VOLATILE TRANSPORT OF METALS IN THE ANDESITIC MAGMATIC-HYDROTHERMAL SYSTEM OF WHITE ISLAND

by

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Abstract

Volcanic gases observed at active volcanoes originate from the magma at depth. These volatiles exsolve as a result of decompression, crystallization and cooling of the silicate melt. The transport of metals in a magmatic volatile phase arises from complexation with the main volatile species, sulfur and halides. Composition of the magma, temperature, pressure and redox state have thus strong implications on metal mobility in these environments. Moreover, a variety of interactions and phase separations can affect these fluids after exsolution from the parental magma. This thesis aims at constraining the volatile transport of trace metals at White Island, a subduction-related magmatic-hydrothermal system, through a characterization and metal budget of the magmatic reservoir and the different atmospheric discharges.

The metal content of the reservoir, as well as the effects of degassing and magma mixing on the magma are explored through the study of ejecta from the 1976-2000 eruptive cycle. CO₂, SO₂ and H₂O are degassing from a mafic melt at ~ 5 km depth, regularly feeding a shallower and evolved reservoir at ~ 800 m. Average contents of 164 ppm of Cu, 73 ppm of Zn, 12 ppm of Pb and 0.4 ppm of Au and Ag were detected in melt inclusions. A fraction of these metals partition into the exsolving aqueous fluid. Onset of magnetite crystallization may trigger exsolution of sulphide melt, found to contain around 30 wt% of Cu, and as much as 36 wt% Ni, 21 wt% Ag, 0.10 wt% Au in small inclusions, representing a considerable source of metals available for an aqueous fluid phase upon resorption.

The volatile transport of metals is indicated by their enrichment in a variety of discharges at the surface. The hyperacidic waters of the crater lake absorb metals from the magmatic gases injected at subaqueous vents. Concentrations of ~ 12 ppm of As and Zn, 6 ppm of Cu and Pb were observed. Hydrolysis of the host rock by the reactive waters is responsible for the high cation contents of the fluids. Precipitation of secondary minerals such as silica, anhydrite, gypsum, sulfur and alunite occurs within and underneath the crater lake. The predicted speciation of metals greatly varies, dominated by Cu^I and Fe^{II} chloride complexes in the more reduced environment at the lake bottom, whereas Cu^{II} and Fe^{III} are stable in the oxidized surficial waters. Arsenic is mainly present as As(OH)₃ at depth, with H₃AsO₄ dominating at the surface. Ag, Pb and Zn are complexed with chloride, and are not redox dependent. The presence of a body of molten sulfur at the bottom of the lake is indicated by sulfur spherules, both floating at the lake surface and in sediments. Pyrite crystals coat the surface of some globules, and chemical analyses reveal an enrichment in a variety of chalcophile metals (Tl, Sb, Bi, Au, As, Ag, Re, Cu).

The volcanic gases emitted at fumaroles are enriched in metals compared to the magma. The effective transport of Se, Te, Sb, B, Au, As, and Bi is indicated by enrichment factors larger than 1000. In contrast, Cu is relatively depleted, suggesting deposition in the subsurface environment. Variations in composition are observed with time, mainly depending on temperature and major composition of the emissions. Values > 100 ppb of Sb, Bi, Ni, Zn, As and Se, > 10 ppb of Te, Pb, and Cu, and up to 8 ppb of Tl were recorded. Chloride is predicted to be the main ligand responsible for metal transport, even at higher temperature.

The lack of thermodynamic data for complex solvated metal clusters may nevertheless bias our results. The low temperature of the studied fumaroles (maximum 192.5 °C) is in accordance with the small abundance of sulfides in the sublimates, whereas the high proportion of sulfates indicates oxidized conditions.

The volcanic plume is enriched in metals such as Bi, Cd, Tl, Se, Te and Sb. The most common particles emitted are sulfates, halides, silicates, sulphuric acid and $\text{Zn} \pm \text{Cu}$ oxides. Metal emission rates are in the range of 1-10 kg/day for As, Se, Cu and Zn, 0.1-1 kg/day for Pb, Tl and Bi. Emissions of high-temperature magmatic gases are indicated by elevated SO_2/HCl ratio and the presence of Au in the particulate phase.

Mass balance calculations in White Island magmatic-hydrothermal system indicate a segregation of around 4900 tons of copper per year, either accumulated from a dense brine at ~ 500 m depth, or deposited by low-density vapors on their way to the surface. Metal-rich sulfide blebs trapped in phenocrysts may also retain Cu at depth. These results thus reinforce the belief that White Island is an actively forming porphyry copper deposit.

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Table of contents

Abstract.....	i
Acknowledgements	iii
Table of contents	v
List of figures.....	vii
List of tables.....	ix
Chapter 1: Introduction	1
1.1 Overview of magmatic-hydrothermal systems.....	2
1.1.1 Deep magmatic fluids	2
1.1.2 Surface fluids	4
1.1.3 Zonation in magmatic-hydrothermal systems.....	5
1.2 Metals in the volcanic environment	6
1.2.1 Formation of ore deposits	7
1.2.2 Surface manifestations of metals	10
1.2.3 Thesis aim, research questions and brief summary	10
Chapter 2: White Island, an overview	13
2.1 Geological setting	13
2.2 Eruptive history and activity	16
2.3 The magmatic-hydrothermal system of White Island	17
2.4 The 1976-2000 eruptive cycle.....	18
2.5 Recent eruptions.....	20
Chapter 3: Magma mixing, volatile degassing and late sulphide saturation: Insights into the 1976-2000 eruptive sequence at White Island.....	25
3.1 Introduction	25
3.2 Samples and analytical methods	25
3.2.1 Samples.....	25
3.2.1 Major elements and volatiles	26
3.2.2 Water	28
3.2.3 Trace elements.....	29
3.3 Results.....	30
3.3.1 Whole rock and phenocrysts.....	30
3.3.2 Melt inclusions.....	34
3.3.3 Cu-Fe sulphides	36
3.4 The role of mafic recharge during the 1976-2000 eruptive sequence	42
3.5 Pressure and temperature constraints	47
3.6 Magma degassing during ascent and crystallization	48
3.6.1 Major species	48
3.6.2 Metals	52
3.7 The occurrence of sulphide melt inclusions and their effect on metals	56
3.8 Conclusions	58
Chapter 4: Hyperacidic crater lake as a sink for metals.....	61
4.1 Introduction	61
4.2 Samples and analytical methods	63
4.2.1 Collection of samples.....	63
4.2.2 Sample preparation and analytical techniques	64

4.3	Results.....	66
4.3.1	Crater lake water.....	66
4.3.2	Solid samples.....	71
4.4	Sources of crater lake water.....	77
4.5	Water speciation and saturation.....	80
4.5.1	Speciation and saturation of surficial oxidized waters.....	80
4.5.2	Speciation and saturation of deeper reduced waters.....	82
4.6	Conclusions.....	84
Chapter 5: Transport and deposition of metals by volcanic gases.....		87
5.1	Introduction.....	87
5.2	Sampling and analytical methods.....	88
5.3	Variations in metal content of fumarolic condensates.....	91
5.3.1	Chemistry of fumarolic discharges.....	91
5.3.2	Metal enrichment in fumarolic gases.....	95
5.4	Sublimates forming in low-temperature fumarole.....	96
5.5	Thermochemical modelling.....	102
5.6	Conclusions.....	109
Chapter 6: Metal emissions in volcanic plumes.....		113
6.1	Introduction.....	113
6.2	Sampling and analytical methods.....	114
6.3	Chemical features.....	118
6.3.1	Major species.....	119
6.3.2	Trace elements.....	120
6.3.3	Aerosols from Yasur and Mount Etna volcanoes.....	122
6.4	Particle morphology and composition.....	125
6.5	Origin of the aerosol.....	129
6.5.1	Variations in major gas compositions.....	129
6.5.2	Variations in trace metals.....	130
6.6	Emission rates.....	131
6.7	Conclusions.....	133
Chapter 7: Mass balance calculations and concluding remarks.....		135
7.1	The copper budget for White Island magmatic-hydrothermal system.....	135
7.2	Transport and deposition of Cu.....	139
7.2.1	Partitioning into immiscible sulfide melt.....	139
7.2.2	Partitioning into magmatic volatile phase.....	139
7.3	Thesis Conclusions.....	147
References.....		151
Appendix.....		173
A.1	LA-ICP-MS analytical precision and accuracy.....	173
A.2	Melt inclusions and matrix glass compositions.....	174
A.3	Cu-Fe sulphide composition maps.....	196
A.4	Sediment core and sulfur globule compositions.....	198
A.5	XRD diffractograms.....	202
A.6	Sediment core 1a collected on 5 June 2015.....	205
A.7	ICP-MS detection limit, accuracy and precision.....	206
A.8	Plume enrichment factors, rock compositions (White Island, Yasur, Etna).....	208
A.9	HSC input files.....	209

List of figures

Figure 1-1: High-temperature part of the water phase diagram.	3
Figure 1-2: Phase diagram of the H ₂ O-NaCl system in T-P-X coordinates.....	4
Figure 1-3: Schematic cross section of a magmatic hydrothermal system.	6
Figure 1-4: Models for the formation of ore-deposits associated with arc volcanoes.....	9
Figure 2-1: Location of White Island with respect to the Taupo Volcanic Zone.....	14
Figure 2-2: White Island crater floor characteristics.	15
Figure 2-3: Picture of White Island taken from the south showing the breached crater floor	16
Figure 2-4: Pictures of the 2012-2013 eruptive sequence.....	21
Figure 2-5: Picture of the crater floor covered by green-colored ash after the 27 April 2016 phreatic eruption. .	22
Figure 3-1: White Island historic and 1976-2000 whole rock.	31
Figure 3-2: Backscattered electron image of olivine Fo76 and olivine Fo92 coexisting in one of the March 1977 bomb, WIDP 6.	31
Figure 3-3: SiO ₂ versus MgO of melt inclusions and matrix glasses for separate rocks erupted during the 1976-2000 eruptive sequence.	35
Figure 3-4: Transmitted light image of Cu-Fe sulphides in a plagioclase phenocryst in WIDP 13 from March 1977.....	36
Figure 3-5: Cu-Fe-S ternary diagram of sulphide inclusions (wt %).	37
Figure 3-6: Cu-Fe sulphide composition maps.	41
Figure 3-7: U versus As in melt inclusions and matrix glasses of rocks from the 1976-2000 eruptive sequence.....	42
Figure 3-8: Transmitted light image of mingled glasses in the March 1977 block WIDP 6.	43
Figure 3-9: Backscattered electron image of a mafic enclave in the October 1993 bomb WIDP 4.....	44
Figure 3-10: Reverse and normal zoning in phenocrysts from the 1976-2000 eruptive sequence.	45
Figure 3-11: CaO versus S of melt inclusions and matrix glasses from the 1976-2000 eruptive sequence.....	49
Figure 3-12: CaO versus Cl of melt inclusions and matrix glasses from the 1976-2000 eruptive sequence.	50
Figure 3-13: Cl versus S of melt inclusions and matrix glasses from the 1976-2000 eruptive sequence.	51
Figure 3-14: SiO ₂ versus Cu of melt inclusions and matrix glasses of rocks from the 1976-2000 eruptive sequence.....	52
Figure 3-15: SiO ₂ versus Zn of melt inclusions and matrix glass for separate rocks of the 1976-2000 eruptive sequence.....	53
Figure 3-16: log Cl/Rb versus log Zn/Rb of melt inclusions and matrix glass for separate rocks of the 1976-2000 eruptive sequence.....	54
Figure 3-17: Lead behavior with degassing and crystallization.....	55
Figure 3-18: Backscattered electron image of orthopyroxene phenocrysts in the bomb from July 2000 WIDP 3 containing sulphide inclusions.....	56
Figure 3-19: Schematic model of White Island magmatic system during the 1976-2000 eruptive sequence.....	59
Figure 4-1: Aerial picture showing the sampling locations (source LINZ).	63
Figure 4-2: Pictures of sulfur spherules floating at the surface of the crater lake.....	66
Figure 4-3: Crater lake time series showing variations in level and temperature.	67
Figure 4-4: Pictures of the crater lake during the different sampling campaigns.	68
Figure 4-5: Pictures of the lake in late 2016.	69
Figure 4-6: Pictures of sediment cores and the analyzed layers.	75
Figure 4-7: Element Transfer Ratio for the crater lake samples and F0 Pool normalized with 1977 andesite.	78
Figure 4-8: Ternary diagram 3*F-Al-3*Mg showing the composition of the crater lake water since its formation in 2001.....	79

Figure 4-9: Isosol plot showing the crater lake water composition against the host dacite.	80
Figure 4-10: R_H -pH stability diagram of various Cu sulfides.	83
Figure 4-11: Formation of metal sulfides on the surface of sulfur spherules	84
Figure 5-1: Aerial picture showing the locations of the three fumaroles sampled (source LINZ).	88
Figure 5-2: Sketch of the sampling train, showing the two types of samples collected.	89
Figure 5-3: Pictures of the sampling train.	90
Figure 5-4: SO_2 - CH_4 *100-Ar*100 ternary diagram for F0 fumarole showing variations between magmatic and hydrothermal endmembers.	91
Figure 5-5: Enrichment factors (EF) estimated for the three fumaroles sampled.	96
Figure 5-6: Description of the mineral species found in the sublimate tubes 1 (June 2015) and 2 (June- October 2016.)	97
Figure 5-7: SEM images of sublimates.	97
Figure 5-8: SEM images of sublimates.	98
Figure 5-9: SEM images of sublimates.	99
Figure 5-10: SEM images of sublimates.	100
Figure 5-11: Speciation of the most abundant gaseous Pb species.	103
Figure 5-12: Speciation of the most abundant gaseous Cu species.	104
Figure 5-13: Speciation of the most abundant gaseous Zn species.	105
Figure 5-14: Speciation of the most abundant gaseous Fe species.	106
Figure 5-15: Speciation of the most abundant gaseous As species.	106
Figure 5-16: Speciation of the most abundant gaseous Bi species.	107
Figure 5-17: Sublimates and condensates formed during cooling.	108
Figure 6-1: Sampling locations and setup at White Island and Yasur volcano, Vanuatu.	115
Figure 6-2: Sampling location at Mount Etna.	115
Figure 6-3: Bivariate plots suggesting different sources.	120
Figure 6-4: Enrichment factors of aerosols from White Island, Mount Etna, and Yasur volcanoes.	121
Figure 6-5: SEM pictures of White Island aerosols.	125
Figure 6-6: SEM pictures of White Island aerosols.	126
Figure 6-7: SEM pictures of Etna aerosols.	127
Figure 6-8: SEM pictures of Etna aerosols.	128
Figure 6-9: SEM pictures of Yasur aerosols.	128
Figure 6-10: Ternary diagram Cu-HCl/50- SO_2 /100 for the volcanic plume.	130
Figure 7-1: Aerial photos showing acid discharges around White Island.	137
Figure 7-2: Pressure-temperature-salinity relations in the H_2O -NaCl system.	141
Figure 7-3: Distribution of gaseous Cu species in high-temperature gases from Kudriavy, Yasur and White Island volcanoes at 1 bar and 100 bar.	145
Figure 7-4: Pressure-temperature phase diagram of the H_2O -NaCl system.	146
Figure 7-5: Sketch of White Island magmatic-hydrothermal system.	149
Figure A-1: Cu-Fe sulphide composition maps 2.	196
Figure A-2: Cu-Fe sulphide composition maps 3.	197
Figure A-3: XRD diffractograms of ash and suspended particles.	202
Figure A-4: XRD diffractograms of sediment cores.	203
Figure A-5: XRD diffractogram of Core 1b-1.	204
Figure A-6: Picture of one of the core sediments collected on 5 June 2015, Core 1a.	205

List of tables

Table 3-1: Description of samples	27
Table 3-2: LA-ICP-MS analytical parameters	30
Table 3-3: Olivine core compositions (wt%)	32
Table 3-4: Whole rock compositions (wt%)	33
Table 3-5: Major and trace element compositions of the Cu-Fe sulphides (wt%)	38
Table 4-1: White Island crater lake and spring compositions.	69
Table 4-2: Composition ($\mu\text{g.g}^{-1}$) of sediments, scum layer, suspended particles, ash, sulfur globules and andesite.	71
Table 4-3: Composition ($\mu\text{g.g}^{-1}$) of black versus yellow sulfur globules.....	73
Table 4-4: Composition (ng.g^{-1}) of selected layers from the sediment cores.....	74
Table 4-5: Calculated dominant metal complexes in the crater lake water from 5 June 2015.....	81
Table 5-1: Composition of White Island fumarolic gases.	92
Table 5-2: List of all the observed sulfates in sublimates and natural encrustations.	101
Table 5-3: Metal content of elemental sulfur condensing from fumarole F0 gases ($\mu\text{g.g}^{-1}$).....	102
Table 6-1: Composition of blank particle filters (ng.g^{-1}).	116
Table 6-2: Acid gases and aerosol compositions of filter packs from White Island plume.	118
Table 6-3: Acid gases and aerosol compositions of filter packs from Yasur volcano plume.	122
Table 6-4: Acid gases and aerosol compositions of filter packs from Mount Etna plume.	123
Table 6-5: Average emission rates (kg/d , unless specified) for White Island, Yasur and Etna and comparison with other studies.	132
Table 7-1: Mass balance calculations for a selection of metals during periods of low activity (t/y).	138
Table A-1: LA-ICP-MS analytical precision (± 1 RSD) and accuracy (bias) estimated with certified reference material GSD-1 for the different spot sizes used.....	173
Table A-2: Melt inclusion and matrix glass compositions.	174
Table A-3: Sediment cores composition, black and yellow sulfur globules composition.	198
Table A-4: ICP-MS detection limit (3 SD), secondary standards (SLRS-4, JB1, BIR-1) measurement values, errors (1 SD) and bias.	206
Table A-5: Enrichment factors in the aerosol and rock composition for White Island, Yasur and Etna	208
Table A-6: Gas composition in mol% used as input for HSC thermochemical modeling.....	209

Chapter 1: Introduction

Volcanoes have given birth to many stories and myths throughout history. The term volcano itself comes from the island of Vulcano in the Mediterranean Sea, where the inhabitants used to think the volcano was the chimney of Vulcan's forge, the god of fire in Roman mythology. Every civilization living nearby volcanoes have their myths and legends about the powerful neighbor. In Hawaii, the goddess of volcanoes, Pele, would cause eruptions in her moments of anger (Westervelt, 1916). Her name was given to the thin shards of glass emitted during eruptions, Pele's hair. As it is still the case nowadays, volcanoes fascinated people despite their danger.

In a different manner, metals are fascinating to people too. Materials such as bronze, brass, or iron have long been recognized for their utility in building tools. Nowadays, many metals are found in electronic components due to their remarkable properties, such as conductivity. The US Environmental Protection Agency (EPA) found that 16 000 kg of copper and 34 kg of gold could be recovered from one million cell phones. Besides their utility, shiny and colorful minerals have also attracted people for their beauty and rarity. First used in art and jewelry, they have acquired an incredible value. They have long been used as a currency and are still a symbol of wealth.

Volcanoes and metals... fascinating and attracting in different ways, but maybe more closely related than one could first think. Volcanoes are considered to be the main natural source of heavy metals in the atmosphere (Lepel et al., 1978; Nriagu, 1989). At the same time, many of the ore deposits on Earth today were formed by magmatic-hydrothermal systems in the past (Burnham, 1979; Henley and Ellis, 1983; Sillitoe and Bonham, 1984; Hedenquist and Lowenstern, 1994; Williams-Jones and Heinrich, 2005; Nadeau et al., 2016). This highlights the source of metals being the magma, but also points to the fact that metals behave differently in the subsurface environment. Not all the metals are released into the atmosphere, some being segregated into what we call ore deposits. We could also argue that not all the metals are segregated into ore deposits, but that some are released into the atmosphere. This brings us to wonder why? What are the processes taking place between the magmatic chamber and the surface, causing metals to partition into a gaseous phase instead of a liquid or solid phase?

Out of the different types of volcanoes present on Earth, andesitic volcanoes are of particular interest, due to several aspects: their high gas content originating from the subducted slab releasing its volatiles (Giggenbach, 1992a), their intermediate viscosity magmas, and their potential to give rise to extensive eruptions. Basaltic volcanoes are known for their effusive activity, during which a large amount of volatiles are released simultaneously with low-viscosity magma. In contrast, rhyolitic volcanoes have too viscous magma to allow volatile separation, thus leading to violent eruptions. At andesitic volcanoes, the large amount of volatiles is able to separate from the melt and often migrates to the surface, leading to passive degassing in quiescent periods. This constant degassing makes arc-volcanoes appropriate places to study volatile metal emissions. The few volcanoes studied thus far, revealed not only differences in the metal species being emitted, but also in their rate of emission. These variations are also observed by economic geologists. Most of the ore deposits on Earth today were formed during the life of a subduction-related volcano (Sillitoe, 1972; Bodnar and

Beane, 1980; Sawkins, 1984; Hedenquist et al., 1993; Sillitoe, 1995). However, the presence of both ore-bearing and barren systems, with very similar setting, suggests that special conditions are required to form economic ore-bodies. What are these conditions? Why are some elements preferentially concentrated and deposited in a magmatic-hydrothermal system while emitted into the atmosphere at another?

Little is known about the transport of metals after they have escaped from the magma. And as we have seen, a lot happens in the few kilometers separating magmatic chambers from the surface. The subsurface environment of magmatic-hydrothermal systems is probably one of the most challenging areas to study from a geochemical point of view. Temperature sharply decreases by hundreds of degrees, redox conditions are shifted due to mixing with atmospheric gases, and meteoric waters infiltrate and interact with deep sourced fluids. This thesis aims at studying the remarkable environments that are magmatic-hydrothermal systems, by focusing on the example of White Island, in New Zealand.

1.1 Overview of magmatic-hydrothermal systems

Inherited from ancient Greek, the term hydrothermal describes the presence and interaction of two key parameters, water (hydros) and heat (thermos), as they circulate in the Earth's crust. In the case of magmatic-hydrothermal systems, energy is supplied dominantly by the shallow underlying magma. In the same manner, we can identify distinct sources for the waters: deep fluids originating from the magma and surface fluids infiltrating the system.

1.1.1 Deep magmatic fluids

The major constituent of volcanic gases is water (H_2O , 40-99 mol%) followed by carbon dioxide (CO_2 , 1-50 mol%), sulfur dioxide and hydrogen sulfide (SO_2 , 0.2-15 mol% and H_2S , 0.1-2 mol%, respectively) and halogen species hydrogen chloride and hydrogen fluoride (HCl , 0.1–6 mol% and HF , < 0.1 mol%, respectively) (Symonds et al., 1992; Symonds et al., 1994; Wahrenberger et al., 2002). These volatiles originate from the magma, from which they separate due to decompression as the melt rises in the crust (Burnham, 1979, 1997). The timing of exsolution depends on the solubility of the gases as a function of magma composition, pressure and temperature. Carbon dioxide is less soluble in silicate melts, and is therefore released early by the magma at depth, followed by water (Holloway, 1976; Wallace, 2005; Blundy et al., 2010). Due to the acidic nature of magmatic-hydrothermal systems, carbon dioxide gas rises towards the surface without interacting much, similar to a noble gas. In contrast, ascending magmatic water condenses/mixes into hydrothermal fluids under appropriate temperature and pressure conditions. Sulfur and the halogens are more soluble (than CO_2) in silicate melts and hence, released at shallower levels (in increasing order of solubility $\text{S} < \text{Cl} < \text{F}$, (Carroll and Webster, 1994)). In the case of sulfur, the solubility and relative proportions of SO_2 and H_2S are strongly dependent on redox conditions and composition of the magma (Haughton et al., 1974; Wallace and Carmichael, 1992; Nilsson and Peach, 1993). Moreover, not only volatile species form, but sulfide and sulfate can precipitate (Carroll and Rutherford, 1985; Luhr, 1990). Regarding chloride, speciation varies

with pressure, with alkali chlorides NaCl and KCl dominating at high pressure in high-density aqueous fluids and HCl at low pressure in low-density vapors (Kilinc and Burnham, 1972; Shinohara et al., 1989; Webster, 1992). The dependence of major volatile solubilities on pressure is the basis of volcanic gas monitoring. As mafic magma rises into a volcanic conduit, CO₂-rich gas will first be emitted, progressively evolving into low C/S ratio mixture.

Figure 1-1: High-temperature part of the water phase diagram. The domains of the different aqueous phases (liquid, vapor, supercritical fluid) and three major types of geological fluids are shown, according to their P-T-density parameters and the degree of our knowledge of metal speciation and solubility. From Pokrovski et al. (2013).

Not only the composition of the exsolved phase varies with pressure and temperature, but also its physical state (Figure 1-1). At high pressure, volatiles can exsolve from silicate magmas as supercritical fluids. The critical point in the NaCl-H₂O system was estimated to occur between ~100-140 MPa and 600-800°C (Sourirajan and Kennedy, 1962; Pitzer and Pabalan, 1986). The decrease in temperature and pressure often leads to separation into a vapor and a high-density hypersaline liquid (Figure 1-2) (Sourirajan and Kennedy, 1962; Bodnar et al., 1985; Pitzer and Pabalan, 1986; Shinohara, 1994; Driesner and Heinrich, 2007). While the low density vapor buoyantly rises towards the surface, the hypersaline liquid tends to remain at depth (Henley and McNabb, 1978). Evidence of these hypersaline liquids are found in fluid inclusions in minerals from many ore deposits (e. g. porphyry copper) (Roedder, 1984; Bodnar, 1995).

Figure 1-2: Phase diagram of the H₂O-NaCl system in T-P-X coordinates. From Driesner and Heinrich (2007).

1.1.2 Surface fluids

Surface groundwater, and seawater in the case of volcanic islands (Chiodini et al., 1995; Delmelle et al., 1998; Christenson et al., 2017), infiltrate hydrothermal systems and interact with the ascending gases and/or liquids. Surface waters percolate the system through a network of fissures and cracks and are heated by contact with hot rocks in the deeper part of the system. They also interact with deep volatiles rising from the magma, forming the so-called hydrothermal fluids. Magmatic SO₂, H₂S, HCl and HF dissolve in aqueous liquids according to the following reactions (Sakai and Matsubaya, 1977; Giggenbach, 1987):

At high temperature (>200°C and >300°C respectively), the low dipole moment of water results in HCl and H₂SO₄ being mostly associated. It is only at lower temperature that they dissociate, reducing the pH of the fluid (Quist et al., 1965; Ruaya and Seward, 1987). There, hot and acidic fluids leach the surrounding rock as they circulate through it, bringing cations into solution (Giggenbach and Glasby, 1977). The alteration types vary depending on the composition of the hydrothermal fluids, the temperature, pressure and the rock type. In the presence of highly acidic sulfate-rich fluids, silicic alteration takes place, leaving a residual

core of vuggy silica after mobilization of the other elements (Ellis and Mahon, 1964; White and Hedenquist, 1990; Hedenquist et al., 2000). This aqueous liquid, although less dense and saline than the brine found at depth, can lead to precipitation of secondary hydrothermal minerals, filling the veins and pores created by intense alteration. A particular case is when the precipitation takes place in the upper part of the hydrothermal system, effectively sealing it from the surface (Browne and Lawless, 2001; Christenson et al., 2007). An example of that process is the 2007 eruption of Ruapehu Crater Lake which arose because of sealing of the system, leading to pressurization and an unexpected phreatic eruption (Christenson et al., 2010).

1.1.3 Zonation in magmatic-hydrothermal systems

There are different zones in hydrothermal systems, depending on their temperature and hence on the distance from the underlying magma and volcanic conduit (Figure 1-3). In the vicinity of the latter, the system is said to be single-phase. Further away from the heat source, forming an envelope around the conduit, vapor and liquid coexist as two-phase systems. Hot acidic springs Cl⁻ and SO₄-rich and crater lakes are associated with these. Fumarolic gas discharges are generally separated from the main conduit and interact with the hydrothermal system in this vapor-liquid envelope. This results in both magmatic and hydrothermal contributions to fumarolic fluids (Cioni and D'Amore, 1984; Giggenbach, 1987; Giggenbach and Sheppard, 1989; Taran et al., 1992; Chiodini et al., 1995). High-temperature fumaroles are usually associated with hot acidic springs in areas close to the vent. Crater lakes may form where the hydrology and topography permit (Christenson and Tassi, 2015). In these lakes, magmatic HCl- and SO₂-rich gases dissolve and accumulate (Rowe et al., 1992a; Christenson and Wood, 1993; Symonds et al., 2001). Further from the vent, the heat and acidity are decreasing though water-rock interactions. Neutral hot springs, mudpots and sometimes geysers are the surface features of these distal fluids. The progressive fluid neutralization creates a sequence of alteration facies, from silicic alteration close to the vent where hot and acidic fluids occur, to advanced argillic and intermediate argillic alteration further away from the vent where neutral fluids dominate. Finally, propylitic alteration develops where alkaline-chlorine fluids interact with the host rock (Fulignati et al., 1998; Fulignati et al., 1999).

Figure 1-3: Schematic cross section of a magmatic hydrothermal system.

1.2 Metals in the volcanic environment

Various metals are reported in diverse forms in and around volcanoes. As an example, 270 tons of mercury are emitted in the volcanic plume of Kilauea every year (Siegel and Siegel, 1987). This is not only a problem locally, as it has been shown that the volcano is the source of the Hg found 320 km away, in Oahu (Siegel and Siegel, 1987). Varrica et al. (2000) reported high concentrations of Br, Cu, Zn and Au in lichens, as a result of volcanic emissions at Vulcano Island.

Menard et al. (2014) reported high levels of B, Li, As and V in a stream flowing down from Lascar volcano into the town of Talabre in Chile. As a comparison, the Talabre river contains 45.4 ppm of arsenic, while the EPA acceptable concentration in drinking water, as of 2001, is 10 ppb.

Another proof of the transport of metals by magmatic fluids is the presence of sublimates around high-temperature fumaroles (Symonds et al., 1987; Kavalieris, 1994; Taran et al., 1995; Fulignati et al., 1998; Taran et al., 2001). Appreciable concentrations of As, Cu, Mo, Pb, Sn and W have been reported in sublimates surrounding volcanic vents (Le Guern and Bernard, 1982; Bernard et al., 1990; Africano et al., 2002; Wahrenberger et al., 2002; Zelenski and Bortnikova, 2005). Korzhinsky et al. (1994) showed the existence of a pure rhenium mineral in high-temperature (910 °C) fumaroles at Kudriavy volcano. Only found at trace levels on Earth, this discovery highlights the efficiency of volcanic gases at transporting and concentrating metals.

All these manifestations indicate that metals escape from the magma at depth. Although they are not, as such, volatiles, they behave like volatiles. More strictly speaking, they are volatile molecular metal complexes. The pressure, temperature, and composition of the fluid they are

carried by constrain their transport towards the surface. Some are retained at depth by hypersaline brines, some are scavenged by waters circulating in the uppermost parts of a volcano, some form sublimation products, and a portion escapes into the atmosphere.

1.2.1 Formation of ore deposits

Ore deposits associated with volcanoes are thought to form throughout the lifespan of their host magmatic-hydrothermal system (Hedenquist et al., 1993; Archibald et al., 2001; Williams-Jones and Heinrich, 2005). Their formation requires four different processes to take place: transport and enrichment of metals, alteration and deposition. Moreover, the existence of both barren and ore-bearing intrusions in arc-related environments suggests that the formation of such deposits is not “compulsory”, but requires special circumstances to occur.

There are two main types of ore deposits, varying primarily in their mineralogy and their location with respect to the magmatic intrusion. Porphyry deposits are closely overlying the magmatic pluton and often contain elevated concentrations of Cu, Mo, Sn, W and Au. Epithermal deposits rich in Au, Ag, (As, Cu, Hg) are usually more distal and closer to the surface.

It is now widely accepted that fluids exsolving from a shallow emplaced magma are responsible for the transport of ore-forming metals to their deposition site (Burnham, 1967; Drummond and Ohmoto, 1985; Hedenquist and Lowenstern, 1994; Sillitoe and Hedenquist, 2003; Nadeau et al., 2016). The enrichment process takes place by selective partitioning of the metals into the ore forming fluid phase. As stated above, depending on pressure and temperature conditions, this fluid phase can be a supercritical fluid, an aqueous solution or a vapor. Although accepted generally, the role of vapor-liquid separation in segregating ore metals is still poorly understood.

The efficiency of aqueous liquids in transporting metals has long been recognized (Barnes and Kullerud, 1957; Burnham, 1967; Romberger and Barnes, 1970; Bodnar and Beane, 1980; Barnes, 1981; Drummond and Ohmoto, 1985; Shinohara, 1994; Barnes, 1997). Many experimental studies since the 1960's have helped build solubility tables for the most common ore-forming metals in hydrothermal systems (Candela and Piccoli, 1995a; Pokrovski et al., 2013; Seward et al., 2014). The development of melt and fluid inclusion studies have also extended our understanding of fluid-melt partitioning (Bodnar, 1995; Audétat et al., 1998; Heinrich et al., 1999; Heinrich et al., 2003; Lerchbaumer and Audétat, 2013). The most common major species forming complexes with metals, i.e. ligands, in aqueous solutions were found to be chloride and sulfide (Burnham, 1979; Hemley et al., 1992; Burnham, 1997; Yardley et al., 2011).

On the other hand, low-density vapor was first thought to be inefficient in carrying large quantities of metals (Krauskopf, 1957; Krauskopf, 1964) and was left aside until recently. Fluid inclusion studies revealing metal-rich vapor coexisting with high-salinity liquid, led to new experiments in that field (Roedder, 1971; Eastoe, 1978; Henley and McNabb, 1978; Candela, 1989; Lowenstern et al., 1991; Heinrich et al., 1992; Bodnar, 1995; Damman et al., 1996; Audétat et al., 1998; Heinrich et al., 1999; Ulrich et al., 1999; Williams-Jones and Heinrich, 2005; Kouzmanov and Pokrovski, 2012; Migdisov et al., 2014). These studies

confirm the more important role of the vapor in transporting ore-metals associated with porphyry and higher temperature deposits. The presence of water, hydrochloric acid and sulfur, not taken into account in early volatility studies, accounts for the high transport of Cu, As, Sb, Ag, Mo and Au (Baker et al., 2004; Simon et al., 2005; Simon et al., 2006; Cauzid et al., 2007; Simon et al., 2007; Nagaseki and Hayashi, 2008; Pokrovski et al., 2008; Zajacz and Halter, 2009; Pokrovski et al., 2014).

The paradox of ore deposits resides in the transition from transport to deposition. What changes suddenly reverse the fluid transport capabilities? Cooling, pressure decrease, mixing with another fluid and fluid-rock interaction stand as the most likely processes driving deposition. The very steep thermal gradient between the magma chamber and the surface leads to a drop in fluid temperature as they rise. Cooling reduces the stability of metal complexes leading to saturation. Similarly, as the metal-rich vapors expand into fractures and veins, the drop in pressure can lead to destabilization of the metal complex species and precipitation (Henley and Berger, 2013). Mixing with groundwater has also been reported as a trigger to precipitation through oxidation and/or cooling of the fluids (Vikre, 2007; Leach and Corbett, 2008). Fluid fluxing was suggested by Blundy et al. (2015) in the form of S-rich vapors exsolving from an underlying mafic magma and interacting with metalliferous high-salinity liquids, the increase in sulfide activity leading to metal-sulfide deposition. Finally, interaction of a sulfur-rich vapor with Fe-bearing wall rock can influence transport in two different ways: 1) leads to Fe-sulfide precipitation thus decreasing the solubility of metals transported as sulfide complexes (Williams-Jones and Heinrich, 2005), 2) reduces SO_2 to H_2S upon cooling thus favoring metal transport as sulfide complexes (Giggenbach, 1992b; Heinrich, 2005). The fluid/rock ratio controls the extent of the previous reactions, with high rock/fluid ratios favoring pyrite deposition, and low rock/fluid ratios favoring transport (Heinrich, 2005).

Figure 1-4 depicts the variation in type and location of ore deposits throughout the life of a magmatic intrusion. The deposition can be seen as a continuous process involving exsolution of fluids from a cooling hydrous magmatic intrusion. Acidic gases of low density and salinity first released by the magma rise towards the surface, mix with meteoric fluids, and produce a halo of alteration. Porphyry deposits form after a carapace has crystallized on the upper part of the magma body. Two different models can explain this type of deposition. The first considers vapor as the transporting phase (Heinrich et al., 2004). Metal-rich vapors of low to intermediate density and salinity ascend from the melt and precipitate ore minerals as they expand through veins and fractures, react with wall rock and cool. The second considers vapor as the trigger for precipitation (Blundy et al., 2015). A metal-rich liquid interacts with sulfur-rich gases rising from an underlying mafic magma chamber leading to sulfide saturation.

Figure 1-4: Models for the formation of ore-deposits associated with arc volcanoes.

Epithermal deposition occurs later, when most of the intrusion has already crystallized. Low salinity vapors exsolving from the deeper and cooler magma undergo contraction to liquid during ascent, efficiently carrying metals to previously altered rocks at shallow level. There, the loss of sulfide triggers precipitation by either of the following processes: mixing with meteoric water (Stoffregen, 1987; Spycher and Reed, 1989), adiabatic boiling of a metal-bearing liquid phase (Drummond and Ohmoto, 1985; Krupp and Seward, 1987; Kouzmanov and Pokrovski, 2012), or reacting with Fe-bearing rocks (Muntean et al., 1990; Kettler et al., 1992).

1.2.2 Surface manifestations of metals

Arc-related volcanoes featuring an active hydrothermal system typically show either signs of volcanic unrest or passive degassing. Despite scrubbing by various fluids at depth, significant quantities of metals are still emitted into the atmosphere. Some studies have estimated an average of 10 000 tons of metalloids, metals and trace elements being emitted by quiescently degassing volcanoes per year (Hinkley et al., 1999; Delmelle, 2003). Sublimates deposited around fumarolic vents and waters flowing downslope also comprise part of the surface metal discharge budget.

As stated above, volcanoes contribute greatly to natural emissions of metals into the atmosphere (Zoller et al., 1974; Buat-Ménard and Arnold, 1978; Lepel et al., 1978; Cadle, 1980; Nriagu, 1989). Volcanic plumes are comprised of H₂O, CO₂, SO₂, H₂S, HCl, HF, HBr, H₂, CO and various particles. The majority of metals is transported as particles, associated with sulfides, halides, oxides and sulfates (Buat-Ménard and Arnold, 1978; Lepel et al., 1978; Vié le Sage, 1983; Varekamp et al., 1986; Gemmell, 1987; Symonds et al., 1987; Pennisi et al., 1988; Quisefit et al., 1989; Hinkley, 1991; Andres et al., 1993; Hinkley et al., 1994; Nho et al., 1996; Stimac et al., 1996; Zreda-Gostynska et al., 1997; Hinkley et al., 1999; Aiuppa et al., 2000; Obenholzner et al., 2003; Mather et al., 2012; Gauthier et al., 2016). As an example, Cu, Zn and Pb emission rates from passively degassing Masaya volcano, Nicaragua, between 2000 and 2001 were estimated at 237-927 kg/d, 49-220 kg/d, 20-38 kg/d respectively (Moune et al., 2010). It should be noted that the fluxes of trace metals into the atmosphere increase greatly during eruptive activity (Gauthier and Le Cloarec, 1998; Mather et al., 2003b; Calabrese et al., 2011).

The studies mentioned above highlight the potential hazard of volcanoes in terms of health and environment, both in the vicinity of the vent and further away. Moreover, metal emissions are not only a concern for the atmosphere, but for the hydrosphere and biosphere as well. A fraction of the particles emitted, containing potential harmful species (As, Cd, Cu, Se, Sb, Tl) is effectively deposited further away from the volcano, affecting the plants and soil and eventually dissolving into the local groundwater (Baxter et al., 1982; Aiuppa et al., 2000; Allen et al., 2000; Delmelle, 2003; Fulignati et al., 2006; Calabrese et al., 2011; Floor et al., 2011; Henley and Berger, 2013).

1.2.3 Thesis aim, research questions and brief summary

This thesis aims at understanding the fate of metals in a magmatic-hydrothermal system. From the mafic magma rising to crustal level to exsolution in a fluid phase, interactions with meteoric water, host rock and mixing with the atmosphere, what actually happens to metals? What carriers, if not the magma, are responsible for their mobility? To answer these questions, we will study the metal content and speciation of magmatic-hydrothermal features. First of all, the reservoir of magma, represented by melt inclusions. Then, we will focus on all the discharges into which metals could partition. These include erupted rocks and secondary minerals, hot springs and crater lake, fumarolic gases and volcanic plume. The goal is to constrain the processes occurring in the magmatic-hydrothermal system responsible for such repartition of metals at the surface. By estimating a mass balance between the reservoir and

the discharges, we also aim at revealing eventual deposition occurring in the sub-surface environment. Finally, monitoring the metal content of volcanic gases throughout this three-year project might highlight a link between changes in eruptive activity and variations in metal emissions.

The geological background of the area of study, White Island, is given in **chapter two**. It describes the eruptive history, past and recent, and reports on the current state of knowledge on New Zealand's most active volcano.

The third chapter is a textural, structural and chemical study of a set of ejecta from the 1976-2000 eruptive sequence, in the view of constraining magma dynamics and volatile degassing. We focus on the evolution of the system throughout the eruptive sequence, tracking any changes in the feeding system. We also assess the metal contents of the mafic magma and their behavior during crystallization, degassing and mixing.

In the fourth chapter, we examine the crater lake environment, where scrubbing of magmatic gases and hydrolysis of host rock take place. We assess the speciation of metals through thermodynamic calculations, and compare the predicted saturated phases with minerals observed in sediment cores, suspended particles, and erupted hydrothermal material. We also constrain metal segregation by elemental sulfur present at the lake bottom, and found as sulfur globules floating at the surface of the lake.

The fifth chapter focuses on the metal content of fumarolic gases. Variations in composition of the metal load are compared to changes in major species, the latter being related to volcanic activity. We also describe sublimates precipitated from fumarolic gases and collected in silica tubes. Thermochemical modeling using HSC Chemistry software is also reported, in the view of constraining the nature of gaseous metal complexes and predicting the species likely to precipitate with cooling.

In chapter six, we focus on metal emissions into the atmosphere via aerosols forming in the volcanic plume. The composition and nature of aerosols emitted at White Island are compared to those from the magmatic-hydrothermal plume of Mount Etna (Italy), and the purely magmatic gases of Yasur (Vanuatu). We also explore the existence of a relationship between changes in metal contents of the plume, and variations in volcanic activity. Metal emission rates are estimated for the three volcanoes.

Chapter seven combines results from the previous chapters in the view of constraining the metal transport in White Island magmatic-hydrothermal system. Mass balance calculations are performed in the view of revealing deposition of ore metals in the subsurface environment.

Chapter 2: White Island, an overview

White Island has fascinated New Zealanders since their arrival. Maoris refer to it as “Te Puia o Whakaari”, or “Whakaari”, meaning “The dramatic volcano”, and different legends have been reported as to its origin (Luke, 1959). The most popular of them states that it was given birth at the same time as the other volcanoes in the Taupo Volcanic Zone. This tale was reported with other Maori legends by Grey (1853) as follows. Ngatoro-i-rangi, a tohunga or spiritual leader from Arawa, a coastal tribe, decided to go explore the heart of the island. As he reached Lake Taupo, he saw a beautiful mountain to the south. The mountain was so majestic that he could not resist climbing to the summit. He and his slave, Aruhoe, began their climb, and as they were getting higher and higher, the cold affected them, freezing their fingers and toes and stiffening their joints. As they were agonizing, Ngatoro-i-rangi prayed his sisters in Hawaiki to send him fire. The sisters heard the prayer and sent Te Pupu and Te Hoata to rescue their brother. The fire demons travelled underwater towards Aotearoa. They reached the surface at Whakaari to see how far they were, bringing the fire that is still burning nowadays. They reached the surface many times before finding Ngatoro-i-rangi, leaving a trail of steam and thermal activity on their path. They finally brought the fire to the top of the mountain and saved Ngatoro-i-rangi from the cold. He later named it Tongariro, to remember the cold south wind that almost killed him.

The first European to report the island was Captain Cook in 1769. He named it White Island due to the constant cloud of white steam above the island. He nevertheless failed to notice that it was a volcano. It was not until the end of 1826 that people landed on the island. The Williams brothers and Cunningham described steam and smoke in all parts of the crater, as well as several boiling lakes. Captain Drury visited the island in 1848, noting the presence of sulphurous lakes and crystalline sulfur covering the crater floor (Luke, 1959). Sulfur mining started in 1885 and was suspended several times because of eruptions. In 1914, a landslide reaching the crater lake produced a lahar that killed the 11 miners present on the island. The lack of profitability and the bad working conditions led to the end of the mining activity in 1934.

2.1 Geological setting

White Island is an andesitic volcano lying on the continental crust, 48 km off the coast of the North Island in the Bay of Plenty, New Zealand (Figure 2-1). It marks the northern end of the Taupo Volcanic Zone (TVZ), a volcanic arc and back-arc basin due to the westward subduction of the Pacific plate under the Australian plate at the Hikurangi trench, 200 km east from the TVZ (Cole and Nairn, 1975; Cole and Lewis, 1981; Wright, 1992). Being 200 km long and 60 km wide on land, the TVZ extends off shore for another 100 km as a 45 km wide graben delineated by the Tauranga Fault Zone to the west and the White Island Fault Zone to the east (Smith et al., 1989; Wright, 1992). The TVZ is characterized by 1 Ma old calc-alkaline volcanism and can be divided into three volcanic zones: 1) andesitic volcanoes on the south represented by the Tongariro Volcanic Center, 2) rhyolitic volcanoes in the central part including the Lake Taupo caldera, and 3) andesitic systems on the northern end with

Edgecumbe, Whale Island and White Island (Figure 2-1) (Cole and Lewis, 1981; Cole, 1990). North-east from White Island is the Tonga-Kermadec arc, a series of volcanic islands and submarine volcanoes associated with the Kermadec-Tonga subduction zone.

Figure 2-1: Location of White Island with respect to the Taupo Volcanic Zone.

White Island is the subaerial part of an 18 by 16 km submarine volcano rising from the sea floor 300-400m under the water (Duncan, 1970; Clark and Cole, 1986). The island, around 2 km in diameter, represents only a small portion of the whole edifice and half its height. Together with the sea stacks Volkner Rocks and Club Rocks, the total volume reaches 78 km³ (Cole et al., 2000). White Island is composed of two overlapping stratocones, the extinct Ngatoro cone on the north-west, and the active Central cone on the south-east (Black, 1970; Duncan, 1970; Cole et al., 2000). Only part of the Ngatoro cone remains, most of it being removed before the construction of the Central cone (Graham and Cole, 1991). The main crater is divided into three subcraters oriented NW-SE (Black, 1970; Duncan, 1970; Nairn and Wood, 1986; Houghton and Nairn, 1989a) as shown in Figure 2-2.

Most of the crater floor is covered by material from the 1914 debris avalanche and is less than 30 meters above sea level. The southeastern crater wall is breached by the sea, giving White Island its peculiar shape (Figure 2-3). The three bays, Crater, Wilson and Shark are thought to have been formed by a large eastward-trending sector collapse that happened in pre-historic times (< 3.4 ka) (Moon et al., 2009; Letham-Brake, 2013).

a)

Figure 2-2: White Island crater floor characteristics. a) The first map of White Island compiled by J. Healy from the New Zealand Geological Survey in 1951. b) Aerial photo showing the three subcraters (Source: LINZ).

Figure 2-3: Picture of White Island taken from the south showing the breached crater floor (5 June 2015). The acid stream discharging into the sea in Crater Bay gives the yellowish color to the sea.

2.2 Eruptive history and activity

White Island is constructed of andesite-dacite lava flows and pyroclastic deposits (Cole and Nairn, 1975; Clark et al., 1979; Cole et al., 2000). The old Ngatoro cone and Troup Head are of andesitic composition, whereas Central cone is dacitic. The eruptive activity appears to be cyclic, with major eruptions of andesite-dacite lava flows alternating with minor basalt-andesite explosive eruptions (Cole et al., 2000).

Thirty-four eruptions, mainly phreatic and phreatomagmatic alternating with Strombolian events, have been reported since the arrival of the first settlers in 1826 (Hamilton and Baumgart, 1959; Cole and Nairn, 1975; Smithsonian Institution, 1976-2000; IGNS, 1986-2001; GeoNet, 2001-2017). White Island has been the most continuously active volcano in New Zealand during the past 40 years, with the longest historic eruptive sequence taking place between December 1976 and September 2000 (Hamilton and Baumgart, 1959; Clark and Cole, 1986; Houghton and Nairn, 1989a; Simkin and Siebert, 1994; Siebert et al., 2010). The last magmatic eruption occurred in August 2012-October 2013 with the formation of a new dome. The volcano is on a state of volcanic unrest since this episode (GeoNet) and small phreatic eruptions have occurred in April and September 2016, ejecting mostly hydrothermally altered material from the conduit.

Magma chambers feeding the eruptions during the last 40 years are thought to be as shallow as 500 m below the surface (Clark et al., 1979). There is also evidence of deeper chambers beneath the central part of the volcano, at depth between 1-2 km and 2-7 km (Houghton and Nairn, 1989a; Cole et al., 2000). A multi-magma chamber model has been proposed by different studies, involving deep storage of mafic melt and shallower levels of chambers where melt differentiation, mixing and contamination occur to different degrees (Cole et al., 2000).

The first estimate of SO₂ emission rate at White Island was done by Radke (1982) using the treated filter method and yielded to a value of 150 t/d. Soon after, Rose et al. (1986) did the first measurements using airborne correlation spectrometry (COSPEC). They repeated the study three different times, allowing estimates of the long-term emission rate (~ 350 t/d from November 1984 to January 1985) and higher emission rates prior to eruptive activity (1230 t/d in November 1983). CO₂, SO₂ and H₂S emissions have been measured ~ monthly since 2003 (Werner et al., 2008; Christenson et al., 2017).

2.3 The magmatic-hydrothermal system of White Island

Giggenbach (1987) described White Island as having a boiling lava surface at varying depth. Magmatic gases exsolving from it either reach the surface in the plume through the main volcanic conduit or discharge from fumaroles after interactions with an envelope of acid brines around the conduit, i.e. the hydrothermal system.

From the study of metal distribution in marine sediments around White Island, Giggenbach and Glasby (1977) concluded that the hydrothermal system must have been active for the past 10 ka. Recent studies (Giggenbach et al., 2003; Bloomberg, 2012; Christenson et al., 2017) have highlighted the presence of a sea water component in subsurface brine composition, thus indicating that the hydrothermal system is not totally isolated from the sea, as was first thought (Stewart and Hulston, 1975; Giggenbach and Sheppard, 1989). The numerous fumaroles and springs found at White Island are the surface expression of the hydrothermal system. The chemistry and temperature of the fumarole discharges have been studied and monitored for more than 40 years (Giggenbach, 1982, 1987; Giggenbach and Sheppard, 1989; Giggenbach and Soto, 1992). From these, Giggenbach and Sheppard (1989) estimated the composition of the magmatic gas phase to be 75 wt% H₂O, 18 wt% CO₂, 5 wt% SO₂ and 1.5 wt% HCl. Temperatures exceeding 770°C have been recorded close to the active vents. Studies of the Donald Mound fumarole show cyclic behavior with periods of high temperature emissions (up to 700 °C) having a magmatic signature (CO₂, SO₂, H₂), alternating with cooler gases of hydrothermal composition (H₂S, CH₄). During heating periods, deposited HCl, HF and elemental sulfur are remobilized, leading to an increase in their emission until they are exhausted and the gas approaches magmatic composition (Giggenbach and Sheppard, 1989). The fumarolic gases are a mixture of hydrothermal fluids and magmatic gases. Fumaroles with decreasing percentages of magmatic gases with distance from the main active vent delineate the shape of the two-phase hydrothermal envelope. Giggenbach and Sheppard (1989) estimated the volume of magma required to maintain a steady-state degassing of 350 t/day of SO₂ on average over the lifetime of the hydrothermal system to be 250 km³. A crater lake intermittently occupies parts of the crater floor. It has been reported as far back as 1826, when settlers first landed on the island (Hamilton and Baumgart, 1959). Werner et al. (2008) and Christenson et al. (2017) showed that, when present, the crater lake is efficient at scrubbing magmatic gases. Such a lake was present at the beginning of the current study in April 2014 and it had completely dried up by the time of writing in February 2017, emphasizing the active character of the magmatic-hydrothermal system at White Island. Fumaroles and hot springs have also been reported on the coastline and underwater on the flanks of the volcano (Grace, 1975; GeoNet, 2001-2017).

Hydrothermal alteration of rocks is a very fast process due to the presence of acid gases and waters circulating in the sub-surface. Hedenquist et al. (1993) studied altered andesite ejected during eruptions in February 1988. The rocks were free of ash at the time of collection, implying a recent eruption, given the frequent ash emission during that period. However, the samples showed signs of alteration at vesicle margins and in fracture selvages. The fractures were filled with alunite, anhydrite, kaolinite and isolated crystals of pyrite. The rock closely surrounding those veins (few millimeters) was completely altered, recrystallized into cristobalite containing some opal-CT phenocrysts with 2-3 wt% Al_2O_3 , 0.9-1.8 wt% Cl, traces of Fe and S. Alteration is thought to have taken place at around 380 °C, as indicated by S-isotope geothermometry of minerals from the veins.

Only a few data for aerosols are available for White Island. Rose et al. (1986) carried out a study using a cascade impactor to study the mineralogy and size of the particles emitted within the volcanic plume. They showed that the majority of the particles in the plume is less than 1 μm in diameter, with the volcanic contribution consisting of H_2SO_4 , FeCl_3 and NaCl. The likely contribution of sea aerosols in the form of salts was however not quantified. Compared to similar sampling at other volcanoes, the authors found that the proportion of particles at White Island is very low (Casadevall et al., 1984; Chuan et al., 1986). They suggested the scrubbing of gases by hydrothermal fluids, the lower temperature of the vapors, or the higher emission velocity as possible explanations. Since the development of spectroscopic methods, fluxes of major volatile species are now well constrained. The sulfur dioxide emission rate has a low-activity average of 300 t/day and can rise up to 2075 t/d during eruptive events and unrest (Christenson et al., 2017). The flux of carbon dioxide has been varying between 500 and 2600 t/d since 2004 (Wardell et al., 2001; GeoNet, 2001-2017; Werner et al., 2008). Emission rates of 275 t/d for HCl and < 1 t/d for HF were reported by Love et al. (2000), higher than the 125-89 t/d, 150 t/d and 70-80 t/d of HCl estimated by Christenson et al. (2017), Werner et al. (2008) and Rose et al. (1986) respectively.

Using the average emission rate of SO_2 , different studies have estimated the trace metal fluxes into the atmosphere. The following emission rates were determined over 16 years using various methods: Pb = 3-125 kg/day, Bi = 1.5-6 kg/day, As = 11.2-140 kg/day, Sb = 1.6-4 kg/day (Patterson and Settle, 1987; Tedesco and Toutain, 1991; Le Cloarec et al., 1992; Wardell et al., 2008).

2.4 The 1976-2000 eruptive cycle

The 1976-2000 cycle is the longest eruptive sequence observed at White Island since the arrival of Europeans. The development of techniques during this period allowed scientists to collect invaluable samples and information throughout the eruptions. This gives us the opportunity to investigate the magmatic processes involved into the injection of fresh mafic magma in the system.

A large body of magma started to rise to the shallow crust beneath White Island in mid-1973. The emplacement, at a depth of around 0.5 km, lasted until 1976 (Clark and Cole, 1989). The eruptive cycle began on 18 December 1976 with phreatic and phreatomagmatic, vent clearing events (Clark et al., 1979; Houghton et al., 1983; Houghton and Nairn, 1989c; Nairn and

Houghton, 1989). Emissions of ash and steam continued for two months leading to the formation of a crater of ~160 m diameter and 100 m depth. Tephras consisted mostly of hydrothermally altered material until 25 January 1977, after which ejecta was mainly juvenile. The first blocks (< 10 cm) were ejected between January 25 and February 15 but it was not until March 12 that vigorous eruptions produced bombs and blocks up to 3 m length (Clark et al., 1979; Houghton et al., 1983; Houghton and Nairn, 1989c). The strongest explosive activity occurred between March 12 and March 25, before resuming to vigorous incandescent ash emissions until the end of April 1977. Almost continuous eruptions, alternating between strombolian and phreatomagmatic, took place until 1982. A crater of 300 m diameter and 250 m deep, later named the 1978 crater complex, resulted from the five years eruption (Houghton and Nairn, 1989a).

The material erupted at the beginning of the cycle in March-April 1977 was characterized by high-Mg bombs and blocks rich in Ni and Cr compared to historic rocks (olivine crystals account for high Mg and Ni, while chromite crystals in phenocrysts and groundmass glass account for high Cr). The isotopic signature also differed, with lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio and higher $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (Graham and Cole, 1991; Cole et al., 2000). Although erupted at the same time, bombs and blocks slightly differ in composition, mineral assemblage and groundmass texture. The denser material was more mafic (~56 wt% SiO_2 against ~58 wt% SiO_2 for bombs), bearing up to 6.2% forsteritic olivines (Fo_{90-92}) (Clark et al., 1979; Clark and Cole, 1986; Cole and Graham, 1989; Graham and Cole, 1991; Shiraki et al., 1994). Clark et al. (1979) suggested that the bombs may originate from the top of the magma column, highly vesiculated and containing lighter plagioclase crystals. The blocks, however, were from the core of the magma column, containing the heavier olivine and magnetite crystals. Nevertheless, the chemical and isotopic signatures of the bombs and blocks are evidence for a more mafic source for the March-April 1977 eruptions compared to historic rocks. The pyroxene and plagioclase phenocrysts formed in a more evolved melt, suggesting different stages of crystallization, in accordance with the multiple magma chambers model. The reverse zoning exhibited by many pyroxenes and plagioclases reinforces this hypothesis. Shiraki et al. (1994) argued that the 1977 ejecta were the products of mixing of high-Mg basaltic andesite injected prior to the eruption with residual dacite supplying plagioclase and pyroxene phenocrysts. The high-Mg basaltic-andesite magmas are thought to form at or near the slab-mantle wedge interface by hydrous melting of the mantle, metasomatized by fluids from the subducting slab (Cole et al., 2000). After a rapid rise through the mantle and lower crust, they reach shallow (e. g. 300 m to 7 km) chambers where dacite melt is stored. Mixing and crustal contamination can occur, as evidenced by xenoliths (microdiorite, gneiss, quartzose) and magma mingling in some of the ejecta (Graham and Cole, 1991; Shiraki et al., 1994; Cole et al., 2001).

The activity resumed in February 1986, with continuous gas emissions and frequent phreatic, phreatomagmatic and Strombolian events until May 1992. New craters formed within the 1978 crater complex. Similar eruptive cycles, alternating between phreatomagmatic and Strombolian events, crater collapse and clearing events, occurred in 1993-1994, 1998-1999 and 2000. A Strombolian eruption in July 2000 marked the end of the eruptive sequence (Smithsonian Institution, 1976-2000). The total volume erupted between 1976 and 2000 was estimated at $\sim 10^7 \text{ m}^3$ (Houghton and Nairn, 1989b; Scott, 1992)

Wood and Browne (1996) showed that the juvenile rocks from the 1991-1992 eruptions were not as rich in Mg, Ni and Cr as the 1977 ejecta, implying differentiation of the mafic melt during the eruptive cycle. The phenocryst assemblage is nevertheless similar, with orthopyroxene, plagioclase and clinopyroxene as major minerals. Olivine is present in most of the rocks in small amounts. Other minor phases include spinel and apatite. Rapien (1998) studied ejecta from 1977, 1988, 1989 and 1991 eruptions. She showed that plagioclases fall in the field of labradorite (An_{62-68}), orthopyroxenes are enstatite (En_{69-72} , Fs_{23-26} , Wo_{3-5}) and clinopyroxenes are augite (En_{45-46} , Fs_{14-16} , Wo_{38-40}). The groundmass glass is sometimes microlite-free, whereas acicular microcrysts of pyroxene, plagioclase and spinel are present in some samples. H_2O , CO_2 , S and Cl contents of melt inclusions and matrix glass have been reported in different studies. On the basis of melt inclusion studies, fumarolic gas compositions and emission rates, Hedenquist et al. (1993) and Rapien et al. (2003) suggested that White Island has the characteristics to produce a porphyry copper deposit throughout its cooling history.

Melt inclusion studies have led to estimates on depth and temperature of the magma chamber. Wardell et al. (2001) suggested an entrapment pressure of 35 to 70 bars due to the low water content they measured in plagioclase- and clinopyroxene-hosted melt inclusions from the 1986 and 1988 eruptions. This is consistent with the depth of < 500 m inferred for the shallower magmatic chamber beneath White Island (Clark et al., 1979; Clark and Cole, 1989). However, this study did not consider olivine-hosted melt inclusions, likely to have been trapped deeper in the system. Rapien (1998) estimated a temperature of ~1100 °C from coexisting pyroxenes (Lindsley and Andersen, 1983) and 1210 °C from homogenization of melt inclusions from 1991 eruption. Using the rhyolite-MELTS software package (Gualda et al., 2012), Esposito et al. (2014) found a liquidus temperature of 1131 °C. Recently, Kilgour et al. (in prep) estimated crystallization temperatures for the different phenocrysts to be ~ 1210 °C for olivine, ~ 1054 °C for orthopyroxene, ~ 999 °C for plagioclase and ~ 982 °C for clinopyroxene.

2.5 Recent eruptions

A new eruptive episode started on 5 August 2012 with emissions of ash, mud and blocks during a small phreatomagmatic eruption (GeoNet, 2012-2013). The rise of fresh magma within the conduit was later indicated by the growth of a spiny lava dome of about 20-30 m diameter within the active crater (Figure 2-4 a and b).

Figure 2-4: Pictures of the 2012-2013 eruptive sequence. a) Aerial pictures of the active crater showing most of the lake had dried by the end of 2012 and a spiny lava dome had formed. b) Close up picture of the lava dome. c) Activity within the south-west pond during January 2013 in the form of expansion and fragmentation of dome-shaped viscous material. d) Dome-shaped viscous liquid during fragmentation and release of steam. e) Vigorous fountaining activity ejecting yellowish material (most likely rich in elemental sulfur) up to 30 m high. f) Aerial picture of the active crater in March 2013 showing the two different active zones. The vent near the lava dome is emitting a dilute blueish plume whereas the furthest vent emits steam. Photos courtesy of GNS.

This dome is thought to have formed mid-November of 2012, and soon became associated with high temperature gas emissions ($> 450\text{ }^{\circ}\text{C}$). This activity was accompanied by changes in the crater lake: the level was high prior to the eruptions in August and rapidly decreased leaving only small ponds distributed across the active crater by the end of 2012. Temperature estimates from late December indicated strong variations between the small lake adjacent to

the dome and a more distant pond (71 °C and 35 °C). Gas fluxes measured at the same time were 400 t/d of SO₂ and 1300 t/d of CO₂. These fluxes slightly increased in 2013, with values up 600 t/d of SO₂ and 2000 t/d of CO₂ at the end of January. The activity in early 2013 was focused in one of the ponds, consisting of bursts of dome-shaped, highly viscous liquid (Figure 2-4 c and d) (Christenson et al., 2017). Towards the end of January, it evolved into spectacular fountaining of yellowish material up to 30 m high (Figure 2-4 e). Similar activity was observed throughout February. The crater lake started reforming in April 2013 following rainfall but disappeared again in June. An eruption occurred on August 20, producing a plume of steam rising up to 4 km. Small lakes soon refilled the crater and persisted until the last eruptions of the sequence in October 2013, depositing mud across the crater floor.

After more than 3 years of unrest, activity resumed in the evening of 27 April 2016 with a phreatic eruption (GeoNet, 2016). The crater floor and parts of the crater walls were covered with green-colored ash, most likely the top of the hydrothermal system consisting of altered andesite (Figure 2-5). No juvenile magma was erupted on that day. Another small phreatic eruption occurred on September 13 of the same year, giving rise to a small ash plume rising from the 2012 lava dome vent.

Figure 2-5: Picture of the crater floor covered by green-colored ash after the 27 April 2016 phreatic eruption. a) Aerial picture showing the extent of the deposit, covering almost all the crater floor and crater walls. b) Picture taken from within the crater. Photo courtesy of GNS.

Besides these two unexpected phreatic eruptions in 2016, the activity was reduced to quiescent degassing during the project timeframe, motivating our decision to study metal emissions at Yasur and Etna. The former is located in Tanna Island, in the southern Vanuatu archipelago. The series of volcanic islands extends over 1200 km following the eastward subduction of the Indo-Australian plate under the Pacific plate. Yasur, a basaltic trachyandesite scoria cone, rises 361 m above sea level and is part of the larger Siwi caldera (Chen et al., 1995; Métrich et al., 2011). The activity during the past several hundred years has been characterized by persistent degassing coupled with continuous Strombolian and sometimes Vulcanian explosions every 2 to 15 minutes (Firth et al., 2014). The presence of magma only meters below the surface suggests hydrothermal contribution to be minor compared to White Island.

Mount Etna is a 3330 m high stratovolcano located in the eastern coast of Sicily in Italy. Being the most active volcano in Europe, Etna is one of the world's largest SO₂ emitter owing to the persistent degassing of its volatile-rich alkaline basalts (Metrich and Clocchiatti, 1989; Allard, 1997; Caltabiano et al., 2004).

The knowledge acquired throughout the years on the hydrothermal system of White Island and its link to the volcanic activity sets a starting point for the present study. Focusing on metals, we will refine our understanding of volatile transport in subduction context by:

- Characterizing the magmatic system: what is the parental magma composition in terms of metals, and how degassing and mixing processes affect the repartition between the melt and any fluid phase.
- Studying the metal distribution at the surface through studies of various types of discharges, and constraining the metal speciation in these phases.
- Making a mass balance for the magmatic-hydrothermal system and comparing it to models obtained through thermodynamic calculations to emphasize processes taking place in the subsurface environment.

Chapter 3: Magma mixing, volatile degassing and late sulphide saturation: Insights into the 1976-2000 eruptive sequence at White Island

3.1 Introduction

The composition of primary magma at depth is an essential parameter controlling the processes happening during the rise and evolution of the melt. It is also one of the most difficult to assess. Volatiles are of special interest due to their role in influencing the eruptive style of a volcano (Wilson, 1980; Woods and Koyaguchi, 1994; Roggensack et al., 1997; Huppert and Woods, 2002; Stock et al., 2016), as well as transporting other species, such as metals (Lowenstern et al., 1991; Williams-Jones et al., 2002; Harris et al., 2003; Foustoukos and Seyfried Jr, 2007; Sherman, 2010; Henley and Berger, 2013; Migdisov et al., 2014). Silicate melt inclusions are small droplets of magma trapped within crystals during their growth. The phenocrysts, due to their incompressible properties, act as pressure vessels and ensure the preservation of inclusions during eruption. Melt inclusions hence provide information on the melt prior to eruption, during the early stages of crystallization at magmatic pressure and temperature (Harris and Anderson, 1983; Roedder, 1984; Anderson et al., 1989; Lowenstern, 1995; Sobolev, 1996; Frezzotti, 2001; Lowenstern, 2003). Inclusions hosted in the first minerals to crystallize, deep in the system (i.e. olivines), are assumed to represent the closest composition to the primary magma. Studies of these archives provide insights into dissolved volatile and metal contents during magma ascent and crystallization (Takenouchi and Imai, 1975; Anderson et al., 1989; Lowenstern, 2003). Combined with petrologic studies, they also highlight the evolution of the magmatic system throughout passive degassing and eruptive activity.

As described in Chapter 2, the December 1976 eruption at White Island was the beginning of a period of eruptive activity that ended in July 2000 (Houghton and Nairn, 1989a). Phreatic, phreatomagmatic and Strombolian events succeeded one another during that time frame. Here, we present results of petrologic and chemical studies of ejecta from the 1976-2000 eruptive sequence.

3.2 Samples and analytical methods

3.2.1 Samples

The samples used in the study come mainly from the GNS archive, and collections of Prof. Jim Cole and the late Werner Giggenbach. They consist of nine scoria bombs covering the 1976 to 2000 eruptive cycle, and two blocks erupted in March 1977 (Table 3-1). All the samples were collected shortly after eruption, hence minimizing hydrothermal alteration. The precise date of eruption is not known for each sample as the access to the island at that time was limited. Eruptions occurring during clear days were reported by people from the Bay of Plenty but periods of unsettled weather in March 1977 made any visit to the island, and

inland observation, difficult (Clark et al., 1979). Five of the rocks studied were collected on April 4th and had been erupted over the period from 12th to 25th of March. Strong activity was reported both from land and during flights over the island during that time. There is however a lack of information to constrain the date of eruption of each sample and to assess the relative chronology between the different bombs and blocks. Two samples were collected during a visit on August 3rd 1977. The crater was then covered with blocks and bombs up to 1m diameter most likely erupted on 29-30 July. Also part of the study is one sample erupted in 1992 and collected by Werner Giggenbach. One of the bombs was collected on October 22nd 1993, after the vent clearing, phreatic eruption of October 19th. Bombs and blocks of up to 2m diameter were erupted during the 17 April 1999 eruptions. One ballistic, collected during a visit on 20 April, was analyzed in this study. The last sample was ejected on July 27th 2000, during what was the last eruption of the cycle, and also the largest one in the past 20 years (Smithsonian Institution, 1976-2000; IGNS, 1986-2001).

2.5.1 Major elements and volatiles

Polished sections were used for microscopic observations and imaging, as well as chemical analyses. A JEOL JXA-8230 Superprobe was used to determine major and volatile (Cl, S and F) element compositions by electron probe microanalysis (EPMA). Melt inclusions and matrix glass were analyzed using 15 kV, 8.0 nA current and a defocused beam with a spot size of 10 μm to minimize Na loss. A bigger spot size was used in matrix glasses containing microlites to encompass the variation in composition due to crystallization. The bulk composition (i.e., residual glass + microlites) was, for these samples, analyzed using a 30 μm beam. Analyses were standardized using rhyolitic glass VG-568 for Si, Al and K, basaltic glass VGA-99 for Ca, Na, Ti, Mg and Fe, synthetic pure oxides for Cr and Mn, Beson apatite for P, fluorite for F, scapolite for Cl and pyrite for S. On-peak counting times were as follows: 15 s for Na, 60 s for S, Cl and F, 30 s for Si, Ca, K, Al, Mg, Fe, Ti, Mn, Cr and P. Na was measured first without peak search to minimize volatilization under the beam. Reference glasses VGA-99 and VG-568 (Jarosewich et al., 1980) were used to verify analyses and gave the following uncertainties: 2% RSD < 8% for alkalis, < 4% for TiO_2 , < 3% for Mg and FeO_t , < 2% for SiO_2 , Al_2O_3 , CaO, 15% for Cl, 21% for P_2O_5 , 24% for MnO and 29% for S.

Olivine crystals were analyzed using 15 kV, 20 nA current and a focused beam. Analyses were standardized using San Carlos NMNH-111312-44 (Jarosewich et al., 1980) olivine for Si, Mg and Fe, Kakanui augite NMNH-122142 (Jarosewich et al., 1980) for Ca, synthetic oxides for Cr, Mn and Ni. On-peak counting times were 30 s for all elements. Reference San Carlos NMNH-111312-44 and Springwater olivine USNM-2566 (Jarosewich et al., 1980) were used to verify analyses and gave the following uncertainties: 2% RSD < 1% for SiO_2 , FeO_t and MgO, 8% for MnO and 6% for NiO.

Table 3-1: Description of samples

Date erupted	Date collected	Sample	Description	Microlite	Small vesicles Spherical	Big vesicles Uneven	Olivine	Fo	Spongy core plagioclase	Normal Zoning	Reverse zoning	Cr-Fe Spinel	Fe ± Ti oxides	Cu-Fe Sulfide
12-25/3/1977	4/4/1977	WIDP 6	Dense black block on edge of crater impact. Not altered.	Y ++	+	+	++	76-78, 90-93	Y	Y	N	Gdm, Ol, Px	Gdm, Opx	N
		WIDP 6 dacitic enclave		Y + (Pla only)	++	+	N		N	N	Y	N	++ Gdm, Opx	N
12-25/3/1977	4/4/1977	WIDP 18	Dense black block.	Y	Nd	Nd	++	~ 90	Nd	Nd	Nd	Nd	Nd	Nd
12-25/3/1977	4/4/1977	WIDP 10	Highly vesiculated grey scoria. Outside quite altered.	N	++	+	+	76-78	Y	N	Y	Gdm, Ol, Px	Cpx	Pla, Gdm
12-25/3/1977	4/4/1977	WIDP 11	Highly vesiculated dark grey scoria. Outside altered.	N	+	++	N		Y	N	N	Gdm, Px	N	N
12-25/3/1977	4/4/1977	WIDP 13	Highly vesiculated black scoria. Not altered.	Y	+	+	+	76-78	Y	N	Y	Px	Cpx, Gdm	Pla
26/7-3/8/1977	8/3/1977	WIDP 9	Highly vesiculated black scoria. Not altered.	Y	+	++	+	76-78	Y	N	Y	Px	Gdm	N
26/7-3/8/1977	8/3/1977	WIDP 8	Highly vesiculated dark grey scoria. Outside altered.	N	+	+	+	76-78	Y	N	Y	Px	Gdm, Pla, Px	Pla
1992	1992	WIDP 17	Highly vesiculated dark grey scoria. Outside altered.	N	++	++	+	76-78	N	N	Y	Px	N	N
10/19/1993	10/22/1993	WIDP 4	Dense vesicular fresh andesite from a broken bomb. Not altered.	Y	+	+	++	91-92	Y	Y	N	Gdm, Ol, Px	Gdm	MI
4/17/1999	4/20/1999	WIDP 7	Black scoria bomb. Not altered.	Y	+	+	+	79-80, 91-92	Y	N	Y	Gdm, Ol	Gdm	N
7/27/2000	7/31/2000	WIDP 3	Dense dark grey scoria. Outside altered.	Y (few)	+	+	+	76	Y	N	N	Gdm, Ol, Px	Gdm	Opx

Notes: Nd: Not determined. Gdm: Groundmass glass. Ol: Olivine. Px: Pyroxene. Cpx: Clinopyroxene. Opx: Orthopyroxene. Pla: Plagioclase. MI: Melt Inclusion. Y: Yes. N: No. +, ++: relative abundance.

Semi-quantitative composition maps of Cu-Fe sulphides were acquired using the same instrument, in WDS mode with a beam current of 20 nA. For sulphides larger than 10 μm , maps were done on stage mode, with a pixel size set to 0.2 μm , and dwell time to 500 ms. For smaller sulphides, the beam mode was used, with a dwell time of 300 ms and 100 x 100 pixels square. The Cu-Fe sulphide compositions were measured with a focused beam, 15 kV, 20 nA, and using pyrite, galena, scapolite and metal standards (pure Cu, Ni, Ag, Au, Zn, Co, Mo). Counting time was 30 s for Cu, Fe and S and 60 s for all the other elements. The pyrite standard was used to verify analyses yielding to the following uncertainties: 2% RSD < 2% for S and Fe. Unfortunately, no copper sulfide standard was available to assess the accuracy of standardization with metal Cu. The analyses should thus be regarded as semi-quantitative.

3.2.2 Water

Phenocrysts from 3 rocks (WIDP 3, WIDP 4 and WIDP 18) were hand-picked from crushed material. Plagioclase, pyroxene and olivine crystals containing melt inclusions apparently unaffected by cracks were mounted separately onto glass slides using Crystalbond™ 509. Crystals were ground using P2500 wet silicon carbide paper until the melt inclusions were exposed. They were then polished with 3 μm and 1 μm diamond DP-suspension. In order to expose the second side of the inclusions, samples were reheated on a hot plate and the crystals were flipped over. Grinding and polishing of the second side was repeated. Parallel polishing of the crystals was controlled by looking at interference colors under crossed-polarized light. Doubly polished wafers were removed by dissolving the Crystalbond™ with acetone.

Samples were analyzed by transmission FTIR spectroscopy using a Nicolet 6700 FTIR spectrometer coupled to a Nicolet Continuum FTIR Microscope and OMNIC software at Massey University, Palmerston North, New Zealand. Absorbance at $\sim 3550\text{ cm}^{-1}$, the fundamental O-H stretching vibration, was used to estimate total H₂O content. Peak heights were measured after applying a linear baseline.

The Beer-Lambert law was used to convert absorbances into H₂O concentrations (wt%):

$$c = MA/d\rho\epsilon$$

where M is the molar mass of the H₂O ($\text{g}\cdot\text{mol}^{-1}$), A is the height of the absorbance peak, d (μm) and ρ ($\text{g}\cdot\text{cm}^{-3}$) are the thickness and density of the melt inclusion, respectively, and ϵ ($\text{mol}^{-1}\cdot\text{cm}^{-1}$) is the molar absorption coefficient.

The absorption coefficient for the $\sim 3500\text{ cm}^{-1}$ band was chosen according to the melt inclusion composition. A value of $68\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ was used for dacitic inclusions in plagioclase and pyroxene (Yamashita et al., 1997) whereas $70\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ was used for andesitic inclusions hosted in olivine (King et al., 2002). Three olivine-hosted inclusions were more mafic and the value of $63\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ from Dixon et al. (1988) was used.

The glass densities were estimated following the calculations of Best (2003), as a function of bulk composition, temperature and pressure. The partial molar volumes are from Lange and Carmichael (1990), Lange (1997) and Ochs and Lange (1997). Values range between 2.46

and 2.82 g.cm^{-3} . Spacing between interference fringes in the region $2000\text{-}2700 \text{ cm}^{-1}$ in reflectance spectrum (Wysoczanski and Tani, 2006) was used to estimate sample thickness. Only one sample showed no interference fringe. We measured its thickness using an Insize micrometer with an accuracy of $\pm 2 \text{ }\mu\text{m}$. The doubly exposed wafers of olivine-hosted melt inclusions were very fragile. For this reason, we kept the inclusions either partially exposed or unexposed and measured their thickness with the method described by Nichols and Wysoczanski (2007). This method involves two subsequent analyses, one of the unexposed or partially exposed inclusion, and one of the host olivine only. The latter causes peaks in the region between 2000 cm^{-1} and 1600 cm^{-1} . Given that the peak height at 2000 cm^{-1} and the amount of olivine in the beam path are proportional, the proportion of the inclusion is calculated by comparing peak heights with and without it. The inclusion thickness is finally derived from the wafer thickness estimated with interference fringe patterns. The refractive index was calculated using the glass composition for the melt inclusions, and the forsterite content for the host olivine. Errors associated with FTIR analysis have been estimated to be $\pm 10\%$ for H_2O (Dixon et al., 1988; Dixon et al., 1995; Macpherson et al., 1999; Agrinier and Jendrzewski, 2000; Danyushevsky et al., 2000; Wysoczanski and Tani, 2006; Wysoczanski et al., 2006).

3.2.3 Trace elements

Melt inclusions and matrix glass were analyzed for trace elements by Laser Ablation ICP-MS (LA-ICP-MS) at Victoria University of Wellington, using a RESolution S155-SE, 193nm excimer laser coupled with an Agilent 7500CS quadrupole ICP-MS in dual detector mode. The laser is equipped with a dual volume cell, allowing ablation to take place in a small volume (wash-out time of 5-7 s). Reference material NIST SRM 612 was used to tune the ICP-MS to high sensitivity, keeping low oxide formation ratio ($\text{ThO}^+/\text{Th}^+ < 5\%$). The ablation was performed in helium environment to enhance the transport efficiency (Gunther and Heinrich, 1999). Each ablation lasted 40 s and was preceded by 30 s of instrument background measurement. Argon and nitrogen were mixed to the carrier gas at the exit of the ablation cell. A N_2 flow of 2 mL.min^{-1} was found to improve the sensitivity in the higher masses. A spot size of $25 \text{ }\mu\text{m}$ was used for the majority of samples. For inclusions with a smaller diameter, the spot size was reduced to $20 \text{ }\mu\text{m}$ or $15 \text{ }\mu\text{m}$. The analytical parameters are listed in Table 3-2. USGS synthetic basalt glasses were used, GSE-1G for standardization, and GSD-1G to verify the analyses (Jochum et al., 2005). We chose Si as the internal standard to calculate absolute values. The reproducibility was assessed in inclusions large enough for multiple ablations. Analytical precision for each element (1% RSD) and deviations of analyzed GSD-1G from preferred values are presented in Appendix A.1.

Table 3-2: LA-ICP-MS analytical parameters

Laser setup		ICP-MS setup	
Laser energy	5 mJ	RF Power	1500 W
Attenuation	25 % T	Carrier gas	0.91 L×min ⁻¹
Spot size	15, 20, 25 µm	Octopole bias	-8.4 V
Repetition rate	5 Hz	Quadrupole bias	-6.7 V
Ablation cell gas	He, 400 mL×min ⁻¹	Dwell times	10-30 ms
Carrier gas	N ₂ , 2 mL×min ⁻¹ , Ar, 910 mL×min ⁻¹	Cones	Aluminum
		Elements	⁷ Li, ¹¹ B, ²⁹ Si, ⁴³ Ca, ⁴⁵ Sc, ⁴⁷ Ti, ⁵¹ V, ⁵³ Cr, ⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁵ Cu*, ⁶⁶ Zn, ⁶⁹ Ga, ⁷⁵ As, ⁸² Se, ⁸⁵ Rb, ⁸⁶ Sr, ⁸⁸ Sr*, ⁹⁵ Mo, ⁹⁸ Mo*, ¹⁰⁷ Ag*, ¹⁰⁹ Ag, ¹¹¹ Cd, ¹¹⁸ Sn*, ¹²⁰ Sn, ¹²¹ Sb, ¹³⁷ Ba, ¹⁷² Yb, ¹⁸² W, ¹⁸⁵ Re, ¹⁹⁷ Au, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi, ²³⁸ U

Notes: * Isotope used

3.3 Results

3.3.1 Whole rock and phenocrysts

All the rocks are glomeroporphyritic andesites with phenocrysts of plagioclase, clinopyroxene and orthopyroxene. A summary of their textural and structural characteristics is presented in Table 3-1. Whole rock compositions for some of the ejecta were analyzed by Peter Wood at GNS, New Zealand (Mike Rosenberg, pers. comm. 2016) and Séverine Moune at the Laboratoire Magmas et Volcans, France (G. Kilgour, pers. comm.) (Table 3-4). Figure 3-1 shows that the 1976-2000 rocks are highly magnesian compared to historic rocks at White Island, as observed by Cole and Graham (1989). Only one scoriaceous block, erupted in October 1991, plots in the dacitic composition. All the other samples are basaltic-andesite and low SiO₂ andesite. The combination of the overall small volume erupted during the sequence (10⁷ m³ in 1976-1990, between 10⁴ and 10⁵ m³ in 1990-1994 and 1997-2000 (Houghton and Nairn, 1989b; Scott, 1992)) and the basaltic-andesite composition of the ejecta suggests this sequence was a minor explosive eruption following the classification of Clark et al. (1979) and Cole et al. (2000). The rarity of this type of ejecta in historic rocks is explained by the small volume produced as compared to the major andesite-dacite lava-flow eruptions. Concentrating on this sequence thus deprives us of the study of metals evolution through differentiation into more evolved magmas.

Some of the samples present microlite-free matrix glass whereas others contain plagioclase and pyroxene microlites. Bombs are vesicular to highly vesicular (~40% to ~70% vesicles) whereas the 1977 block is denser (~20% vesicles). Some samples exhibit large, uneven globular vesicles, evidence of nucleation, growth and coalescence, coexisting with smaller roundish bubbles. The latter are thought to form later, before coalescence can occur.

Figure 3-1: White Island historic and 1976-2000 whole rock. a) TAS diagram (Bas et al., 1986). b) MgO versus SiO₂. Data for historic rocks from Cole et al. (2000).

Clinopyroxene and orthopyroxene phenocrysts range in size from 0.5 mm to 5 mm and are mostly euhedral to subhedral. Crystal rims with normal and reverse zoning are found in different rocks (Table 3-1). Plagioclase crystals have a similar size range, although two types of crystals are found: 1) subhedral to euhedral crystals with compositional zoning, and 2) subhedral to euhedral crystals with spongy cores, surrounded by rims with compositional zoning. Olivines are present in 9 samples out of 11 as a minor phase ($\leq 1\%$). Two distinct populations of olivine were observed, as shown in Figure 3-2.

Figure 3-2: Backscattered electron image of olivine Fo76 and olivine Fo92 coexisting in one of the March 1977 bomb, WIDP 6. Note the resorption and recrystallization of orthopyroxene (grey) and plagioclase (dark grey) of the Fo76 olivine. The “white” minerals in the Fo92 olivine are Cr-rich spinel.

The first olivine population, present in only 4 samples, consists of small euhedral to subhedral (100-500 μm) crystals, although some larger skeletal phenocrysts (up to 2.5 mm) occur, implying a rapid growth rate. Microprobe analyses gave compositions ranging from Fo90 to Fo93 (Table 3-3). These highly magnesian olivines are thought to originate from the

slab-mantle interface, implying a rapid rise of the magma to the surface to preserve the phenocrysts (Cole et al., 2000). The second population, found in 8 samples, consists of partly resorbed olivine, recrystallized as orthopyroxene and plagioclase. They are less primitive, with composition ranging from Fo76 to Fo80. These differences in composition imply crystallization from melts at different stages of differentiation.

Fe oxides and Fe-Ti oxides are present in the matrix glass of all the rocks apart from WIDP 10, WIDP 11 and WIDP 17 (see Table 3-1). They are also sometimes found as inclusions in pyroxenes or plagioclases. Cr-rich spinels are found in all the rocks, as inclusions in phenocrysts of olivine whenever present, and in pyroxenes. They are also found in the groundmass glass of all the rocks except WIDP 13, WIDP 9 and WIDP 8 from March and July-August 1977 eruptions. A dacitic enclave found in the March 1977 block WIDP 6 contains the largest population of Fe-Ti oxides in the matrix glass and in pyroxenes but is free of Cr-spinel.

Table 3-3: Olivine core compositions (wt%)

Sample	SiO ₂	Cr ₂ O ₃	FeO	MnO	MgO	NiO	CaO	Total	Fo
WIDP3_OI21	38.21	0.02	21.55	0.27	38.79	0.27	0.19	99.30	76
WIDP4_OI07	40.34	0.30	7.77	0.13	50.37	0.24	0.18	99.34	92
WIDP4_OI11	40.38	0.07	8.46	0.11	50.07	0.23	0.19	99.51	91
WIDP4_OI15	40.40	0.07	8.97	0.14	49.82	0.23	0.27	99.89	91
WIDP4_OI18	40.68	0.15	8.28	0.12	50.15	0.25	0.20	99.81	91
WIDP4_OI20	40.35	0.10	8.53	0.14	50.19	0.28	0.23	99.83	91
WIDP4_OI24	40.53	0.09	8.10	0.12	50.34	0.24	0.16	99.58	92
WIDP4_OI25	40.60	0.11	8.30	0.14	49.99	0.26	0.18	99.58	91
WIDP6_OI01	40.55	0.07	9.09	0.13	49.03	0.29	0.17	99.35	90
WIDP6_OI 02	40.36	0.05	10.64	0.16	47.94	0.21	0.19	99.55	89
WIDP6_OI03	40.79	0.08	8.34	0.11	50.11	0.31	0.18	99.91	91
WIDP6_OI04	38.61	0.01	20.38	0.29	39.50	0.26	0.17	99.22	77
WIDP6_OI05	38.24	0.01	21.07	0.26	38.90	0.27	0.19	98.94	76
WIDP7_OI01	38.06	0.02	18.25	0.25	40.92	0.14	0.16	97.80	80
WIDP7_OI02	38.02	0.05	18.51	0.26	40.64	0.16	0.15	97.79	79
WIDP7_OI03	38.10	0.01	19.21	0.25	40.27	0.16	0.19	98.19	79
WIDP7_OI04	40.05	0.12	8.46	0.14	49.43	0.16	0.19	98.55	91
WIDP7_OI05	40.39	0.17	7.70	0.13	50.10	0.17	0.17	98.83	92
WIDP10_OI24	38.47	0.02	20.35	0.28	40.43	0.22	0.18	99.95	78
WIDP18_OI03	40.21	0.12	6.99	0.12	51.73	0.29	0.18	99.64	93
WIDP18_OI20	40.60	0.01	7.33	0.11	50.74	0.21	0.23	99.23	92
WIDP18_OI19	40.00	0.08	8.18	0.12	50.82	0.21	0.20	99.60	92
WIDP18_OI10	40.45	0.09	7.39	0.12	50.51	0.29	0.17	99.03	92

Table 3-4: Whole rock compositions (wt%)

Eruption	Type	Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Total
March 1977	Andesite block	P41600	55.84	0.63	13.24	1.76	5.73	0.14	10.12	8.94	2.39	1.14	0.07	100.00
March 1977	Andesite block	26592	55.95	0.61	13.48	8.40	-	0.11	9.26	8.63	2.30	1.19	0.07	100.00
March 1977	Scoria bomb	P41599	57.84	0.65	13.95	1.52	5.51	0.12	7.81	8.50	2.57	1.45	0.08	100.00
March 1977	Scoria bomb	26589	57.63	0.60	13.80	7.88	-	0.17	7.88	8.10	2.44	1.38	0.11	99.99
July-August 1977		26595	58.55	0.63	14.04	-	6.86	0.12	7.57	8.21	2.50	1.42	0.10	100.00
May 1979		7905JWC	58.39	0.63	13.55	-	7.27	0.14	7.55	8.39	2.49	1.46	0.13	100.00
1986		860210	57.45	0.62	13.72	7.65	-	0.13	7.23	8.02	2.64	1.43	0.08	98.98
1988		880210	57.24	0.6	13.73	7.73	-	0.13	7.42	8.38	2.41	1.34	0.08	99.06
1989		891129	57.24	0.62	13.43	7.98	-	0.14	7.94	8.23	2.36	1.36	0.09	99.38
August 1991		23411A	58.01	0.57	13.68	7.79	0.00	0.13	7.81	8.21	2.35	1.36	0.09	100.00
August 1991		23142A	58.29	0.62	13.86	7.57	0.00	0.13	7.38	8.08	2.54	1.44	0.10	100.00
October 1991	Scoriaceous block	911023B	63.58	0.68	14.75	6.34	-	0.09	3.50	5.68	3.06	2.19	0.12	99.99
November 1991	Scoria bomb	911128	58.01	0.57	13.53	7.83	-	0.14	7.80	8.29	2.38	1.35	0.09	99.99
December 1991	Scoria bomb	911206A	57.70	0.58	13.84	7.66	-	0.13	7.58	8.29	2.79	1.36	0.08	100.01
January 1992	Scoria bomb	920100	57.95	0.57	14.00	7.60	-	0.13	7.50	8.35	2.44	1.36	0.09	99.99
February 1992	Scoria bomb	920220	57.63	0.57	13.64	7.80	-	0.14	7.96	8.27	2.54	1.36	0.10	100.01
1992		920512	57.91	0.63	13.43	7.75	-	0.13	7.63	8.34	2.26	1.41	0.09	99.58
1994	Scoria bomb	WI16c*	57.82	0.62	13.76	8.49	-	0.13	7.65	8.32	2.45	1.31	0.10	100.65
July 2000	Scoria bomb	000731A	57.60	0.60	13.72	7.79	-	0.13	8.05	8.31	2.36	1.35	0.09	100.00
July 2000	Scoria bomb	000731B	57.69	0.62	13.66	7.77	-	0.13	7.95	8.27	2.46	1.37	0.09	100.00
July 2000	Scoria bomb	WI-18c*	56.63	0.62	13.14	8.87	-	0.14	9.54	8.46	2.28	1.15	0.09	100.92
July 2000	Scoria bomb	WI1c*	56.95	0.62	13.29	8.76	-	0.14	8.26	8.46	2.67	1.28	0.10	100.53

Notes: Data from Clark et al. (1979) and Peter Wood (M. Rosenberg, pers. comm.), besides * = data from Severine Moune (G. Kilgour, pers. comm.)

3.3.2 Melt inclusions

Melt inclusions are common in phenocrysts, ranging in size from 5 μm to >100 μm . A total of 204 melt inclusions were analyzed for major, volatiles (S and Cl) and trace elements. Olivine-hosted melt inclusions were corrected for post-entrapment crystallization (Sobolev and Danyushevsky, 1994) by incrementally adding (0.1%) olivine back into the melt inclusion until equilibrium with the host was reached. Given the low H_2O content of the melt inclusions, we used an exchange coefficient (K_D) value of 0.3 (Roeder and Emslie, 1970). Clark et al. (1979) analyzed the FeO and Fe_2O_3 content in a bomb and a block from the March 1977 eruptions. We used their average $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ value of 0.216 for the post-entrapment crystallization correction. The corrected melt inclusion compositions as well as the matrix glass compositions are shown in Appendix A.2.

Inclusions have SiO_2 content ranging from 48.20 wt% to 71.55 wt%, whereas matrix glasses range from 61.44 wt% to 67.68 wt%. The dacitic enclave in the March 1977 sample exhibits the highest SiO_2 content in the matrix glass, with 73.22 wt%. The continuous composition from mafic to more evolved melts (Figure 3-3) suggests a similar source of magma during the 1976-2000 eruptive sequence. Differentiation of mafic magma through crystallization of olivine, pyroxene, and plagioclase seems to explain the range of SiO_2 content observed. Olivine-hosted inclusions are the most primitive, while inclusions hosted in plagioclase and pyroxenes are more evolved.

The matrix glass in WIDP 13 (erupted in March 1977), WIDP 8 and 9 (erupted in July-August 1977) is more evolved than melt inclusions, as expected for differentiation through crystallization. In contrast, all the other rocks have matrix glass more mafic than previously trapped inclusions (Figure 3-3), implying that mixing with a more mafic magma occurred after melt inclusions entrapment. WIDP 7, erupted in April 1999, contains melt inclusions with the most evolved compositions (up to 71.55 wt% SiO_2). These trapped silicate melts are in the same range as the dacitic enclave found in the March 1977 block. This is consistent with the long break in activity within the sequence, the last sizeable eruption occurring in 1994. The unerupted magma left in the reservoir had time to differentiate, attaining these felsic compositions. The matrix glass has a markedly more primitive signature (64.36 wt% SiO_2), further suggesting the occurrence of magma mixing.

The sulfur content ranges from 16 ppm to 1332 ppm in melt inclusions and from 41 ppm to 105 ppm in matrix glasses. These values are greater than the maximum of 384 ppm reported by Rapien (1998); Wardell et al. (2001); Esposito et al. (2014), in accordance with their analyses of inclusions hosted in plagioclase and pyroxene only. Cl ranges from 410 ppm to 4388 ppm with most of the melt inclusions between 1000-2000 ppm, and matrix glass between 429 ppm and 1918 ppm. F was below detection limit (~ 420 ppm) in all the melt inclusions and matrix glasses. SIMS analyses by Rapien (1998) and Esposito et al. (2014) of melt inclusions from White Island ejecta (1977, 1986, 1988, 1991) resulted in F contents of 400-800 ppm and 163-169 ppm respectively.

Figure 3-3: SiO_2 versus MgO of melt inclusions and matrix glasses for separate rocks erupted during the 1976-2000 eruptive sequence.

Water content is available for only 23 melt inclusions, three of them being hosted in olivine phenocrysts, ranging from 0.21 wt% to 0.97 wt%. These low concentrations (< 1 wt% H_2O) are consistent with earlier findings (Rapien, 1998; Wardell et al., 2001; Esposito et al., 2014). The rarity of olivine crystals and the difficulty of finding melt inclusions larger than $10\ \mu\text{m}$ without bubbles or daughter crystals made it challenging to obtain H_2O data for the deep crystallizing magma. The water content of melt inclusions hosted in olivines from the 1977 block WIDP 18 are very low and most likely reflect difficulties in analyzing melt inclusions smaller than $10\ \mu\text{m}$ with FTIR (Nichols and Wysoczanski, 2007). Five other olivine-hosted

melt inclusions were analyzed, giving the highest observed water contents (1.01-2.25 wt%). Their major element compositions were however affected by crystallization of daughter minerals after entrapment. As we did not proceed to homogenization of such inclusions containing shrinkage bubble and/or daughter minerals, these results were not included. They nevertheless witness higher water content for the most primitive melt, as we would expect.

No CO₂ was detected in any of the melt inclusions. Behrens et al. (2004) reported the difficulties in analyzing CO₂ with FTIR in intermediate magmas and recommended the use of SIMS. Previous studies of White Island rocks used the latter technique (Rapien, 1998; Esposito et al., 2014) showing CO₂ contents of 39 to 3508 ppm (mostly < 200 ppm) in melt inclusions hosted in plagioclase and pyroxene. The presence of a shrinkage bubble in olivine-hosted inclusions might also explain the very low concentration of dissolved CO₂ in the glass (Cervantes and Wallace, 2003; Wallace et al., 2015).

3.3.3 Cu-Fe sulphides

Cu- and Fe-rich sulphides were observed in 5 different samples: two bombs from March 1977, WIDP 10 and WIDP 13, one of the August-July 1977 bombs WIDP 8, the dense vesicular bomb from October 1993 WIDP 4, and WIDP 3 from the last eruption of the sequence in July 2000. These sulphide inclusions have a size range of 4-20 µm and they are found in a variety of hosts: five of these inclusions were found in plagioclase, two within melt inclusions hosted in orthopyroxene, one in an orthopyroxene, and one in the matrix glass. The plagioclase hosting one of the sulphides in WIDP 13 contains many other similar inclusions, as shown in Figure 3-4.

Figure 3-4: Transmitted light image of Cu-Fe sulphides in a plagioclase phenocryst in WIDP 13 from March 1977. All the black features in the plagioclase core correspond to Cu-Fe sulphides trapped at different depths within the crystal. A total of 8 inclusions were observed, although only one is exposed at the surface (Sulphide 2).

Qualitative WDS maps show interesting zoning of these unaltered sulphides (Figure 3-6, Appendix A.3). The distribution of the three main constituents, S, Fe and Cu, is not uniform. The highest concentrations of sulfur and iron generally coincide with each other, and are associated with low Cu content. The highest copper concentrations, conversely, usually exhibit lower sulfur and iron contents. Results of point analyses in S- and Fe-rich zones give 28-34 wt% S, 24-33 wt% Fe and 24-40 wt% Cu. In the Cu-rich zones, we measured similar S contents (24-33 wt%) but as low as 6 wt% for Fe. The highest Cu content analyzed was 52 wt%. The results of point analyses are presented in Table 3-5. The distribution of compositions in the Cu-Fe-S system (Figure 3-5) suggests exsolution from a precursor intermediate solid solution (iss), forming Cu-rich sulfides towards the bornite endmember and Fe-rich sulfides trending towards pyrite.

Moreover, we observed Fe-rich and S-poor clusters in two different sulphides, having composition of 56 wt% Fe, 10 wt% S and 6 wt% Cu for the inclusion in WIDP 10 (Figure 3-6 a, c and Figure 3-5). These may reflect the release of sulfur and copper associated with sulfide oxidation, as reported in other studies (Keith et al., 1997; Larocque et al., 2000; Halter et al., 2002; Nadeau et al., 2010).

Figure 3-5: Cu-Fe-S ternary diagram of sulphide inclusions (wt %). Also plotted, the composition of some common Cu-Fe sulphides. bn: bornite, ccp: chalcopyrite, cct: chalcocite, co: covellite, cu: cubanite, po: pyrrhotite, py: pyrite. Phase data from Yund and Kullerud (1966) showing solid solution fields at 700 °C. bnss: bornite solid solution, iss: intermediate solid solution, poss: pyrrhotite solid solution.

Table 3-5: Major and trace element compositions of the Cu-Fe sulphides (wt%)

	WIDP3 Sulf2- 01	WIDP3 Sulf2- 02	WIDP3 Sulf2- 03	WIDP3 Sulf2- 05	WIDP3 Sulf2- 06	WIDP3 Sulf2- 07	WIDP3 Sulf2- 08	WIDP3 Sulf3- 01	WIDP3 Sulf3- 02	WIDP3 Sulf3- 03	WIDP3 Sulf3- 04	WIDP3 Sulf3- 05	WIDP3 Sulf3- 06	WIDP8 Sulf1- 02	WIDP8 Sulf1- 04	WIDP8 Sulf3- 01
S	30.23	30.81	30.96	32.07	33.11	32.99	33.15	33.18	33.16	33.50	33.78	33.59	33.83	28.54	30.60	30.65
Mo	0.40	0.39	0.39	0.40	0.43	0.41	0.40	0.44	0.42	0.41	0.45	0.42	0.46	0.36	0.39	0.36
Fe	22.33	26.74	24.67	29.70	31.49	33.10	31.12	33.31	33.35	34.35	35.24	34.95	35.49	31.36	37.78	30.76
Zn	0.05	0.07	0.04	0.05	0.05	0.07	0.04	0.05	0.01	0.01	0.02	0.07	0.08	0.03	0.03	-
Ni	1.33	1.55	1.22	1.68	2.61	1.73	2.87	1.73	3.88	1.20	1.05	1.16	1.08	0.21	1.09	36.31
Co	0.43	0.52	0.28	0.51	0.64	0.65	0.90	0.65	0.66	0.62	0.89	0.67	0.68	0.81	0.68	1.22
Pb	-	0.00	-	0.05	-	-	-	0.10	0.03	0.02	0.06	0.01	0.03	0.07	0.02	0.14
Ag	0.02	-	-	0.02	-	-	0.02	-	0.03	0.01	-	-	0.00	0.00	-	0.23
Cu	41.05	36.18	39.63	29.20	28.35	28.12	28.59	28.09	27.08	27.28	27.13	27.17	26.84	22.33	17.48	3.59
Au	0.01	-	0.02	0.02	0.00	0.01	-	0.01	0.03	-	0.03	-	-	-	0.01	-
Cl	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02	0.03	0.02	0.03	0.03	0.08	0.04	0.04
Total	95.86	96.27	97.21	93.69	96.68	97.07	97.09	97.54	98.66	97.39	98.66	98.05	98.47	83.70	88.08	103.27

Table 3-5 (continued)

	WIDP8 Sulf3- 02	WIDP8 Sulf3- 03	WIDP8 Sulf3- 04	WIDP8 Sulf3- 05	WIDP8 Sulf3- 06	WIDP8 Sulf3- 07	WIDP8 Sulf3- 08	WIDP8 Sulf3- 09	WIDP10 Sulf1-01	WIDP10 Sulf1-02	WIDP10 Sulf1-03	WIDP10 Sulf1-04	WIDP10 Sulf1-05	WIDP10 Sulf1-06	WIDP10 Sulf1-07	WIDP10 Sulf1-08
S	31.34	30.51	30.57	29.42	28.89	31.30	29.84	31.38	26.78	28.46	31.32	31.63	30.16	27.49	9.86	29.40
Mo	0.41	0.38	0.42	0.36	0.36	0.37	0.40	0.38	0.36	0.39	0.40	0.38	0.37	0.38	0.11	0.36
Fe	31.56	28.75	29.42	26.38	25.34	30.82	29.48	31.27	22.27	22.75	29.00	30.07	26.95	24.35	55.91	27.72
Zn	0.03	0.03	0.02	0.04	0.03	0.05	0.04	0.07	0.05	-	0.08	0.05	0.01	0.09	0.03	-
Ni	35.05	17.54	8.50	0.89	0.44	0.41	0.33	0.41	1.28	0.88	1.70	1.84	28.16	6.20	0.53	1.35
Co	1.24	1.03	0.85	0.54	0.40	0.63	0.34	0.65	0.39	0.24	0.26	0.49	0.73	0.34	0.49	0.42
Pb	0.12	0.10	0.09	0.08	0.03	0.02	0.02	0.03	-	-	-	0.03	0.02	0.06	0.02	0.06
Ag	0.23	0.09	0.07	-	0.02	-	0.02	0.00	0.04	0.02	0.02	-	0.28	0.81	0.01	0.04
Cu	4.00	18.85	22.45	30.73	31.39	25.19	25.59	24.69	35.38	35.92	26.73	26.96	9.47	23.98	5.79	29.40
Au	0.02	0.03	-	0.03	-	0.02	0.02	0.01	0.03	0.02	0.02	-	0.04	0.06	0.03	0.10
Cl	0.04	0.06	0.03	0.02	0.02	0.02	0.03	0.02	0.06	0.06	0.12	0.10	0.04	0.02	0.01	0.05
Total	104.02	97.30	92.39	88.46	86.90	88.79	86.07	88.89	86.59	88.67	89.52	91.44	96.18	83.75	72.77	88.85

Table 3-5 (continued)

	WIDP10 Sulf1-09	WIDP10 Sulf1-10	WIDP10 Sulf1-11	WIDP10 Sulf2-01	WIDP10 Sulf2-02	WIDP10 Sulf2-03	WIDP10 Sulf2-04	WIDP10 Sulf2-05	WIDP10 Sulf2-06	WIDP10 Sulf2-07	WIDP13 Sulf1-01	WIDP13 Sulf1-02	WIDP13 Sulf1-04	WIDP13 Sulf1-05	WIDP13 Sulf1-06	WIDP13 Sulf1-07
S	20.99	30.88	8.57	28.28	28.57	31.51	31.48	25.46	26.20	27.20	23.54	24.00	31.47	32.69	31.84	28.88
Mo	0.25	0.37	0.12	0.35	0.39	0.42	0.38	0.34	0.33	0.37	0.29	0.30	0.38	0.38	0.39	0.37
Fe	12.04	26.81	57.33	26.38	23.59	30.34	30.42	15.71	17.33	19.61	5.87	14.63	31.99	32.29	31.31	23.93
Zn	0.01	0.02	0.01	0.08	0.07	0.08	0.11	0.07	0.09	0.10	0.07	0.06	0.04	0.05	0.04	0.02
Ni	1.46	1.97	0.33	1.50	0.69	1.61	1.77	-	-	0.07	-	0.22	0.95	1.06	0.97	0.71
Co	0.29	0.41	0.43	0.27	0.39	0.57	0.42	0.26	0.26	0.15	0.13	0.11	0.55	0.53	0.66	0.46
Pb	0.11	0.00	0.01	-	0.00	0.06	-	-	-	-	0.04	-	-	0.05	0.05	-
Ag	21.10	0.46	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.01	0.06	0.02	-	0.01	-	-
Cu	16.87	27.04	4.53	36.83	40.36	32.89	32.21	52.55	50.43	47.49	52.19	45.17	25.21	25.01	26.12	35.59
Au	0.02	0.02	0.03	0.01	-	0.01	-	-	-	-	-	-	-	0.01	-	0.00
Cl	0.03	0.04	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.08	0.06	0.03	0.03	0.03	0.03
Total	73.15	88.00	71.37	93.73	94.10	97.52	96.81	94.42	94.65	94.98	82.18	84.52	90.59	92.07	91.38	89.96

Table 3-5 (continued)

	WIDP13 Sulf1-08	WIDP13 Sulf1-09	WIDP13 Sulf1-10	WIDP13 Sulf1-11	WIDP13 Sulf1-12	WIDP13 Sulf1-13	WIDP13 Sulf1-14	WIDP13 Sulf2-02	WIDP13 Sulf2-03	WIDP13 Sulf2-04	WIDP13 Sulf2-05	WIDP13 Sulf2-06	WIDP13 Sulf2-07	WIDP13 Sulf2-08	WIDP13 Sulf2-09	WIDP13 Sulf2-10
S	29.83	31.71	30.29	30.90	30.28	31.70	30.61	28.79	27.82	27.93	29.33	30.78	30.05	29.06	29.08	29.66
Mo	0.38	0.40	0.37	0.39	0.40	0.39	0.41	0.35	0.35	0.35	0.38	0.38	0.35	0.36	0.38	0.40
Fe	31.29	30.31	33.60	27.88	33.69	29.52	26.59	25.56	25.35	24.50	25.27	29.47	27.51	21.62	23.34	27.14
Zn	0.05	0.02	0.02	0.01	0.05	0.06	0.02	0.05	0.05	0.08	0.07	0.03	0.09	0.06	0.06	0.07
Ni	0.84	14.63	4.13	28.84	2.50	4.57	16.60	10.67	12.09	7.77	2.07	1.33	1.52	0.44	0.74	1.08
Co	0.64	0.54	0.44	1.01	0.47	0.46	0.83	0.57	0.59	0.53	0.35	0.45	0.40	0.15	0.54	0.37
Pb	-	0.04	0.01	0.03	0.02	-	0.02	-	0.02	0.04	-	0.02	0.02	-	-	-
Ag	-	0.05	0.02	0.15	0.02	0.02	0.04	0.18	0.34	0.23	0.07	0.01	0.04	-	0.02	0.01
Cu	26.11	19.07	22.29	9.34	23.02	24.20	20.54	17.78	15.77	20.02	26.87	24.68	24.25	36.54	27.30	23.97
Au	0.01	-	-	-	0.00	-	-	0.01	0.03	-	-	0.01	-	0.01	-	0.02
Cl	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Total	89.16	96.77	91.17	98.53	90.44	90.92	95.66	83.95	82.40	81.42	84.40	87.16	84.22	88.23	81.45	82.71

Note: – not determined.

The sulphide trapped in the matrix glass in WIDP 10 is richer in Cu than any other sulphides, with values of 32 wt% to 53 wt%. This is also the only sulphide found in the matrix glass, probably suggesting a later formation than the other sulphides trapped in phenocrysts. These concentrations are extremely high and demonstrate the efficiency of sulphide melts in concentrating chalcophile metals.

A variety of trace elements were observed in the different sulphides, usually concentrated in clusters rather than distributed uniformly. This is the case for Ni, with concentrations up to 36 wt% in one of the sulphides in WIDP 8 from late July 1977 (Appendix A.3, Figure A-1 c). These Ni-rich areas are usually Cu-poor, highlighting stability of a Ni-S-Fe phase. The other notable trace elements forming clusters are Ag and Au. One of the clusters in sulphide 1 from WIDP 10 has elevated silver content (21 wt%) (Figure 3-6 a). The other Ag-rich clusters usually exhibit contents in thousands of ppm. The highest concentration of gold observed is 1000 ppm in the same sulphide from WIDP 10 (Figure 3-6 a). Clusters rich in zinc are less common. One of the sulfides from WIDP 13 nevertheless exhibits a concentration of 880 ppm. The highest contents for zinc are observed in the sulphide hosted in the matrix glass from WIDP 10, with values up to 1140 ppm, which is also the most concentrated in copper. The concentration of Mo is quite uniform in all the sulphides, ranging from 3000 ppm to 4500 ppm. Co shows more variability and notably the highest concentrations of up to 1 wt% associated with Ni-rich clusters. All the sulphides have low Pb concentrations, the highest being found with Ni- and Ag-rich clusters, at around 1000 ppm.

The composition of these metal-rich sulfides is in agreement with the experimentally determined partition coefficients between sulphide and silicate melts: 250-1300 for Cu, 790-5500 for Au, 300-19000 for Ag, 210-4400 for Ni, 18-164 for Co, 3-200 for Mo, 0.28-130 for Zn and 7-48 for Pb (Peach et al., 1990; Lodders and Palme, 1991; Gaetani and Grove, 1997; Ripley et al., 2002; Mengason et al., 2006; Mengason et al., 2011; Li and Audétat, 2012). In spite of the wide range of partition coefficients obtained due to varying silicate melt composition, fugacity of oxygen and sulfur during experiments, all of the metals besides Zn show a compatible behavior. It is interesting to note that Cl is present in the sulphides, even up to concentrations of 1160 ppm in small cluster found in the plagioclase-hosted sulphide in WIDP 10 (Figure 3-6 a).

a) WIDP 10 _ 12-25 March 1977 _ Sulfide 1

b) WIDP 10 _ 12-25 March 1977 _ Sulfide 2

c) WIDP 13 _ 12-25 March 1977 _ Sulfide 1

Figure 3-6: Cu-Fe sulphide composition maps. The reflected light image on top left corner shows the position of quantitative point analyses. The other images are composition maps acquired using WDS detectors and show the distribution of each species within the sulphide. a) Sulphide in plagioclase phenocryst from WIDP 10, March 1977. b) Sulphide in matrix glass from WIDP 10, March 1977. c) Sulphide in plagioclase phenocryst from WIDP 13, March 1977.

Arsenic was below detection limit in almost all the sulphides. Figure 3-7 however shows that the latter behaves incompatibly during crystallization. The lack of As in sulphides might be explained by preferential partitioning into a volatile phase. The high concentrations observed in fumarolic gases (123-1090 ppm, cf. Chapter 5) support the idea of arsenic degassing.

Figure 3-7: U versus As in melt inclusions and matrix glasses of rocks from the 1976-2000 eruptive sequence.

3.4 The role of mafic recharge during the 1976-2000 eruptive sequence

Magma mixing is suggested by enclaves of different compositions. The mingled glass in WIDP 6 (erupted in March 1977) is a dacitic enclave with a high silica content (73.22 wt% SiO₂) compared to the matrix of the block (62.99 wt% SiO₂, Mix 1) (Figure 3-8). The matrix glass of Mix 2 has a similar silica content (63.51 wt% SiO₂) as Mix 1, although they exhibit slightly different textures. Glass 1 contains a lot of acicular microlites up to 30 µm, whereas microlites in glass 2 are rarely exceeding 10 µm in size. These two melts might represent a different mixing ratio between the mafic and dacitic magmas, with more dacitic component in Mix 2. Variation in degassing could also explain such a difference, given the effects of degassing on microlite crystallization (Cashman, 1992; Hammer et al., 1999; Szramek et al., 2006; Johnson et al., 2008).

Figure 3-8: Transmitted light image of mingled glasses in the March 1977 block WIDP 6. Three different glasses are present, Mix 1, Mix 2 and Dacitic enclave.

We suggest the dacitic enclave arises from a shallow stored chamber that had undergone crystallization, and was incorporated by magma on the move. The uplift seen prior to the eruptive sequence in 1973-1976 and thought to be associated with emplacement of a magma body at ~500 m depth, indicates crystallization in this shallow reservoir (Clark and Cole, 1989; Houghton and Nairn, 1989b). The mafic recharge probably mixes with the bottom part of the differentiated magma, leaving the upper zone unmixed. As mentioned by several authors (Reubi and Blundy, 2009; Kent et al., 2010), the majority of magmas erupted at arc volcanoes where mixing is a recognized process, are of intermediate composition. Only a small portion of the two endmembers, mafic and felsic, is erupted. Kent et al. (2010) showed that volcanoes erupting andesites with constant composition through time, are the ones relying the most on mafic recharge and magma mixing to erupt.

Another enclave was found in WIDP 4. It contains a 2.4 mm skeletal Fo90 olivine phenocryst, suggesting a mafic origin, and is isolated from the rest of the rock by a crystallized clinopyroxene border (Figure 3-9). The composition of the glass within the pocket is slightly more evolved and Cl-rich, in contrast to what would be expected for a mafic enclave. This might be explained by crystallization of microlites within the isolated, small volume of melt, after crystallization of the clinopyroxene border. The inset in Figure 3-9 shows different clinopyroxene composition on either side of the border, supporting crystallization from different melts, the enclave being isolated from the rest of the magma.

Figure 3-9: Backscattered electron image of a mafic enclave in the October 1993 bomb WIDP 4. Skeletal olivine and surrounded glass isolated from the rest of the melt by a border of clinopyroxene. Zooming into the border reveals two distinct pyroxene compositions in and out of the enclave.

Magma mixing is further supported by zoned crystals. When recharge occurs, the phenocrysts crystallizing in the felsic melt end up surrounded by a more primitive magma. This results in disequilibrium textures (Eichelberger, 1975; Sakuyama, 1981; Gerlach and Grove, 1982), observed as reverse zoning in some of the crystals. Figure 3-10 shows such a zonation in rocks erupted in March 1977, October 1993 and April 1999. In contrast, in the WIDP 6 dacitic enclave where no mixing occurred (Figure 3-10 a), orthopyroxene phenocrysts exhibit normal zoning, reflecting fractional crystallization of the magma. The same normally zoned rims are observed in magnesian olivines formed at depth in the mafic melt (Figure 3-10 a and c).

Figure 3-10: Reverse and normal zoning in phenocrysts from the 1976-2000 eruptive sequence. All images are backscattered electron images. a) Block erupted in March 1977, WIDP 6. Normal zoning in orthopyroxenes from the dacitic enclave and in a magnesian olivine from the block. Reverse zoning in orthopyroxenes from the block. b) Bomb erupted in March 1977, WIDP 10. Reverse zoning in an

orthopyroxene phenocryst and in an orthopyroxene overgrowth in a resorbed olivine. c) Bomb erupted on 19 October 1993, WIDP 4. Reverse zoning in orthopyroxene and clinopyroxene, normal zoning in magnesian olivine. d) Bomb erupted on 17 April 1999. Reverse zoning in orthopyroxene.

The presence of normally zoned, stable mafic olivine next to resorbed, less magnesian olivine, indicates repeated recharge events (Figure 3-2). Zellmer et al. (2016) showed that such resorption results from uptake in a silicic magma. Fe enrichment of the crystal rim and dissolution continue until a microlite isolates the mineral from the melt. The resorption process then stops, and growth of the microlite (orthopyroxene or plagioclase) is favored. Isolation before complete dissolution preserves the core of the olivine, as observed in our samples. The growth of orthopyroxene from the rim indicates that no eruption closely followed the mafic injection. In contrast, the magnesian Fo92 olivine shows Fe-enrichment of the rim but no resorption, implying the residence time in the felsic magma after injection was short (i.e. eruption occurred shortly after mixing). This time constraint is also supported by matrix glass being more mafic than trapped inclusions in most of our samples (Figure 3-3). A prolonged residence time would allow crystallization to proceed, leading to an evolved matrix glass composition.

As no diffusion study was done, we could not assess whether the observed forsteritic content of the resorbed olivine is primary or not. The different size of crystals from the two populations nevertheless suggests different sources. Repeated injections from these more mafic reservoirs into a shallow felsic chamber would then lead to the observed assemblage. Mafic recharge can lead to eruption due to: 1) increase of material into a fixed-volume chamber, 2) exchange of heat and volatiles between the two melts leading to volatile solubility modifications, 3) formation of a new magma with different physical properties, 4) depressurization of the chamber due to fracturing of the overlying rocks (Anderson, 1976; Sparks et al., 1977; Eichelberger, 1980; Sparks and Marshall, 1986; Watts et al., 1999). Such a magma mixing hypothesis has already been suggested by different authors (Graham and Cole, 1991; Shiraki et al., 1994; Cole et al., 2001). Moreover, it is a well known process, recognized as one of the mechanisms triggering eruptions at subduction-related volcanoes (Anderson, 1976; Sparks et al., 1977; Eichelberger, 1980; Murphy et al., 1998; Watts et al., 1999; Kent et al., 2010).

The composition of matrix glass and melt inclusions shows that mixing was closely followed by eruption for 8 samples out of 11. The 3 rocks (WIDP 13, 8, 9) having more evolved matrix glass than melt inclusions contain resorbed Fo76-78 olivines, suggesting that recharge events occurred but did not lead to eruption, enabling the melt to evolve towards more felsic composition again. Two silicic melt inclusions (70.21 wt% and 71.47 wt% SiO₂) in WIDP 8 support long residence time in the shallow chamber. A low mixing ratio with such felsic melt could also explain the more evolved composition of WIDP 8 and 9, erupted in late July 1977. It is interesting to note the high Cl contents (1477 and 1593 ppm respectively) and low S and Cu contents (99 and 77 ppm, 85 and 38 ppm respectively) of these two felsic inclusions.

To summarize, ejecta from the 1976-2000 eruptive sequence highlight mixing of an evolved shallow stored melt with a more mafic component shortly before eruption, in the form of: 1) enclaves with different composition than the host rock, 2) stable magnesian olivines coexisting with resorbed less primitive olivines, 3) matrix glass less evolved than melt

inclusions hosted in phenocrysts. Such mixing was observed for most of the eruptions during the sequence, suggesting a potential role in triggering eruptions.

3.5 Pressure and temperature constraints

Some mineral-melt thermometry was carried out on the same samples by Geoff Kilgour and co-workers (pers. comm., 2016). They estimated the melt temperature at which olivine, orthopyroxene, clinopyroxene and plagioclase phenocrysts were crystallizing. Their results are in agreement with our findings, indicating higher temperature for the olivines as compared to the rest of the phenocrysts. The former crystallized in melts with temperature ranging between 1183 °C and 1270 °C. The latter show a broader range of temperature, 965 °C to 1082 °C for plagioclase, 903 °C to 1077 °C for clinopyroxene, and 949 °C to 1176 °C for orthopyroxene. This is also consistent with differentiation of the cooler magma in the shallow chamber, and varying degrees of mixing between the mafic and dacitic melts.

Entrapment pressures were estimated using the H₂O-CO₂-melt solubility model of Papale et al. (2006). Calculations were performed for melt inclusions hosted in each of the phenocryst phases to assess different depths of crystallization, using the temperatures reported above (G. Kilgour, pers. comm., 2016). For melt inclusions in WIDP 4 (ejected October 1993), we used the average temperature for orthopyroxene (1026 °C), clinopyroxene (945 °C) and plagioclase (978 °C) determined in the same rock. For the melt inclusion in WIDP 3 from July 2000, we used the average temperature for orthopyroxene (1103 °C) determined in the same rock. For melt inclusions from WIDP 18 from March 1977, we used the average temperature for olivine (1209 °C) determined in WIDP 6. For each inclusion, we calculated the Fe₂O₃ and FeO contents using the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 0.216$ ratio for White Island whole rock from Clark et al. (1979), measured in bombs and blocks from the 1977 eruptions. Esposito et al. (2014) and Rapien (1998) reported CO₂ contents from SIMS analyses of 39-3508 ppm in melt inclusions hosted in plagioclase and pyroxene phenocrysts. Given that CO₂ was not detected in our samples and that the majority of their results were < 200 ppm, we performed our calculations with values of 0 and 100 ppm of CO₂ for melt inclusions hosted in these phenocrysts.

Our results yield entrapment pressures of 15.0-21.7 MPa (no CO₂) and 14.2-46.4 MPa (100 ppm CO₂) for orthopyroxene-hosted inclusions from October 1993 (500-700 m and 470-1550 m respectively) with SiO₂ contents ranging from 62.53 to 67.31 wt%. The pressures estimated from clinopyroxene-hosted inclusions without and with CO₂ were 18.4 MPa and 29.7 MPa respectively (i.e. depths of 600 m and 1000 m), and 12.6 MPa and 23.5 MPa (420 m and 780 m) for inclusions in plagioclase. We obtained similar results from melt inclusions hosted in orthopyroxene from the July 2000 eruption, 13.3 MPa and 26.4 MPa (440 m and 880 m). Our estimates are in agreement with the values of 21.5 to 32 MPa (720-1100 m) obtained by Esposito et al. (2014) using the same model, a temperature of 1100 °C and $\text{Fe}^{3+}/\text{Fe}_{\text{tot}} = 0.2$.

These pressures correspond to depths of about 420-1550 m, thus confirming crystallization in the shallow environment. The higher pressures might reflect onset of crystallization during ascent in the conduit, or crystallization in intermediate chambers/accumulation zones along

with olivine Fo76-80. This is consistent with the higher sulfur content of some of these inclusions, reaching 535 ppm, reflecting deeper entrapment during SO₂ degassing. Given the range in pressure estimated, a model with multiple accumulation zones of small volume in the shallow environment (420 to 880 m) and maybe deeper ones (at 1000-1500 m depth) seems more realistic than a single, voluminous magmatic chamber.

For the olivine-hosted inclusions, we used the estimate of 500 ppm CO₂ from Werner et al. (2008) for a magma at a depth of 7 km and 1 wt% H₂O. We obtained entrapment pressures of 142.3 MPa and 82.8 MPa for two different melt inclusions (60.2 MPa and 63.1 MPa respectively using CO₂ = 100 ppm). These values correspond to much greater depths of 2.7 km to 4.7 km, supporting deeper crystallization of the olivines from the mafic magma. The high CO₂ contents (up to 3508 ppm) obtained by Rapien (1998) and Esposito et al. (2014) in plagioclase- and pyroxene-hosted silicate inclusions suggest our estimates are minimum depths of entrapment. Moreover, the extremely magnesian nature of the olivines, as noted above, suggests a source at the crust/mantle boundary. We thus assume that the more mafic reservoir is at a minimum depth of 5 km depth.

3.6 Magma degassing during ascent and crystallization

3.6.1 Major species

Figure 3-11 and Figure 3-12 show degassing of sulfur and chlorine as the melt crystallizes. The few olivine-hosted melt inclusions allow us to look at the sulfur and chlorine contents of the primary melt. The highest concentrations recorded, in crystal-free melt inclusions, are 1020 ppm for S and 4388 ppm for Cl (Appendix A.2). The inclusions hosted in olivine Fo76 and Fo78 exhibit the highest Cl contents (WIDP3-IN21, WIDP10-IN26) but have only intermediate CaO concentrations. These high Cl contents resemble the paralava described by Wood and Browne (1996) and might reflect regassing of the samples. The mafic enclave of WIDP 4 also exhibits really high Cl content, possibly due to similar regassing. On the other hand, the highest S contents are found in the most primitive olivines Fo90-93 (Figure 3-11).

Figure 3-11: CaO versus S of melt inclusions and matrix glasses from the 1976-2000 eruptive sequence.

This is consistent with the earlier hypothesis that the two populations of olivines are produced at different depths by more and less differentiated magmas. Sulfur is less soluble in silicate melts than Cl and thus starts exsolving earlier as the magma rises and crystallizes (Carroll and Webster, 1994; Aiuppa et al., 2002; Spilliaert et al., 2006). The entrapment pressures determined above suggest most of the S exsolves at depth between 4.7 and 2.7 km, with the majority of inclusions hosted in plagioclase and pyroxene already degassed. This is consistent with the findings of Werner et al. (2008), indicating that degassing of CO₂ and SO₂ occurs at depth greater than 300 m. Experimental results on the partitioning of sulfur between a silicate melt (basalt to basaltic andesite) and aqueous fluids also supports efficient degassing, with $D_s^{v/m}$ between 6 and > 1000, the highest values reached as pressure decreases to 25 MPa (Moune et al., 2009; Lesne et al., 2011; Webster and Botcharnikov, 2011). The less magnesian olivines trapped melt that has already lost some of its sulfur and is CaO-poor, indicating a depth in the lower range (i.e. ≤ 2.7 km), potentially as an intermediate magma chamber.

Some inclusions hosted in plagioclase and pyroxene show higher S contents (Figure 3-11). Onset of crystallization of these minerals in the deeper reservoir(s) might explain entrapment of less degassed melt, although regassing of magma in the shallow chamber through fluxing of S-rich vapors should not be ruled out. The S-rich melt inclusion in WIDP 13 (1391 ppm) is also the most evolved and Cu-rich of the samples, pointing to possible destabilization of Cu-Fe sulfide bleb responsible for such enrichment.

In contrast, the behavior of chlorine in pyroxene- and plagioclase-hosted inclusions is not as marked as for S, broadly ranging from 600 to 1700 ppm, without a clear trend (Figure 3-12). The estimated entrapment pressures indicate a depth in the range of 420-880 m. Experimental

work on basalts from Mt. Etna by Alletti et al. (2009) indicates that the partition coefficient of chlorine between a hydrous vapor and a basaltic melt changes from 6 at 200 MPa, to 11-14 at 1 MPa and 25 MPa at NNO, supporting partitioning of chlorine into a H₂O-rich vapor phase at low depth. Degassing is nevertheless not as efficient as for S, with the more evolved inclusions in WIDP 8 and WIDP 7 having high Cl contents, possibly reflecting diffusion-limited degassing (Watson, 1991; Alletti et al., 2007; Balcone-Boissard et al., 2009).

Figure 3-12: CaO versus Cl of melt inclusions and matrix glasses from the 1976-2000 eruptive sequence.

Figure 3-13 supports efficient degassing of S compared to Cl, pointing towards a balance between degassing and incompatible behavior of Cl in the magma. Similar degassing was reported at Stromboli, where > 75% of the sulfur is exsolved between 6 and 2 km (Métrich et al., 2010). It also highlights the multiple injections of mafic melt described earlier, with the absence of a degassing pattern throughout the eruptive sequence.

The dacitic enclave in WIDP 6 contains many small spherical bubbles whereas the rest of the block has mainly big uneven globular vesicles (Figure 3-8). As shown by Schipper et al. (2017), as much as 99% of the vesicles are interconnected in the April 1999 ejecta (WIDP 7), providing a path for the deeply exsolved volatiles to escape the magma under open-system conditions. We interpret volatile degassing to occur in three stages: 1) early exsolution of less soluble CO₂, H₂O and SO₂ at depth with effective coalescence, building the network of vesicles observed, 2) exsolution of Cl in H₂O-rich vapor in the shallow chamber as described by Métrich et al. (2010) under open-system conditions, and 3) late exsolution of residual H₂O and HCl during ascent to the vent (Métrich and Rutherford, 1992) without possibility to coalesce. The observed trends for chlorine and sulfur are qualitatively consistent with the

fluxes of SO₂ and HCl emitted at the surface: 171-1230 t/d of SO₂ between 1983 and present (Rose et al., 1986; Love et al., 2000; Wardell et al., 2001; GeoNet, 2001-2017), 89-275 t/d of HCl (Love et al., 2000; Werner et al., 2008; Christenson et al., 2017).

Figure 3-13: Cl versus S of melt inclusions and matrix glasses from the 1976-2000 eruptive sequence.

Despite the persistent degassing observed at White Island, only a very small volume of magma has been erupted throughout the whole sequence. We propose convection within the deep magmatic reservoir (2.7 to 4.7 km) to explain such consistent flow of gases. This process was first introduced by Kazahaya et al. (1994) to explain excess degassing at Izu-Oshima volcano, Japan. It implies overturn of dense degassed magma with less dense, gas-rich melt, within a vertical conduit overlying a magmatic chamber. Their model has since

been refined and suggested to be the driver of persistent degassing at many others volcanoes (Tazieff, 1994; Shinohara et al., 1995; Allard, 1997; Stevenson and Blake, 1998; Kazahaya et al., 2002; Witter et al., 2005). In the case of White Island, convection within the deep reservoir, and potentially, extended to the overlying conduit, would explain the more or less constant flux of CO₂, SO₂ and H₂O observed at the surface. As shown above, Cl most likely exsolves at shallower level, probably due to second boiling in the crystallizing dacitic magma at a depth of 420-880 m.

3.6.2 Metals

Copper content of silicate melt inclusions from the 1976-2000 sequence varies between 2 ppm and 1004 ppm, with the majority of them containing less than 300 ppm (Figure 3-14). Cu content first increases with crystallization, until the melt reaches a silica content of ~ 60 wt%, at which point the Cu content starts to decrease. A dozen melt inclusions in the March 1977 block WIDP 6 and in one of the late July 1977 bombs WIDP 9, have copper concentrations much greater. This enrichment might reflect breakdown of a Cu-rich sulphide melt following fluxing of the shallow environment with deep-derived SO₂-rich gas (Hattori, 1993). This argument is reinforced by the absence of such sulfide in both samples, whereas WIDP 8, erupted in the same period, does not show such Cu enrichment and contains sulphides. It should be noted that the most evolved inclusions in WIDP 8 have low S and Cu contents, supporting depletion in Cu with differentiation due to degassing and/or sulfide melt formation.

Figure 3-14: SiO₂ versus Cu of melt inclusions and matrix glasses of rocks from the 1976-2000 eruptive sequence.

Partitioning of copper into a magmatic vapor phase ($D_{Cu}^{v/m}$ varies from 10 to 20 but can reach up to 2700) and the role of S as a ligand are well known (Giggenbach and Matsuo, 1991; Candela and Piccoli, 1995b; Harris et al., 2003; Halter et al., 2005; Zajacz et al., 2008; Johnson and Canil, 2011). This is in agreement with the composition of fumarolic gases at White Island, containing 5-93 ppb of copper (cf. Chapter 5). The presence of sulphide inclusions in some of the rocks, as mentioned above, should also be considered as a sink for chalcophile metals.

Figure 3-15: SiO₂ versus Zn of melt inclusions and matrix glass for separate rocks of the 1976-2000 eruptive sequence.

Melt inclusions have zinc contents of 22-196 ppm. The numerous olivine-hosted melt inclusions in WIDP 4 from October 1993 allow us to see the behavior of Zn through crystallization. Figure 3-15 shows that Zn first behaves incompatibly during olivine crystallization at depth, and then decreases in the magma in the shallow environment. It has been shown that zinc is compatible in ferromagnesian minerals such as orthopyroxenes and in some oxides (Core et al., 2005; Johnson et al., 2013). Given that we did not analyze Zn in such phases, we cannot rule out that the decreasing content in WIDP 4 is due to partitioning into these minerals. This late compatibility is however absent in many of the other rocks, pointing to different behavior of zinc.

Figure 3-16: $\log \text{Cl/Rb}$ versus $\log \text{Zn/Rb}$ of melt inclusions and matrix glass for separate rocks of the 1976-2000 eruptive sequence.

When plotting Zn/Rb and Cl/Rb ratios, the effect of crystallization on both species is removed, due to the incompatible behavior of Rb in silicate magmas (Griffin and Rama Murthy, 1969). We now see in Figure 3-16 that zinc and chlorine are positively correlated. This suggests zinc partitions into crystallizing phases and/or magmatic vapor phase. Zinc degassing is observed at the surface, with fumarolic gases containing 8-250 ppb (cf. Chapter 5), and supported by experimental estimates of the partition coefficient between magmatic vapor phase and silicate melt ($D_{Zn}^{v/m}$ varies from 7.6 to 44, (Candela, 1989; Candela and Piccoli, 1995b; Keppler, 1996)).

Figure 3-17: Lead behavior with degassing and crystallization. U versus Pb. b) log Cl/Rb versus log Pb/Rb. C) log Cl/Rb versus log Pb/Rb.

Lead content varies from 2 ppm to 23 ppm. These concentrations are much lower than for Cu and Zn. Magnesian olivines have low values, and Figure 3-17 shows an increase with differentiation, with the magma progressively becoming enriched. We observe a slight decrease of Pb with decreasing S and Cl. Again, the composition of fumaroles at the surface supports lead degassing, with 1 ppb to 23 ppb in the volatile phase. Partition coefficients between magmatic vapor phase and silicate melt for Pb is also consistent with Pb degassing ($D_{Pb}^{v/m}$ varies from 4.2 to 20, (Urabe, 1987; Candela, 1989; Keppler, 1996)).

To summarize, this study of melt inclusions from the 1976-2000 eruptive sequence indicates efficient degassing of the least soluble species CO_2 , H_2O and SO_2 before the magma reaches the shallow environment (420-880 m). The interconnected network formed through coalescence allows volatiles to escape the magma and degas at the surface. Convection within the deeper reservoir and/or overlying conduit (2.7 to 4.7 km) is a potential process to explain the persistent degassing of White Island despite the very low volume of magma erupted. HCl is more soluble and starts exsolving in the shallow environment (~420 to 880 m), augmented by crystallization. The repeated mafic injections bring volatiles and heat to the shallow crystallizing dacitic magma. Metals such as Cu, Zn, Pb behave incompatibly, progressively enriching the residual magma through crystallization. Correlations with S and Cl nevertheless suggest degassing of these metals, and/or segregation by a sulphide melt.

3.7 The occurrence of sulphide melt inclusions and their effect on metals

The sulphide hosted in the matrix glass in one of the 1977 bombs, WIDP 10, exhibits a perfectly spherical shape (Figure 3-6 b). Minimizing surface tension during mixing of two immiscible liquids results in the least abundant species to adopt a shape with minimum surface area for a given volume (i.e. a sphere). This physical process implies that the sulfide was trapped as an immiscible melt within a liquid silicate melt.

Figure 3-18: Backscattered electron image of orthopyroxene phenocrysts in the bomb from July 2000 WIDP 3 containing sulphide inclusions. The silicate melt inclusion containing one the sulphides (WIDP3_IN02), and a close by inclusion (WIDP3_IN01) were analyzed for their volatile content.

In order to constrain the sulfur content at sulfide saturation, we analyzed silicate melt inclusions containing sulphides or hosted in phenocrysts containing sulphides. In WIDP 3, the inclusion containing one of the sulphides (IN02) and a nearby inclusion (IN01), have sulfur contents of 359 ppm and 299 ppm respectively (Figure 3-18). In WIDP 4, the small sulphide phase is hosted in a melt inclusion containing 310 ppm of sulfur. Entrapment pressure of this silicate inclusion was estimated following the H_2O - CO_2 -melt solubility

model of Papale et al. (2006) as described above, using 100 ppm CO₂ from Esposito et al. (2014). The resulting pressure of 21 MPa is in agreement with the proposed late saturation, after the magma has reached depth of ~ 600 m.

The absence of sulphide in olivine phenocrysts suggests late saturation with respect to a sulphide melt. Given the low (< 1332 ppm) sulfur content of olivine-hosted melt inclusions (typically 900-2500 ppm S in arc magmas (Wallace and Edmonds, 2011)), an oxidized mafic magma at ~1200 °C will most likely become saturated with sulfur due to decompression, at depths where a magmatic volatile phase is present (CO₂ and most likely H₂O already saturated), favoring exsolution of S into the aqueous fluid phase instead of formation of an immiscible sulfide liquid. This is in accordance with the composition of gases emitted by Donald Mound fumarole in 1988 of about 92 mol% H₂O, 6 mol% CO₂, 1 mol% SO₂ and 0.2 mol% HCl (Giggenbach and Matsuo, 1991). It also agrees with the onset of sulfur exsolution from mafic melts into a vapor phase at pressures around 140-100 MPa observed in natural systems (Spilliaert et al., 2006; Johnson et al., 2010), determined experimentally (Webster and Botcharnikov, 2011), and calculated with models (Scaillet and Pichavant, 2005). Further rise of this magma into the shallow (~420-880 m) accumulation zones and mixing with cooler, partly crystallized dacitic magma induces cooling and decompression. The effects of both these processes have been determined experimentally and tend to decrease sulfur solubility in hydrous silicate melts (Carroll and Rutherford, 1985; Poulson and Ohmoto, 1990; Mavrogenes and O'Neill, 1999; Holzheid and Grove, 2002).

Additionally, crystallization taking place in the shallow reservoirs will reduce the total volume of residual melt, thus increasing the sulfur content (S incompatible in crystallizing phases). Experimental studies have shown that sulfur solubility is also dependent on FeO content of the silicate melt and oxygen fugacity f_{O_2} (Carroll and Rutherford, 1985; Luhr, 1990; Wallace and Carmichael, 1992; Metrich and Clocchiatti, 1996; Jugo, 2009). The dacitic enclave in WIDP 6 contains more Fe-oxides than any other rocks of the eruptive sequence, suggesting increased crystallization in the felsic melt. Onset of crystallization of such phases would not only reduce the total Fe content of the melt, but would also lower f_{O_2} , by decreasing the Fe³⁺/Fe²⁺ ratio. This, in turn, would convert the highly soluble sulphate (S⁶⁺) into less soluble sulphide (S²⁻) (Carroll and Rutherford, 1988). Jenner et al. (2010) showed that crystallization of magnetite at SiO₂ > 60 wt% acts as a trigger to sulphide saturation by reducing the silicate melt (i.e. decreasing f_{O_2}). All of these processes (i.e. cooling, crystallization, shift in redox conditions) lead to formation of an immiscible sulphide melt.

The small amount of magnetite crystallizing in White Island magma may not be sufficient to trigger sulphide saturation on its own, but might be efficient when coupled with the processes described previously. It may also promote sulphide saturation on a local scale, as suggested by Bacon (1989). Late sulphide saturation in arc settings has been proposed by several authors, supported by silicic magmas saturated with a sulphide melt whereas their mafic counterparts are not (Larocque et al., 2000; Luhr, 2008; Parat et al., 2011). Timing of sulphide saturation is a critical parameter in the formation of ore deposits (Keith et al., 1997; Halter et al., 2002; Halter et al., 2005; Nadeau et al., 2010; Richards, 2011; Wilkinson, 2013). Jenner et al. (2010) and Park et al. (2015) showed that late sulphide saturation is not a barrier to the formation of ore-bearing systems. On the contrary, fractional crystallization permits

enrichment of the silicate melt in incompatible metals (Au, Cu, Zn) efficiently segregated into the sulphide melt upon saturation.

Destabilization of this sulphide phase by volatile exsolution would provide metals to newly formed hydrothermal fluids. Resorption of the sulphide melt before complete crystallization of the melt thus prevents small blebs of metal-rich sulphides to be disseminated in a large volume of magma. Various authors have explored processes leading to destabilization of an immiscible sulphide phase, including, 1) oxidation through fluxing of SO₂-rich magmatic volatile phase rising from underlying mafic magmas (Hattori, 1993; Blundy et al., 2015), 2) oxidation through volatile exsolution (Keith et al., 1997; Larocque et al., 2000; Halter et al., 2002; Halter et al., 2005), and 3) pressure decrease (Keith et al., 1997). In the case of White Island, deep SO₂-rich fluids and ongoing volatile exsolution within the shallow environment would promote oxidation of the sulfide blebs. Nevertheless, the importance of such processes in generating ore-forming fluids inevitably depends on the amount of immiscible sulfide melt exsolved from the magma.

3.8 Conclusions

This study of ejecta from the 1976-2000 eruptive sequence revealed textural, structural and chemical evidence for magma mixing in a shallow environment, between a crystallizing dacitic melt and mafic recharge. The estimated entrapment pressure indicates that the shallow reservoir is at ~ 400 to 800 m depth, probably in the form of multiple accumulation zones interacting together and mixing with the mafic melt. The source of this more primitive magma is deeper than 5 km depth, probably at the crust-mantle interface as suggested by the extremely magnesian olivines. The presence of intermediate reservoir(s) between 1-2 km, in which Fo₇₆₋₇₈ olivines and some of the pyroxenes crystallize, is suggested. A schematic view of the magmatic system of White Island is proposed in Figure 3-19. Mafic injections are frequent and do not always lead to eruption. Short residence times of mafic minerals into more evolved melt nevertheless suggest these recharge events might act as a triggering mechanism in some instances. The repeated injections of magma lead to zonation within the shallow magmatic chambers, indicated by enclaves of different composition in erupted material.

The persistent flux of gases observed at White Island is mainly due to degassing of the less soluble species CO₂, H₂O and SO₂ from the deepest reservoir. Magma convection within a large chamber and/or within the overlying conduit might be responsible for overturn of dense degassed magma with less dense gas-rich melt. Efficient degassing is then possible without erupting large volumes of magma. More soluble chlorine degasses in the shallow reservoirs, most likely through second boiling.

Figure 3-19: Schematic model of White Island magmatic system during the 1976-2000 eruptive sequence.

Metals exhibit an incompatible behavior in the mafic melt yielding an enriched magma through crystallization. Degassing occurs in the shallow environment favoring volatile transport of Cu and Pb, although partitioning into crystallizing phases cannot be ruled out in the case of zinc. The presence of Cu-Fe sulphides rich in Ag, Au and Zn implies saturation of an immiscible sulphide phase, potentially triggered by magnetite crystallization in the dacitic melt. Destabilization of these sulfides would act as an additional source of metal-rich fluids, assuming remobilization within a magmatic volatile phase.

Chapter 4: Hyperacidic crater lake as a sink for metals

4.1 Introduction

In the last chapter, we explored the metal content of the magma responsible for volcanic activity at White Island. We saw that many of the metals are being exsolved along with the major volatile species, sulfur and chlorine. Here, we follow these fluids on their path towards the uppermost part of the system, where they encounter accumulating and infiltrating, cooler meteoric water.

Of all the Holocene or younger volcanoes worldwide, around 16% of them feature a crater lake (Delmelle and Bernard, 2000). These lakes can be subdivided into two categories: hot, mineralized acidic waters, and cooler and diluted, slightly acidic to neutral waters. The former are usually associated with active volcanoes releasing high fluxes of magmatic gases, whereas the latter generally sit on top of dormant volcanoes where deep-seated magma releases less gas (Delmelle and Bernard, 2000; Rouwet et al., 2014; Christenson et al., 2015). Scientific interest was first driven by the risk associated with these systems. In spite of the harmless characteristics of the cool and neutral crater lakes at first glance, a hidden hazard arises from them: the accumulation of carbon dioxide at the bottom of the stratified waters suddenly released in a deadly asphyxiating gas cloud. Such an event occurred in Cameroun at the now famous Lake Nyos in 1986, killing the population and livestock living nearby (Kling et al., 1987; Sigurdsson et al., 1987; Kusakabe et al., 1989). In the case of active volcanoes, additional hazard arises from the presence of a crater lake. Drainage of these waters following eruption or rim/flank collapse can generate lahars (Simkin and Siebert, 1994; Delmelle and Bernard, 2000; Delmelle et al., 2015; Manville, 2015). Another potential risk is associated with pollution of the local groundwater by seepage or overflow of the acidic and mineralized waters, as observed for instance at Kawah Ijen, Poas or Copahue volcanoes (Rowe et al., 1992a; Simkin and Siebert, 1994; Rowe et al., 1995; Sriwana et al., 1998; Delmelle and Bernard, 2000; Varekamp et al., 2001; Löhr et al., 2005; van Hinsberg et al., 2010a; Manville, 2015). In addition, phreatic eruptions are frequent, and usually unheralded, at volcanoes where a lake occupies the crater. They are often associated with sealing of the hydrothermal system by secondary precipitation of mineralized fluids (Browne and Lawless, 2001; Christenson et al., 2007; Christenson et al., 2010).

The interest in crater lakes also arises from their chemical “scrubbing” capabilities, making them potential tools to monitor the volcanic activity. Indeed, changes in water chemistry, temperature and/or color have been observed preceding and following eruptions at different volcanoes (Giggenbach, 1974; Giggenbach and Glover, 1975; Takano, 1987; Brown et al., 1989; Takano and Watanuki, 1990; Brown et al., 1991; Rowe et al., 1992b; Christenson and Wood, 1993; Oppenheimer, 1993; Badrudin, 1994; Christenson, 2000; Martínez et al., 2000; Ohba et al., 2000; Varekamp et al., 2001; Ohba et al., 2008; Bani et al., 2009; Christenson et al., 2010; Rouwet and Tassi, 2011; Rouwet et al., 2014).

Hyperacidic crater lakes ($\text{pH} < 2$) are rare and remarkable environments, which contain the most acidic natural waters on Earth. They occupy craters of active volcanoes where the hydrology and geomorphology allow ponding of meteoric waters and condensation of rising volcanic vapors from the underlying conduit (Symonds et al., 2001; Christenson and Tassi,

2015). Their hyperacidic nature arises from scrubbing of magmatic gases, notably HCl and SO₂, and their subsequent dissolution (Sakai and Matsubaya, 1977; Giggenbach, 1987; Rye et al., 1992; Kusakabe et al., 2000) as described by the reactions:

Such disproportionation of magmatic gases leads to strong enrichment in sulfate and chloride in crater lake waters, as well as the formation of elemental sulfur. These reactive waters promote hydrolysis of the host rock, enriching the lake in cations resulting in high total dissolved solids (Henley and Berger, 2011). Such extensive alteration results in silica-enriched residual rock beneath and around volcanic lakes (Rowe and Brantley, 1993; Wood, 1994; Christenson et al., 2010; van Hinsberg et al., 2010b). At Kawah Ijen, Delmelle and Bernard (1994) reported incongruent dissolution leading to residual rock with as much as 85 wt% SiO₂.

Crater lakes thus represent perfect environments to study water/gas/rock interactions in magmatic-hydrothermal systems. The metal load of acidic crater lakes has mostly been ignored at the expense of sulfur and chlorine species in the past studies. It nevertheless represents a potential hazard in terms of water pollution in inhabited areas. Moreover, crater lakes have been shown to act as metal sinks, in the same way as they scrub gaseous HCl and SO₂ (Henley, 2015). The study of metal behaviour in such environments will thus help us understand metal segregation in hydrothermal systems.

The presence of a lake occupying portions of the crater floor at White Island has been reported as far back as 1826, by the first settlers to visit the island (Luke, 1959). It nevertheless appears to be ephemeral, and linked to the activity of the volcano. No lake was present during the 1976-2000 eruptive sequence, but water accumulation in the eruption crater complex started as soon as the activity stopped in mid-2000. It was not until 2003 that a crater lake as such filled the western subcrater. The volume at the overflow level has been estimated at $\sim 2.5 \times 10^6 \text{ m}^3$ (Christenson et al., 2017). Three complete cycles of filling and evaporation took place since the lake's re-appearance in 2003 (Werner et al., 2008; Christenson et al., 2017). Its composition is characteristic of hyperacidic lakes, with chloride and sulfate contents of 35-150 g/L and 5-45 g/L respectively, pH of -1 to 1.5, and temperatures ranging from 31 °C to 78.8 °C (GeoNet, 2001-2017). The lake dried again at the end of 2016, and remains absent at the time of writing.

This study aims to constrain the behaviour of metals in White Island's hyperacidic crater lake, from magmatic-gas injection at the bottom of the lake, to elemental sulfur scrubbing, secondary mineral deposition and evaporation.

4.2 Samples and analytical methods

4.2.1 Collection of samples

The crater lake samples were collected from the southern shore (Figure 4-1) using a polyethylene bottle attached to a sampling pole. The temperature of the lake was measured during collection with a thermocouple. Three different water samples were collected each time: 1) rubber seal bottle, removing any head space, for the analysis of pH and H₂S, 2) filtered (0.45 µm Millipore and 0.45 µm Whatman) for anions and trace elements (Nalgene and Teflon bottle respectively), 3) filtered (0.45 µm) and acidified (7M HNO₃) for major cations and Cu (Nalgene bottle). The suspended particles collected onto one of the filters (0.45 µm Whatman) were kept for X-ray powder diffraction (XRD) and bulk analysis. The acidity of the lake and hazard due to the unpredictable nature of phreatic eruptions, prevented collection of water samples further from the shore and at deeper levels.

Figure 4-1: Aerial picture showing the sampling locations (source LINZ). North rim is where the ashes from the 27 April 2016 eruption were collected.

Sediments were collected from the bank and lake bottom at the shore line. Cores were also taken near the shore, at shallow levels. A cleaned plastic tube was hammered into the bottom of the lake and carefully removed with its sediment core. The tube was closed with two lids and later allowed to dry in a desiccator in the laboratory. During one of the sampling visits, a greenish foamy layer containing elemental sulfur spherules was floating at the surface of the lake. Some of this material was collected in a bottle and subsequently dried in a desiccator.

Another sample used for this study comprised ejecta of the phreatic eruption of 28 April 2016. Most of the crater floor and part of the rim was covered with greenish wet ash during the event (cf. Chapter 2). The sample was collected the day after the eruption, with no rain

occurring since deposition, by Michael Rosenberg from GNS Science. As no juvenile material was erupted during this phreatic blast, we assume the ash to represent material altered and /or deposited by the hydrothermal system underneath the lake.

We also sampled a spring discharging in the crater floor, F0 Pool, and the active fumarole F0 located close by (Figure 4-1). The water was collected using a 0.5 L Nalgene bottle to fill our small Teflon vessels. Two samples of fumarolic gases were also collected: a condensate, using a glass condenser connected to a silica tube inserted into the fumarole; a Giggenbach flask, using a titanium tube inserted into the fumarole (cf. 5.2). The major and minor species are analysed by gas chromatography and wet chemistry, as part of the GeoNet volcanic hazards monitoring. The trace metal content of fumarolic gases was retrieved from ICP-MS analysis of the condensate.

4.2.2 Sample preparation and analytical techniques

All chemical treatments for trace elements analysis by ICP-MS were done using SeaStarTM ultra-pure acids and Milli-Q water. All the sample preparations were done in a class 100 clean room at Victoria University of Wellington.

4.2.2.1 Water samples

The pH and major element analyses were done by GeoNet scientists at Wairakei (New Zealand), as part of an on-going volcanic hazards monitoring program. pH and H₂S were measured in the laboratory as soon as possible after collection. Flow injection analysers were used for H₂S and NH₃. SO₄²⁻, Br⁻ and the cations were measured by ion chromatography. The high concentration of Cl⁻ makes titration analysis more suitable than ion chromatography. F⁻ was measured by ion selective electrode.

The trace elements were analysed at Victoria University of Wellington with a Thermo Scientific Element2 sector-field ICP-MS. As some precipitates formed after collection, the samples had to be analysed as bulk samples. They were weighed using a high precision balance (± 0.00001 g). We first dried down the samples and subsequently digested them in 5 mL 15M HNO₃ + 5 mL 12M HCl at 120 °C in Teflon beakers. In some cases, a white residue remained in solution which was then digested by addition of 0.1 mL of 36M HF. After complete dissolution, the samples were evaporated again to near dryness, refluxed in 15M HNO₃ and finally taken up in 30 mL of 3M HNO₃. Fumarolic condensates were treated the same way.

Samples were analysed with different dilution factors in order to determine major and trace elements. The final dilution was done using 1% HNO₃. A synthetic solution was used to calibrate the ICP-MS, running 4 different dilutions to obtain a calibration curve. Instrument background was assessed by running 1% HNO₃ blank solution every 2 samples. The detection limit was taken as 3 standard deviations of the acid blank, whereas the limit of quantification was 6 standard deviations. SLRS-4 reference material (Yeghicheyan et al., 2001) was run to determine precision and accuracy of the analyses (Appendix A.7). In

addition, we ran JB1 and BIR-1 standards (Jochum et al., 2016) to verify rock and sediment analyses.

4.2.2.2 Solid samples

The cellulose 0.45 μm Whatman filter used for collection of suspended particles was weighed before and after sampling, along with the water bottle for which the filter was used. We could then recover a mass fraction of suspended particles per kilogram of water. The filter and suspended particles were digested in a Teflon beaker at 120 $^{\circ}\text{C}$ in a mixture of 5 mL 15M HNO_3 + 5mL 12M HCl + 1 mL 36M HF . The samples were evaporated after complete dissolution and taken up in 5 mL 6M HCl to ensure no solid remained. After drying, the samples were refluxed in 2 mL 15M HNO_3 , and then taken to final volume (10 mL) with 1M HNO_3 . The composition of the Whatman cellulose filter was assessed by digesting 10 weighed blank filters following a similar procedure. Another filter used to collect suspended particles was dried in a desiccator and kept for XRD analysis.

Sediment cores were pushed out of the sampling tube in a half tube using a plastic plunger. The core was then cut in half with a clean fishing line. Different layers within the core were observed and aliquots of each layer taken for ICP-MS analysis. The material was first dried in a desiccator, crushed using an agate mortar and pestle, and 0.05 g of each layer was precisely weighed. The digestion was performed in 0.5 mL of 15M HNO_3 + 2 mL of 36M HF . After dissolution, the samples were dried to near dryness to prevent the formation of insoluble salts and refluxed in 15M HNO_3 . After complete evaporation, 5 mL of 6M HCl were added to ensure no solid remained and the samples were dried again. We then refluxed them in 15M HNO_3 and finally dissolved them in 10 mL 1M HNO_3 . A block of sediment collected on 6 June 2015 from the bottom of the lake had the same thin black layer surrounded by sulfur-rich yellow precipitates as in the sediment cores (Figure 4-6). We powdered an aliquot of both the black and the yellow layers and analysed it by XRD to assess the mineral phases present.

The foamy layer collected from the surface of the lake was dried in a desiccator and digested using the same protocol as the sediments. The sulfur spherules it contained were also analysed separately to assess the metals scavenged by elemental sulfur. The globules are usually spherical, although some of them present flattened surfaces. Contrary to many sulfur spherules found at other lakes (e.g., Poas, Ruapehu, Santa Ana, Kawah Ijen, Kawah Puti, Keli Mutu, Kusatsu-Shirane (Giggenbach, 1974; Takano and Watanuki, 1990; Rowe et al., 1992b; Delmelle and Bernard, 1994; Pasternack and Varekamp, 1994; Sriwana et al., 2000; Martínez et al., 2002; Colvin et al., 2013), the samples at White Island were rarely hollow. Most of them exhibit a hole but their interior is mostly solid. Their size ranges from 0.5 mm to 2 mm. The color varied from bright yellow to shiny, metallic-like black, most likely due to the presence of trace metals compounds (Figure 4-2).

Spherules of different colors were picked for analysis in order to ascertain the differences in composition between metal-poor and metal-rich spherules. 0.05 g of the scum and spherules were precisely weighed and digested in Teflon beakers at 120 $^{\circ}\text{C}$. A mixture of 1 mL 15M HNO_3 + 1 mL 12M HCl + 0.5 mL 36M HF was added to the foam sample. The solution was dried to incipient dryness after complete dissolution to prevent for the formation of insoluble salts. After reflux in 15M HNO_3 , 5 mL of 6M HCl was added to the sample. It was dried

down after couple of hours, refluxed in 15M HNO₃ and finally taken up in 10 ML 1M HNO₃. The sulfur spherules were treated similarly although they did not require HF during the dissolution procedure due to the absence of silicates.

Figure 4-2: Pictures of sulfur spherules floating at the surface of the crater lake.

The ash from the 28 April 2016 eruption was powdered using an agate mortar and pestle. We also crushed part of a bomb erupted during the 12-25 March 1977 active period. The sample was first crushed using a Boyd crusher at Victoria University of Wellington, then powdered using an agate ball mill. We precisely weighed an aliquot of 0.05 g for each sample and digested them following the same protocol as for the sediments. The major elements were analysed by XRF by SpectraChem Analytical, CRL Energy Limited, Lower Hutt, New Zealand. BIR-1 was analysed to determine accuracy of the analysis (< 4% bias for Na₂O, < 2% for Fe₂O₃, < 1% for SiO₂, Al₂O₃, MgO, CaO).

Samples for XRD analysis (sediments, suspended particles and ash) were analysed with a PANalytical X-Pert Pro Multi-Purpose Diffractometer (Victoria University of Wellington), using copper K alpha ($K = 1.54187 \text{ \AA}$) radiation, with a beam intensity of 45 kV and 40 mA.

The lake sediments, including the thin black layer in the core from 5 June 2015, along with the April 2016 ash, sulphur spherules and suspended particles were imaged and analysed using a JEOL JSM-53000LV SEM coupled with EDS detector at Victoria University of Wellington. The analyses were performed with an acceleration voltage of 20 kV, a spot size of 57, and a load current of 69-72 μA .

4.3 Results

4.3.1 Crater lake water

The crater lake was sampled on three occasions between October 2014 and December 2015. Changes in lake level (Figure 4-3) and color were also observed throughout this period. The level on 24 October 2014 was ~ 3.6 meters above the reference level, slowly rising after

complete dry-down during the 2012-2013 eruptive activity. The lake had a temperature of 68 °C and consisted of a main uniform pool, of light greyish green color reflecting the amount of particles in suspension (Figure 4-4 a). Smaller pools without signs of convection were observed on the sides. Evaporation from the lake surface is evident on Figure 4-4-a. Bubbling was also observed, indicating direct gas escape in addition to evaporation.

Figure 4-3: Crater lake time series showing variations in level and temperature. Green arrows represent the three sampling campaigns. The grey area delineates the 2012-2013 eruptive sequence, during which the crater lake disappeared.

The level had slightly increased on 5 June 2015, accompanied by a decrease in temperature down to 57.4 °C. A scum layer containing sulfur globules was floating at the surface of the lake (Figure 4-4 c). As noted in October 2014, Figure 4-4-c shows that evaporation and bubbling were still taking place. The lake was not as uniform as during the first visit, with various colors of grey and yellowish green observed at the surface (Figure 4-4 b), indicating that convection was not sufficient to completely homogenize the system.

The lake level had increased again on 23 December 2015. Despite this rise, the shore at the sampling site consisted of a thick layer (at least 30 cm) of smooth, unpacked mud-like sediments, emphasizing drying and precipitation of this portion of the lake (Figure 4-4 d). The temperature had risen to 74.5 °C. The warming of the system was also observed around fumarole 0, where hot springs and mud pools had dried. Despite the lake looking more uniform than during the previous visit, pools of different colors were still observed. Overall, the grey coloration of the lake indicates stronger convection, in accordance with the rise in temperature. Such a grey pool was present at the sampling site, where water and suspended particles were collected.

Figure 4-4: Pictures of the crater lake during the different sampling campaigns. a) Photo taken from the helicopter on 24/10/14 showing a mostly uniform lake (looking north). Small pools with different colors are seen only on the sides. Many fumaroles are visible at the back of the lake. b) Picture taken from the western rim on 5/06/15 showing different pools in the lake, varying in color from bright green to pale greyish green. The vigorous fumarole at the back of the lake is well exposed. c) Photo taken from the crater floor on 5/06/15. The scum layer rich in sulfur globules is the darker layer close to the shore. Note the two persons at the sampling location on the left for scale. d) Picture taken from the crater floor on 23/12/15 showing the thick smooth layer of dried sediments extending from the shore. A zone with a grey color is present on the left side of the lake. Note the black arrow indicating north. Pictures: Celine Mandon, GeoNet.

The lake level kept on rising until early 2016, when a rapid decrease began, preventing further water sampling. It consisted of a shallow pool in June and October 2016, which had completely disappeared by December (Figure 4-5).

Figure 4-5: Pictures of the lake in late 2016. a) Photo taken from the crater floor on 30/09/16 showing the almost dried lake, with only small pools remaining. b) Picture of the dried lake on 20/12/16 taken from the crater floor (drone). Photo courtesy of GeoNet.

In terms of chemistry, White Island crater lake has a composition similar to those of other hyperacidic lakes, with average contents of 140 335 mg.L⁻¹ for chlorine and 27 075 mg.L⁻¹ for sulfate over the studied period. The pH is negative, fluctuating between -0.71 to -0.87 and the total dissolved solids (TDS) is around 200 000 mg.L⁻¹. Some trace metals are very concentrated: 6.3-8.6 µg.g⁻¹ of Cu, 10.6-17.2 µg.g⁻¹ of Zn, 6.7-18 µg.g⁻¹ of Pb, 11.6-12.7 µg.g⁻¹ of As, 0.3-1.3 µg.g⁻¹ of Hg, 3.0-7.5 µg.g⁻¹ of Tl. The complete analyses of the water are presented in Table 4-1.

Table 4-1: White Island crater lake and spring compositions.

	Crater Lake	Crater Lake	Crater Lake	F0 Pool	F0 Pool
Sampling date	24/10/14	5/06/15	23/12/15	5/06/15	15/10/15
T (°C)	68.0	57.4	74.5	99.3	101.2
pH	-0.77	-0.83	-0.85	-0.84	-0.8
Major and minor elements (µg.g ⁻¹)					
Cl	142 454	153 300	134 198	142 285	141 313
SO ₄	27 209	27 337	28 147	1410	1218
B	282	316	259	134	587
Na	7372	6401	4829	27	26
Ca	4417	5305	5619	48	49
Mg	4076	3292	2687	34	37
Al	9492	7902	6766	89	89
Fe	4678	3879	3046	198	460
K	2716	2425	1850	27	29
As	11.60	12.30	14.30	36	64

	Crater Lake	Crater Lake	Crater Lake	F0 Pool	F0 Pool
Sampling date	24/10/14	5/06/15	23/12/15	5/06/15	15/10/15
Li	9.9	8.6	6.1	0.03	0.05
Si	39	41	43	51	45
H ₂ S	<0.01	0.22	0.20	0.13	0.17
Br	455	465	600	3.1	16.3
F	3067	1793	1470	1.2	2.2
NH ₃	277	275	236	0.38	0.41
Rb	11.81	5.81	5.50	0.08	0.09
Sr	28.82	20.78	21.17	0.25	0.23
Zr	1.67	1.99	1.88	0.48	0.68
Sn	1.14	0.79	0.69	0.01	0.02
Sb	1.67	1.49	1.60	0.69	2.36
Ba	32.81	2.49	2.20	0.95	2.44
Tl	7.53	3.32	3.02	0.01	0.02
Pb	18.00	7.68	6.70	0.03	0.08
Bi	5.74	2.64	2.68	0.01	0.01
Sc	2.81	2.29	2.37	0.05	0.04
Ti	54.10	41.98	48.30	24.57	45.13
V	25.98	20.84	19.25	0.37	0.43
Cr	41.93	23.95	19.36	0.89	2.09
Mn	172.0	100.1	82.29	0.92	1.27
Co	1.99	1.55	1.35	0.23	0.31
Ni	7.07	5.04	5.19	0.62	1.39
Cu	5.70	5.80	6.00	2.50	2.28
Zn	17.24	10.62	12.50	0.13	0.28
Ga	1.74	1.33	1.16	0.03	0.02
Trace elements (ng.g ⁻¹)					
Mo	81.68	439.9	89.27	30.22	36.97
Ag	41.10	34.05	36.05	5.20	7.24
Cd	253.5	138.6	95.18	1.04	2.04
In	165.9	101.0	72.14	0.37	0.78
Re	0.52	0.36	0.29	0.07	0.10
Au	2.07	1.36	0.58	0.11	0.33
Hg	584.0	270.1	1281	43.55	34.31

Reproducibility (1 RSD): Hg $\pm$ 110%; Te $\pm$ 71%; Sn $\pm$ 61%; Se, Tl, Au, W, Ag, Na $\leq$ $\pm$ 40%, B, Cd, Sb, Re, Pb, Bi, Mg, Sc, Ti, Cr, Zn, K $\leq$ $\pm$ 20%; $\leq$ $\pm$ 10% for the rest of the elements (Appendix A.7).

Bubbling at the surface of the lake provides evidence of fumarolic discharge at the bottom. The numerous vents observed at lower lake levels also confirm direct gas discharge into the lake. These gases are responsible for the highly acidic nature of the lake through disproportionation of HCl and hydrolytic reaction of SO₂ (Christenson et al., 2017). They also maintain the lake temperature due to enthalpy loss during steam condensation (e.g. Brown et al., 1989).

4.3.2 Solid samples

4.3.2.1 Suspended particles

The suspended particles are rich in Ti, Ba and Ag compared to the lake water (Table 4-2). The sample collected in June 2015 is richer in As, Ba, B and Tl than the later sample from December 2015. Collection in December led to an estimate of 14g of suspended particles per kilogramme of water. Calcium sulfate (gypsum and/or anhydrite), barite, SiO₂, TiO₂ and Al-K sulfate (most likely alunite) were observed by SEM in the suspended particles. This is consistent with the results from X-ray powder diffraction, highlighting the presence of anhydrite, gypsum and cristobalite, with minor amounts of alunite, halite and quartz (Appendix A.5). Halite, instead of being saturated in the lake water, most likely formed after collection, by evaporation of residual water on the filter. The proportion of barite and TiO₂ is too small to be detected by XRD. Moreover, we observe a broad hump in the XRD spectra at $2\theta = 20-22.5$ (Appendix A.5), probably highlighting the presence of amorphous silica. Particulate amorphous silica has in fact been reported as abundant in the suspended solids of Kawah Ijen crater lake (Delmelle and Bernard, 1994).

Table 4-2: Composition ($\mu\text{g.g}^{-1}$) of sediments, scum layer, suspended particles, ash, sulfur globules and andesite.

	Sediments	Scum	Suspended particles	Suspended particles	Ash	S globules	Andesite
Sampling	5/06/15	5/06/15	5/06/15	23/12/15	28/04/16	5/06/15	4/04/77
Na	7334	9013	21404	27389	12945	105.5	16988
Ca	53932	57915	25706	18117	48276	211.8	57819
Mg	4193	4247	8700	10247	4776	47.0	48185
Al	22240	8503	21401	19573	37334	104.8	69966
Fe	15306	19095	8296	9605	20762	18679	56096
K	6760	2585	6170	6563	10329	35.7	11871
B	26.47	17.40	339.5	194.7	nd	0.21	25.12
Rb	30.75	10.25	25.64	24.09	33.76	0.08	46.89
Sr	171.0	96.79	108.7	87.69	683.9	0.61	161.0
Zr	91.30	16.68	59.30	46.38	93.83	0.31	97.84
Mo	1.33	2.04	1.46	1.22	1.52	0.85	1.01
Ba	631.9	108.0	132.5	50.54	610.0	7.07	509.8
Tl	5.73	5.37	19.67	9.93	2.85	1.11	0.19
Pb	12.69	11.40	15.04	14.52	7.69	2.66	7.73
Bi	1.87	4.66	6.52	7.93	1.40	1.23	0.76
Sc	8.75	5.75	8.22	9.17	13.77	0.07	30.43
Ti	3522	1000	3203	2507	3902	26.44	3701
V	68.16	28.09	67.96	71.57	113.6	0.76	211.3
Cr	74.96	35.35	63.50	66.44	119.3	5.90	355.8
Mn	123.2	102.5	211.1	254.5	197.9	2.47	1059
Co	9.09	22.28	4.57	5.57	18.53	21.00	31.81
Ni	22.64	52.56	12.42	16.89	43.70	49.78	114.3
Cu	55.69	91.01	30.30	29.11	84.41	80.94	81.29

	Sediments	Scum	Suspended particles	Suspended particles	Ash	S globules	Andesite
Zn	13.41	16.14	28.76	39.28	18.91	0.86	46.67
Ga	5.45	1.81	4.73	4.98	7.47	0.04	12.95
As	26.33	762.5	309.0	92.31	46.70	291.2	4.76
Se	31.39	314.7	nd	nd	39.18	938.3	nd
Ag	0.89	0.23	0.66	0.63	0.89	0.08	0.04
Cd	0.13	0.16	0.37	0.31	0.18	0.02	0.05
In	0.06	0.11	0.23	0.26	0.06	0.01	0.05
Sn	1.36	1.06	2.88	2.57	7.37	0.06	1.47
Sb	2.16	1.96	5.66	6.00	1.80	0.27	0.19
Te	3.34	42.62	0.36	0.40	3.78	142.99	0.001
Sm	2.20	0.77	0.98	0.82	2.14	0.01	2.39
Yb	0.90	0.27	0.67	0.57	1.36	0.004	1.99
W	0.87	0.38	0.74	0.51	1.07	0.08	1.25
Re	0.05	0.22	0.05	0.05	0.15	0.17	0.001
Au	0.09	0.10	0.06	0.06	0.06	0.19	0.0001

Notes: nd: Below detection limit.

4.3.2.2 Sulfur spherules

The composition of mixed color sulfur globules is presented in Table 4-2. They are enriched in various elements such as Se ($\sim 900 \mu\text{g.g}^{-1}$), As ($\sim 300 \mu\text{g.g}^{-1}$), Te ($\sim 150 \mu\text{g.g}^{-1}$), Cu ($\sim 80 \mu\text{g.g}^{-1}$), Co ($\sim 21 \mu\text{g.g}^{-1}$), Re ($\sim 169 \text{ ng.g}^{-1}$), and Au ($\sim 189 \text{ ng.g}^{-1}$). This partly explains the enrichment of the sediments in the latter species. Pyrite crystals up to $20 \mu\text{m}$ were observed with the SEM at the surface and in cavities of black sulfur globules, as reported at other crater lakes (Delmelle and Bernard, 1994). This is also in agreement with the findings of Takano et al. (1994), who reported native sulfur with a black color to contain $\sim 10\%$ of pyrite. ICP-MS analyses of black and yellow globules showed that the former are richer in metals (

Table 4-3 and Appendix A.4). The high metal contents in the dark globules may be explained by the presence of metal sulfides, as observed on the surface of sulfur spherules at Kawah Ijen (Delmelle and Bernard, 1994; Henley, 2015).

Table 4-3: Composition ($\mu\text{g.g}^{-1}$) of black versus yellow sulfur globules.

	Sulfur globules yellow	Sulfur globules black
Fe	442.1	20582
Tl	0.17	1.31
Pb	0.35	3.30
Bi	0.15	1.71
Co	0.20	27.14
Ni	0.34	62.20
Cu	0.79	98.97
Zn	0.51	1.37
Se	305.8	701.2
Ag	0.009	0.096
Cd	0.007	0.032
Te	186.982	128.643
Re	0.003	0.294
Au	0.010	0.124
Hg	nd	0.059

Note: nd: Below detection limit.

4.3.2.3 Sediments

SEM observations and EDS analyses of the sediments collected on the lake bottom on 5/06/15 revealed the presence of barite, TiO_2 , SiO_2 , altered silicates, gypsum/anhydrite, Al-Na sulfate and pyrite.

Cores from June 2015 (Core 1a and 1b) have a crystalline yellow layer at the top, most likely formed by evaporation during crater lake level fluctuations (Figure 4-6 and Appendix A.6). As the cores were sampled close to the shore, a small variation in lake level would result in drying of the shallow parts. This is consistent with the variation in chemistry of the sediments (Appendix A.4). XRD analysis of this crystalline layer (Core 1b-1) revealed that it is mostly composed of gypsum, with small amounts of anhydrite, cristobalite and halite (Appendix A.5). It is also enriched in Sr, Sc, As, Cd and In (Table 4-4). On the other hand, we note that Ba is depleted in the evaporite material. The dark thin layer (Figure 4-6) observed in the upper section arises from the presence of black sulfur spherules within the gypsum crystals. As previously noted, the black globules are covered with small crystals of pyrite.

Table 4-4: Composition (ng.g⁻¹) of selected layers from the sediment cores.

	Core 1b-1	Core 1b-6	Core 1b-9	Core 2-1	Core 2-6	Core 2-10	Core 2-13
Date	5/06/15	5/06/15	5/06/15	23/12/15	23/12/15	23/12/15	23/12/15
Na	9516	3614	5596	3525	4445	4498	3512
Ca	137766	39832	35178	22008	30663	4224	8999
Mg	4795	3672	4006	1842	2232	2153	1863
Al	13335	8227	24378	5785	11878	16298	10833
Fe	6887	9792	13100	15594	8695	12747	8984
K	4266	2757	7115	1570	2953	4543	2499
Sr	264.8	75.94	131.2	285.0	492.1	147.5	186.0
Ba	120.8	225.1	508.4	300.8	563.6	384.6	597.1
Tl	6.28	1.93	2.32	3.10	3.81	4.48	3.22
Pb	14.71	5.15	10.52	5.43	5.29	5.73	3.83
Bi	5.19	1.63	1.30	3.01	2.39	2.08	1.89
Sc	20.25	4.13	8.66	2.48	4.81	4.91	3.52
Ti	753.3	1097	3474	967.1	3006	3269	3196
Cr	49.50	35.33	71.99	23.28	29.02	26.99	25.17
Co	3.48	6.54	5.87	13.20	5.99	9.72	6.17
Ni	10.33	17.12	14.34	34.35	14.40	24.48	14.98
Cu	17.16	27.47	36.30	76.18	37.73	54.41	47.88
Zn	24.11	7.43	12.09	18.43	10.78	12.35	9.27
Ga	2.90	1.72	5.27	1.21	2.06	2.88	1.77
As	52.26	138.4	21.07	549.5	333.3	86.11	238.2
Se	nd	296.3	29.61	540.4	169.3	227.1	202.6
Ag	0.18	0.23	0.80	0.21	0.64	0.97	0.70
Cd	0.23	0.07	0.13	0.09	0.10	0.13	0.09
In	0.15	0.04	0.05	0.07	0.08	0.06	0.06
Sn	0.98	0.48	0.88	0.87	8.85	1.29	1.11
Sb	2.25	1.02	1.82	1.21	1.75	1.73	1.62
Te	nd	1.23	0.15	52.97	15.10	21.51	16.76
Re	0.01	0.03	0.02	0.22	0.12	0.11	0.12
Au	0.04	0.03	0.10	0.02	0.03	0.05	0.03

Note: nd: Below detection limit

One of the cores (Core 1b) contained a second layer of yellowish crystalline material (Figure 4-6), the composition of which is similar to the one at the top (Core 1b-1, see Table 4-4). This most likely reflects an earlier episode of evaporation that did not occur at the location of the other sediment core. Underneath this layer is a horizon (Core 1b-6) very rich in sulfur spherules, with high Se and Te contents (296 µg.g⁻¹ and 1.2 µg.g⁻¹ respectively, see Table 4-4). The lower part of both cores is quite uniform, made of coarse grey to whitish particles. It also contains larger clasts, up to 5 cm in length, probably from blocks falling into the lake. Yellow sulfur globules are visible in some of the horizons. XRD results show gypsum, alunite, sulfur and Al-rich silicate to be the main components, with minor amounts of pyrite (Appendix A.5). Two broad humps are also visible on the spectra, at around 2θ = 11-14 and

$2\theta = 20\text{-}23.5$, corresponding to altered silicates and amorphous silica, respectively. Small dark particles are found in the bottom layers, consisting of glassy silica with holes filled with white milky crystals (most likely sulfates).

Figure 4-6: Pictures of sediment cores and the analyzed layers. Core 1b was sampled on 6 June 2015. Note a very thin black layer in the top yellow layer. Core 2 was sampled on 23 December 2015.

The sediment core collected in December 2015 (core 2) is very different. It consists of soft sediments, mud-like, from the dried accessible shore, in which we were sinking by more than twenty centimetres at each step. The coarser horizon at the bottom of core 1b is not present, in agreement with a formation by evaporation rather than sedimentation and/or alteration of silicates falling into the lake. The absence of a crystalline layer as seen in June implies different conditions of evaporation.

The most striking difference between horizons in Core 2 arises from the presence or absence of sulfur spherules. Sediments are darker and coarser when sulfur spherules are present (Layers 1, 2, 3, 4, 5, 8, 10), whereas layers without globules appear greener and are comprised of smaller particles (Figure 4-6) similar to the suspended material collected on the cellulose filter. This is reflected in the composition (Table 4-4 and Appendix A.4), with high Fe and Te contents in the first five layers, as well as in layers 2-8, and 2-10 (dark and coarse).

XRD analysis reveals that the pale greenish thin horizons at the middle of the core (e.g. Core 2-6) consist of anhydrite and sulfur, with minor amounts of cristobalite and gypsum (Appendix A.5). The high contents of sulfur and anhydrite is responsible for the cement-like aspect of the sediments in these horizons. The broad hump at $2\theta = 11-14$ is visible on the diffractogram, pointing to the probable presence of altered silicates. Pale greenish layers at the bottom (e.g. 2-13) are similar to the analysed layer 2-6 (Table 4-4 and Appendix A.4), although their composition point to a higher sulfur to anhydrite ratio, given the lower Ca content. The very high content of calcium in layers 2-1 and 2-2 most likely corresponds to observed gypsum crystals. It is interesting to note that layer 2-13 is enriched in Ag ($0.70 \mu\text{g.g}^{-1}$) compared to the top ($0.21 \mu\text{g.g}^{-1}$ in Core 2-1), which is rich in sulfur spherules. Core 2 is very different from the sediments sampled in June 2015, highlighting sedimentation of gypsum and sulfur spherules at times, changing to sulfur and anhydrite.

The differences observed in the sediment cores indicate changes in precipitating minerals with time, switching from gypsum, alunite, sulfur and Al-rich silica as main components in June 2015, to sulfur and anhydrite in December 2015 (Appendix A.5). The overall composition of sediments and suspended particles is similar to what has been reported at other hyperacidic crater lakes (Wood, 1977; Brantley et al., 1987; Delmelle and Bernard, 1994). Sulfur spherules in such lakes are thought to originate from molten sulfur present at the bottom, through which gases are injected, forming these spherical, sometimes hollow globules (Rowe et al., 1992b; Delmelle and Bernard, 1994; Pasternack and Varekamp, 1994). The presence of such a sulfur body has also been inferred by Christenson et al. (2017), to explain the sulfur-rich eruptions witnessed in 2013 (cf. Chapter 2). The sporadic presence of sulfur globules in the lake sediments suggests differences in the gas discharge regime (bubbling) as well as convection within the lake itself as a function of time. It might also reflect variations in water level, with deposition occurring only on the lake shore due to their low densities.

4.3.2.4 Ash

The ash ejected during the April 2016 phreatic eruption represents material from deeper within the hydrothermal system. It is thus not surprising to find abundant anhydrite and alunite, detected by SEM and XRD. In lesser amount, cristobalite, gypsum, pyrite and quartz were also identified (Appendix A.5), with altered silicates and traces of a Fe- and Cr-rich compound. This mineralogy is similar to that in the suspended particles and sediments from the crater lake, as well as the altered assemblage described by Hedenquist et al. (1993). This highlights recirculation of lake fluids in the upper part of the hydrothermal system. It is worth noting that the pyrite/anhydrite assemblage can also result from gas-rock interactions. Henley et al. (2015) showed that SO_2 -rich gases may react with Ca-bearing silicates producing Ca sulfate and H_2S , the latter efficiently capturing Fe from the gas to form iron sulfides.

Precipitation of secondary minerals in the residual porous rock beneath the lake is of importance as it reduces permeability (Heap et al., 2017). Anhydrite and alunite might indeed be responsible for the sealing of the system, leading to overpressure and phreatic eruption, as reported at other volcanoes (Christenson and Wood, 1993; Wood, 1994; Christenson et al., 2007; Christenson et al., 2010). This process was most likely responsible for the phreatic eruption that occurred in April 2016 without warning. ICP-MS analyses indicate that the bulk Cu content of the ash is higher than that of the andesite (Table 4-2). This suggests deep precipitation of Cu-rich minerals, probably as halides or sulfides, subliming from the high-temperature gases (Bernard, 1985; Symonds et al., 1987). It may also occur through saturation of deep brines scrubbing volatile metals from the gas phase. Silver is very concentrated in the ash and sediments compared to the andesite, although no silver containing particles were observed with SEM nor XRD.

The presence of SiO₂, gypsum/anhydrite, alunite, pyrite and barite in suspended particles and ash indicates that the sediments filling the eruption crater complex at White Island are partly comprised of secondary minerals. Andesite falling from the lake rim and subsequently altered by the acidic waters is another source of material, as evidenced by the coarser particles found on the shore and the Si-rich grains. Finally, elemental sulfur is present at the lake bottom, most likely in a molten form, and appears to be effective at sequestering chalcophile elements such as Fe, Se, Te, As, Cu, Co, Au and Re. This body of molten sulfur is thought to form through disproportionation of SO₂, oxidation of H₂S and polythionates (Takano and Watanuki, 1990; Rowe, 1994). The presence of pyrite on the sulfur spherules suggests a more reduced environment close to subaqueous vents, where the H₂S-bearing gases meet metal-rich waters and form sulfides.

4.4 Sources of crater lake water

As previously discussed in the introduction, hyperacidic crater lakes derive their extremely low pH by accumulation or scrubbing of magmatic vapors. The strong enrichment in Cl⁻ and SO₄²⁻ observed in White Island crater lake manifests such a magmatic input. The sulfur content is controlled by several reactions. For example, the elemental sulfur and sulfates observed in the sediments have an impact on the S content of the water, lowering it by precipitating and increasing it during remobilization of previously crystallized phases. On the other hand, Cl is conservative and only affected by variations in magmatic input and evaporation/dilution processes (Giggenbach, 1974). Rock-water interactions between the reactive, acidic fluid and the host andesite are responsible for the high total dissolved solids (TDS) values.

The element transfer ratio (ETR), introduced by Pasternack and Varekamp (1994), highlights the three processes occurring in hyperacidic crater lakes: 1) magmatic gas input, 2) rock dissolution (constant HCl input enables on-going titration of the host rock), 3) precipitation of secondary minerals. The ETR is defined as:

$$ETR = (X/Mg)_{water} / (X/Mg)_{andesite}$$

where $(X/Mg)_{\text{water}}$ is the ratio of element X to magnesium in the water and $(X/Mg)_{\text{andesite}}$ is the same ratio in the andesite. We use Mg as a reference element, as it is considered to remain in solution in acidic fluids (i.e. it does not form secondary minerals) (Giggenbach, 1974). The calculated ETR are presented in Figure 4-7. Three groups of elements are observed: 1) elements with ETR ~ 1 showing a similar dissolution from the andesite as Mg; 2) elements with ETR > 1 showing an enrichment due to either dissolution of earlier precipitated minerals, and/or input through magmatic gases; 3) elements with ETR < 1 reflecting limited dissolution, and/or precipitation of secondary minerals.

Figure 4-7: Element Transfer Ratio for the crater lake samples and F0 Pool normalized with 1977 andesite.

The phases observed in lake sediments (i.e., $BaSO_4$, TiO_2 , SiO_2) suggest that precipitation of secondary minerals explains the ETR < 1 for Ba, Ti and Si. In the case of silica, limited dissolution may also be responsible for the low ETR, as indicated by Si-rich residual rocks found underneath crater lakes. Calcium has an ETR ~ 1 despite its presence as sulfate in the suspended particles and sediments. In contrast, the enrichment of elements on the left side is most likely due to gaseous input at the lake bottom. Most of these species are in fact transported by volcanic gases (Lambert et al., 1985; Rose et al., 1986; Varekamp et al., 1986; Symonds et al., 1987; Quisefit et al., 1989; Symonds et al., 1992; Hinkley et al., 1994; Cheynet et al., 2000). Enrichment of Hg, Tl, Sb, B, Au, Bi, As, Cd and In is particularly high, as reported at other hyperacidic crater lakes (Delmelle and Bernard, 1994; Pasternack and Varekamp, 1994; Sriwana et al., 2000; Varekamp et al., 2009; van Hinsberg et al., 2010a). It is interesting to note the low enrichment factor for Cu, as previously reported in brines from White Island (Giggenbach et al., 2003) and interpreted to reflect enargite precipitation at depth by Hedenquist et al. (1993).

Figure 4-8 shows the relative abundances of F, Mg and Al of the water since the lake formation in 2001. The dacite is the average composition of historic dacitic rocks from Graham and Cole (1991), whereas andesite is one of the 1977 ejecta. We clearly see the influence of both dissolution of the rock, mostly dacite, and magmatic gases on the composition of the water. The enrichment of Mg relative to Al emphasizes precipitation of Al-rich secondary minerals, compared to the conservative nature of magnesium. The rock endmember is closer to the dacitic composition than andesite, in agreement with the findings of Cole et al. (2000), reporting dacite as the product of major eruptions.

Figure 4-8: Ternary diagram 3*F-Al-3*Mg showing the composition of the crater lake water since its formation in 2001. The historical data is from GeoNet. Also shown are the composition of the host rocks, both andesite and dacite, and the composition of fumarolic gases on 23/12/14 and 05/06/15.

The ETR for F0 Pool is plotted for a comparison in Figure 4-7. Values near 1 for rock-forming elements (Ca, alkali metals, Mn, Sm, Sr, Rb) emphasize the extent of rock dissolution in this hot and acidic spring. Differences in Ag and B might be explained by precipitating phases rich in these elements in the lake, as shown by their greater concentration in the sediments, ash and suspended particles in comparison to the lake water and andesite (Table 4-2). Similarly, the higher abundances of chalcophile Au, As, Re, Cu and Mo in the acid spring might reflect scavenging by elemental sulfur at the bottom of the lake. Only Si has a negative ETR, emphasizing that most of the secondary minerals precipitating in the crater lake (i.e., BaSO_4 , TiO_2) are not saturated in F0 pool. Overall, the similarities between crater lake water and F0 pool support the findings of Christenson et al. (2017), suggesting comparable source components resulting from water-rock-magmatic gas interactions.

The isolol plot (Figure 4-9) shows that a congruent dissolution of 100 g of dacite per liter of water explains the observed composition for most of the elements. This value is slightly higher than the one reported by Delmelle and Bernard (1994) for the crater lake at Kawah Ijen and Christenson and Wood (1993) for Ruapehu crater lake. Si and Ba are depleted in the lake water, in agreement with the ETR plot and the observed secondary minerals in the sediments.

Figure 4-9: Isosol plot showing the crater lake water composition against the host dacite. The dacite composition was taken from Graham and Cole (1991).

4.5 Water speciation and saturation

Thermodynamic calculations performed to constrain the speciation and saturation of natural waters assume a system in equilibrium. White Island crater lake, as we have demonstrated earlier, is a very active system: magmatic gases are continually injected at the bottom of the lake, where elemental sulfur forms. In contrast, surficial waters are in contact with the cooling and oxidizing atmosphere. Pools of various colors indicate convection and mixing of fluids within the lake. The varying secondary minerals in sediment cores moreover reflect changes in temperature and/or redox and/or composition with time. In summary, an evolving thermal gradient, as well as a redox gradient, exist between the bottom and surface of White Island crater lake, at odds with the equilibrium state assumed for calculations. Our approach to overcome the complexity of this natural system for thermodynamic modelling, is to consider two systems with redox conditions representative of the bottom and the surface of the lake respectively. The lake water is likely to be reduced at depth where magmatic gases are injected (Delmelle and Bernard, 1994) and more oxidized at the surface.

Calculations were performed using the SpecE8 module within The Geochemist's Workbench software (Bethke, 2007). Activity coefficients applicable to the electrolyte solution of the crater lake are derived using the extended Debye-Hückel expression of Helgeson (1969) and the B-dot deviation function. Given no major changes were observed between different water samples from the crater lake, we only report results from the June 2015 sample. Speciation and saturation calculations were also performed for the June 2015 F0 pool sample. The LLNL database (Delany and Lundeen, 1989) was used for calculations, allowing variations of pH to satisfy charge balance.

4.5.1 Speciation and saturation of surficial oxidized waters

We first estimated the speciation in the surficial waters, assumed to be in equilibrium with the atmosphere. The redox state was thus controlled by f_{O_2} in air (i.e. $\log f_{O_2} = -0.68$). The following results are all computed results. HSO_4^- is the dominant sulfur species, as expected

in these acidic waters, more than two orders of magnitude higher than H_2SO_4 and SO_4^{2-} . Free Cl^- is dominant, associated HCl being 5 orders of magnitude lower. Free ions are also expected to be the dominant species for the major cations Na^+ , Al^{3+} and K^+ . Complexes are nevertheless quite stable, as indicated by the high molalities of AlF^{2+} , NaCl , KCl and AlSO_4^+ , less than an order of magnitude lower than the free ions. The stability of AlF^{2+} reflects the high concentration of F in the crater lake (i.e. $1793 \mu\text{g.g}^{-1}$). The dominant Ca species is found to be CaCl^+ , followed by Ca^{2+} . MgCl^+ and Mg^{2+} dominate in the case of Mg. The oxidized $\text{Fe}^{(\text{III})}$ species are stable in the surficial waters, dominated by FeCl_2^+ , FeCl_3 and FeCl^{2+} . Ionic complexes are the most stable species concerning trace metals (Table 4-5). CuCl^+ , followed by CuCl_2 and Cu^{2+} , are the most abundant Cu species. Complexes with Cl ligands are also dominant for Zn and Pb, as ZnCl_4^{2-} and PbCl_4^{2-} . Calculations suggest H_3AsO_4 (As^{V}) is the dominant arsenic species in the crater lake.

Table 4-5: Calculated dominant metal complexes in the crater lake water from 5 June 2015 ($\Sigma\text{Cl} = 5.93 \text{ mol/kg}$) under oxidized ($\log f_{\text{O}_2} = -0.68$) and reduced ($R_{\text{H}} = -3.5$, equivalent to $\log f_{\text{O}_2} = -65$) conditions.

	Σelement (molarity)	Oxidized surficial environment Dominant complexes (molarity)	Reduced deep environment Dominant complexes (molarity)
Ag	4.02E-07	AgCl_4^{3-} (4.00E-7), AgCl_3^{2-} (2.24E-9)	AgCl_4^{3-} (4.00E-7), AgCl_3^{2-} (2.38E-9)
As	2.10E-04	H_3AsO_4 (2.09E-4)	$\text{As}(\text{OH})_3$ (2.09E-4)
Cu	1.17E-04	CuCl^+ (5.73E-5), CuCl_2 (3.70E-5), Cu^{2+} (1.32E-5), CuCl_3^- (7.14E-6)	CuCl_3^{2-} (1.14E-4), CuCl_2^- (2.87E-6)
Fe	8.87E-02	FeCl_2^+ (5.23E-2), FeCl_3 (1.78E-2), FeCl^{2+} (1.47E-2), FeCl_4^- (1.95E-3), FeHSO_4^{2+} (1.63E-3)	FeCl_2 (4.39E-2), FeCl^+ (3.99E-2), Fe^{2+} (4.86E-3)
Pb	4.73E-05	PbCl_4^{2-} (4.38E-5), PbCl_3^- (2.75E-6)	PbCl_4^{2-} (4.35E-5), PbCl_3^- (2.91E-6), PbCl_2 (7.31E-7)
Zn	2.07E-04	ZnCl_4^{2-} (1.91E-4), ZnCl_3^- (1.30E-5)	ZnCl_4^{2-} (1.90E-4), ZnCl_3^- (1.37E-5)

In addition, the saturation index (SI) for a number of minerals was determined using the expression:

$$SI = \log Q/K$$

where Q and K are the activity quotient and the equilibrium formation constant of the respective mineral. Values equal to 0 indicate saturation with respect to a mineral whereas $SI > 0$ and $SI < 0$ reflect supersaturation and undersaturation respectively.

In surficial waters in equilibrium with the atmosphere, barite and silica phases (quartz, tridymite, chalcedony, cristobalite and amorphous silica) are calculated to be slightly supersaturated. We nevertheless favor the presence of cristobalite, following the XRD results of the sediments and the altered assemblage reported by Hedenquist et al. (1993). In both cases, anhydrite and gypsum are computed slightly undersaturated. We calculated SI at 30

°C, 100 °C, 200 °C and 300 °C to assess the effect of temperature on the precipitating phases. No change occur at 30 °C and 100 °C. At 200 °C, only quartz, tridymite and chalcedony are supersaturated. Quartz remains the only saturated phase at 300 °C. It should be noted that Al-bearing minerals such as diaspore, boehmite and gibbsite, as well as alunite, show SI tending towards 0, following their retrograde solubility. This is an important fact, confirming the assumption that alunite plays a role in sealing the system at depth, where these higher temperatures exist. Natroalunite saturation at lake temperature is observed in the sediments and suspended particles, although not confirmed due to lack of thermodynamic data.

Calculations show that F0 pool is supersaturated with silica (quartz, tridymite, chalcedony, cristobalite and amorphous silica), with all the sulfates predicted close to saturation in crate lake water far from saturation ($\log Q/K < 1.8$). This is in line with the ETR calculated above, showing Si only to be precipitating.

4.5.2 Speciation and saturation of deeper reduced waters

When modelling the speciation at the lake bottom, we used R_H ($R_H = \log (f_{H_2} / f_{H_2O}) \approx \log (x_{H_2} / x_{H_2O})$, (Giggenbach, 1987)) measured in White Island fumarolic gases to control the redox state. We took an average value of $R_H = -3.5$ from fumarole F0 gases. The computed speciation of chloride and most of the major cations is not affected greatly by changes in redox state. In contrast, the distribution of sulfur species changes drastically, with $H_2S_{(aq)}$ becoming the dominant phase. The dominant $Fe^{(III)}$ species in oxidized waters are replaced by $Fe^{(II)}$ species, as shown in Table 4-5. This table also shows that Ag, Zn and Pb speciation is not affected by changes in redox state, in contrast to Cu, Fe and As. $As^{(V)}$ species are replaced by $As^{(III)}$ arsenous acid ($As(OH)_3$), whereas $Cu^{(I)}$ chloride complexes become the dominant species.

The predicted saturated species in the more reduced environment present at the lake bottom vary greatly, with precipitation of various metal sulfides. Orpiment and realgar are highly supersaturated, with SI of 28 and 12 respectively. These really high values suggest that additional minerals such as arsenolite or arsenate, not taken into account in our calculations, may be saturated. Pyrite, bornite and covellite are supersaturated (SI of 2.7, 1.8 and 1.4 respectively), chalcopyrite and chalcocite are slightly supersaturated (SI of 0.5 and 0.4 respectively), whereas galena, sphalerite and pyrrhotite and undersaturated ($SI < -3$). Elemental sulfur is also predicted to be precipitating ($SI = 0.3$) under these conditions, in agreement with the observed sulfur globules.

The results from these thermodynamic calculations generally agree with the minerals observed in the suspended particles and sediments. We should note the absence of Ag-rich minerals in the calculations despite the high enrichment in both the sediments and ash. Sulfur and alunite are other species observed in sediments and suspended particles (alunite only) that are not predicted in the computations. This disagreement might reflect incorrect thermodynamic database. It may also emphasize the active character of the crater lake, with different redox and temperature conditions with depth, ignored in our modelling. It is worth noting that Na-bearing alunite (i.e. natroalunite) may also be forming instead of the pure phase. The chemistry of sulfur in hyperacidic crater lakes is rather complex and has been detailed in several studies (Takano, 1987; Takano and Watanuki, 1990; Takano et al., 1994;

Delmelle and Bernard, 2015). Elemental sulfur is thought to form through deposition reactions involving magmatic SO_2 and H_2S , and/or intermediate sulfur species such as polythionates, polysulfides and thiosulfate (see Figure 4-11).

The presence of pyrite in the ash erupted in April 2016 and on the sulfur globules reflects reducing environment underneath the lake. Pyrite precipitation in reduced environment has been shown to incorporate various metals as minor elements (Fleischer, 1955; Craw et al., 2003; Yamaguchi and Ohmoto, 2006; Berner et al., 2013), and might explain the strong enrichment of the Tl, Pb, Bi, Co, Ni, Cu, Ag, Cd, Re and Au in the dark globules (

Table 4-3). The absence of any other metal sulfides may reflect pyrite precipitation at temperatures slightly over 250°C , at which FeS_2 becomes less soluble in contrast to other sulfides, which solubility increases (Reed and Palandri, 2006). It is also possible that we did not observe sulfides other than pyrite due to their low amount. This is especially relevant given that Fe concentration in the lake water is more than two orders of magnitude higher than that of Cu and Pb (Table 4-1).

Figure 4-10: R_H -pH stability diagram of various Cu sulfides. The fields representing the oxidized surficial waters (S) and the reduced environment at the lake bottom (B) are shown. The stability of sulfur species is also represented to emphasize coprecipitation of sulfides and elemental sulfur.

The elevated metal concentrations of sulfur spherules and the predicted precipitation of sulfides in reduced environment nevertheless highlights removal of metals from these fluids deeper in the system. Figure 4-10 shows the stability field of Cu sulfides as a function of the redox and acidity of the crater lake. Covellite is the stable mineral in the reduced environment at the lake bottom, coprecipitating with elemental sulfur. In contrast, sulfide minerals are not stable in the oxidized surficial waters.

Another potential mechanism (Figure 4-11) responsible for the metal enrichment of elemental sulfur arises from the properties of sulfur in aqueous solutions. In fact, given the point of zero charge (pzc) of sulfur at pH = 2.3 (Garcia and Druschel, 2014, and references therein), the surface of sulfur molecules will be positively charged in the highly acidic crater lake waters. Adsorption of neutral and negatively charged metal chloride complexes, predominant at the bottom of the lake, is thus promoted. Considering that hydrolysis of elemental sulfur is an ongoing reaction (although slow at $T < 150\text{ }^{\circ}\text{C}$, (Ellis and Giggenbach, 1971)), small amounts of H_2S will be present in the vicinity of elemental sulfur (i.e. at the sulfur-water interface). Metal sulfides are formed through reaction of the adsorbed metals and the H_2S produced.

Figure 4-11: Formation of metal sulfides on the surface of sulfur spherules

4.6 Conclusions

The chemistry of the crater lake waters indicates that high-temperature magmatic volatile input is responsible for their strong acidity, in turn leading to water-rock interactions with the host rock. Congruent dissolution of ~ 100 g of dacite per liter of water explains the major cation concentrations in solution. It is also responsible for the formation of residual vuggy silica associated with hyperacidic crater lakes (Christenson and Wood, 1993; Rowe and Brantley, 1993; Wood, 1994; van Hinsberg et al., 2010b). Species such as B, As, Hg, Tl, Au, Bi, Sb, As, Zn are enriched in the lake waters through magmatic gas input.

The magmatic gases injected at subaqueous vents favor the formation and accumulation of a body of molten sulfur at the bottom of the lake, effectively scavenging chalcophile elements (Te, Se, Cu, As, Ag, Cd, Sb, Re, Au). Reduced conditions in this deep environment are

responsible for sulphide precipitation, as evidenced by pyrite crystals on sulfur spherules. Adsorption of metal chloride complexes on the surface of positively charged sulfur spherules and subsequent reactions with H₂S could also explain the elevated metal content.

Saturated phases in the oxidized surficial waters determined by thermodynamic modelling are in agreement with the observed minerals in suspended particles and sediments. Silica, most likely in the form of cristobalite, anhydrite, gypsum and barite are saturated at the observed temperature. Saturation of alunite occurs deeper in the system, at higher temperature, as evidenced in the April 2016 ash. Precipitation of anhydrite and alunite/natroalunite from fluids recirculating within the porous rocks beneath the lake is an efficient mechanism for sealing the system, with implications on generating phreatic eruptions.

Sulfur is predicted to precipitate in the deeper, more reduced environment, together with metal sulfides. The low enrichment factor of copper in the lake waters and the saturation of bornite, covellite, chalcocite and chalcopyrite in this more reduced environment strongly suggest precipitation at depth. Together with the assemblage alunite-cristobalite-pyrite and the intense alteration of the host rock, the predicted copper precipitation is reminiscent of conditions occurring around “high sulfidation” ore depositing environments (Stoffregen, 1987; White and Hedenquist, 1990; Izawa, 1991; Hedenquist et al., 1993; Hedenquist et al., 1994b).

Chapter 5: Transport and deposition of metals by volcanic gases

5.1 Introduction

After highlighting the role of magmatic gases in enriching crater lake waters and hydrothermal fluids in metals, we now focus on the gaseous phase itself. In this chapter, we follow the path of magmatic gases throughout the hydrothermal system and out to the surface as fumaroles. Which metals are present, at what concentration, and which ligand are they complexed with? We also explore the effects of mixing with the cool and oxidized atmosphere.

The path of magmatic gases after their exsolution from the magma is rather chaotic: they make their way through porous fractured rock, hot and acidic brine, mix with cool meteoric water, each time a little altered by such interactions. All of these processes are imprinted in the composition of the volcanic gases emitted at the surface. Fumaroles have long been of interest to volcanologists, as they carry valuable information on the magma at depth. Sadao Matsuo, a Japanese pioneer gas geochemist, described volcanic gases as “a telegram from the Earth’s interior”. The development of sampling and analytical methods enables complete gas analyses: from major elements to minor and trace, organic species and even isotopes (Giggenbach, 1975a, 1982; Tassi et al., 2005; Vaselli et al., 2006; Tassi et al., 2009). This provides a snapshot of the state of the magma at depth, together with a picture of the hydrothermal system encountered by the gases on their way to the surface. Some volcanoes, such as Etna, Vulcano, and White Island, have been extensively studied over the past few decades. The long trend datasets enable scientists to discern a certain link between volcanic activity and gas composition (Giggenbach, 1975b, 1983; Capasso et al., 1992; Chiodini et al., 1993; Chiodini et al., 1995; Capasso et al., 1999). Magmatic components (CO_2 , CO , H_2 , SO_2) were identified, as opposed to their hydrothermal counterparts (CH_4 , H_2S). Variations of elemental ratios (e.g., $\text{SO}_2/\text{H}_2\text{S}$, CO_2/CH_4) thus highlight predominance of either endmember. Based on the pressure dependence of elements’ solubility (Carroll and Webster, 1994), we can also follow the path of magma as it rises into a volcanic conduit. CO_2 and H_2O are the first species to exsolve from the melt, followed by sulfur and the halogens as pressure decreases. Monitoring volcanic gases at the surface thus tells us about magma movements at depth (Tassi et al., 2005; Aiuppa et al., 2007; Tassi et al., 2009).

Pressure, temperature and redox variations as the gases arrive at the surface lead to mineral deposition in the form of sublimates. Such encrustations found around high-temperature fumaroles are of importance as they provide clues about metal transport by volcanic gases (Le Guern and Bernard, 1982; Symonds et al., 1987; Quisefit et al., 1989; Bernard et al., 1990; Symonds et al., 1992; Getahun et al., 1996; Cheynet et al., 2000; Africano et al., 2002; Wahrenberger et al., 2002; Zelenski and Bortnikova, 2005). These studies reveal the existence of exotic minerals, found exclusively in these environments, and emphasizing the role of major ligands in forming complexes with metals.

Despite their trace concentrations, many of these metal species are toxic, and as we saw in the last chapter, enriched in the gas phase. Furthermore, ancient dissected volcanoes show us that extreme deposition of economically valuable metals (Cu, Au, Ag, Mo) is taking place at depth, over magmatic systems’ lifetime (Henley and Berger, 2013).

In this chapter, we characterize the volatile transport of metals at White Island, focusing on fumarolic gases emitted across the crater floor. We determine the metal content of fumarolic discharges and how it is affected by variations of the major species with time. We also describe minerals precipitating from these gases and perform thermodynamic calculations to constrain the speciation of gaseous metal species.

5.2 Sampling and analytical methods

Three different fumaroles located across the crater floor as shown in Figure 5-1, were sampled during the study. Fumarole F9a, also called Noisy Nellie, is an old vent, in which the temperature and flow were previously much higher in the 1970's and 1980's. The flow is currently very low with a temperature around boiling point. F13a is also an old fumarole, which temperature has been fluctuating between 100 °C and 120°C since the 1980's. F0, the youngest fumarole, first appeared in 2005 during the first cycle of crater lake growth (Christenson et al., 2017). It also had the highest temperature amongst the accessible fumaroles, at around 160 °C at the beginning of the study, rising to ~ 190 °C in June 2016. Despite their similar distance from the main vent, F0 has a stronger magmatic component, highlighting preferential pathway from the main conduit (Christenson et al., 2017). Sublimates were exclusively collected from this vent, due to its higher temperature and flux.

Figure 5-1: Aerial picture showing the locations of the three fumaroles sampled (source LINZ).

Two different types of samples were collected in order to obtain the bulk composition as well as the trace element concentrations. A Giggenbach flask is used to collect the former, whereas condensates allow determination of the latter (Figure 5-2). Prior to a collecting trip, the Giggenbach bottles are filled with a known volume of 6N KOH and subsequently

evacuated. During sampling, soluble and acidic species (including H₂O) react with the caustic solution, thus increasing the liquid fraction. The non-soluble and non-reactive species (CO, H₂, CH₄, He, N₂) occupy the head-space. The gaseous fraction is analyzed by gas chromatography whereas water and reactive species contents are determined by wet chemistry and ion chromatography. These analyses are done at GNS Science, Lower Hutt, as part of the GeoNet volcanic hazards monitoring. Condensates were sampled using a glass condenser, immersed in ice-water to ensure efficient condensation. After ~ 30 mL of condensate was collected, the liquid was transferred to acid-cleaned Teflon bottles. The temperatures were measured at the fumarole outlet with a thermocouple. Elemental sulfur droplets deposited on the sampling train during collection were collected and analyzed following the procedure described in 4.2.2.2.

Figure 5-2: Sketch of the sampling train, showing the two types of samples collected.

The sampling train consists of a tube, made of titanium for bulk composition and silica for trace metals, inserted into the fumarole in one end, and connected to the collecting device with nylon tubing on the other end (Figure 5-2 and Figure 5-3 a). For fumaroles with a low gas flow, we dug into the fumarole to insert the tube, and covered with soil and rocks to minimize atmospheric contamination. The N₂/Ar ratio is used to identify likely atmospheric contamination.

The condensates were weighed (± 0.00001 g), dried at 120 °C and subsequently digested in a mixture of 2 mL 15M HNO₃ and 4 mL 12M HCl. After complete digestion, the samples were dried, refluxed in 15M HNO₃ and finally taken up in 10 mL 1M HNO₃. Appropriate dilutions for both minor and trace elements were made using 1% HNO₃. The analyses were done with

a Thermo Scientific Element2 sector-field ICP-MS at Victoria University of Wellington, following the procedures described in 4.2.3.1.

Sublimates were collected in a silica tube inserted into fumarole F0 (Figure 5-3 b) as described by Le Guern and Bernard (1982). The tubes were 130 cm long, 2.1 cm inner diameter, with a bent section finished with a narrow mouth on the upper end. The first tube was left 20 days in the fumarole. The temperature at the inlet was 160 °C on 5 June 2015 and 168 °C on 25 June when it was collected. The second tube was inserted into the fumarole for almost 4 months, starting on 17 June 2016 (temperature inlet: 189.6 °C, temperature outlet: 112.0 °C) and collected on 14 October (temperature inlet: 192.5 °C). The tube had broken, causing the small upper section to fall lower into the fumarole. The bent upper part was clogged with elemental sulfur, forming a plug of around 3 cm in length. The last tube (only 75 cm long) was put into the fumarole on 14 October 2016 and left for 2 months. During a visit on 9 November, we noticed that the thin opening on the upper part was clogged up with precipitated elemental sulfur. We broke the narrow mouth and ensured the gases were flowing freely. The temperature was 191.6 °C. We took the tube out on 20 December 2016. The temperature (182 °C) was measured using an infrared pyrometer, usually yielding values 2 to 10 °C lower than with a thermocouple (Brad Scott, pers. comm.). The tubes were sealed with Parafilm M[®] after collection to reduce contact with air. The last tube had liquid inside when opened in the laboratory, due to minor condensation after collection.

Figure 5-3: Pictures of the sampling train. a) Collection of condensate at fumarole F0 using the silica tube inserted into the vent. Note the presence of the titanium tube used to collect Giggenbach flasks. b) Silica tube inserted in F0 for sublimate collection. Photo Courtesy of GNS.

Each tube was cut into 5 to 10 cm sections and subsequently halved. All the cutting was done without water, using a diamond cutter to pre-cut sections, gently broken afterwards. Crystals from the tube walls were transferred onto a stub for subsequent SEM observations, using the same instrument and analytical conditions as described in 4.2.3.3.

We also collected natural incrustations by breaking a large block hanging over the fumarole outlet. These incrustations were also observed and analyzed by SEM and EDS.

5.3 Variations in metal content of fumarolic condensates

5.3.1 Chemistry of fumarolic discharges

The composition of major species in F0 condensates highlights variations in magmatic and hydrothermal contributions (Table 5-1 and Figure 5-4). Fumarolic gases from 23 December 2014 indicates high hydrothermal contribution. This is illustrated by low sulfur oxidation state of -0.95 (S_n varies from -2 (for S^{2-} in H_2S) to 4 (for S^{+4} in SO_2)), low CO_2/H_2S and high CH_4 content.

Figure 5-4: SO_2 - CH_4 *100- Ar *100 ternary diagram for F0 fumarole showing variations between magmatic and hydrothermal endmembers. The post-November 2014 sample with hydrothermal signature is the 23 December 2014 sample.

A shift towards more magmatic signature commenced in June 2015, with S_n of 2.64, showing that SO_2 was becoming the dominant sulfur species. This trend was confirmed in September and October of the same year, with $S_n > 3.3$. The concurrent decrease in CO_2/SO_2 ratio may reflect less hydrothermal scrubbing, allowing a greater proportion of soluble SO_2 to escape to the atmosphere. At high temperature, such “scrubbing” is due to the reactivity of SO_2 according to (Kusakabe et al., 2000),

At low temperature and elevated redox potentials, the SO_2 hydrolysis may proceed as,

June 2015 was also the beginning of a heating period, with gas temperature rising above the average 160 °C measured over the previous year. This continued to a maximum of 192.5 °C

in October 2016. A rapid shift towards hydrothermal signature was nevertheless observed. The November 2016 sample has a S_n value of 0.94 indicating increasing H_2S content, despite the elevated temperature of 191.6 °C. We should note that the crater lake was drying out during the same period. The increasing hydrothermal signature may thus reflect evaporation of the hydrothermal system due to increasing heat input, rather than a decrease in the magmatic contribution. Remobilization of elemental sulfur during heating, for example, would increase H_2S content of the gases at the expense of SO_2 following (Mizutani and Sugiura, 1966):

Two moles of H_2S for one mole of SO_2 result from this reaction, leading to gases with a hydrothermal signature despite increasing input of hotter magmatic gases.

Table 5-1: Composition of White Island fumarolic gases.

Vent	F0	F0	F0	F0	F0	F0	F0	Donald Mound*	F9a	F9a	F13a
Date	23 Dec 2014	5 Jun 2015	30 Sep 2015	15 Oct 2015	23 Dec 2015	14 Oct 2016	9 Nov 2016	1988	23 Dec 2014	9 Nov 2016	9 Nov 2016
T °C	160.7	160	174	174	178.6	192.5	191.6	495	100.3	99.7	103.8
Major elements (mol%)											
H ₂ O	92.22	89.18	85.47	83.12	87.88	89.39	90.33	94.44	-	-	-
CO ₂	6.18	8.78	12.34	13.53	9.85	8.52	7.82	4.00	-	-	-
SO ₂	0.074	0.82	1.47	1.28	0.81	0.71	0.42	0.59	-	-	-
H ₂ S	0.35	0.24	0.12	0.15	0.35	0.32	0.44	0.17	-	-	-
St	0.42	1.06	1.59	1.43	1.15	1.03	0.86	0.75	-	-	-
Sn	-0.95	2.64	3.55	3.38	2.2	2.15	0.94	-	-	-	-
HCl	0.82	0.80	0.52	1.73	1.04	0.97	0.93	0.60	-	-	-
HF	3.6E-04	1.4E-04	6.1E-04	8.9E-04	1.0E-03	5.0E-04	1.3E-03	9.8E-03	-	-	-
H ₂	3.2E-01	1.0E-01	5.3E-05	1.1E-01	1.8E-04	2.0E-04	1.3E-04	2.5E-02	-	-	-
N ₂	3.3E-02	7.7E-02	8.4E-02	8.4E-02	7.7E-02	8.6E-02	6.0E-02	1.7E-02	-	-	-
CH ₄	1.5E-03	9.0E-04	7.5E-04	4.1E-04	6.0E-04	9.9E-04	1.5E-03	4.6E-04	-	-	-
CO	5.8E-03	2.5E-06	4.2E-06	1.8E-06	-	-	-	1.5E-04	-	-	-
He	3.3E-07	4.1E-05	5.4E-05	5.1E-05	4.1E-05	3.7E-05	2.4E-05	1.4E-05	-	-	-
O ₂	-	1.6E-03	1.4E-03	1.4E-03	-	-	-	-	-	-	-
Ar	7.7E-05	1.3E-04	1.2E-04	1.2E-04	1.3E-04	1.8E-04	1.1E-04	-	-	-	-
HBr	4.9E-05	1.2E-04	2.4E-04	4.8E-04	4.0E-04	5.3E-03	3.8E-04	-	-	-	-
Minor and trace elements (ng.g ⁻¹)											
B	32440	31549	16536	23102	19005	19702	11527	35100	6.65	2.40	176
Na	77.13	206.1	1989	1277	21253	20642	514.5	870	-	-	-
Ca	1409	1197	1757	1706	19811	21136	724.6	-	94.6	-	-
Rb	0.06	0.05	1.98	1.34	17.17	12.65	0.78	2	0.13	0.37	nd
Sr	0.26	0.63	11.36	8.28	84.35	-	-	-	0.19	-	-
Zr	0.21	0.36	1.62	1.33	10.14	53.37	1.81	-	0.03	0.06	0.91
Mo	0.16	0.10	0.59	1.48	0.59	0.86	0.76	3	0.02	0.11	nd

Vent	F0	F0	F0	F0	F0	F0	F0	Donald Mound*	F9a	F9a	F13a
Date	23 Dec 2014	5 Jun 2015	30 Sep 2015	15 Oct 2015	23 Dec 2015	14 Oct 2016	9 Nov 2016	1988	23 Dec 2014	9 Nov 2016	9 Nov 2016
Ag	0.05	0.07	0.19	0.33	0.40	0.38	0.08	nd	0.01	0.01	0.18
Cd	0.01	0.01	0.10	0.18	0.21	0.28	0.04	2	0.003	0.01	0.14
In	0.00	0.00	0.03	0.01	0.26	0.79	0.03	-	nd	nd	0.00
Sn	5.32	7.10	31.36	18.13	45.69	241.1	52.01	-	0.02	0.04	0.48
Sb	97.49	285.3	114.8	133.2	90.09	392.8	205.9	80	0.04	0.19	2.67
Te	10.08	3.52	1.10	3.13	15.97	6.93	46.11	60	0.56	2.96	10.4
Ba	1.50	0.85	97.21	37.67	186.6	508.4	97.29	-	0.83	2.96	16.6
Sm	0.00	nd	0.08	0.06	0.68	0.95	0.05	-	nd	0.001	0.01
Yb	0.00	nd	0.04	0.03	0.37	0.57	0.02	-	nd	0.001	0.01
W	0.13	0.16	0.14	0.32	0.13	0.13	0.16	-	0.02	0.02	0.04
Au	0.05	nd	0.02	0.03	0.02	0.03	0.04	nd	0.01	0.02	0.04
Tl	0.01	0.01	0.21	0.22	1.68	8.15	0.34	70	0.01	0.02	0.03
Pb	0.96	1.51	22.67	2.56	16.49	24.64	3.28	180	0.79	0.46	6.04
Bi	0.37	0.59	5.23	3.20	18.99	165.0	3.49	70	0.02	0.02	0.06
Mg	24.41	47.72	664.8	621.5	6428	5914	178.3	460	20.7	11.3	76.2
Al	579.1	52.95	3747	2163	29154	14922	2192	3460	52.9	18.1	150
Sc	0.02	0.01	0.79	0.74	8.15	7.50	0.57	10	0.002	0.01	0.04
Ti	332.0	5.13	-	-	-	-	-	-	-	-	-
V	0.20	0.06	26.77	10.82	111.4	59.17	29.61	70	0.04	0.05	0.42
Cr	1.73	0.35	37.50	114.0	104.6	68.27	10.50	30	0.18	0.69	1.18
Mn	0.98	0.22	18.61	30.21	157.0	277.4	8.73	-	0.64	2.95	1.38
Fe	60.18	8.81	555.3	849.9	2769	5064	383.2	950	75.46	68.4	155
Co	0.05	0.02	0.27	2.24	0.83	3.76	0.42	-	0.02	0.05	0.09
Ni	3.41	1.21	18.11	206.7	10.32	40.22	10.46	20	0.42	3.10	2.86
Cu	4.95	4.22	92.58	54.42	11.79	19.18	38.83	30	0.82	1.49	13.0
Zn	49.39	8.42	250.4	82.50	97.27	66.16	15.09	1200	7.56	9.78	20.70
Ga	1.20	0.82	7.98	3.78	53.20	261.5	6.84	-	nd	0.02	0.06
K	29.71	20.19	1236	980.1	8853	1064	854.7	-	23.5	97.9	92.4
As	123.1	1090	469.7	125.0	221.2	131.8	340.5	2700	3.19	3.82	53.2
Se	75.31	26.04	16.60	68.03	97.28	21.50	191.6	330	3.27	16.5	38.9

Notes: nd: Below detection limit. -: Not analyzed. St: Total sulfur. Sn: Sulfur oxidation state.

*: From Tedesco and Toutain (1991)

Reproducibility (1 RSD): Hg $\pm$ 110%, Te $\pm$ 71%, Sn $\pm$ 61%, Se, Tl, Au, W, Ag, Na $< \pm$ 40%; B, Cd, Sb, Re, Pb, Bi, Mg, Sc, Ti, Cr, Zn, K $< \pm$ 20%; $< \pm$ 10% for the rest of the elements (Appendix A.7).

These variations in major gas composition emphasize the active character of White Island magmatic-hydrothermal system, and especially changes in the spatial distribution of the two-phase hydrothermal envelope described by Giggenbach (1987).

The composition of fumarolic gases of higher temperature sampled in February 1988 at Donald Mound fumarole are presented for a comparison (Table 5-1). This vent reached the highest temperature ever recorded at White Island in October 1987, 730 °C, but had cooled down to 495 °C at the time of sampling (Giggenbach and Matsuo, 1991). The sample

collected in February 1988, despite different absolute compositions, show similarities to F0 gases from June and September 2015 in terms of CO₂/SO₂, SO₂/HCl and SO₂/H₂S ratios. Contrastingly, the sample from December 2014 has very different composition, with more HCl than SO₂, and H₂S dominating over SO₂ (Table 5-1), reflecting a greater contribution from the hydrothermal system. The oxygen fugacity f_{O_2} of some samples was estimated using:

and

and thermodynamic data from Robie and Hemingway (1995). The similar f_{O_2} values (see Appendix A.9) obtained with the two methods for the high temperature (495 °C) gases of Donald Mound suggest that they are in equilibrium, slightly above the Nickel-Nickel Oxide (NNO) buffer ($\Delta NNO = + 2.56$ using CO/CO₂ and $\Delta NNO = + 2.35$ using H₂/H₂O). Contrastingly, the obtained f_{O_2} values from CO/CO₂ and H₂/H₂O for fumarole F0 gases differ by up to 4 log units. Disequilibrium is however expected in such low temperature gases. F0 sample from December 2014 is more reducing ($\Delta NNO = - 4.90$ and $\Delta NNO = - 0.62$ using CO/CO₂ and H₂/H₂O respectively) than the samples from June 2015 ($\Delta NNO = + 2.25$ and $\Delta NNO = + 0.36$) and September 2015 ($\Delta NNO = + 2.32$ and $\Delta NNO = + 6.91$).

Some metals show variations following that of the major species, with Cu, Zn, Ga, Pb, Bi, Ag, Cd having higher contents in the more magmatic samples. In contrast, the metalloids As, Se, Te and Sb show more erratic variations, with a quite high content in the November 2016 sample, indicating different behavior during volatilization of the hydrothermal system. Copper varies between 4.2 and 92.6 ng.g⁻¹, As between 123.1 and 1090 ng.g⁻¹ and Zn between 8.4 and 250.4 ng.g⁻¹ (Table 5-1). We notice that As maximum corresponds to Cu and Zn minima, in the June 2015 sample. These concentrations are in the same range as those reported in high temperature fumaroles at Merapi and Vulcano (Cheynet et al., 2000; Nadeau, 2011). The content of Pb is, in contrast, quite low (1.0-24.6 ng.g⁻¹) compared to the 8000 ng.g⁻¹ at Merapi and 3200 ng.g⁻¹ at Vulcano. The only previous metal data available for White Island gases is from Tedesco and Toutain (1991), who sampled Donald Mound fumarole in February 1988 (Table 5-1). The reported Pb, Tl, As and Zn contents were almost one order of magnitude higher (180 ng.g⁻¹, 70 ng.g⁻¹, 2700 ng.g⁻¹ and 1200 ng.g⁻¹ respectively), whereas Cu was in the same range (30 ng.g⁻¹). This suggests that less Pb, Tl, Zn and As is lost in the subsurface environment in the 495 °C fumarolic gases. In contrast, the similar Cu concentration in the current low-temperature gases and the 495 °C gases from Donald Mound, suggests that it is deposited at $T > 500$ °C. Comparing with lower temperature fumaroles (Table 5-1), we observe that F13a is an order of magnitude more concentrated than F9a in Cu, Pb and As and many other metals. It is nevertheless almost 10 times lower than fumarole F0, reflecting its hydrothermal nature.

5.3.2 Metal enrichment in fumarolic gases

Enrichment factors are used to emphasize preferential partitioning into gaseous phase compared to the residual magma (Zoller et al., 1974; Lepel et al., 1978). The enrichment factor, EF, of an element i is defined as follows:

$$EF_i = (C_i/C_R)_{gas} / (C_i/C_R)_{rock}$$

where (C_i/C_R) is the ratio of concentrations of the element i to a reference element R in the gas, divided by the same ratio in the host rock. The reference element is a major non-volatile species, Al in this case. We used the composition of the andesite (Appendix A.8) erupted in 1977 to calculate the EF.

Enrichment factors are shown in Figure 5-5. Elements with $EF > 1$ are mainly volatiles and chalcophiles, in accordance with their enrichment in volcanic gases. As expected, all the refractory elements have $EF \sim 1$. We nevertheless observe quite a wide range in enrichment factor for a single element with time, probably linked to changes in major composition. Antimony for example, varies from 4 orders of magnitude from June to December 2015. It is also interesting to note the highest EF for the sample from June 2015, despite its quite low temperature (160 °C). Interestingly, F9a and F13a, which have lower concentrations compared to F0, have similar enrichment factors. For some elements such as Au, Tl, Cu and Zn, they are even in the high range. Given these fumaroles are most likely originating from boiling of the hydrothermal envelope (Giggenbach, 1987), these high EF's values may reflect the refractory character of Al, partitioning strongly in the brine during phase separation, or preferential partitioning of the metals into the vapor. It might also represent efficient deposition occurring in the conduit of F0. Despite the higher general concentrations of hotter gases from Donald Mound, the enrichment factors are comparable to the present day gases. We note high enrichment for Tl, Pb and Zn, emphasizing the magmatic origin of these species and their volatile behavior. Cu, in contrast, has an enrichment factor similar to the average found in this study. We should note the $EF \sim 1$ for Cu in F0 condensates from December 2015 and October 2016.

Figure 5-5: Enrichment factors (EF) estimated for the three fumaroles sampled. Data from Donald Mound are from Tedesco and Toutain (1991). The Se value of 0.92 ppm in White Island andesite was taken from Wells (1967).

5.4 Sublimates forming in low-temperature fumarole

Despite F0 being the hottest accessible fumarole, its temperature is still low compared to vents usually chosen for sublimate studies (i.e. $> 400\text{ }^{\circ}\text{C}$) (Garavelli et al., 1997; Cheynet et al., 2000; Africano et al., 2002; Wahrenberger et al., 2002; Zelenski and Bortnikova, 2005). A sketch of the tubes and zones of the commonly observed minerals collected in them is shown in Figure 5-6.

Salammoniac (NH_4Cl) is common in tube 2, from June-October 2016, as colorless arborescent euhedral crystals, sometimes rounded, displaying an adamantine luster (Figure 5-7 a, b). Small heavy (i.e. bright in backscattered image) crystals and euhedral in form, were commonly found on large salammoniac crystals. We could unfortunately not analyze them due to their very small size requiring high magnification, causing volatilization of the salammoniac host. Vapor deposited SiO_2 is very common in the silica tubes. Some euhedral crystals were observed having a morphology similar to cristobalite, along with aggregates of spheres that could either be cristobalite or opal. Some silica crystals are rich in Al, and a few Ti-rich and Sn-rich particles were observed.

Figure 5-6: Description of the mineral species found in the sublimate tubes 1 (June 2015) and 2 (June-October 2016.) The second tube was broken at 38 cm from the top and had a hole of around 8 cm length at 40 cm from the bottom. The bent section was clogged with elemental sulfur.

Elemental sulfur is present in the form of solidified droplets from 37 to 75 cm and 113 cm to the top in tube 1 and from 45 cm to the top in tube 2 (Figure 5-6). This is in accordance with the condensation of sulfur reported to occur at $T < 200\text{ °C}$ (Le Guern, 1988; Quisefit et al., 1989; Cheynet et al., 2000; Africano et al., 2002). The zone between 75 and 113 cm in tube 1 contains almost no sublimate at all.

Figure 5-7: SEM images of sublimates. Salammoniac crystals showing both rounded (b) and cubic shape (a) in tube 2 and incrustations respectively (Backscattered electron (BSE) images). Thin plates of S and N in tube 2 thought to be mascagnite (c and d) (Secondary electron (SE) images).

Figure 5-8: SEM images of sublimates. Pyrite crystals covering entire surfaces in tube 2 (a) or occurring as single octahedral crystals in tube 3 (b). Iron ammonium sulfates thought to be pyracmonite in tube 1 (c and d). All BSE images.

Pyrite is the only identified sulfide, occurring as euhedral grains up to 15 μm in size (Figure 5-8 a, b). It is found in the three tubes, from 0 to 80 cm in tube 1 and as far as 105 cm in tube 2. Prismatic crystals of ammonium iron sulfate, thought to be pyracmonite ($(\text{NH}_4)_3\text{Fe}(\text{SO}_4)_3$ (Demartin et al., 2010) were found in tube 1 (Figure 5-8 c, d). Mascagnite ($(\text{NH}_4)_2\text{SO}_4$) occurs as thin plates growing on top of existing crystals, giving them the appearance of white balls (Figure 5-7 c, d). We are not certain whether the mascagnite crystals formed within the fumarole or later on, during reactions with condensed gases. This uncertainty arises from observation of sections of tube coated with mascagnite, weeks after opening and cutting segments.

Barite is present in all the tubes as euhedral crystals up to 20 μm in size, between 10 and 35 cm in tube 1 and 0 to 80 cm in tube 2. Some barite crystals in the second tube were Sr-rich according to EDS analysis. A wide variety of sulfates were present as euhedral crystals and are reported in Table 5-2. Some of them displayed an adamantine luster (Al sulfates) and others a vitreous luster (Ca sulfates).

We observed a common unidentified phase in tubes 1 and 3 (Figure 5-9 a, b and c), displaying a euhedral arborescent shape, although quite rounded, translucent and pale yellow in color, with adamantine luster. The only detected species in EDS were S and O. They appear very different compared to elemental sulfur droplets under the SEM, dark and almost translucent in backscattered images (Figure 5-9 a, b, c). This suggests the likely presence of light elements (H, B, N, F), hardly detected by EDS.

Figure 5-9: SEM images of sublimates. Unidentified compounds in tube 1 bearing S and O, pale yellow (a, b, c) and dark bright yellow (d, e, f). a) Euhedral rounded arborescent crystals with bright spots containing up to 16% As. b) Euhedral rounded arborescent crystals (up to 2.5% As) on top of an elemental sulfur droplet. c) Euhedral rounded arborescent crystals with bright spots containing up to 5% Hg, 2% As, 0.7% Cu and 0.5% Sb. d) Euhedral skeletal crystals with bright blobs containing up to 18% As. e, f) Euhedral skeletal crystal bearing up to 11% As). All SE images except BSE image for d. As and Hg contents are qualitative.

In some of these crystals, small blobs appearing brighter in backscattered images contain metals and/or metalloids. Arsenic is the most common element, up to 16% in qualitative EDS analyses, corresponding to the yellower parts. Higher up in the tube (75-80 cm and 125-130 cm), the same minerals were found with similar bright spots, rich in As (up to 18%), Hg (up to 5%), Cu (up to 0.7%) and Sb (up to 0.5%). These were found in a thin layer of euhedral crystals, completely covering the inside of the tube. Translucent to pale yellow crystals only contain S and O, whereas the darker yellow crystals are rich in As. The Hg-rich blobs, in contrast, were dark with a metallic luster. Cinnabar precipitation was predicted by thermodynamic calculations during cooling of White Island fumarolic gas (Christenson and Mroczek, 2003) supporting our observations.

Similar crystals were observed in the bottom part of tube 3. Again, only the yellow crystals contained As (up to 10%), while the translucent parts are composed of S and O. There is only one occurrence of a similar phase in tube 2, at around 25 cm from the bottom. The small blobs contain up to 12% As, and less than 1% Cu. A similar type of mineral was observed in tube 1 (0-15 cm and 75-80 cm), also containing S, O and As (up to 18%), although exhibiting euhedral skeletal morphology, a bright yellow color and adamantine luster (Figure 5-9 d, e, f). The distribution of arsenic is not quite uniform, and appears as bright blobs in the cooler specimen.

Some unidentified phases were observed in tube 1: Ti-S-K-Si between 10 and 15 cm (Figure 5-10 c), Fe-Cr-Ni crystal (35-40 cm), Cl-Fe-Ca-S compound at 50-55 cm and a dark red plate made of Fe-Cl-P-Zn-Br (Figure 5-10 b).

Sublimate tube 2 contained platy minerals, made of light elements only, at 15-20 cm and thought to be sassolite ($B(OH)_3$), a common mineral around fumaroles at Vulcano (Garavelli et al., 1997). A variety of unidentified phases was found: small blue particles with an ellipsoidal shape containing S with minor Si-Cl-As-Al between 30 and 52 cm. Some compounds rich in Cl and Fe and bearing Cr, Ni, As with trace amounts of Cu, as well as a crystal containing S-Cr-Fe were observed at 74-85 cm. We observed more compounds bearing Cl-S-Al in the upper part of the tube that had fallen into the fumarole after breaking, as well as a shiny translucent Al-S-Si-Ca crystal, and a white ball made of small plates of S-Ti-Fe.

Figure 5-10: SEM images of sublimates. a) Aggregate of unidentified Sn-S compounds on salammoniac in natural incrustations. The bright leaf in the middle is elemental sulfur. b) Unidentified dark red plate containing Fe-Cl-P-Zn-Br in tube 1. c) Unidentified euhedral crystals of S-Ti-K-Si in tube 1. d) Unidentified euhedral crystals bearing Ti-S-O in tube 1. a and b are BSE images, c and d are SE images.

Table 5-2: List of all the observed sulfates in sublimates and natural encrustations.

Tube 1	Tube 2	Tube 3	Encrustations
Mg sulfate	Mg-Fe sulfate	Mg sulfate	Fe-Mg sulfate
Barite	Barite (crystal with 2% Sr)	Barite	Barite
Al sulfate (crystal with 0.8% Ga)	Al sulfate	Al sulfate	Al sulfate
Ca sulfate	Ca sulfate	Ca sulfate	Ca sulfate
Fe-N sulfate	Fe-N sulfate		Fe-N sulfate
K-Ca-N sulfate	Ca-K sulfate		Ca-K sulfate
Mg-N sulfate	Fe-Na-N sulfate		Ca-K-Fe sulfate
Al-Fe sulfate	Na-Fe sulfate		Fe-K-N sulfate
Al-Mg-Fe sulfate	Na-K-Fe-Ti sulfate		Mg-Fe-Al sulfate
			Al-Na-K sulfate

The third tube was quite wet when we opened it in the lab, suggesting dissolution reactions may have occurred after collection. We only analyzed crystals from the first 10 cm and found salammoniac, silica, a lot of silicate particles most likely dragged from the conduit by the gases, mascagnite, pyrite and the unidentified compound bearing S, O and As. A variety of sulfates was also observed and is detailed in Table 5-2.

Sulfur is a ubiquitous phase around fumaroles, as evidenced by the yellow color of the sublimate chimneys and sulfur flows leaking away from them. The slab of fumarole wall collected was covered with natural incrustations. The top of the block was coated with colorless to pale yellow euhedral arborescent crystals of salammoniac up to 2 to 3 mm long. Some were also covered with elemental sulfur. Small crystals had grown on the salammoniac, such as tiny spheres of silica, radiant acicular aggregates of S-Fe-Ga-Cu compounds, needles containing Cl-S-Br-Al-Na-Sn and Bi, euhedral plate (4 μm) containing Sn-S-Si-Al-Ti, cubes of sylvite up to 10 μm , pyrite, and small spheres of unidentified S-Sn compounds (Figure 5-10 a). An area on the side of the block was covered by dull pink filamentous crystals most likely made of B, H, N and/or F given the dark color in backscattered images. We found tiny grains of W-Cl-Na-Al-K-Ca, S-Fe-Cu-As, pyrite and sylvite in these pink crystals. The sides and bottom of the block was covered with grey amorphous silica, forming cavities in which minerals had crystallized. A variety of crystals were found such as acicular gypsum, orange platy anhydrite, pyrite and a variety of other sulfates (Table 5-2). Silica occurs as different colors and structures, such as orange vitreous crystals (1 mm in length) similar to opal, euhedral crystals up to 50 μm with the morphology of cristobalite, dark vitreous amorphous silica thought to be opal, red amorphous silica comparable to jasper.

Sulfates are the most common sublimates both in the tubes and in natural incrustations, suggesting quite oxidized conditions, as reported by Bernard (1985) and Taran et al. (2001) and modelled by Africano et al. (2002). The oxidizing nature of White Island low-temperature fumarolic gases is the likely consequence of elemental sulfur precipitation in the conduit (Christenson et al., 2010). The latter may also explain the rarity of sulfides, owing to the elevated metal contents measured in elemental sulfur (Table 5-3). Values of ~ 1 ppm for Cu, Pb and Bi were reported, two orders of magnitude higher than in the condensate, suggesting high solubility of metals in liquid sulfur.

Table 5-3: Metal content of elemental sulfur condensing from fumarole F0 gases ($\mu\text{g.g}^{-1}$).

F0 elemental sulfur			
Mo	0.11	Pb	1.27
Ag	0.05	Bi	1.29
Cd	0.005	Co	0.27
Sn	2.93	Ni	0.75
Sb	0.16	Cu	1.68
Te	387.3	Zn	4.38
Re	0.001	Ga	2.93
Au	0.0005	As	103.3
Hg	0.43	Se	640.5
Tl	0.10	Cr	2.27

Of the previous studies of this kind, the majority was realized in very high temperature fumaroles (usually $> 500\text{ }^{\circ}\text{C}$) resulting in a variety of sulfides, sulfosalts and metal chlorides to be observed (Korzhinsky et al., 1994; Garavelli et al., 1997; Cheynet et al., 2000; Africano et al., 2002; Wahrenberger et al., 2002; Zelenski and Bortnikova, 2005; Garavelli et al., 2013). As noted by several studies, many metals such as Cu, Bi and Sn are not as volatile as Tl, As or B and tend to deposit at temperature $> 350\text{ }^{\circ}\text{C}$ by chemical vapor deposition (Symonds et al., 1987; Bernard et al., 1990; Symonds et al., 1990). The relative absence of minerals containing Cu and their overall low concentrations in the fumarolic condensates suggest that deposition might occur deeper in the subsurface, as the gases cool and expand on their way to the surface (Henley and Berger, 2013). Conversely, As and Sb are quite concentrated in the gases yet no major phase is reported in the sublimates. This points to unfavorable conditions for deposition, as was observed in similar studies (Symonds et al., 1992; Getahun et al., 1996).

5.5 Thermochemical modelling

Gas speciation was calculated using the software HSC Chemistry (version 9.1.1, Outotec Research Oy, Finland), based on Gibbs free energy minimization calculations. Modeling was facilitated using measured mole % gas compositions at 1 bar, in a 15 element system (H, O, C, S, Cl, F, N, Br, Cu, Zn, Pb, As, Fe, Bi, Tl). The lack of HBr data for Donald Mound sample (Tedesco and Toutain, 1991) prevented us from comparing it with the other gases. The input files are reported in Appendix A.9. We also added gas, liquid and solid phases expected to be present in the volcanic gases or form during cooling. We assumed a constant gas flow, and therefore modeled deposition in closed-system conditions. Such an assumption is supported by results from Africano et al. (2002), who showed that closed-system conditions reproduced more closely the observed assemblage than an open-system in Satsuma-Iwojima fumarolic gases. The use of solids as pure phases ignores both solid solutions and the presence of trace elements in minerals, and thus deviates from real conditions. Gases were assumed to mix ideally. Equilibrium calculations were first performed at the sampling temperature to assess gaseous speciation. Cooling was then modeled by incrementally decreasing the temperature down to $50\text{ }^{\circ}\text{C}$, by $10\text{ }^{\circ}\text{C}$ steps.

Samples collected at fumarole F0 on 23 December 2014, 5 June 2015 and 30 September 2015 were used for modeling, as well as the higher temperature (495 °C) gas from Donald Mound fumarole collected in 1988 by Tedesco and Toutain (1991). As described above, the fumarolic gases from F0 collected in December 2014 are more reducing, and have a $\text{SO}_2/\text{H}_2\text{S}$ ratio < 1 (see Table 5-1). F0 gases from June and September 2015, as well as Donald Mound sample from 1988 are more oxidized, SO_2 being the dominant sulfur species.

Figure 5-11: Speciation of the most abundant gaseous Pb species.

The distribution of Pb amongst gaseous species is shown in Figure 5-11 and emphasizes the role of chloride and bromide complexes in transporting lead. PbBr_4 and PbCl_4 are the dominant species even at low temperature, indicating $\text{Pb}^{(\text{IV})}$ is the most stable in the gas. Stability of $\text{PbCl}_{4(\text{g})}$ at $T < 800$ °C was reported in gases from Ert'a Ale, Kudriav'y and Merapi (Symonds et al., 1987; Wahrenberger et al., 2002; Renggli et al., 2017). PbCl_2 , PbBr_2 , PbCl and the sulfide complex PbS are the second most abundant species.

The speciation of Cu amongst gaseous species is depicted in Figure 5-12. $\text{Cu}^{\text{I}}\text{Cl}$ dominates at high temperature in Donald Mound gases, replaced by the dichloride complex $\text{Cu}^{\text{II}}\text{Cl}_2$ at $T < 300$ °C. Similar distribution is observed in the 2015 samples from F0, although we see that bromide complexes CuBr and CuBr_2 are also quite stable. Cu_4Br_4 becomes more stable at $T < 100$ °C. The more reduced sample from December 2014 shows a slightly different

distribution, with the bromide complex dominating at the sampling temperature, and similar abundances for CuCl and CuCl₂. It is interesting to note that the general abundance of gaseous copper species is very low compared to Pb. In the F0 samples, PbCl₄ had an equilibrium amount between 10⁻⁶ and 10⁻⁸ kmol, whereas CuCl₂ is at most 10⁻¹⁷ kmol. This depletion in the gas phase is likely to reflect loss by deposition of solid species.

Figure 5-12: Speciation of the most abundant gaseous Cu species.

The predominance of chloride complex prevails for Zn as well, with ZnCl₂ being the most abundant species in all the samples (Figure 5-13). The bromide complex ZnBr₂ is orders of magnitude less abundant whereas other species such as Zn₂Br₄, Zn(OH)₂, ZnF₂, ZnCl and Zn are very low.

Fe^{II}Cl₂ is the most stable species in the high temperature gas of Donald Mound (Figure 5-14), replaced by Fe^{III}Cl₃ at T ≤ 170 °C. This shift in redox state of iron is observed in the 2015 gases from F0, where FeCl₃ and FeCl₂ have similar abundances at the sampling temperature, the former becoming more important with cooling. In contrast, the more hydrothermal sample from 2014 indicates greater stability of FeCl₂ at all temperatures. The hydroxide complex, Fe(OH)₂, is predicted to be quite abundant at high temperature, rapidly decreasing in cooler gases, where FeF₃ becomes increasingly stable, in accordance with a shift in redox state. Bromide complexes in F0 samples somewhat lowers the overall abundance of FeF₃.

Figure 5-13: Speciation of the most abundant gaseous Zn species.

As and Tl are the only species predicted to be mainly transported as volatile oxide species. As_4O_6 is only stable until $\sim 240^\circ\text{C}$ and with further cooling is replaced by the chloride complex, AsCl_3 (Figure 5-15). The valence is the same in the two species, indicating the lower stability of the molecular As_4O_6 species at lower temperatures. All of the gaseous species show a marked decrease at that same temperature ($\sim 240^\circ\text{C}$), related with removal of As from the gas phase by condensation of AsS (see below). The presence of AsBr_3 in the 2015 F0 samples increases the stability of As_4O_6 over AsF_3 , as predicted from cooling of Donald Mound discharge gas to $\sim 160^\circ\text{C}$. The sulfide complex, AsS , is also quite abundant at high temperature. Once again, we observe discrepancies in the 2014 sample from F0. AsCl_3 is still the most abundant complex, followed by As_4 and AsH_3 in these more reduced and HCl-rich gases. In the case of Tl, TlO dominates at all temperatures and even in the more reduced sample (F0 fumarole, December 2014), with TlCl the second most abundant gaseous species. TlCl was found to be the dominant complex in fumarolic gases from Vulcano (Cheynet et al., 2000) and Kudriav (Wahrenberger, 1997). The distribution of Bi is divided between $\text{Bi(OH)}_2\text{Cl}$ and BiCl_3 in the four samples studied. The sulfide complex BiS is predicted to be quite stable in the higher temperature gas of Donald Mound, similar to what was observed for As and Pb.

Figure 5-16: Speciation of the most abundant gaseous Bi species.

In addition to speciation in the gas phase, we modeled solid and liquid phases depositing as the gas is cooled to 50 °C. Figure 5-17 shows the species predicted to form during such a process. The most noticeable result is the near absence of chloride minerals, in contrast with the abundance of gaseous chloride complexes. Molysite (FeCl_3) and lafossaite (TlCl), for instance, may occur in volcanic sublimates (Menyaylov et al., 1983; Getahun et al., 1996; Zelenski and Bortnikova, 2005; Roberts et al., 2006). The results from Donald Mound show a deposition sequence of minerals containing Fe, Cu, As, Zn and Bi, from high to low temperature. The stable phases tend to be sulfides at high temperature, replaced by sulfates with cooling. We observe magnetite deposition at the highest temperature, supplanted by pyrite (FeS_2), and finally hydrated iron sulfates at $T < 160$ °C. At high temperature, the Cu-containing minerals are iron or arsenic sulfosalts, whereas covellite is precipitating at $T < 180$ °C. The only chloride mineral is BiCl_3 , depositing at very low temperature. We also observe condensation of liquid phases, elemental sulfur and AsS, commencing at ~ 240 °C. Elemental sulfur is known to condense at $T < 350$ °C, following (Matsuo, 1962; Mizutani and Sugiura, 1966):

This is in agreement with our observations of solidified droplets of elemental sulfur in the sublimates tubes at temperature < 160 °C. Condensation of AsS is likely to be responsible for the drop in As gaseous species stability discussed above.

As expected from the cooling of Donald Mound gases, the calculations show that the 2015 F0 samples have low-temperature mineral assemblages. ZnSO_4 replaces sphalerite at $T < 155^\circ\text{C}$, whereas hydrated iron sulfates are precipitating at all temperature. Pyrite is not predicted to deposit at $T < 171^\circ\text{C}$, although it was observed in the two tubes at temperature lower than 160°C . Covellite, however, deposits over the whole temperature range in the computation. The lack of minerals containing Cu and Zn in our observations may reflect their segregation by elemental sulfur, owing to the elevated metal content in the condensing liquid (see Table 5-3). ZnSO_4 is also very soluble in water, which is likely to be present at $T < 100^\circ\text{C}$. Condensation of liquid sulfur and AsS is predicted in the two F0 samples from 2015. It is worth noting that AsS liquid might be at the origin of the unidentified As bearing crystals observed in the tubes, solidifying after condensation. The predominance of sulfates in the model is in agreement with minerals observed both in the sublimate tubes and in the natural incrustations.

Figure 5-17: Sublimates and condensates formed during cooling.

The modeled assemblage depositing from the more hydrothermal gases from December 2014 differs greatly from the three other gases (Figure 5-17). Sulfides and sulfosalts are the only minerals precipitating, as would be expected from reduced gases. The absence of elemental sulfur may arise from the low total sulfur content of the gas (0.42 mol%).

We modeled the effect of mixing with oxidized atmospheric air by incrementally adding N₂ and O₂ to the F0 June 2015 sample. The speciation of gaseous species is mostly unchanged, with predominance of chloride and bromide complexes. Changes arise for bismuth, with Bi(OH)₂Cl_(g) becoming more abundant than BiCl_{3(g)}. AsCl_{3(g)} remains the most stable phase until high f_{O_2} , when it is replaced by As₄O_{10(g)}. The modeled depositing phases, in contrast, reflect oxidation, with a shift to CuSO₄, ZnSO₄, Fe₂(SO₄)₃ and As₂O₅ depositing at 160 °C. Such oxidizing conditions are likely to occur during deposition of the natural incrustations on the fumarole walls. Minerals observed in natural incrustations from fumarole F0 were mainly sulfates, in accordance with mixing with atmosphere. We however noted the presence of pyrite crystals, not predicted to deposit at such low temperature and high f_{O_2} .

No Pb-bearing minerals are predicted to deposit. PbS (galena) and PbCl₂ (cotunnite) are the most common species reported in sublimates from reduced gases at T < 400 °C (Stoiber and Rose, 1974; Bernard, 1985; Symonds et al., 1987; Quisefit et al., 1989; Cheynet et al., 2000; Africano et al., 2002; Wahrenberger et al., 2002). Sulfosalts of Bi, Pb, and As are also often observed (Le Guern, 1988; Quisefit et al., 1989; Garavelli et al., 1997; Cheynet et al., 2000; Africano et al., 2002; Zelenski and Bortnikova, 2005). Lead sulfate (anglesite) is common in more oxidized gases (Taran et al., 2001). As we did not detect Pb-containing sublimates, we cannot be sure that the lack of predicted solid species reflects reality and that it is not due to incomplete thermodynamic data. No Tl mineral is predicted to deposit, suggesting most of it is dispersed into the atmosphere. However, as noted above, thallium-containing minerals such as lafossaite (TlCl), steropesite (Tl₃BiCl₆) and hephaistosite (TlPb₂Cl₃) have recently been found in fumarole sublimates at Vulcano (e.g. Roberts et al., 2006), whereas Nataliyamalikite (TII) was discovered at Avacha volcano, in Kamchatka (Okrugin et al., 2017).

To summarize, chloride appears to be the main ligand responsible for metal transport in the gas phase. This result supports findings from Chapter 2, suggesting correlation between Cl and metals during degassing of the magma, and exsolution from the shallow dacitic chamber. Despite the low abundance of HBr in volcanic gases (HCl/HBr > 2000), bromide complexes are extremely stable, especially at lower temperature, as reported in gases from Kudriav and Vulcano (Wahrenberger, 1997). The role of sulfur is minor in this context. Metal sulfide complexes appear to be stable only at high temperature (T > 500 °C). However, the presence of sulfur in the gas phase, and its oxidation state, strongly influence the metal speciation. This emphasizes the indirect control of sulfur on metal transport and deposition.

5.6 Conclusions

Rapid changes in fumarolic gas composition and temperature are observed at White Island, in response to changes in the magmatic feeding system. Giggenbach (1987) ascribed such variations to an evolving two-phase hydrothermal envelope surrounding the conduit. Cooling periods are reflected by invading liquids, reflected at the surface by emissions with a hydrothermal signature (e.g. H₂S, CH₄). In contrast, periods of higher activity are characterized by fumarolic gases of magmatic composition, indicating expansion of the single-phase vapor envelope. During heating period, the two-phase envelope is volatilized, retracting further away from the conduit.

This study has demonstrated that metals are enriched in volcanic gases and that they respond similarly to interactions with the hydrothermal system. The lower metal concentrations in gases with hydrothermal signature emphasize metal “scrubbing” in shallow aquifers. Moreover, we observed a link with changes in magmatic activity. More Tl, Pb, Bi, Zn and Ag are transported by high-temperature magmatic gases, suggesting that these species are deposited and/or scrubbed at temperatures $< 495\text{ }^{\circ}\text{C}$. In contrast, the copper load of gases at $< 200\text{ }^{\circ}\text{C}$ and $495\text{ }^{\circ}\text{C}$ is very similar, emphasizing efficient deposition at $T > 495\text{ }^{\circ}\text{C}$, deeper within the system.

The oxidized nature of low-temperature fumarolic gases is reflected by the predominance of sulfate minerals precipitating around the vent. This assemblage may greatly differ during emissions of reduced gases with high hydrothermal contribution, dominated by precipitation of various sulfide and sulfosalt minerals. Pyrite is the only sulfide mineral observed, likely reflecting the higher abundance of iron compared to other metals. The absence of the predicted phases CuS, ZnS and sulfosalts in the sublimate tubes may be due to the very low metal concentrations in the discharging gas. In addition, uptake of chalcophile elements into condensing elemental sulfur at $T < 240\text{ }^{\circ}\text{C}$ may prevent sulfide precipitation. Lead and thallium show very volatile behavior, with no solid phases precipitating according to thermodynamic calculations. Sulfur removal by condensation of elemental sulfur is a very efficient process, as observed in the field. Several compounds rich in As or Hg are associated with sulfur, most likely forming through solidification of condensed liquids. The predicted formation of $\text{AsS}_{(l)}$ at $T < 240\text{ }^{\circ}\text{C}$ supports this interpretation. The results from thermodynamic modelling show an overall good agreement with species observed in nature, especially when considering oxidation following atmospheric mixing.

Thermochemical modelling emphasizes the role of chloride and bromide complexes in transporting Pb, Cu, Zn, Bi and Fe. In contrast, oxide complexes are dominant in the case of Tl, and As at high temperature. The role of S as a ligand appears to be minor, with increasing importance for Bi, As and Pb as temperature increases. However, sulfur remains a critical species given the control it exerts on the redox conditions of volcanic gases, themselves influencing metal transport.

Chapter 6: Metal emissions in volcanic plumes

6.1 Introduction

The white cloud which sits over White Island, and for which the island is named, is the last piece of our puzzle. Having studied the metal composition of the magma itself, the crater lake and springs and the fumaroles, we now turn our attention to the plume.

Volcanoes represent a significant natural source of metals in the atmosphere by way of the plumes emitted both during eruptions and quiescent activity (Nriagu, 1989; Hinkley et al., 1999). The gas species of interest are similar to the fumarolic ones and include SO₂, H₂S, HCl, HF (minor HBr and HI), as well as some highly volatile trace components such as Hg (Kyle et al., 1990; Christenson and Mroczek, 2003; Delmelle, 2003; Mather et al., 2003b; Nriagu and Becker, 2003; Pyle and Mather, 2003; Bagnato et al., 2007; Witt et al., 2008; Bagnato et al., 2011). In addition to gaseous species, volcanic plumes also contain aerosols. These particles have various origins: 1) silicates swept up from the volcanic conduit and/or resulting from magma fragmentation, 2) condensation of droplets, 3) gas-to-particle conversion. The last two processes are responsible for the formation of H₂SO₄, halides, sulfates, sulfides, elemental sulfur and oxides in the particulate aerosols. Trace metals (Cu, Cr, As, Zn, Se, Cd, Sn, Sb, Pb, Tl and Bi) are concentrated in such aerosols as a result of strong partitioning into the particulate phase during cooling and dilution of the plume (Hinkley, 1991; Aiuppa et al., 2000; Allard et al., 2000; Obenholzner et al., 2003; Moune et al., 2010; Martin et al., 2012; Menard et al., 2014; Allard et al., 2015; Calabrese and D'Alessandro, 2015). The particle size in volcanic plumes ranges from < 0.01 to > 25 µm, with most of the solids smaller than 2 µm originating from gas-to-particle conversion within the plume (Hobbs et al., 1982; Vié le Sage, 1983; Rose et al., 1986; Allard et al., 2000; Watson and Oppenheimer, 2000; Martin et al., 2009a).

The impact of volcanic clouds on the environment and human health arises from the acidic gases and the heavy metals they carry. Not only are they a threat locally through gravity deposition and rain remobilization (Fulignati et al., 2006; Martin et al., 2009b; Calabrese et al., 2011; Floor et al., 2011; Calabrese and D'Alessandro, 2015), but also at a global scale due to their capacity to be dispersed into the troposphere (Siegel and Siegel, 1987; Delmelle, 2003).

The common method used to simultaneously collect the gas and particle fractions of a plume is by the use of filter packs. This technique was first introduced by Naughton et al. (1975) and further improved by Finnegan et al. (1989). The main advantages are the possibility to sample volcanic plumes from distance (both ground-based and airborne), thus allowing collection even during periods of higher activity. In conjunction with SO₂ fluxes measured by remote sensing techniques (DOAS, COSPEC, UV camera), it also provides estimates of metal emission rates. The discrete character of collection however neglects the spatial and temporal variations of a plume. It also leaves behind any species transported in a different form than particle or acid gas, such as H₂O and Hg.

Many volcanoes are difficult or dangerous to access, leaving the filter pack technique as the only means to assess acidic gases and trace element emissions. As such, it has been widely

used and improved over the years (Zoller et al., 1974; Varekamp et al., 1986; Pennisi et al., 1988; Finnegan et al., 1989; Kyle et al., 1990; Zreda-Gostynska et al., 1997; Gauthier and Le Cloarec, 1998; Allard et al., 2000; Allen et al., 2000; Aiuppa et al., 2003; Mather et al., 2003a; Martin et al., 2008; Moune et al., 2010; Calabrese et al., 2011; Martin et al., 2012; Mather et al., 2012; Zelenski et al., 2013; Menard et al., 2014; Allard et al., 2015; Gauthier et al., 2016).

The aim at White Island has been to estimate the amount of metals released by the super-heated vent located at the back of the crater lake, at the root of the volcanic plume. The output flow suggests these gases are being discharged through the main conduit, most likely bearing a more magmatic signature compared to the other fumarolic discharges. We also compare the signature of White Island plume to magmatic-hydrothermal emissions from Mt Etna (Italy), and purely magmatic plume from Yasur (Vanuatu).

6.2 Sampling and analytical methods

Collection of plume material at White Island was performed from the western crater rim (Figure 6-1 a-b). The gases, entrained by the wind, rise as a vortex along the crater wall. Care was taken not to sample fumarolic gases emitted from the walls underneath. This setup relies on the wind direction to be constant. For this matter, the last sampling campaign was performed with a drone (Figure 6-1 c). All the equipment was mounted on the flying device and flown into the plume. The flight time, limited by the battery lifetime, was around 5 minutes. Background air samples for White Island were collected at Maketu, in the Bay of Plenty (-37.75051° S, 176.46285° E).

In addition to White Island, we also sampled acidic gases and aerosols at Yasur volcano, in Vanuatu, and at Mount Etna in Italy. At Yasur, the trade winds commonly blow from the southeast, giving rise to the ash plain at the north west of the volcano. We installed our equipment on the western rim (Figure 6-1 d), at the margin of the volcanic plume (due to safety reasons). Background sample was collected from the southeast coast of Tanna island, close to the village of Manuapen (-19.54838° S, 169.47821° E).

The samples from Mt Etna were collected on 3 August 2016 during the Etna International Training School of Geochemistry, from the southeast rim of Bocca Nuova crater (Figure 6-2). The eruption that took place in May of the same year resulted in the crater being filled with lava, hence depriving Etna from its usual plume. We sampled what was thought to be the plume making its way through the lava, emitted along a fissure in the south east sector of the Bocca Nuova crater (37.74957° S, 14.99561° E).

Figure 6-1: Sampling locations and setup at White Island and Yasur volcano, Vanuatu. a) Aerial picture (source: LINZ) showing the sampling location on the western rim and the two flight paths of the drone on 20 December 2016. The first flight is drawn in blue (sample WI S1), the second in red (sample WI S4). It should be kept in mind that the lake was dried during drone sampling in December 2016 (see Figure 4-5), with mainly the superheated vent emitting. b) Picture of the sampling settings on the western rim. Note the pole holding the filter packs in the middle of the plume. c) Picture of the flying device used for sampling. The filter pack is mounted at the front of the flying device. d) Picture of the sampling settings at Yasur volcano on the western rim. The inset (source: Google Earth) shows the location of sampling. The ash plain extends to the northwest.

Figure 6-2: Sampling location at Mount Etna. a) Aerial picture (source Google Earth) showing the sampling location on the southeast rim of Bocca Nuova (BN). NE: Northeast crater. NSE: New southeast crater. V: Voragine. b) Picture of the pole holding the filter packs in front of the now filled Bocca Nuova crater. The arrow points to the fissure from which the plume is thought to escape.

Filter pack sampling was done by pumping the plume through a PFA filter holder containing 4 filters in series. The first filter is a membrane collecting the particulate phase. On June 2016, we used two different types of membrane, a Millipore AAWP mixed cellulose esters membrane filter (diameter 47 mm, pore size: 0.8 μm) and a Whatman® PTFE membrane (diameter 47 mm, pore size 2 μm). The sampling campaigns in June and December 2016 at White Island, as well as Etna and Yasur, were done using Pall® Zefluor membranes (diameter 47 mm, pore size 1 μm). In December 2016, we also sampled using a Sterlitech® membrane (diameter 47 mm, pore size 0.1 μm) to collect particles smaller than 1 μm . This particle membrane is followed by three paper filters (Whatman®, ashless grade 41, diameter 47 mm) impregnated with a solution of 1M KOH + 5% Glycerol (Finnegan et al., 1989). The KOH solution reacts with the acid gases (SO_2 , HCl, HF) in the plume. The sampling flow and duration were monitored in order to avoid saturation of the impregnated filters with respect to SO_2 . Such saturation results in non-quantifiable S measurements and was assessed by the total amount on the last (final) filter to be < 5% of the total amount. At White Island, we sampled for 20 to 30 minutes at a flow of 5-10 $\text{L}\cdot\text{min}^{-1}$. The range used at Yasur volcano was 8-40 min at 8-13 $\text{L}\cdot\text{min}^{-1}$. The flow and duration were reduced to 4 $\text{L}\cdot\text{min}^{-1}$ and 15-20 min at Etna due to the much higher SO_2 flux. The flow rates and total volume of air pumped were measured by Bronkhorst® Mass View digital mass flow meters. The Zefluor membrane used at White Island in December 2016 and at Yasur were pre-washed with a dilute HCl solution to reduce the amount of background trace metals. Filter blanks for the different types of membrane are presented in Table 6-1.

As the amount of aerosol collected with the filter pack is limited (to avoid saturation of impregnated filters), we also used a single-stage holder with a PTFE filter (Pall® Zefluor) to collect particles for trace elements analysis. Samples for SEM analysis were collected on polycarbonate filters (Nuclepore®, diameter 25 mm). In this case, air was drawn at a flow of 12-15 $\text{L}\cdot\text{min}^{-1}$ for 20 to 40 min.

Table 6-1: Composition of blank particle filters ($\text{ng}\cdot\text{g}^{-1}$).

	Sterlitech 0.1 μm	Pall 1 μm	Pall pre- washed	Whatman 2 μm	Millipore Cellulose
B	10.7	29.3	8.35	34.8	31.9
Na	18.2	381.2	33.6	na	na
Ca	365.8	na	168.0	167.2	5556.4
Rb	0.04	0.04	0.01	0.003	4.1
Sr	na	0.91	1.71	0.12	32.2
Zr	0.34	2.29	0.29	0.06	0.21
Mo	0.12	0.29	0.29	0.08	2.0
Ag	0.08	0.14	0.01	0.01	0.46
Cd	0.09	0.03	0.01	0.001	0.13
In	0.001	1.28	1.35	nd	0.16
Sn	3.70	406.6	499.8	0.14	51.9
Sb	0.08	0.07	0.11	na	0.64
Te	-	-	-	0.02	0.08
Ba	1.27	1.62	0.39	0.05	21.5

	Sterlitech 0.1 μm	Pall 1 μm	Pall pre- washed	Whatman 2 μm	Millipore Cellulose
Sm	0.01	0.003	0.003	-	0.05
Yb	0.003	0.002	0.001	-	0.02
W	-	0.02	0.02	0.09	4.0
Re	-	0.002	0.001	-	0.001
Au	0.04	1.36	0.46	0.004	0.01
Tl	0.15	0.01	0.01	0.004	0.03
Pb	0.09	0.23	0.11	0.02	12.9
Bi	0.01	0.01	0.003	0.003	0.04
Mg	6.91	46.7	11.0	5.16	1376
Al	94.4	74.4	37.4	16.6	31.3
Sc	0.02	0.01	0.002	-	0.01
Ti	3.04	2.02	40.2	0.46	16.0
V	0.08	0.14	0.07	0.002	0.16
Cr	17.8	4.78	2.08	5.81	316.0
Mn	0.25	15.6	0.23	na	na
Fe	10.3	50.8	16.6	7.84	115.6
Co	0.005	0.06	0.02	0.02	0.17
Ni	0.19	2.89	0.66	0.80	9.4
Cu	0.90	0.87	0.55	0.10	130.3
Zn	12.8	18.2	5.34	1.80	148.9
Ga	0.03	0.03	0.01	0.01	0.01
K	8.28	99.5	40.3	1.99	2857
As	0.36	-	-	0.10	2.1
Se	2.15	-	-	0.31	3.4

Notes: na: Not analyzed. - Below detection limit.

The filter cassettes were prepared and taken apart in a class 100 clean lab, in a fume hood and using nitrile gloves. Filters were handled using polypropylene or Teflon tweezers. The packs were transported in doubly sealed bags, and, when possible, were stored at -18 °C until analysis. Impregnated filters were extracted in 30 mL of distilled de-ionized water, to which a drop of H₂O₂ was added to oxidize any sulfide into sulfate. The solutions were analyzed after a week by ion chromatography (Dionex ICS-3000, GNS Science, Lower Hutt, New Zealand) for F⁻, Cl⁻ and SO₄²⁻. Interferences created by the paper filters in the region of F⁻ prevented quantification of the low amount present in White Island samples. SO₂, HCl and HF abundances in the plume were derived from the sulfate and halide ions concentrations. Dionex seven anion standard solution was used for calibration, with a reproducibility of 7% (1 RSD).

Aerosol components on the PTFE membranes were digested in PTFE beakers with a solution of 3 mL 8M HNO₃ + 3 mL 6M HCl and left on a hot plate at 120 °C. After two days, the filters were rinsed with 2M HNO₃ and removed from the beaker. The solutions were then dried down, refluxed in 15M HNO₃ and dried down again. Finally, the samples were taken up in 10 mL of 1% HNO₃ and analyzed by double focusing magnetic sector field ICP-MS (Element 2™, Thermo Fisher Scientific) at Victoria University of Wellington following the

procedure described in 4.2.3.1. A synthetic solution was used to calibrate the ICP-MS. Acid blanks and certified reference material SLRS-4 (Yeghicheyan et al., 2001) were run throughout the analysis. The accuracy, as the deviation from the certified value in percent, is as follows: 97% for Ag and Te, 70% for Zn, <30% for Na, Zr, Cd, Sb, W, Tl, V, Mn, Co, Ga, As, Se and less than 10% for the other elements (Appendix A.7).

A round section of the polycarbonate filters was cut for observation with the SEM. EDS analyses, despite being semi-quantitative, suggests the nature of the particles.

6.3 Chemical features

The results are presented in Table 6-2 for White Island. All the results were corrected for the contribution of the filter, by subtracting the respective background content presented in Table 6-1. The great variability of the results reflects spatial and temporal variations of volcanic plumes (e. g. density), as well as changes in wind directions in some cases (Aiuppa et al., 2002).

Table 6-2: Acid gases and aerosol compositions of filter packs from White Island plume.

	WI S4	WI S2	WI S3	WI P5	WI S2	WI S3	WI P	WI S1*	WI S4*	Maketu
Date	26 Jun 2015	26 Jun 2015	26 Jun 2015	26 Jun 2015	17 Jun 2016	17 Jun 2016	17 Jun 2016	20 Dec 2016	20 Dec 2016	4 Mar 2017
Vol. (m ³)	0.102	0.141	0.055	0.529	0.154	0.148	0.289	0.012	0.013	
SO ₂ (t/day)	343	343	343	343	246	246	246	402	402	
Acid gases µg.m ⁻³										
HCl	4414	3940	4546		11159	8885		2521	484	414
SO ₂	20175	19308	18894		20986	17764		4519	5138	247
SO ₂ /HCl	4.57	4.90	4.16		1.88	2.00		1.79	10.61	
Aerosols ng.m ⁻³										
B	796.4	352.2	2864	61.1	na	na	na	2285	1948	-
Na	na	na	na	na	303.5	-	-	199.0	1640	25750
Ca	31059	16931	25347	3201	1382	3750	1011	107583	11266	70505
Rb	2.5	4.8	11.1	1.3	0.48	0.41	0.21	5.1	1.0	1.9
Sr	12.3	48.6	74.6	7.4	na	na	na	na	na	na
Zr	3.0	12.7	16.4	1.6	-	-	-	69.2	31.8	71.3
Mo	42.8	1.6	2.7	1.0	-	-	-	-	24.0	0.81
Ag	-	1.9	4.3	1.2	-	-	-	-	7.0	0.56
Cd	0.92	0.82	0.88	0.65	1.2	0.16	0.07	-	-	0.12
In	-	0.31	0.32	0.30	-	-	-	-	-	-
Sn	-	14.0	20.6	7.1	na	na	na	na	na	na
Sb	26.1	20.3	60.6	10.4	16.9	14.1	8.4	26.9	-	0.63
Te	31.5	46.9	31.1	39.4	13.5	9.2	2.9	-	-	0.29
Ba	1.9	97.7	120.1	15.6	53.5	22.3	3.1	496.0	76.7	274.4
Sm	0.12	0.26	0.31	0.04	0.01	0.05	0.01	2.7	0.73	2.0
Yb	0.05	0.13	0.14	0.02	0.01	0.03	0.01	0.80	0.18	0.59
W	54.2	0.2	-	0.16	-	0.03	-	-	-	1.5
Re	0.22	0.09	0.16	0.02	-	-	-	-	-	-
Au	0.62	1.9	5.5	0.05	-	-	-	-	0.62	-
Tl	54.7	42.6	35.5	37.5	9.2	4.5	9.9	10.5	-	0.28

	WI S4	WI S2	WI S3	WI P5	WI S2	WI S3	WI P	WI S1*	WI S4*	Maketu
Pb	79.9	87.1	102.4	74.0	31.3	28.3	18.3	11.1	9.5	7.9
Bi	37.2	24.8	21.7	22.9	2.4	1.5	1.1	-	5.4	0.14
Mg	75.5	2792	6288	487.4	153.2	327.7	83.4	1656	501.9	3248
Al	3755	20185	44345	4531	442.9	959.8	137.7	49105	10407	34088
Sc	0.85	2.8	4.2	0.36	0.12	0.18	0.04	6.5	1.1	3.4
Ti	-	431.6	844.7	78.9	19.8	43.9	4.1	-	272.3	1097
V	8.0	25.9	44.2	4.0	1.7	1.1	1.1	14.4	5.5	18.4
Cr	-	2333	5068	589.0	-	-	-	-	2153	15.7
Mn	-	-	-	-	-	-	-	5.5	47.4	20.1
Fe	1518	5243	9303	1142	254.7	169.1	-	448.0	1722	810.7
Co	0.36	1.2	2.5	0.38	0.31	-	-	-	0.81	1.0
Ni	-	14.2	21.8	3.0	-	-	-	-	53.0	5.3
Cu	-	47.3	469.9	11.3	7.5	15.9	3.8	-	109.8	1.3
Zn	-	248.6	549.1	83.7	-	-	628.8	-	-	37.7
Ga	0.90	3.7	7.4	0.79	0.38	0.45	0.24	12.5	2.7	7.2
K	-	2451	4262	509.1	924.6	87.1	109.7	-	1125	1488
As	572.8	277.7	312.2	270.4	230.8	236.6	97.4	44.0	-	2.8
Se	189.8	98.0	208.5	91.1	318.3	307.2	259.0	-	-	-

Notes: - Below detection limit. na: Not analyzed.

SO₂ (t/day) is the SO₂ flux measured by GeoNet with airborne COSPEC.

*: Samples collected with a drone.

The particle filters WI P5 and WI P only collected the particulate phase (no acid gases).

Background air sampled on mainland at Maketu.

Reproducibility (1 RSD): Te $\pm$ 71%; Sn $\pm$ 61%; Se, Tl, Au, W, Ag, Na $< \pm$ 40%; B, Cd, Sb, Re, Pb, Bi, Mg, Sc, Ti, Cr, Zn, $< \pm$ 20%; $< \pm$ 10% for the rest of the elements (Appendix A.7).

The atmospheric background for White Island was measured on the beach in Maketu, in the Bay of Plenty. The strong wind on that day was most likely carrying droplets of sea water, indicated by very high values in major elements, Ba and Zr compared to background in Vanuatu (see Table 6-3). In White Island samples, many elements are nevertheless well above atmospheric background, emphasizing a volcanic origin.

6.3.1 Major species

The SO₂ and HCl contents of the volcanic plume are 4.8-19.1 mg.m⁻³ and 1.5-10.0 mg.m⁻³ respectively. The SO₂/HCl ratio in June 2016 is low compare to June 2015 (1.94 and 4.54 respectively) suggesting either a change in the magmatic settings, or variations of response from the hydrothermal system. It is possible that the 27th April phreatic eruption induced changes in the surficial vent environment. The increase in temperature observed at fumarole F0 (from ~160 °C in June 2015 to ~190 °C in June 2016, cf. Chapter 5) might also be linked to this variation in SO₂/HCl ratio. This ratio is very different in the two samples from December 2016, ranging from 1.79 to 10.61. The sampling time was drastically reduced during drone sampling, and might explain these variations (less time to average temporal variations in the plume). During the second flight, we approached the vent more closely and flew at lower altitude, potentially collecting a greater proportion of the main vent compared to neighboring fumaroles. The higher SO₂/HCl ratio might thus represent gases less affected by hydrothermal interactions. Overall, our understanding of the system is limited by the small

number of sampling campaigns and the absence of direct comparison between drone and ground-based samples on the same day.

6.3.2 Trace elements

The most abundant elements in the volcanic plume are B, Na, Ca, Mg, Al, Ti, Cr, Fe, K, with concentrations $> 1000 \text{ ng.m}^{-3}$ in some occasions, besides Ti exhibiting a maximum of 845 ng.m^{-3} . Arsenic and selenium are often higher than 100 ng.m^{-3} , whereas Ba, Pb, Cu and Zn sometimes exceed this value. The rest of the elements have contents $< 100 \text{ ng.m}^{-3}$, and less than 15 ng.m^{-3} for Rb, Ag, Cd, In, Re, Au, Sc, Co, Ga and Rare Earth Elements (Sm and Yb).

Figure 6-3: Bivariate plots suggesting different sources. The constant ratio between thallium and volatile elements such as Bi indicates they originate from a similar magmatic volatile phase. In contrast, the constant ratio between titanium and lithophile elements such as Sc suggests silicate nano-particles as the common source. Conversely, Bi does not correlate with Ti, nor does Sc with Tl.

We observe a correlation between some chalcophile elements (e. g. Cd, Te, Pb, Bi) and highly volatile Tl (cf. Chapter 5 (Patterson and Settle, 1987; Hinkley et al., 1994; Baker et al., 2009)), whereas lithophile elements (e. g. Cr, Sc, Al, Sm, Yb, Ba) correlate with Ti (Figure 6-3). These correlations suggest two different sources for the particles within the plume. Lithophile elements are transported by solid nano-particles, either formed through magma fragmentation or swept up from the conduit walls. Chalcophile elements, in contrast, are transported by a magmatic volatile phase.

The contents of Pb, Bi and Tl show strong variations with time, around one order of magnitude higher in June 2015 (Table 6-2). Arsenic shows a strong decrease during the

studied period, from $\sim 358 \text{ ng.m}^{-3}$ in June 2015 to 44 ng.m^{-3} in December 2016. Most elements are notably less concentrated in the June 2016 plume, with the exception of Se, Zn, Ni, and Ba. Samples collected closer to the source with the drone contain more lithophile elements (Zr, Ba, Yb, Sm, Mn), suggesting that silicate particles from the conduit wall settle before the plume reaches the crater rim.

Enrichment factors (Lepel et al., 1978; Vié le Sage, 1983) were calculated by dividing each element in the aerosol by the concentration of the same element in the host rock, both divided by a reference element. We chose Al for the latter as it is refractory and abundant in both aerosols and rocks. The rock composition used for White Island is the 1977 andesite, a lava reported by Aiuppa et al. (2003) for Etna and ash erupted during sampling at Yasur (Appendix A.8). Elements with $EF \sim 1$ are transported as silicate whereas species with $EF > 1$ are volatile, transported in aerosols formed through gas-to-particle conversion (Vié le Sage, 1983).

Figure 6-4: Enrichment factors of aerosols from White Island, Mount Etna, and Yasur volcanoes. The andesite from 1977 eruption was used for White Island, with Se content of $0.92 \text{ } \mu\text{g.m}^{-3}$ from Wells (1967). We used ash collected during sampling for Yasur and composition of lava from Etna reported by Aiuppa et al. (2003).

The results presented in Figure 6-4 show lithophile elements (Sc, Ba) with $EF \sim 1$, in accordance with the correlation with Ti reported above. On the other hand, chalcophile and siderophile elements show volatile to extremely volatile behavior, with $EF > 10\,000$ for Se, Te and Au, similar to what was observed in fumarolic gases (cf. Chapter 5) and at other volcanoes (Aiuppa et al., 2003; Moune et al., 2010; Menard et al., 2014; Gauthier et al., 2016). Volatile elements with lower EF in December 2016 are likely reflecting the higher proportion of silicates in the aerosols sampled with the drone.

6.3.3 Aerosols from Yasur and Mount Etna volcanoes

Results from the filter pack studies at Yasur and Etna volcanoes are presented in Table 6-3 and Table 6-4 respectively. Despite the short collection time at Etna, the two filter packs were saturated with respect to SO₂, with 25% and 30% of the total sulfate present on the last filter. Such saturation indicates that we cannot quantify the total amount of SO₂, leading to underestimated concentration of the latter species.

At Etna, our results indicate mean values of 60.4 mg.m⁻³, 7.2 mg.m⁻³ and 0.13 mg.m⁻³ for SO₂, HCl and HF respectively, with a SO₂/HCl ratio of 8.4. These results are within the range previously measured by Calabrese et al. (2011) and Aiuppa et al. (2002), despite underestimation of SO₂. At Yasur, average concentrations of 7.5 mg.m⁻³ of SO₂, 0.7 mg.m⁻³ of HCl and 75 µg.m⁻³ of HF respectively were measured, with a SO₂/HCl molar ratio of 7.7. FTIR measurements of Yasur emissions reported by Oppenheimer et al. (2006) show SO₂/HCl molar ratio of ~ 2 during passive degassing, whereas the same ratio rises to ~30 during Strombolian eruptions. Our value of 7.7 agrees with these previous estimates, as it represents average ratio of both types of emission (sampling time 8 to 40 minutes).

Table 6-3: Acid gases and aerosol compositions of filter packs from Yasur volcano plume.

	S2	S3	S4	S5	S6	S7	N1	P	Manuapen
Vol. (m ³)	0.221	0.282	0.158	0.066	0.176	0.077	0.130	0.153	
Acid gases µg.m ⁻³									
HF	52	23	54	123	38	161	-		-
HCl	582	205	904	721	423	2036	142		-
SO ₂	6541	3000	7850	13759	5110	17756	2801		17
SO ₂ /HCl	11.23	14.61	8.69	19.09	12.09	8.72	19.77		-
Aerosols ng.m ⁻³									
Na	6507	3007	65025	2106	66993	2947	1713	4607	1235
Ca	10402	2785	86322	313.7	132431	25259	2409	4812	1042
Rb	7.0	2.9	55.5	3.4	66.7	4.9	4.2	11.2	0.10
Zr	13.0	5.0	148.5	-	179.6	1.6	9.8	2.2	0.20
Mo	10.5	-	22.4	-	12.7	-	9.1	12.8	2.9
Ag	0.4	0.22	2.3	0.21	2.3	0.59	0.26	1.1	0.06
Cd	6.1	3.2	8.2	9.3	3.2	12.9	4.9	22.3	0.02
In	7.2	15.4	50.9	-	49.2	-	20.0	25.6	-
Sb	11.8	0.05	3.1	-	0.72	0.02	-	-	0.03
Te	12.4	0.92	13.6	0.59	7.0	1.4	6.3	16.7	0.16
Ba	110.4	37.2	1151	5.8	1431	35.0	36.0	28.6	3.4
Sm	0.92	0.31	9.4	0.02	12.4	0.20	0.37	0.23	0.02
Yb	0.52	0.18	5.2	0.01	7.0	0.08	0.21	0.10	0.02
W	0.42	-	0.49	-	2.8	-	2.9	-	-
Re	0.56	0.26	0.63	1.0	0.3	1.2	0.28	1.5	-
Tl	10.6	5.1	11.4	10.8	4.5	17.9	6.8	31.3	0.16
Pb	51.4	26.8	79.3	77.2	59.3	99.9	26.6	119.7	0.12
Bi	6.6	1.0	7.2	0.04	4.6	0.47	3.9	17.2	0.03

	S2	S3	S4	S5	S6	S7	N1	P	Manuapen
Mg	2952	1117	39367	13468	38630	877.8	917.5	767.6	234.4
Al	17107	4599	153258	3074	205838	3751	6986	4363	462.9
Sc	3.5	1.1	32.7	0.10	50.1	0.47	1.3	0.68	0.08
Ti	1037.3	733.3	9877.0	-	11635.6	-	1526.3	112.3	3.5
V	51.5	14.1	439.0	0.42	597.1	6.9	23.7	15.0	1.0
Cr	0.65	3.1	42.2	-	33.9	-	-	0.08	0.02
Mn	235.7	80.7	2775.9	7.3	3156.2	21.1	86.1	55.3	6.1
Fe	11045	3535	122761	786.0	138772	1312	3711	3490	253.1
Co	3.6	1.3	49.4	0.10	46.9	0.33	1.2	1.3	0.09
Ni	0.77	-	86.3	-	34.7	2.9	8.3	2.5	0.78
Cu	238.4	113.3	841.0	348.3	928.3	394.8	142.0	646.4	3.1
Zn	51.5	10.2	200.3	12.0	198.7	66.2	-	136.6	-
Ga	3.7	1.1	35.0	0.46	44.8	1.0	1.8	0.90	0.10
K	5873	1859	45571	2156	49119	2683	2186	6023	236.4
As	172.7	40.5	146.9	17.7	53.3	67.7	43.7	233.6	0.83
Se	18.9	16.9	24.9	-	-	-	-	58.2	47.1
Ash%	2.5	1.9	23.2	0.04	39.6	0.08	2.3	1.5	

Notes: - Below detection limit.

Background air sampled at Manuapen.

The particle filter P only collected the particulate phase (no acid gases).

Ash%: Estimated assuming Mn originates from silicates only and using Yasur ash composition.

We notice high Cu concentrations with average content of 327 ng.m^{-3} and 457 ng.m^{-3} at Etna and Yasur respectively, against average of 176 ng.m^{-3} , 9 ng.m^{-3} and 110 ng.m^{-3} (see Table 6-2) during the three sampling campaigns at White Island. This is in accordance with the results from the previous chapters, reporting overall low Cu contents in White Island emissions. Given the temperature dependence of Cu solubility in vapor, the lower temperature of White Island plume is likely to explain the lesser amount of Cu transported (Symonds et al., 1987). It is worth noting that the Cu concentration reported by Calabrese et al. (2011) at Etna from 2004 to 2007 is one order of magnitude higher ($\sim 2200 \text{ ng.m}^{-3}$).

Table 6-4: Acid gases and aerosol compositions of filter packs from Mount Etna plume.

	Etna S3	Etna S4	Etna P	Etna N*
Vol. (m^3)	0.082	0.070	0.455	Blank
Acid gases $\mu\text{g.m}^{-3}$				
HF	102	159		-
HCl	7351	7056		2
SO ₂	68025	52803		12
SO ₂ /HCl	9.25	7.48		5.30
Aerosols ng.m^{-3}				
Na	-	-	1975.0	39.4
Rb	10.4	7.5	19.8	0.02
Zr	26.6	-	-	0.20
Mo	3.1	-	6.0	-

	Etna S3	Etna S4	Etna P	Etna N*
Ag	-	-	0.004	-
Cd	5.5	3.0	11.6	0.01
Sb	1.9	0.88	1.7	0.07
Te	-	-	13.9	-
Ba	-	-	3.1	0.23
Sm	0.41	0.01	0.03	0.001
Yb	0.12	-	0.01	0.001
Re	0.06	0.04	0.20	-
Tl	16.3	14.6	38.0	0.12
Pb	55.2	52.4	98.1	0.09
Bi	2.4	0.73	13.1	-
Al	5538	-	80.5	33.6
Sc	0.71	0.01	0.03	0.01
Ti	289.3	51.8	80.0	1.3
V	6.1	3.9	5.3	0.07
Mn	-	-	0.39	1.6
Fe	-	-	249.8	90.1
Co	-	-	0.64	0.11
Cu	236.1	334.3	411.2	0.90
Zn	-	-	205.3	6.1
Ga	1.4	-	0.07	0.02
K	1960	515.8	3278	24.5
As	9.9	9.9	64.4	-
Se	93.3	96.2	179.8	-

Notes: - Below detection limit.

The particle filter Etna P only collected the particulate phase (no acid gases).

*: Field blank in $\mu\text{g.g}^{-1}$ and ng.g^{-1}

Enrichment factors for Mount Etna, and especially for volatile elements (Se, Re, Tl, As, Cd, Pb, Bi), are higher than those for White Island (Figure 6-4). Different magma compositions may be responsible for these discrepancies. However, the greater concentrations of volatile elements at Etna might also reflect a more important magmatic contribution. In fact, discrete eruptions occurred in the evening following sampling, emphasizing the proximity of the magma. In contrast, the last magmatic eruption at White Island occurred in 2013. Moreover, the low temperature of emissions (plume and fumarolic gases) measured at White Island suggests that the two-phase envelope surrounding the conduit (Giggenbach, 1987) is well developed. Cooling of the metal-transporting vapors on their way to the surface is likely to trigger metal precipitation (Bernard, 1985; Symonds et al., 1987; Bernard et al., 1990) explaining the lower EF for White Island. Note the really high enrichment in Bi (EF = 390 000) in Mount Etna plume, in agreement with the bismuth iodide particles observed on the polycarbonate filter (see below).

Enrichment factors of volatile elements at Yasur are, on the other hand, in the same range as those at White Island. The Strombolian eruptions occurring every 2-10 minutes at Yasur are likely to be responsible (dilution effect), owing to the ash emitted during such events and collected onto the filters. The amount of ash on each filter was assessed by assuming Mn to

be solely of silicate origin, and using the ash composition ($\text{Mn} = 1285 \mu\text{g.g}^{-1}$, Appendix A.8). The high concentration of aluminum in the aerosol fraction due to the presence of silicates, lowers the enrichment factors for volatile elements, depleted in the juvenile magma. Despite this dilution effect, Bi, Cd and Tl show substantial enrichment. These values are similar to those reported at Ambrym, another volcano of the Vanuatu volcanic archipelago (Allard et al., 2015).

6.4 Particle morphology and composition

Single particles in White Island aerosols consist of euhedral sulfates, larger than $2 \mu\text{m}$ in size (Figure 6-5 a). Two types of sulfates were observed, Ca sulfate and Al-K sulfate. Euhedral crystals of halite of up to $10 \mu\text{m}$ were also found (Figure 6-6 a).

Figure 6-5: SEM pictures of White Island aerosols. a) Euhedral crystal of Ca sulfate. b) Zn oxide with minor amount of Al, Cu, Al and S. All SE images.

Figure 6-6: SEM pictures of White Island aerosols. a) Euhedral crystals of halite. b) Particle containing Si-S-O thought to be silica coated with sulfur. c) Aggregate of particles, coated with S, showing a round shape suggesting drying of a H₂SO₄ droplet. Particles include silicates, pyrite and euhedral SiO₂. d) Unidentified Cl, S, P, Al round particle. Note the presence of dried material next to the particle assumed to be H₂SO₄. All SE images.

Numerous particles are rich in Si, with minor amounts of Al-K-Fe-Mg-Na indicating that they are silicates, likely originating from conduit wall erosion. Their shape is often irregular and they usually contain sulfur. Some of them have a smoother surface and are comprised almost exclusively of Si, suggesting they might be silica particles forming by gas-to-particle conversion (Chuan et al., 1986; Lefevre et al., 1986; Toutain et al., 1995; Moune et al., 2010). A thin shard more than 10 µm long was observed (Figure 6-6 b), containing Si and S, suggesting it might be coated with sulfur. We found three unidentified rounded particles, with similar appearance and composition (Figure 6-6 d). EDS analyses revealed Cl, S, P, Al and/or Na, with minor Br. They easily volatilize under the beam. The presence of H₂SO₄ is indicated by dried material on the filter (Figure 6-6 c, d) and aggregate of particles all containing S and deposited with a circular shape. The aggregate in Figure 6-6-c is mainly composed of small fragments of silicates coated with sulfuric acid, although a grain of pyrite (~ 2 µm) was found. Elemental sulfur particles were also detected by EDS.

The second most common type of particles after silicates was Zn ± Cu oxides (Figure 6-5 b). The majority of them contained more than 50% Zn, with smaller amount of Cu. Only one particle was Cu-dominant, and another had equal proportions (37% Zn, 33% Cu and 30% O). The morphology differs, with particles appearing as aggregates of small grains whereas others look uniform and smooth. Their sizes range from 0.5 µm to 6 µm. Rose et al. (1982) reported the occurrence of Zn ± Cu oxides in the non

cooling and reacting with the atmosphere to form oxides. Similarly, Toutain et al. (1995) reported unidentified particles containing major Cu and Zn in the plume of Mount Etna.

Figure 6-7: SEM pictures of Etna aerosols. a) Small crystals of Zn (93 %) on a particle. b) Metallic plate containing 72 % Cu and 27 % Zn. All BSE images.

Comparable $\text{Zn} \pm \text{Cu}$ oxides were found in the particulates from Mount Etna plume. A number of zinc- and copper-rich grains apparently do not contain oxygen, suggesting they might be pure metals. One of them (Figure 6-7 b) is a 10 μm long plate which contains 72% Cu and 27% Zn, which corresponds to a compound with formula $\text{Cu}_{2.9}\text{Zn}_{1.1}$. This is very similar to α -Brass (Cu_3Zn), observed as inclusions in plagioclase from Miyake volcanic island (Japan) (Li et al., 1989). Small roundish grains of Zn (93%) were also observed on a sulfur particle (Figure 6-7 a). Moreover, we found elongated euhedral rosette crystals of zinc sulfate, absent in the plume of White Island (Figure 6-8 a).

The presence of H_2SO_4 is highlighted by similar dried material on the polycarbonate filter surrounding particles of SiO_2 and silicate (Figure 6-8 b). A round aggregate of Ca sulfate crystals also suggests presence of liquid droplets (Figure 6-8 d). Interesting irregular masses of Bi iodide were present on the filter (Figure 6-8 c).

The filter collected at Yasur contained mainly ash. These had a very smooth surface under the SEM, and a variety of shapes reflecting magma fragmentation (Figure 6-9 c). Fe-Cr-Ni oxide was observed, as well as comparable $\text{Zn} \pm \text{Cu}$ oxides than the ones found at White Island and Etna (Figure 6-9 a). Euhedral crystals of Ca sulfate and halite were also observed (Figure 6-9 d).

Figure 6-8: SEM pictures of Etna aerosols. a) Zn sulfate rosette. b) Silica in a H_2SO_4 droplet. c) Aggregate of bismuth iodide. d) Round aggregate composed of Ca sulfate and thought to have been transported in a droplet of liquid. All SE images.

Figure 6-9: SEM pictures of Yasur aerosols. a) Zn oxide with minor amount of Al, Cu, S, Cl, Ca. b) Silicate. c) Ash. d) Halite. All SE images except BSE image for b.

To summarize, silicates are ubiquitous in the aerosols, resulting from conduit erosion and magma fragmentation in the case of Yasur. Sulfates are also found in the particulate phase of

the three volcanoes, as well as Zn oxides ($\pm$ Al-Cu). The only chloride particulate found is halite, in the plume of White Island and Yasur. The presence of this compound at the two volcanic islands could suggest a marine origin. However, NaCl was previously observed at Etna (Andres et al., 1993; Toutain et al., 1995; Calabrese and D'Alessandro, 2015) and the mineral is common in fumarolic sublimates (Quisefit et al., 1989; Bernard et al., 1990; Africano et al., 2002; Wahrenberger et al., 2002; Zelenski and Bortnikova, 2005) emphasizing a magmatic origin as well. Sulfur is present in small amounts in many particles at White Island, indicating possible coating. Moreover, the presence of sulfuric acid is suggested by dried droplets containing S, as reported in the past by Rose et al. (1986). Formation of sulfuric acid is likely occurring after SO₂ emission into the atmosphere and subsequent oxidation in water droplets (Eatough et al., 1994).

6.5 Origin of the aerosol

6.5.1 Variations in major gas compositions

As previously noted, we observed variations in the SO₂/HCl ratio of White Island plume between the three sampling campaigns, with values around 4.5 in June 2015 dropping to around 1.9 in June 2016. The two samples collected in December 2016 vary greatly, from 1.8 to 10.6. For a comparison, values of the same ratio in Yasur and Etna plumes are 13.5 and 8.4 respectively, showing that magmatic signature is indicated by high SO₂/HCl ratios.

The composition of plume emissions measured by GeoNet during flight surveys are used to constrain the nature of the changes observed. Variations in CO₂/SO₂, CO₂/H₂S and SO₂/HCl are the result of both changes in the magmatic feeding system and varying contribution from the hydrothermal system. Increase in CO₂ indicates rise of mafic magma within the conduit. SO₂ is also of magmatic origin, although it is easily scrubbed by the hydrothermal system (cf. Chapter 4). H₂S mainly arises from the hydrothermal system, whereas HCl is a combination of both magmatic and hydrothermal contributions (see Symonds et al., 2001).

Emission rates measured during flights in the plume show increase in CO₂/SO₂ from 4.8 (on 16 June 2015) to 8.2 (on 2 June 2016) whereas CO₂/H₂S decreases from 115 to 33 (GeoNet, 2016). The SO₂ emissions decrease while H₂S increases. A process that can explain such variations is the remobilization of sulfur dissolved in the hydrothermal system as H₂S_(g) following heating. Because of scrubbing into a two-phase hydrothermal envelope, SO₂ emissions are likely to stay low until complete vaporization. These variations are similar to the dry-out process described by Symonds et al. (2001). The parallel decrease in SO₂/HCl ratio between June 2015 and June 2016 (Table 6-2) may also indicate increasing HCl emissions due to the vaporization of hydrothermal fluids. The rise in temperature observed in fumarolic gases (cf. Chapter 5) over the same period further supports this assumption.

Contrastingly, the average CO₂/SO₂ ratio decreases from 8.2 in June 2016 to 3.8 in December 2016, back into the field of magmatic vapors described by Christenson et al., 2017 (molar C/S of 3 to 6), suggesting only minor SO₂ scrubbing. The accompanying increase in CO₂/H₂S ratio from 33 to 68.1 also supports low contribution from the hydrothermal system.

The contrasting SO_2/HCl ratio (1.8 and 10.6) measured in December 2016 (Table 6-2) indicates collection of very different gases. The SO_2/HCl ratio of 10.6 is similar to magmatic values reported at Etna and Yasur, whereas the lower ratio of 1.8 reflects hydrothermal contribution. Such disparity may either reflect rapid changes in emission with time (the sample with a ratio = 10.6 could be a burst of magmatic gases), or greater contribution from the crater lake evaporation and/or low-temperature fumaroles with changing wind conditions to explain the lower SO_2/HCl ratio. Collection closer to the high-temperature vent at the back of the crater lake (see Figure 6-1) during the second drone flight (SO_2/HCl = 10.6) further suggests sampling of gases of magmatic origin.

6.5.2 Variations in trace metals

Partitioning of gold into the gas phase at magmatic conditions was reported by several experimental studies (Heinrich, 2005; Simon et al., 2005; Simon et al., 2007; Frank et al., 2011). Elevated Au concentrations are also observed in high-temperature fumarolic gases (Symonds et al., 1987; Quisefit et al., 1989; Hedenquist et al., 1994a; Kavalieris, 1994; Taran et al., 1995; Taran et al., 2000; Yudovskaya et al., 2006; Yudovskaya et al., 2008). The presence of Au in the samples with high SO_2/HCl only (Table 6-2) is an indicator of their magmatic origin. Considering that the ability of volcanic vapors to transport gold decreases with cooling, the temperature of the plume sampled in June 2016 must have been too low to efficiently carry gold complexes, explaining its absence in the particulate phase. The presence of Au in White Island aerosols thus appears as indicative of high-temperature magmatic gases emitted from the inaccessible vent at the back of the currently active crater.

Figure 6-10: Ternary diagram Cu-HCl/50-SO₂/100 for the volcanic plume.

Similar behavior is observed for Cu, as shown in Figure 6-10. Samples from June 2015 and December 2016 with higher SO₂/HCl ratios contain more copper than was carried by the plume in June 2016. It is interesting to note that increasing Cu content with increasing HCl could also be expected, given the predominance of Cu chloride complexes predicted by thermodynamic calculations in fumarole F0 gases (cf. Chapter 5). The opposite trend observed however seems to indicate the more important control of temperature on copper transport by volcanic vapors.

6.6 Emission rates

Combination of SO₂ flux measured independently and filter pack studies allow estimate of halogens and metal emission rates through:

$$X_{flux} = X/SO_2 * SO_2_{flux}$$

where X_{flux} and SO_{2flux} are the flux of element X and SO₂ respectively, and X/SO₂ is the concentration ratio of element X to SO₂. The flux of SO₂ is measured at White Island as part of the GeoNet volcanic hazards monitoring, with an airborne COSPEC instrument. The SO₂ emissions have ranged from 50 to 500 t/d in periods of low activity in the last 14 years and rising as high as 2075 t/d during the 2012-2013 eruption (Christenson et al., 2017).

In order to estimate the trace metal emission rates for the three sampling campaigns at White Island, we used the SO₂ flux measured within the same month as aerosol collection. 343 t/d of SO₂ were emitted on 16 June 2015, 246 t/d on 2 June 2016, and 402 t/d in November 2016-January 2017 (Table 6-2).

For Yasur, Bani and Lardy (2007) measured an average flux of 683 t/d between April 2004 and November 2005, while Métrich et al. (2011) reported daily emissions of 940 tons and 620 tons on 20-21 and 29-30 October 2007 respectively. The measured flux on the day of sampling was higher than average, with a value of 1683 t/d (± 530) (Benjamin Simons, pers. comm., 2017). The latter flux of 1683 t/d was used in our calculations.

The average emission rate at Etna during 1987-2000 was estimated by Caltabiano et al. (2004) at ~ 5560 t/d and at ~ 3530 t/d from 2005-2008 by Salerno et al. (2009). We used the rate of 3530 t/d in our calculations, taking into consideration that lava filling the Bocca Nuova crater during the May 2016 eruption would have reduced the total emission.

Table 6-5: Average emission rates (kg/d, unless specified) for White Island, Yasur and Etna and comparison with other studies.

	White Island	Yasur	Etna	White Island	Etna	Erta Ale ^e	Lascar ^f	Masaya ^g	Ambrym ^h
	This study			Other studies					
HCl (t/d)	106.2	161.7	420.9						
HF (t/d)	-	17.0	7.6						
Cu	3.62	103.11	19.12	300 ^b	657 ^d	0.7	16.9	582	1300
As	4.58	21.91	2.11	11.2 ^a	85 ^d	0.4	80.3		300
Pb	1.07	15.25	4.01	23.3 ^a , 125 ^b , 12 ^c	85 ^d	0.17	7.7	29.1	90
Se	3.15	6.71	7.19	1.3 ^a	52 ^d	0.8	125.2		360
Bi	0.34	1.16	0.31	6 ^b , 55 ^c	26 ^d	0.058	1.4	9.8	32
Tl	0.53	2.78	1.34	11 ^c	107 ^d	0.037	1.9	33.8	160
Zn	6.16	21.79	12.00		246 ^d	0.68	50.1	135	350
Sb	0.63	0.71	0.09	1.6 ^a	24 ^d	0.0014	0.91	0.9	
Te	0.43	1.66	0.81			0.59	1.28	17.2	
Cd	0.04	1.98	0.39	9 ^b	36 ^d	1	0.17	22	46
Au	0.12	-	-						

Notes: - Below detection limit.

^a: Wardell et al. (2008). ^b: Le Cloarec et al. (1992). ^c: Rose et al. (1986). ^d: Calabrese et al. (2011). ^e: Zelenski et al. (2013). ^f: Menard et al. (2014). ^g: Moune et al. (2010). ^h: Allard et al. (2015).

The average emission rates for White Island, Yasur and Etna are presented in Table 6-5. The flux of HCl at White Island estimated from filter pack study is ~ 106 t/d, in agreement with previous estimates of 70-80 t/d, 150 t/d and 89-125 t/d from Rose et al. (1986), Werner et al. (2008) and Christenson et al. (2017) respectively. In terms of trace metals, our results show emission rates of ~ 4 kg/d of Cu, As, Se, ~ 6 kg/d of Zn, and ≤ 1 kg/d of Pb, Bi, Tl, Sb, Te, Au and Cd during quiescent degassing at White Island. Besides Se and Sb, these values are one to two orders of magnitude lower than reported in previous studies (see Table 6-5).

The daily emissions at Yasur are ~ 162 tons of HCl and ~ 17 tons of HF, close to the filter packs estimates of 164 t/d and 23 t/d respectively, reported by Métrich et al. (2011). Trace metal emission rates are higher at Yasur than at White Island, with up to ~ 100 kg/d of Cu, 22 kg/d of As and Zn, 15 kg/d of Pb and ~ 2 kg/d of Tl and Cd. These values are nevertheless substantially lower than those reported at Ambrym, the second largest volcano of the Vanuatu archipelago (Allard et al., 2015).

Metal emission rates from Etna are likely to be overestimated due to saturation of the filters with respect to SO₂. Results in Table 6-5 show that they are slightly higher than at White Island. In contrast, they are an order of magnitude lower than previous estimates, as expected after the decrease in plume emissions following the May 2016 eruption.

Comparison with other volcanoes (Table 6-5) emphasizes the relatively low trace metal emissions at White Island measured during the quiescent activity encompassing this study. Results from the thermodynamic calculations in Chapter 5 exhibited a drop of four orders of magnitude in the Cu, Fe and Zn contents of Donald Mound fumarolic gases between 500 °C and 300 °C. Moreover, the stability of all metal sulfur complexes rapidly decreased as the

temperature fell below 500 °C. The lower fluxes of metals recorded at White Island are thus likely the result of contrasting emission temperatures. Thermal images of the superheated vent giving rise to the volcanic plume at White Island using a FLIR camera, revealed temperatures ranging from 142 °C to 337 °C (mean of 255 °C), between June 2015 and November 2016 (Bruce Christenson, pers. comm.). The temperatures inside the fumarole vent are probably appreciably higher. In contrast, fumarolic gas discharges in excess of 300 °C were recorded at Mount Etna on the day of sampling, suggesting higher temperature for the volcanic plume. The elevated temperature of gas emissions at Yasur are obvious, owing to the proximity of the magma, only meters below the surface. Métrich et al. (2011) estimated the silicate melt to be ~ 1107 °C at a shallow depth (< 4 km), suggesting plume temperature above 900 °C. The more elevated trace metal emissions at these two volcanoes is thus explained by the currently higher temperature of emissions, favoring transport of metal complexes. In fact, metal fluxes from White Island reported by Le Cloarec et al. (1992), Wardell et al. (2008) and Rose et al. (1986) are about an order of magnitude or more higher (Table 6-5). These three studies were conducted during the 1976-2000 eruptive sequence, when emission temperatures were much higher than presently.

6.7 Conclusions

To summarize, this study showed that Bi, Cd, Tl, Se, Te, Au and Sb are the most enriched trace metals and metalloids in volcanic plumes. Despite its enrichment at Etna and Yasur, Cu is not very concentrated in White Island plume, once again emphasizing the importance of temperature in volatile transport of metals. The most common observed particles at the three volcanoes are silicates, sulfates, halite, SiO₂, sulfuric acid droplets, and most interestingly Zn ± Cu oxides.

Three main sources for volcanic aerosols are: 1) the magmatic contribution, represented by volatile elements emitted directly from the magma, 2) silicate contribution, as particles originating from magma fragmentation, or dragged from the conduit during wall erosion, 3) hydrothermal contribution, important when a well-developed, two-phase hydrothermal system is present in the subsurface. The variations in aerosol composition reflect changes in the relative contributions of these three endmembers, and is linked to changes in volcanic activity. The presence of Au in the plume of White Island, for instance, indicates emission of magmatic gases of high temperature. Further study, and especially during higher activity at White Island, is required to constrain the variations in metal content induced by injection of mafic magma. The development of technology, and especially of drones, should greatly improve aerosol sampling, by removing the dependence on wind direction and allowing collection in remote and dangerous locations.

Metal emission rates were estimated, yielding to values in the range of 0.1 to 10 kg/d of Cu, As, Se, Zn, Pb, Bi, Tl, Sb and Te at White Island. These emissions are not negligible and should be taken into consideration where populations are living nearby volcanoes. The case of Yasur is of importance, where as much as 100 kg of Cu and 10-20 kg of As, Pb and Zn are emitted daily in the volcanic plume, in an area where populations rely on local water and food supply.

Chapter 7: Mass balance calculations and concluding remarks

In the previous chapters, we provided detailed analyses of different features from the White Island magmatic-hydrothermal system, focusing on the distribution and speciation of metals. Melt inclusions and erupted rocks enable determination of the effects of crystallization and degassing on metals present in the magma. Analysis of volatiles discharging at the surface helped us in constraining metal degassing and revealed interactions with the active hydrothermal system.

Exsolution of aqueous fluid from magma residing at depth is at the root of hydrothermal systems in volcanic environments (Burnham, 1979). What happens to this fluid subsequently is the focus of this concluding chapter: does it separate into a low-density vapor (observed at passively degassing volcanoes) and a high-density brine, and if so, at what depth and temperature. What is the relative role of each phase in transporting metals? Here, we constrain the transport of metals in the subsurface environment, after volatile exsolution from the magma. Using our results and data from past studies at White Island, we also estimate the copper budget for the magmatic-hydrothermal system.

7.1 The copper budget for White Island magmatic-hydrothermal system

White Island has been depicted in different studies as a favorable system for the formation of a porphyry copper deposit (Hedenquist et al., 1993; Rapien et al., 2003). The data collected during this project enables us to undertake mass balance calculations for copper within the magmatic-hydrothermal system and to highlight potential deposition occurring in the subsurface environment.

First, we need to estimate the volume of magma that degasses over a period of time at White Island. The SO₂ flux is routinely measured by GeoNet (since 2003), using airborne COSPEC (GeoNet, 2003-2017). Christenson et al. (2017) determined a molar C/S ratio between 3 and 6 to represent the magmatic vapor. The main assumption in estimating the volume of degassed magma is that the SO₂ measured at the surface represents all the sulfur exsolved from the silicate melt. We therefore used only SO₂ fluxes measured on days when scrubbing was minimal (i.e. molar C/S ratio between 3 and 6). The SO₂ emission rate obtained is ~ 423 t/d, similar to the average flux of 430 t/d measured during a period of higher activity (1986-1999) by Wardell et al. (2001). The original S content of White Island magma is taken as that of olivine-hosted melt inclusions, 1200 ppm, whereas erupted dacite containing 100 ppm (Giggenbach, 1996) represents the final S content. The amount of magma required to produce the observed flux of SO₂ is ~ 190 000 t/d, or ~ 7×10^7 tons every year. Considering that magma has a density of 2700 kg/m³, it corresponds to 0.026 km³ of silicate melt degassing annually. This volume is in the range of previous estimates from Werner et al. (2008) and Giggenbach and Sheppard (1989) of ~ 0.022 km³/y and ~ 0.025 km³/y respectively.

The average Cu content of olivine-hosted melt inclusions, 128 ppm, is thought to represent the amount of copper in the magma before degassing. Considering the 7×10^7 tons of magma degassed annually, this corresponds to a total of 9010 tons of Cu per annum. Taking the Cu

content of White Island dacite of 58 ppm determined by Graham and Cole (1991), it implies that 45% of the total Cu stays in the silicate melt, amounting to 4083 tons. Consequently, the other 55%, corresponding to 4927 tons of Cu, escapes from the magma.

It is important to consider all the potential sinks for Cu in order to obtain realistic mass balance estimate. In the case of White Island, we have defined them as follows:

- Gas discharges
- Spring discharges
- Elemental sulfur scrubbing/sequestration
- Sulfide melt scrubbing/sequestration
- Cu-rich mineral deposition

The copper content of most of these components was determined and reported in previous chapters or in past studies. For the mass calculation, an estimate of emission/formation rate for each of the potential sinks is required.

The gaseous emissions at White Island have been detailed in Chapter 6 and resulted in Cu emission rates of ~ 4.65 kg/d during low, quiescent activity, corresponding to 1.7 t/y. Le Cloarec et al. (1992) collected aerosols from White Island in 1988, during a period of higher volcanic activity. They estimated the temperature of the gases to be ~ 1000 °C. Their results yield a flux of copper in the range of 300 kg/d, or 110 t/y. Despite this value being two orders of magnitude higher than our current estimate, it is still very low compared to the 4927 t of Cu leaving the magma every year.

Acidic springs are discharged into the sea at various locations around the island. The discolored plume resulting from precipitation of various hydroxides after mixing with sea water makes them easily identifiable (Figure 7-1). Acid Stream drains waters within the crater floor, flowing southeastward and discharging in Crater Bay (Figure 7-1 a and d). The flow has been regularly monitored by GeoNet over the period 2004-2015, with an average value of 2765 t/d (GeoNet, 2004-2015). Its Cu content was reported by Giggenbach and Glasby (1977) at ~ 0.2 ppm, leading to ~ 0.20 tons of copper discharged every year. The flow and composition of the other discharges observed in Figure 7-1 have not been studied. The minor discharges observed in the southeastern bays are attributable to Acid Stream, discharging beneath the tide line (Bruce Christenson, pers. comm.). Two major seepages exist on the northwest coast of the island (Figure 7-1 b and c). We estimated their total discharge to equal that of Acid Stream by comparing the size of discolored plume they produce after mixing with sea water. Considering the same Cu content of 0.2 ppm, the annual flow of copper from spring discharges corresponds to 2 x Acid Stream emission rate, or about 0.40 t/y.

Figure 7-1: Aerial photos showing acid discharges around White Island. Photo: courtesy of GNS.

The crater lake that periodically floods the main crater, despite its ephemeral nature, has been present most of the time since its reappearance in 2003. The occurrence of similar features has also been reported in the past (Luke, 1959), indicating that sulfur scrubbing of metals in the lake should be considered in our calculations. The formation of elemental sulfur in the crater lake environment may be described by the hydrolysis mediated redox reaction,

as well as reaction between sulfur gaseous species during expansion and cooling,

and through the simple oxidation of H_2S by atmospheric oxygen,

Christenson et al. (2017) estimated the rate of formation of elemental sulfur during the 2003-2006 lake cycle by looking at the SO_2 deficit due to reaction (7.1). Difficulties in constraining S loss through reactions (7.2) and (7.3) implies these estimates are minimum values. Their results show that at least 44 000 tons of elemental sulfur deposited during that time frame,

corresponding to ~ 14 000 t/y. For comparison, rates of deposition have been estimated at ~ 11 500 t/y at Poas volcano (Rowe et al., 1992a) and 20 880 t/y at Copahue volcano (Varekamp et al., 2001). Taking an average Cu content of 80 ppm in sulfur globules (cf. Chapter 4) leads to 1.12 tons of copper sequestered by elemental sulfur in the crater lake every year.

Mass balance calculations were performed according to:

$$X_{Seq} = X_{PM} - (X_{DM} + X_P + X_{AS} + X_{ES})$$

where X_{Seq} is the amount of element X sequestered at depth annually, X_{PM} is the amount of X in the primary magma degassing every year estimated from concentration in olivine-hosted melt inclusions, X_{DM} is the amount of X that stays in the silicate melt estimated from concentration in erupted dacite (Graham and Cole, 1991) for Cu and Zn and andesite for Au and Ag, X_P is the amount of X discharged in the aerosol annually, X_{AS} is the amount of X discharged by acid springs annually, and X_{ES} is the amount of X scavenged every year by elemental sulfur depositing at the bottom of the crater lake. Results from these calculations are presented in Table 7-1.

Table 7-1: Mass balance calculations for a selection of metals during periods of low activity (t/y).

Element	Initial amount in magma (X_{PM})	Final content in silicate rock (X_{DM})	Discharged at the surface*	Sequestered at depth (X_{Seq})
S	84471	7039	77431	0
Cu	9010	4083	3.22	4924
Zn	5843	4505	3.68	1334
Ag	65	21	0.11	44
Au	62	23	0.02	39

* Total discharge at the surface = gas discharge (X_P) + spring discharge (X_{AS}) + elemental sulfur scrubbing (X_{ES}).

Gaseous and liquid emissions, together with elemental sulfur deposition at the lake bottom are the main copper discharges at White Island. They add up to ~ 3 tons of Cu released per year during passive degassing periods when a crater lake floods the upper portion of the conduit. During more active periods when no crater lake is present, 110 t/y are discharged. This value is very small compared to the 4927 tons of Cu escaping the magma each year, implying most of it is trapped within the subsurface environment. Giggenbach and Glasby (1977) estimated that White Island magmatic-hydrothermal system has been active for the last 10 000 years. If we consider a constant flow of magmatic gases over the lifetime of the system, this corresponds to deposition of ~ 50 megatons of Cu. This is a considerable amount, and within the range of porphyry copper deposits presently mined. The Bingham Canyon and El Teniente porphyry deposits for example, contain 30 Mt and 94 Mt of Cu respectively (Hattori and Keith, 2001; Cooke et al., 2005). The common copper-containing ore minerals are chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4), chalcocite (Cu_2S), covellite (CuS) and enargite (Cu_3AsS_4), emphasizing the role of sulfur in forming such deposits. The

formation of porphyry copper deposits of economic grade (> 1 wt% Cu), relies on efficient metal transport and deposition, which we will try to constrain for White Island.

7.2 Transport and deposition of Cu

We have determined that around 4900 tons of copper are sequestered in White Island hydrothermal system every year. Given that this copper leaves the magma, two possibilities arise: 1) Cu is segregated into an immiscible sulfide melt, and/or 2) Cu partitions into an exsolving magmatic volatile phase.

7.2.1 Partitioning into immiscible sulfide melt

Droplets of sulfide melt were observed in some of the ejecta from the 1976-2000 eruptive cycle, containing on average 30 wt% Cu. Given the rarity of these phases, if we assume the sulfide melt represents 0.01 % of the magma degassing per year, we obtain a total of 7039 tons of sulfide melt, containing 2112 tons of Cu. This estimate drops to 1056 tons of Cu sequestered by sulfide melt if we assume sulfide melt is only 0.005 % of the total magma. As already mentioned in Chapter 3, late sulfide saturation has been reported as a factor promoting porphyry copper deposit formation (Jenner et al., 2010; Park et al., 2015). Sulfides that are not trapped into phenocrysts are likely to be destabilized during crystallization and degassing of the silicate melt, being replaced by iron oxides (Candela and Holland, 1986; Hattori, 1993; Keith et al., 1997; Halter et al., 2005; Audetat and Pettke, 2006; Nadeau et al., 2010). The most efficient process linked with sulfide removal appears to be related to oxidation following degassing (Candela and Holland, 1986; Candela, 1989; Halter et al., 2005; Stavast et al., 2006; Di Muro et al., 2008), although Hattori (1993) postulated that SO_2 -rich gas fluxing could also lead to sulfide oxidation.

The cases of Bingham Canyon and Tintic District in Utah are particularly interesting. Larocque et al. (2000) showed that more than 90 % of the original magmatic sulfides were removed in slowly cooled rocks associated with porphyries, by degassing and oxidation. In contrast, dykes emplaced at high pressure preventing degassing, contained a higher proportion of preserved sulfide blebs. Following these arguments, rapid ascent and cooling experienced by the sulfide inclusions found in White Island ejecta would inhibit their resorption. However, given the low total volume of magma erupted, we can assume that the majority of sulfide melt formed in the dacitic magma experiences slow cooling and degassing, favoring resorption. In the likely presence of an aqueous fluid, the metals released from the sulfide melt (Cu, Zn, Ni, Ag, Au) would partition into the aqueous phase, given their preferential partitioning into an aqueous fluid over silicate melt (Candela, 1989; Candela and Piccoli, 1995b; Keppler, 1996; Harris et al., 2003; Simon et al., 2006, 2007; Pokrovski et al., 2008; Simon et al., 2008; Zajacz et al., 2008; Johnson and Canil, 2011).

7.2.2 Partitioning into magmatic volatile phase

A critical step in porphyry copper deposit formation is the exsolution of Cu into a volatile phase, and the nature of the latter (i.e. a supercritical fluid, a low-density vapor, or a high-density aqueous fluid) (Hedenquist and Lowenstern, 1994; Burnham, 1997; Candela and Piccoli, 2005; Williams-Jones and Heinrich, 2005; Simon and Ripley, 2011). We determined in Chapter 3 that Cu exsolves from the shallow magmatic chamber. Despite the bulk of S degassing occurring at depth greater than 800 m, plagioclase- and pyroxene-hosted melt inclusions entrapped in shallow storage, contain up to 500 ppm S, indicating only minor sulfur degassing from the dacitic melt. In contrast, due to its greater solubility, Cl degasses mainly from the shallow magmatic reservoir. Moreover, the deeper CO₂- and S-rich magmatic volatile phase is likely to be fluxing the shallow chamber (Wallace and Edmonds, 2011), suggesting that a Cl- and S-bearing magmatic volatile ($\pm$ CO₂) phase is present in the shallow dacitic chamber.

Metrich and Rutherford (1992) and Shinohara (1994) showed that the exsolution of an aqueous fluid from a silicate magma at conditions below the critical point of the H₂O-NaCl system (i.e. at 800 °C and pressure lower than 1.3 kbar) is a two-step process:

- The first step is the exsolution of a homogeneous aqueous fluid from the magma.
- With further crystallization and cooling, fluid phase exsolution occurs but with simultaneous exsolution of both vapor and a liquid.

Of course, the continuously exsolving homogeneous aqueous fluid accumulates, cools and decompresses until the pressure-temperature conditions of the solvus are encountered. Separation then occurs with the formation of a saline fluid with liquid-like density and a less dense, volatile-rich, more gas-like phase.

Sowat, a program kindly provided by Thomas Driesner, allows estimation of the state of a fluid in the H₂O-NaCl system. Under the pressure and temperature conditions determined for the shallow dacitic magma chamber (~ 900 °C, 800 m depth, that is 240 bar), the volatile phase exsolving from the silicate magma is a two-phase fluid (vapor + liquid). Considering an initial salinity of 5 wt% NaCl (typically 4-10 wt% in porphyry Cu environments) (Burnham, 1979; Cline and Bodnar, 1991; Shinohara and Hedenquist, 1997; Ulrich et al., 2001; Klemm et al., 2007; Rusk et al., 2008; Pudack et al., 2009; Landtwing et al., 2010), at 900 °C and 240 bar, the vapor has a density of 0.05 g.cm⁻³ and a salinity of 0.07 wt% NaCl, whereas the liquid has a density of 1.4 g.cm⁻³ and contains 94.6 wt% NaCl (see Figure 7-2). This suggests that both a low-density vapor and a saline liquid are exsolving from the shallow dacitic melt, the former containing both chlorine and sulfur.

Figure 7-2: Pressure-temperature-salinity relations in the H₂O-NaCl system. At the low pressure of exsolution (240 bar), the volatile phase is in the two-phase field at 900 °C. It changes into halite + vapor with decreasing temperature and pressure. The blue line represents the critical curve. Constructed using SOWAT program and data from Driesner (2007).

Fluid inclusion studies have reported high concentrations of Cu (Lowenstern et al., 1991; Heinrich et al., 1992; Lowenstern, 1993; Cauzid et al., 2007) in the vapor phase that cannot be explained by chloride complexes alone. In fact, experimental and fluid inclusion studies have shown the role of sulfur in transporting ore metals such as Cu and Au in a low-density vapor phase (Heinrich et al., 1999; Simon et al., 2006, 2007; Seo et al., 2009; Zajacz and Halter, 2009; Etschmann et al., 2010; Zajacz et al., 2011). Moreover, recent studies indicated the effect of hydration in transporting considerable amounts of copper in low-density vapor, in the form of solvated cluster-like species (Archibald et al., 2002; Zajacz et al., 2011; Migdisov et al., 2014). In terms of partition coefficient between aqueous vapor and liquid, Simon et al. (2006) reported $D_{\text{Cu}}^{\text{v/l}} = 0.69 \pm 0.16$ at 800 °C, 140 MPa and S- and Cl-bearing system. At lower pressure (100 MPa), Frank et al. (2011) reported $D_{\text{Cu}}^{\text{v/l}}$ values from 0.14 ± 0.5 to 0.01 ± 0.025 . Experiments at 600 and 800 °C, and 70 and 130 MPa (Lerchbaumer and Audétat, 2012), yielded $D_{\text{Cu}}^{\text{v/l}}$ in the range of 0.11 ± 0.04 to 0.15 ± 0.04 . The highest partition coefficient obtained experimentally is 1.0 in the presence of ~ 1 wt% total S for temperature 350 °C and 500 °C (Pokrovski et al., 2008). These studies suggest that, despite growing evidence for the capabilities of low-density vapor to transport metals, our current knowledge favors preferential partitioning of Cu into the high-density and salinity liquid. Given the complexity of real systems and the difficulties related to experiments on high-temperature vapors, we consider the two case scenarios in our discussion. This choice is further supported by the results of Pokrovski et al. (2005), who showed that even using metal partition coefficients favoring the dense liquid, boiling of 90% of a metal-bearing sulfur-poor

brine at 600 °C, would result in more than half of the total amount of Cu extracted into the vapor.

7.2.2.1 Cu partitioning into high-density saline liquid

Partitioning of metals into dense saline liquids relies on efficient chloride complexing and is supported by fluid inclusion analyses, and the aforementioned experimental studies (Barnes and Kullerud, 1957; Burnham, 1967; Roedder, 1971; Henley and McNabb, 1978; Candela and Holland, 1986; Hemley et al., 1992; Bodnar, 1995; Candela and Piccoli, 1995b). Considering that a vapor phase is predicted to exsolve simultaneously with a brine, any sulfur, CO₂ and H₂ left in the shallow emplaced dacitic magma, would partition into the vapor. This results in the brine containing predominantly metal chloride complexes, with minor sulfur complexes. The high density (1.4 g.cm⁻³) predicted for the aqueous liquid prevents it from rising to shallower levels (Henley and McNabb, 1978; Bodnar et al., 1985; Shinohara, 1994). Instead, it may accumulate at the depth of formation, retaining metals underneath the solidifying magmatic carapace (Williams-Jones and Heinrich, 2005). The shift from accumulation to deposition can be induced by different mechanisms, related to changes in pressure, temperature and composition (i.e. concentration of metals and ligands, redox conditions, pH).

Water-rock interaction is an efficient mechanism associated with ore deposition. As detailed in Chapter 3, andesite-dacite lava is the most common rock at White Island, containing plagioclase, orthopyroxene, and minor olivine, magnetite and chromite. Phenocryst compositions were reported by Cole et al. (2000) showing Fe-rich orthopyroxenes and Ca-rich clinopyroxenes. Alteration products on andesite blocks ejected in February 1988 consist of veins bearing alunite, anhydrite, and Al-rich chlorite (Hedenquist et al., 1993). Some crystals of pyrite were also reported in contact with alunite. The host rock adjacent to the veins was completely altered, with cristobalite replacing all primary minerals. In contrast, porous tuff ejected during the same eruptive event contained disseminated cristobalite, alunite, anhydrite and pyrite (Hedenquist et al., 1993). The authors estimated that alteration occurred at ~ 380 °C.

Two different processes are related to water-rock interactions. The first one is enrichment through selective dissolution of minerals, whereas the second involves precipitation due to variations in the fluid chemistry along specific reaction pathways (e.g. pH, composition). The relative proportions of fluid and rock is also of importance, with high and low water-rock ratios inducing different changes in fluid composition and mineral dissolution/precipitation (Reed, 1997). Reactions with Fe-bearing rocks described by Hemley et al. (1992) would, for instance, increase the pH and Fe²⁺ of the fluid, favoring precipitation of chalcopyrite. Dissolution of White Island Fe-rich orthopyroxenes would thus promote sulfide precipitation.

Besides water-rock interactions, a pressure-related mechanism is often thought to be responsible for ore deposition. The thermal contraction of the solidified carapace overlying the accumulating dense saline liquid results in the creation of a network of fractures and cracks. Assuming that hydrostatic pressure controls the fluids above the carapace (Fournier, 1999), the transition from lithostatic to hydrostatic regime would induce boiling of the high-salinity metal-rich liquid, with exsolution of a low-density vapor. The volatile species (i.e.

CO₂, H₂S, H₂, HCl, SO₂) partition in the vapor phase, whereas NaCl and KCl stay in the liquid (Ellis, 1979; Drummond and Ohmoto, 1985). The effects of boiling on the remaining liquid are diverse and include: 1) rise in pH due to partitioning of CO₂ and H₂S into the vapor, 2) decrease in S ligand concentration, and 3) concentration of species remaining in the liquid. Any metal complexed with reduced sulfur (i.e. Au and Cu) in the aqueous liquid would become oversaturated with the loss of H₂S and precipitate. Drummond and Ohmoto (1985) demonstrated that the saturation state before boiling is critical, with only species already close to saturation actually precipitating during boiling.

Saturation of gangue minerals (quartz, anhydrite, pyrite) is the result of both water-rock reactions and boiling, due to increasing activity of certain elements in the aqueous fluid. Changes in mineral solubility are also efficiently promoted by cooling, especially in the case of mixing with another liquid. In this regard, infiltration of cool and oxidized meteoric water within the volcanic edifice could influence ore deposition. In fact, oxidation results in a drop in reduced sulfur activity as well as a change in pH, both of which would destabilize metal sulfide complexes. The meteoric fluids are also likely to be cooler, which, as mentioned above, can lower the solubility of some metals (Seward, 1981).

To summarize, the most important processes affecting ore deposition from a high-density, high-salinity liquid appear to be changes in the fluid composition (i.e. redox state, pH, activities) and cooling, induced by a variety of mechanisms such as fluid-rock interaction, mixing with meteoric fluids or boiling.

7.2.2.2 Cu partitioning into low-density vapor

We know from fumarolic gas compositions that a Cl- and S-bearing fluid is exsolving from the magma. Such a low-density vapor would also be formed by a boiling dense saline liquid, as discussed above. Assuming that some metals, such as Cu, partition into this vapor phase, we will try to constrain the mechanisms affecting transport and deposition.

Thermodynamic modeling showed that Cu is mainly transported as a chloride complex in fumarolic gases from White Island. Copper chloride CuCl dominates at high temperature (300-495 °C) whereas the dichloride species CuCl₂ is more abundant with decreasing temperature. Many experimental studies nevertheless emphasize the role of sulfur complexes in transporting Cu (Simon et al., 2006; Seo et al., 2009; Zajacz et al., 2011). We thus modelled volcanic gases at higher magmatic temperatures to constrain speciation of gaseous Cu species. Yasur was chosen for calculations as the magma is only meters below the surface, insuring that minimal hydrothermal interaction occurs. The major gas composition was taken from MulltiGas and filter pack data collected by Métrich et al. (2011). The same authors estimated the temperature of Yasur basaltic trachyandesite to be around 1107 °C, and we used the trace metal contents from our filter pack campaign in October 2016 (cf. Chapter 6) in these calculations. The second case study uses the 984 °C gas composition reported by Wahrenberger et al. (2002) from Kudriavy volcano. We also modelled the major gas composition of high-temperature (772 °C) fumarolic gases from White Island collected in February 1984 (Giggenbach and Sheppard, 1989), and the trace metal contents from lower temperature (495 °C) emissions (Tedesco and Toutain, 1991). The gas compositions used for input are reported in Appendix A.9.

HSC modelling shows that chloride complexes are responsible for Cu transport at these higher temperatures (Figure 7-3). For the three volcanic gases, the content of the dominant complex CuCl is almost constant with cooling until a certain temperature is reached, after which it starts decreasing. This temperature, indicating onset of Cu-containing minerals deposition, is slightly over 700 °C for Yasur and White Island gases, and ~ 800 °C for Kudriavy gases (see Figure 7-3). The mineral predicted to precipitate in White Island gases at $T < 700$ °C is bornite (Cu_5FeS_4), replaced by chalcopyrite (CuFeS_2) at temperature between ~ 570 °C and ~ 370 °C. Formation of enargite (Cu_3AsS_4) is restricted to temperature between ~ 340 °C to ~ 310 °C.

Simulation for higher pressure (100 bar) affects only slightly the speciation of Cu gaseous species, increasing CuCl_2 stability. Increasing the metal content to 0.001 mol % does not change the speciation of gaseous copper species. The minor role of S in transporting Cu might reflect the lack of thermodynamic data compared to the complexity of natural systems: many studies showed the importance of water in increasing metal transport through the formation of hydrated complexes (Pokrovski et al., 2008; Zajacz et al., 2011), for which no thermodynamic data are available. Moreover, complexes such as $\text{CuHS}(\text{H}_2\text{S})$, CuHS , $\text{Na}(\text{K})\text{Cu}(\text{HS})_2$, $\text{Na}(\text{K})\text{ClCuHS}$ are associated with Cu transport in experimental studies (Seo et al., 2009; Zajacz et al., 2011), although not considered in our calculations due to the lack of thermodynamic data.

Figure 7-3: Distribution of gaseous Cu species in high-temperature gases from Kudriavy, Yasur and White Island volcanoes at 1 bar and 100 bar.

Nuccio et al. (1999) showed that high temperature fumaroles such as those recorded at Kudriavy, are the result of quasi-isenthalpic expansion. This assumption is realistic in the case of White Island, taking into account that the maximum temperature recorded in fumarolic gases was 772 °C in February 1984 (Giggenbach and Sheppard, 1989). Assuming that these gases were exsolved from the shallowly emplaced magma at ~ 240 bar and 900 °C, the decompression path obtained in the H₂O-NaCl system is close to isenthalpic expansion (Figure 7-4). The lower temperatures recorded in periods of low activity are likely the result

of interactions with hydrothermal fluids invading the magmatic conduit following cooling of the magmatic intrusion.

Figure 7-4: Pressure-temperature phase diagram of the H_2O - NaCl system. Isenthalpic expansion paths (in $\text{kJ}\cdot\text{kg}^{-1}$) are shown. The decompression path for White Island magmatic gases from the shallow magma chamber at 900 °C and 240 bar, to their emission at the surface at 772 °C (Giggenbach and Sheppard, 1989) is close to isenthalpic. Constructed using the Sowat program (Driesner, 2007).

Many ore deposits are thought to form between 1 and 5 km from cooling intrusions emplaced at 5 to 15 km depth (Seedorff et al., 2005; Sillitoe, 2010, and references therein). The shallow depth (400-800 m) of White Island dacitic reservoirs is, in that regard, quite unusual. If we assume that the fluid exsolving from the magma in the dacitic reservoirs is ascending to the surface through a network of fractures, the confining pressure is that of the overlying groundwater column. Such hydrostatic pressure at a depth of 800 m corresponds to around 80 bar. The vapor phase exsolving at the base of this array of fractures open to the atmosphere, with a temperature around 900 °C, would expand from 240 bar to 80 bar. Such expansion leads to a drop in gas density, destabilizing solvated complexes and driving precipitation (Rusk et al., 2008; Mavrogenes et al., 2010; Henley and Berger, 2011; Henley and Berger, 2013; Henley et al., 2015). This mechanism was, for instance, responsible for the formation of the Pascua high-sulfidation deposit (Chile-Argentina), in the previously altered vuggy silica environment underlying a crater lake (Chouinard et al., 2005).

The drop in halite solubility during quasi-isenthalpic expansion of magmatic vapor modelled by Henley and Berger (2011) is accompanied by sulfide and sulfosalt deposition. In a recent review, Taran and Zelenski (2015) observed the impact of halite precipitation on Na and HCl contents of volcanic gases at different temperatures. A similar scenario could be responsible

for deposition of the Cu load carried by White Island low-density vapors exsolving from the shallow dacitic magma. This is especially relevant given the low pressure of exsolution, placing the magmatic vapor close to the halite + vapor field (Figure 7-4). Isenthalpic or quasi-isenthalpic expansion, with loss of heat to the surrounding rocks, would result in the vapor intersecting the vapor + halite field. In turn, halite precipitation would destabilize chloride-complexed metals, thus favoring metal deposition.

Other deposition mechanisms involve gas-rock reactions. The SO₂ contained in the gas can react with Fe-bearing rock (Giggenbach, 1987):

and/or with Ca-bearing rock (Henley et al., 2015):

These two processes are quite relevant given the presence of Fe-rich and Ca-rich minerals in White Island dacitic lava and in the alteration assemblage. Both reactions lead to formation of H₂S, further driving sulfide deposition. Moreover, the solubility of copper chloride complexes in vapor decreases dramatically between 400 °C and 300 °C (Crerar and Barnes, 1976; Bernard, 1985; Symonds et al., 1987; Hemley et al., 1992; Xiao et al., 1998; Landtwing et al., 2005; Klemm et al., 2007) most likely due to hydrolysis of SO₂ into H₂S and H₂SO₄ at T < 400 °C (Holland, 1965; Burnham, 1967; Sakai and Matsubaya, 1977; Kusakabe et al., 2000), leading to sulfide and sulfate (anhydrite) deposition.

7.3 Thesis Conclusions

- The 1976-2000 eruptive sequence of White Island was related to repeated injections of partly degassed mafic magma from > 5 km depth into more evolved reservoirs located at ~ 400 to 800 m depth. Convection within the deeper chamber is thought to be responsible for the efficient degassing of the less soluble CO₂, H₂O and SO₂ without erupting large volumes of magma (see Figure 7-5). Crystallization of plagioclase and pyroxene in the shallow reservoirs led to chlorine exsolution from the silicate melt. The latter, in conjunction with deeper sulfur fluxing through the chamber, supplied ligands for metal degassing. Magnetite precipitation, in turn, may have triggered saturation of a sulfide melt, efficiently segregating Fe, Cu, Ni, Ag and Au from the magma.

- The crater lake absorbs high enthalpy magmatic gases forming highly acidic and reactive fluids. Seeping underneath the lake and/or recirculation explains the intense alteration observed in ancient dissected volcanoes and at Kawah Ijen for example. As can be seen in Figure 7-5, elemental sulfur is forming at the bottom of the crater lake, efficiently scavenging metals either through saturation of metal sulfides in this reduced environment, or through adsorption on the positively charged surface of sulfur particles and subsequent

reaction with H_2S produced by sulfur hydrolysis. The lake itself is a very active system, with thermal, redox and compositional gradients with depth. The speciation of metals is greatly affected by these variations, with Cu^{I} , Fe^{II} chloride complexes and $\text{As}(\text{OH})_3$ present in the reduced waters at depth and Cu^{II} , Fe^{III} chloride complexes and H_3AsO_4 in the oxidized surficial environment. Zn, Pb and Ag chloride complexes are not affected by redox variations. Dissolution of host rock and precipitation of various secondary minerals (i.e. anhydrite, gypsum, alunite, sulfur, barite, silica) are occurring.

- Low temperature gases emitted at fumaroles have interacted with the two-phase envelope surrounding the magmatic conduit described by Giggenbach (1987) and shown in Figure 7-5. The extent of these interactions is dependent on volcanic activity, due to retraction/expansion of the envelope. More metals are transported into the atmosphere during periods of heightened activity. Decreasing temperature leads to destabilization of metal complexes and subsequent deposition, at $T < 350\text{ }^\circ\text{C}$ for metals such as Bi and Pb. Copper deposition starts at higher temperature ($\sim 700\text{ }^\circ\text{C}$) as evidenced by similarly low contents in present day $\sim 190\text{ }^\circ\text{C}$ fumarolic gases and $495\text{ }^\circ\text{C}$ gases sampled in 1988. Although the dominant ligand appears to be Cl, sulfur is equally important given the control it exerts on redox conditions, further controlling gas speciation and saturated minerals. Cooling and oxidation as the gases approach the surface lead to precipitation of sublimates (dominated by various sulfates) and condensation of elemental sulfur, at White Island.

- The volcanic plume is more enriched in metals than the fumarolic gases, owing to the assumed higher temperature and decreased interactions with the hydrothermal system. Cu is nevertheless depleted in White Island's plume compared to other species such as Bi, Cd, Tl, Se, Te and Sb. The aerosol fraction consists of halides, sulfates, oxides, silicates and sulfuric acid, formed through gas-to-particle reactions or erosion of the conduit wall. Changes in volcanic activity are reflected by the plume composition, not only in terms of major elements, but with potential insights from metal contents. The presence of gold in the White Island plume (i.e. aerosol), for example, is related to emissions of higher temperature gases with a magmatic signature (i.e. high SO_2/HCl ratio). Fluxes of metals are significant, with an annual emission of ~ 2 tons of Cu, As, Zn, ~ 0.4 tons of Pb and ~ 16 kg of Au during quiescent degassing.

- Mass balance calculations predict that 51-55% of the total Cu is segregated at depth. 45% remains in the silicate melt and $< 4\%$ is emitted into the environment. Gold and silver may also be efficiently segregated at depth. These results support earlier assumptions that White Island is a favorable environment for ore deposition processes to occur. The segregated metals either accumulate at depth in a high-density and high-salinity aqueous liquid exsolving from the dacitic magma, and/or are deposited by low-density vapors on their way to the surface (Figure 7-5). The metal-transporting hydrothermal fluid will deposit metals (e.g. as sulfides) in response to: reactions with Fe- and/or Ca-bearing rocks, mixing with meteoric fluids, and rapid expansion during the transition from lithostatic to hydrostatic

regime. A very small fraction of Cu may also be segregated by metal-rich sulfide blebs trapped within phenocrysts.

Figure 7-5: Sketch of White Island magmatic-hydrothermal system. The model for the two-phase hydrothermal envelope is taken from Giggenbach (1987).

This thesis has detailed the fate of metals in an active andesitic-dacitic magmatic-hydrothermal system. We constrained the transport of metals after their exsolution from the magma and showed that, despite significant emission at the surface, certain elements such as Cu, Au and Ag, are predominantly sequestered in the subsurface environment.

Questions nevertheless still arise. Further study, particularly in better constraining the depth and temperature of the magmatic reservoirs at White Island, is needed in order to gain more understanding on the processes occurring in an ore deposition environment. Similarly, petrologic studies and especially mineral analyses would help constraining the P-T conditions of crystallization, as well as trace metal partitioning between mineral/melt/volatile phase. The redox state of sulfur in matrix glass and melt inclusions would also help constraining the

evolution of redox conditions in the silicate melt during crystallization, degassing and immiscible sulfide melt exsolution. Moreover, long term monitoring of White Island discharge features (fumarolic gases and volcanic plume) in terms of metals is required to define potential variations in composition related to shifts in volcanic activity. Such a monitoring tool would improve our ability to forecast changes in volcanic activity. Finally, the new drone sampling technique needs to be refined and improved in the view of developing a method for monitoring volcanic emissions that is not weather dependent.

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Appendix

A.1 LA-ICP-MS analytical precision and accuracy

Table A-1: LA-ICP-MS analytical precision (± 1 RSD) and accuracy (bias) estimated with certified reference material GSD-1 for the different spot sizes used.

Spot size	1% RSD			Bias (%)		
	25 μm	20 μm	15 μm	25 μm	20 μm	15 μm
Li	3.15	2.44	2.32	1.35	0.54	-4.22
B	5.21	4.33	1.28	2.54	4.14	5.26
Sc	4.00	5.36	3.99	9.42	11.11	5.49
Ti	3.98	2.89	7.76	4.86	6.21	-2.50
V	4.70	2.94	11.33	0.00	1.33	-6.41
Cr	10.78	10.70	28.14	3.70	10.81	28.00
Mn	3.87	2.61	6.37	-0.59	-0.79	-3.90
Co	3.21	2.97	3.48	-2.73	-2.00	-6.94
Ni	4.65	4.91	11.43	-1.33	-1.11	2.79
Cu	4.15	6.01	9.17	-0.86	-2.61	-2.40
Zn	6.45	5.32	2.18	-1.87	-11.12	-5.43
Ga	2.29	2.79	2.12	3.57	4.74	4.35
As	6.21	5.24	7.38	-3.26	-3.58	-4.06
Se	44.13	52.97	-	57.78	152.62	137.96
Rb	4.28	6.85	7.56	-2.65	-3.13	-8.60
Sr	6.07	3.99	5.53	-0.51	-1.36	-8.66
Mo	3.73	4.30	8.16	0.72	0.45	2.04
Ag	5.05	3.87	8.06	-1.17	-3.61	-1.76
Cd	9.57	15.56	6.99	-0.99	-8.16	-20.95
Sn	4.85	5.03	5.94	-3.57	-1.86	-11.03
Sb	4.96	2.98	9.01	2.91	-0.11	-2.27
Ba	9.50	9.00	10.10	4.91	2.30	-8.91
Yb	6.57	5.44	7.25	-1.04	2.65	-11.59
W	4.74	4.20	3.74	-1.55	-4.25	-5.99
Re	7.86	12.93	8.11	-	-	-
Au	10.23	24.61	8.36	6.94	11.83	-11.26
Tl	13.14	21.94	21.78	4.37	-7.77	23.79
Pb	4.55	3.46	6.20	-3.49	-5.11	-2.61
Bi	4.50	6.40	6.78	-8.20	-6.87	-10.57
U	3.90	4.18	10.60	1.32	0.02	-4.76

Notes: - not determined

Bias: Deviation between the certified and measured values, in percent.

A.2 Melt inclusions and matrix glass compositions

Table A-2: Melt inclusion and matrix glass compositions.

	WIDP6- IN01	WIDP6- IN02	WIDP6- IN05	WIDP6- IN06	WIDP6- IN07	WIDP6- IN09*	WIDP6- IN10	WIDP6- IN12	WIDP6- IN14	WIDP6- IN15
Major elements (wt%)										
SiO ₂	64.49	64.01	68.26	67.53	68.39	65.34	64.69	64.06	63.19	65.14
TiO ₂	0.84	1.01	1.52	0.88	0.94	0.68	0.99	1.05	0.99	1.01
Al ₂ O ₃	13.57	15.12	14.70	14.52	14.06	14.93	14.39	13.70	14.20	13.12
FeO _i	6.00	6.42	5.10	4.51	4.07	3.78	6.02	6.34	7.56	7.66
MnO	0.14	0.11	0.07	0.12	0.07	0.09	0.09	0.11	0.11	0.11
MgO	1.85	2.01	0.32	1.84	1.30	2.25	1.95	2.26	1.89	1.49
CaO	5.09	5.52	2.09	4.54	4.15	4.69	5.28	4.23	5.46	4.74
Na ₂ O	3.27	3.26	3.41	3.46	3.17	3.40	3.17	3.37	3.25	3.19
K ₂ O	3.02	3.05	4.10	2.78	3.13	2.90	2.57	2.91	2.37	2.78
P ₂ O ₅	1.28	0.01	0.11	0.01	0.06	nd	0.00	0.01	0.01	0.06
Cr ₂ O ₃	0.02	0.00	0.01	0.02	0.02	0.00	nd	0.00	0.01	0.01
Cl (ppm)	1460	820	1815	1013	1100	1283	1130	1010	1177	1050
S (ppm)	72	60	90	128	152	461	108	147	382	400
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.74	100.62	99.88	100.32	99.49	98.23	99.28	98.15	99.18	99.47
Hosting phenocryst	Opx	Opx	Pla	Opx	Cpx	Opx	Opx	Pla	Opx	Opx
Trace elements (ppm)										
Li	22.78	29.27	na	24.48	26.51	33.75	22.74	82.72	26.47	19.49
B	45.40	39.29	na	43.84	40.33	38.43	40.94	40.15	33.67	36.22
Sc	33.32	35.72	na	23.91	33.99	23.11	26.60	25.67	31.03	30.41
Ti	5276.26	7052.29	na	5683.93	6206.96	4289.31	6026.12	6369.96	6241.30	6081.06
V	165.08	295.37	na	230.11	240.14	238.97	252.30	239.95	291.61	341.33
Cr	7.91	91.51	na	8.92	2.88	11.06	nd	17.55	10.60	6.21
Mn	1197.63	900.51	na	690.45	764.11	707.16	708.49	749.98	876.96	860.93
Co	12.27	22.73	na	10.11	11.07	11.54	11.79	16.56	18.56	15.93
Ni	nd	44.74	na	5.17	7.39	6.30	2.92	27.59	22.79	9.89
Cu	163.29	149.60	na	167.79	168.67	174.12	155.54	474.02	1004.12	375.27
Zn	63.94	64.30	na	60.65	66.81	56.99	67.82	67.67	79.43	85.61
Ga	240.64	163.31	na	207.40	249.15	213.01	204.19	200.56	185.74	200.39
As	6.43	4.62	na	3.67	6.53	5.19	5.08	4.60	4.65	4.04
Se	nd	1.65	na	nd	nd	nd	nd	nd	nd	nd
Rb	94.77	88.17	na	90.89	111.91	84.92	86.24	90.15	70.27	81.93
Sr	208.32	145.88	na	178.30	164.89	175.15	168.18	140.83	194.31	179.75
Mo	1.69	1.68	na	1.13	2.15	1.37	1.75	1.45	1.31	1.58
Ag	0.38	0.19	na	nd	0.25	0.17	nd	0.32	0.24	nd
Cd	nd	nd	na	nd	nd	0.46	0.37	nd	0.52	nd
Sn	1.60	nd	na	2.01	2.27	nd	1.69	0.86	2.45	1.86
Sb	0.53	0.75	na	0.43	nd	0.46	0.81	0.36	0.44	nd
Ba	1149.98	779.94	na	1150.62	1348.78	1140.74	1085.39	1003.17	981.50	1003.87
Yb	6.27	3.61	na	3.51	4.74	2.77	3.07	2.71	3.30	2.63
W	1.71	1.18	na	2.33	1.81	1.59	0.84	1.52	0.77	2.28
Re	nd	nd	na	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	na	nd	nd	nd	nd	0.34	nd	nd
Tl	0.34	0.41	na	0.50	0.58	0.38	0.22	0.38	0.30	0.25
Pb	16.51	13.40	na	13.58	12.66	14.99	13.23	12.14	13.61	13.20
Bi	0.16	0.11	na	0.36	0.14	0.14	0.21	0.11	0.06	nd
U	3.06	1.59	na	1.95	1.58	1.71	1.90	1.83	1.72	2.04

Table A-2 (continued)

	WIDP6- IN16	WIDP6- IN17*	WIDP6- IN18*	WIDP6- IN19*	WIDP6- IN20*	WIDP6- IN21	WIDP6- IN23	WIDP6- IN24	WIDP6- IN25	WIDP6- IN26
Major elements (wt%)										
SiO ₂	61.54	67.77	64.68	64.44	64.43	62.20	66.32	66.48	65.98	63.72
TiO ₂	0.75	0.78	0.55	0.63	0.62	0.95	1.19	1.06	1.15	1.06
Al ₂ O ₃	19.21	15.07	17.52	15.85	16.66	14.88	14.42	14.14	13.68	14.20
FeO _t	4.14	4.26	3.65	4.55	3.70	7.85	6.15	6.30	6.51	5.90
MnO	0.06	0.09	0.05	0.06	0.08	0.14	0.05	0.08	0.11	0.09
MgO	1.36	1.62	2.05	2.29	2.09	2.15	0.93	1.00	1.62	2.24
CaO	7.70	4.17	5.07	5.84	5.16	6.19	4.71	4.69	3.73	4.99
Na ₂ O	3.34	3.48	4.05	3.18	3.67	3.39	2.70	3.10	3.25	3.67
K ₂ O	1.77	3.26	3.31	2.72	3.24	1.83	2.76	2.83	3.00	2.90
P ₂ O ₅	nd	0.01	0.01	nd	nd	nd	0.07	0.09	0.03	0.03
Cr ₂ O ₃	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.02	0.00
Cl (ppm)	713	937	980	970	967	787	1043	1003	1007	963
S (ppm)	89	127	499	279	535	427	36	93	112	56
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.96	100.63	101.10	99.68	99.80	99.71	99.41	99.89	99.18	98.90
Hosting phenocryst	Cpx	Opx	Opx	Opx	Opx	Opx	Opx	Opx	Cpx	Pla
Trace elements (ppm)										
Li	27.17	27.29	29.95	16.58	31.63	27.75	24.26	20.74	26.65	35.25
B	37.64	41.65	26.11	15.76	34.92	27.51	39.64	39.90	42.44	13.71
Sc	26.88	24.54	20.48	42.19	18.27	29.89	27.27	32.24	31.07	12.06
Ti	6772.54	4836.82	3159.07	2741.91	3697.51	5491.68	7059.10	6519.46	7082.17	1853.63
V	305.15	145.72	111.00	153.13	116.09	271.92	266.72	276.40	318.61	72.65
Cr	nd	109.79	325.53	777.15	16.88	7.00	38.23	122.01	45.17	7.31
Mn	769.22	1012.25	772.18	1740.31	454.20	898.90	772.28	954.48	809.11	216.54
Co	12.06	20.46	26.17	64.59	11.46	18.79	17.63	22.89	15.75	4.87
Ni	2.67	59.56	127.80	410.89	22.87	15.54	40.69	51.48	10.66	8.76
Cu	172.15	137.72	234.26	48.78	151.67	212.11	158.40	139.91	184.42	155.61
Zn	76.12	83.87	57.18	90.76	35.35	79.57	72.71	82.91	80.78	26.59
Ga	194.60	235.53	148.01	82.13	172.58	140.24	185.98	204.53	216.52	91.17
As	4.03	12.69	3.17	2.81	5.37	2.70	5.22	4.26	6.29	nd
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb	77.51	91.89	65.59	47.74	86.57	54.83	83.87	85.51	94.64	25.30
Sr	161.25	171.57	231.87	118.76	248.76	186.99	158.22	154.25	163.89	391.75
Mo	1.21	1.63	0.71	0.49	1.01	0.47	1.52	2.10	1.51	nd
Ag	nd	nd	nd	nd	nd	0.21	nd	nd	nd	0.39
Cd	nd	nd	nd	nd	nd	nd	0.72	nd	nd	nd
Sn	0.93	2.29	nd	nd	nd	2.63	nd	nd	1.19	nd
Sb	0.59	1.04	0.01	0.06	nd	0.44	1.06	1.04	0.51	0.62
Ba	1076.47	1268.31	823.15	407.59	881.71	737.96	1018.05	1043.66	1171.13	431.80
Yb	3.52	2.27	0.94	1.65	1.29	3.24	1.71	5.09	3.32	nd
W	1.91	1.70	1.73	0.46	1.22	0.69	1.50	1.14	1.71	nd
Re	nd	0.75	nd	nd	nd	nd	nd	nd	0.27	nd
Au	nd	nd	nd	0.29	nd	nd	nd	nd	nd	nd
Tl	0.46	0.37	0.45	nd	0.32	0.45	0.29	0.34	0.37	nd
Pb	13.36	19.84	15.94	5.69	14.03	8.99	12.71	9.81	14.51	4.98
Bi	0.20	0.37	0.16	nd	0.18	0.11	nd	nd	0.11	nd
U	1.90	1.87	1.50	0.82	1.57	1.14	1.97	2.19	1.87	0.47

Table A-2 (continued)

	WIDP6- IN28	WIDP6- IN29	WIDP6- IN30	WIDP6- IN31	WIDP6- IN32	WIDP6- IN33	WIDP6- IN34	WIDP6- Matrix glass 1	WIDP6- Matrix glass enclave	WIDP6- Matrix Glass 2
Major elements (wt%)										
SiO ₂	64.40	65.09	65.86	64.60	63.80	65.13	64.93	62.99	73.22	63.51
TiO ₂	0.58	1.02	1.05	1.06	1.19	1.04	1.11	0.97	0.78	0.93
Al ₂ O ₃	15.69	13.49	13.65	13.85	13.98	13.95	13.90	14.81	12.21	14.72
FeO _t	4.78	6.34	5.80	5.95	6.37	5.89	6.00	6.29	3.54	5.70
MnO	0.07	0.09	0.12	0.10	0.13	0.09	0.11	0.14	0.07	nd
MgO	2.23	1.72	1.70	2.22	2.51	2.09	2.12	3.08	0.73	2.49
CaO	5.45	4.61	4.69	4.90	5.19	4.78	4.73	6.01	1.99	6.24
Na ₂ O	3.58	3.20	3.11	3.50	3.51	3.25	3.34	3.39	3.04	3.20
K ₂ O	2.28	2.81	3.02	2.78	2.78	2.84	2.81	2.39	3.55	2.47
P ₂ O ₅	0.01	0.08	0.01	0.03	0.05	0.01	nd	nd	nd	nd
Cr ₂ O ₃	0.01	0.02	0.01	0.01	0.01	0.00	0.01	0.12	0.12	nd
Cl (ppm)	1173	933	1077	887	920	960	990	698	690	691
S (ppm)	171	100	96	76	112	67	155	105	76	28
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.22	98.56	99.14	99.09	99.63	99.17	99.15	100.22	99.26	99.33
Hosting phenocryst	Cpx	Opx	Opx	Pla	Pla	Pla	Pla			
Trace elements (ppm)										
Li	26.30	23.47	25.59	109.77	89.08	74.04	70.23	22.54	na	na
B	33.94	44.96	46.00	42.78	44.82	41.65	38.33	39.44	na	na
Sc	24.36	25.57	27.09	27.71	23.46	27.21	25.21	32.85	na	na
Ti	3554.12	6179.52	6213.83	6754.00	7124.35	6475.37	5898.24	5918.48	na	na
V	124.91	253.37	253.09	265.57	283.50	263.97	251.29	260.33	na	na
Cr	5.85	8.95	nd	12.30	19.71	16.48	12.42	137.27	na	na
Mn	632.70	715.06	734.11	727.71	775.56	738.15	692.81	911.40	na	na
Co	14.08	13.74	13.38	15.39	18.24	15.95	16.21	20.45	na	na
Ni	15.38	12.25	7.08	29.51	32.60	12.11	13.33	43.38	na	na
Cu	173.73	161.33	168.92	826.65	634.86	333.15	336.06	141.67	na	na
Zn	55.67	67.06	61.54	70.77	66.04	65.55	56.72	67.43	na	na
Ga	169.61	197.57	205.56	202.94	203.04	202.23	187.30	160.12	na	na
As	4.09	6.56	7.24	5.26	4.95	4.59	3.61	4.73	na	na
Se	nd	nd	nd	1.07	nd	nd	nd	2.21	na	na
Rb	75.71	97.43	97.95	90.99	91.27	85.34	82.45	69.63	na	na
Sr	239.43	142.43	137.22	142.32	144.21	144.68	131.20	167.07	na	na
Mo	1.35	1.67	1.87	1.20	1.99	1.41	1.46	1.02	na	na
Ag	nd	nd	nd	nd	0.37	nd	0.34	0.40	na	na
Cd	0.30	nd	0.71	nd	nd	nd	0.33	nd	na	na
Sn	1.73	1.43	1.93	2.61	1.11	1.72	2.17	1.67	na	na
Sb	0.72	0.68	0.31	0.42	0.52	0.30	0.56	0.53	na	na
Ba	868.48	1058.62	1073.74	1043.44	989.72	1081.53	1009.78	857.40	na	na
Yb	1.74	2.37	2.67	3.20	2.95	2.70	2.93	2.75	na	na
W	1.34	1.59	1.63	0.97	1.60	1.74	2.01	1.26	na	na
Re	nd	nd	nd	nd	nd	nd	nd	0.23	na	na
Au	nd	nd	nd	nd	0.22	nd	nd	0.43	na	na
Tl	0.31	0.34	0.37	0.43	0.29	0.27	nd	0.32	na	na
Pb	9.03	12.98	13.93	12.45	12.51	11.03	11.29	9.74	na	na
Bi	nd	0.17	0.18	nd	0.27	0.12	nd	0.14	na	na
U	1.67	2.14	2.31	2.05	2.12	1.86	1.89	1.57	na	na

Table A-2 (continued)

	WIDP18 -Ctx21- IN01	WIDP18 -Ctx21- IN02	WIDP18 -Ctx01- IN01	WIDP18 -Ctx23- IN02	WIDP18 - Ctx03- IN02-R2	WIDP18 - Ctx03- IN03-R2	WIDP18 - Ctx03- IN04-R2	WIDP18 - Ctx20- IN01-R2	WIDP18 _ Matrix glass	WIDP10 -IN01
Major elements (wt%)										
SiO ₂	67.18	65.17	63.64	66.75	53.02	51.58	55.53	48.20	61.73	63.45
TiO ₂	0.83	0.81	0.83	0.84	0.16	0.92	0.85	0.85	0.96	0.99
Al ₂ O ₃	13.98	14.00	14.16	16.21	24.98	19.89	18.19	19.64	15.25	14.56
FeO _t	5.09	6.42	6.70	3.47	2.10	3.52	4.05	4.72	5.75	5.82
MnO	0.06	0.09	0.08	0.06	0.06	0.06	0.07	0.10	0.08	0.10
MgO	1.07	1.25	1.74	0.98	5.29	4.46	4.81	4.45	2.42	2.55
CaO	4.18	4.76	4.74	4.95	11.68	14.78	11.98	15.27	6.28	5.61
Na ₂ O	1.70	2.25	3.56	2.20	2.99	2.50	2.00	2.27	3.41	3.08
K ₂ O	3.11	2.86	2.61	2.69	0.39	0.93	1.44	0.63	2.37	2.78
P ₂ O ₅	0.03	0.04	0.03	nd	nd	nd	nd	nd	0.04	nd
Cr ₂ O ₃	0.05	0.04	0.05	nd	0.04	0.04	0.07	0.05	0.04	nd
Cl (ppm)	1175	1260	1140	1487	257	1703	1583	2027	616	1245
S (ppm)	203	150	108	4	72	1030	713	1179	62	57
H ₂ O (wt%)	0.21679	na	0.28651	na	0.97	na	0.21	0.32	na	na
Total	97.41	97.83	98.28	98.29	100.71	98.68	98.99	96.18	98.39	99.08
Hosting phenocryst	Opx	Opx	Opx	Opx	Ol	Ol	Ol	Ol		Pla
Trace elements (ppm)										
Li	22.43	21.00	35.91	na	13.90	5.17	21.52	7.46	na	25.03
B	43.10	43.15	35.90	na	11.95	13.46	16.72	12.82	na	37.96
Sc	23.35	21.87	21.23	na	25.23	44.64	41.96	60.79	na	28.59
Ti	5231.22	4776.72	5336.80	na	2184.32	4522.82	3662.79	4580.30	na	5864.93
V	256.30	251.63	231.44	na	120.53	278.58	243.93	370.73	na	231.78
Cr	25.43	nd	4.17	na	327.27	343.59	389.47	88.43	na	35.80
Mn	675.33	644.65	731.44	na	1655.63	861.53	1138.64	724.38	na	736.70
Co	17.57	14.39	13.86	na	115.99	57.90	63.09	19.01	na	17.53
Ni	25.00	17.57	5.05	na	1776.84	939.29	926.68	173.04	na	31.83
Cu	150.45	160.68	264.60	na	643.79	91.81	153.17	6.49	na	156.97
Zn	64.00	54.69	71.57	na	117.27	33.85	50.96	42.76	na	61.89
Ga	191.91	193.50	199.19	na	55.25	73.53	78.44	66.34	na	183.41
As	5.86	4.32	4.63	na	2.64	3.48	6.52	nd	na	3.77
Se	nd	nd	nd	na	nd	9.49	17.08	nd	na	nd
Rb	97.01	90.29	81.55	na	24.25	19.99	18.78	14.65	na	83.27
Sr	145.51	161.54	173.23	na	48.08	169.31	170.17	206.49	na	165.87
Mo	0.85	2.25	1.29	na	nd	nd	2.25	1.44	na	1.32
Ag	nd	0.46	nd	na	nd	nd	1.26	nd	na	0.28
Cd	1.31	nd	nd	na	2.18	nd	5.86	5.35	na	nd
Sn	2.16	nd	2.29	na	nd	nd	7.43	nd	na	0.97
Sb	1.87	nd	nd	na	nd	nd	nd	nd	na	0.43
Ba	1031.08	985.89	1078.72	na	256.42	340.39	326.27	302.16	na	932.99
Yb	3.14	3.26	2.52	na	0.63	3.74	4.41	nd	na	2.45
W	1.49	3.12	1.59	na	nd	nd	nd	nd	na	1.39
Re	0.63	nd	nd	na	nd	nd	nd	nd	na	nd
Au	nd	nd	nd	na	nd	nd	nd	nd	na	nd
Tl	0.51	nd	0.34	na	nd	nd	nd	nd	na	0.29
Pb	13.27	13.96	12.89	na	1.99	3.54	7.60	4.97	na	10.91
Bi	nd	nd	0.28	na	nd	nd	0.56	nd	na	0.14
U	2.03	1.81	1.97	na	0.69	nd	0.72	0.57	na	1.58

Table A-2(continued)

	WIDP1 0-IN02	WIDP10 -IN03	WIDP10 -IN04	WIDP10 -IN05	WIDP10 -IN06	WIDP10 -IN07	WIDP10 -IN08	WIDP10 -IN09	WIDP10 -IN10	WIDP10 -IN11
Major elements (wt%)										
SiO ₂	67.14	63.10	64.69	65.76	65.46	65.23	63.80	64.93	64.31	64.33
TiO ₂	0.85	1.06	1.28	0.91	0.97	1.40	1.01	0.86	0.92	1.08
Al ₂ O ₃	13.51	14.40	13.15	13.77	13.91	13.83	14.09	14.07	14.15	13.46
FeO _t	5.82	6.01	7.63	6.42	6.45	6.49	6.81	6.81	6.56	6.53
MnO	0.10	0.09	0.12	0.12	0.10	0.11	0.13	0.11	0.11	0.11
MgO	1.64	2.59	1.99	1.76	2.10	2.23	2.24	2.21	2.26	2.04
CaO	4.09	5.84	5.10	4.99	4.96	5.06	5.46	5.15	5.41	5.21
Na ₂ O	1.47	3.06	1.90	2.29	2.55	2.36	2.48	2.26	2.83	2.24
K ₂ O	3.59	2.63	2.78	2.82	2.89	2.99	2.53	2.63	2.70	2.71
P ₂ O ₅	0.02	nd	0.01	0.01	nd	0.02	nd	nd	0.00	nd
Cr ₂ O ₃	0.01	0.03	0.01	0.01	0.02	0.04	0.01	0.02	0.01	0.04
Cl (ppm)	1490	1340	1283	1283	1274	1340	1321	1611	1340	1340
S (ppm)	100	84	35	84	96	51	318	356	266	152
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	98.39	98.94	98.81	99.01	99.56	99.89	98.71	99.25	99.43	97.90
Hosting phenocryst	Cpx	Cpx	Cpx	Opx	Opx	Opx	Opx	Opx	Opx	Opx
Trace elements (ppm)										
Li	nd	24.75	17.15	22.40	27.06	23.20	22.88	25.18	24.66	22.12
B	nd	38.92	33.09	32.75	41.85	36.21	33.11	32.01	31.71	31.38
Sc	nd	31.56	78.23	30.34	30.51	34.67	34.80	30.26	29.83	36.38
Ti	nd	6216.19	7366.77	4519.55	5810.20	6950.62	7005.89	5371.21	5524.57	6054.79
V	nd	251.26	444.41	223.25	251.14	276.51	303.42	263.91	260.89	276.99
Cr	nd	43.90	157.70	150.53	14.58	167.75	34.63	9.74	17.82	183.46
Mn	nd	733.43	1504.96	1018.13	766.30	1353.95	891.77	811.69	810.58	1249.13
Co	nd	16.79	30.99	31.53	16.18	34.61	17.55	17.16	17.14	34.60
Ni	nd	29.46	78.66	87.43	15.94	100.28	19.93	16.36	15.90	89.86
Cu	nd	158.24	107.70	129.02	155.71	125.54	141.90	79.44	166.25	118.70
Zn	nd	60.75	63.41	74.00	72.99	88.73	72.20	74.63	51.80	80.09
Ga	nd	180.75	160.44	155.80	203.89	165.23	201.48	219.39	177.37	165.62
As	nd	3.56	4.91	2.80	4.94	5.19	2.81	5.33	4.96	2.83
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb	nd	76.82	63.00	73.15	88.74	77.25	69.22	82.18	82.78	73.22
Sr	nd	173.16	125.91	125.08	156.54	128.91	251.65	222.65	191.26	148.56
Mo	nd	1.27	1.56	1.20	1.43	0.66	1.65	1.14	1.02	1.40
Ag	nd	nd	nd	nd	nd	nd	nd	nd	0.45	0.33
Cd	nd	nd	nd	nd	nd	0.13	nd	nd	nd	nd
Sn	nd	1.90	3.42	1.55	0.99	nd	nd	3.27	0.04	nd
Sb	nd	0.29	0.27	nd	0.75	nd	0.76	nd	nd	nd
Ba	nd	895.04	843.48	809.64	1032.51	898.91	1020.01	1136.88	875.98	890.52
Yb	nd	2.79	3.37	2.18	2.76	2.83	4.37	3.90	4.60	3.77
W	nd	1.74	1.62	1.57	1.34	1.08	1.48	1.59	1.28	1.72
Re	nd	nd	nd	nd	nd	nd	0.95	nd	nd	nd
Au	nd	0.45	nd	nd	nd	nd	nd	nd	nd	nd
Tl	nd	0.30	0.02	nd	0.39	0.34	0.45	0.33	0.36	nd
Pb	nd	10.72	9.17	10.43	12.71	11.29	13.51	13.18	12.03	9.70
Bi	nd	0.16	nd	nd	nd	0.16	nd	0.09	0.18	nd
U	nd	1.84	1.46	1.53	2.18	1.90	1.75	2.06	1.97	2.18

Table A-2 (continued)

	WIDP1 0-IN12	WIDP10 -IN13	WIDP10 -IN14	WIDP10 -IN15	WIDP10 -IN16	WIDP10 -IN18	WIDP10 -IN19	WIDP10 -IN20	WIDP10 -IN21	WIDP10 -IN22
Major elements (wt%)										
SiO ₂	65.05	65.56	65.96	65.20	63.59	63.92	64.27	63.34	63.58	64.35
TiO ₂	0.91	0.92	0.86	0.86	1.29	1.32	1.35	0.88	0.91	1.04
Al ₂ O ₃	13.74	13.84	13.60	13.93	14.41	14.47	14.38	13.80	13.62	14.14
FeO _t	6.48	6.39	6.21	6.69	6.02	5.91	6.00	7.29	7.43	6.42
MnO	0.12	0.10	0.10	0.12	0.10	0.12	0.09	0.12	0.12	0.09
MgO	2.03	1.97	1.89	1.97	2.11	2.22	2.35	2.29	2.29	2.01
CaO	4.85	4.75	4.56	4.98	5.40	5.33	5.33	5.97	5.84	5.32
Na ₂ O	2.44	2.45	2.56	2.09	2.71	2.15	1.68	2.59	2.58	2.94
K ₂ O	2.91	2.97	3.14	2.85	2.77	2.86	2.87	2.26	2.24	2.92
P ₂ O ₅	0.06	0.01	0.08	0.01	0.12	0.16	0.09	nd	nd	nd
Cr ₂ O ₃	0.02	0.01	0.00	0.00	0.00	0.02	0.03	0.01	0.04	0.01
Cl (ppm)	1269	1226	1250	1345	1350	1264	1283	1521	1559	1440
S (ppm)	182	184	119	298	97	85	96	375	467	120
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	98.75	99.11	99.10	98.86	98.67	98.63	98.58	98.73	98.86	99.40
Hosting phenocryst	Opx	Opx	Opx	Opx	Pla	Pla	Pla	Cpx	Cpx	Opx
Trace elements (ppm)										
Li	24.59	24.54	25.33	24.86	24.39	21.57	23.06	25.83	24.60	23.18
B	41.98	38.15	44.12	40.15	48.91	41.73	37.81	32.83	32.01	42.51
Sc	31.35	27.88	24.16	26.89	28.66	26.22	25.86	33.38	34.07	27.84
Ti	6114.09	5436.94	4922.05	4727.33	7387.82	7007.24	7530.31	4967.95	5299.68	6086.04
V	248.51	234.51	204.26	218.83	279.20	266.59	267.06	191.89	222.00	248.25
Cr	12.36	15.66	8.67	24.37	16.85	8.46	11.69	16.61	11.15	91.14
Mn	797.05	815.32	699.58	795.36	730.02	661.04	701.76	874.22	900.64	823.32
Co	16.14	20.04	15.79	17.94	16.28	15.05	15.18	17.24	17.44	22.06
Ni	14.87	25.72	12.81	26.59	28.45	26.92	22.49	15.45	12.68	55.55
Cu	122.03	135.59	151.14	141.00	155.48	144.42	142.27	118.27	73.12	161.58
Zn	69.02	77.75	65.95	79.04	64.77	59.05	56.29	71.31	88.33	72.59
Ga	228.47	199.51	194.12	194.07	187.57	185.11	195.56	140.06	157.71	182.25
As	4.40	5.04	5.49	4.48	6.37	4.90	4.94	4.96	3.38	4.62
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb	85.38	88.43	92.68	80.33	72.58	71.74	69.90	61.92	56.47	84.79
Sr	176.82	179.32	144.08	159.39	158.16	169.69	198.79	156.70	172.97	141.17
Mo	1.34	1.81	0.93	1.40	1.64	1.53	1.72	0.91	1.78	1.35
Ag	nd	nd	nd	nd	nd	nd	nd	nd	0.34	nd
Cd	nd	nd	nd	nd	0.88	nd	nd	nd	nd	nd
Sn	3.67	1.25	nd	2.00	0.58	nd	nd	2.90	1.69	2.19
Sb	nd	0.37	nd	nd	nd	0.33	nd	nd	1.55	nd
Ba	1247.29	1041.62	991.23	1008.91	972.79	930.38	971.18	710.33	748.24	929.36
Yb	2.64	2.60	2.15	2.61	4.06	2.71	2.58	2.75	3.47	3.26
W	0.94	1.39	1.33	1.30	1.50	2.46	1.44	1.04	1.20	2.05
Re	nd	nd	nd	nd	0.20	nd	nd	0.83	nd	nd
Au	nd	nd	0.44	nd	nd	nd	0.32	0.33	nd	nd
Tl	0.21	0.72	0.17	0.45	0.61	0.49	nd	nd	nd	0.29
Pb	14.13	11.72	12.30	11.76	12.60	11.53	11.94	9.37	11.13	11.15
Bi	nd	0.07	0.04	0.16	nd	0.17	0.22	0.36	nd	0.31
U	2.13	1.89	2.07	2.09	2.47	2.27	2.55	1.98	1.67	1.69

Table A-2 (continued)

	WIDP1 0-IN23	WIDP10 -IN24	WIDP10 -IN25	WIDP10 -IN26- R2	WIDP10 - Matrix glass	WIDP10 - Glass around Sulfide	WIDP11 -IN01	WIDP11 -IN02	WIDP11 -IN03	WIDP11 -IN05
Major elements (wt%)										
SiO ₂	63.79	63.10	62.91	54.88	63.38	63.39	65.51	65.13	67.43	63.35
TiO ₂	0.89	1.32	1.33	2.52	1.04	0.89	0.94	0.79	0.83	1.17
Al ₂ O ₃	14.34	14.28	14.21	14.95	14.62	14.47	14.53	14.56	13.61	13.12
FeO _t	6.93	6.90	6.70	9.05	5.95	5.94	5.44	5.70	5.57	8.51
MnO	0.09	0.11	0.10	0.16	0.09	na	0.10	0.08	0.07	0.15
MgO	2.19	2.56	2.49	4.45	2.75	2.65	1.86	1.81	1.60	1.98
CaO	5.64	5.32	5.24	8.01	5.87	5.89	4.93	5.07	4.09	5.38
Na ₂ O	2.12	2.36	2.28	2.41	3.21	3.12	2.98	2.82	2.17	2.62
K ₂ O	2.69	2.78	2.82	2.29	2.66	2.39	2.90	2.81	3.56	2.49
P ₂ O ₅	0.00	0.03	0.06	1.39	0.04	na	0.05	nd	0.01	nd
Cr ₂ O ₃	0.00	0.01	nd	0.00	0.03	na	0.03	0.01	0.02	0.06
Cl (ppm)	1347	1606	1502	3938	998	825	1117	1226	1768	1202
S (ppm)	110	111	69	630	71	27	92	29	147	290
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	98.84	98.94	98.30	98.71	99.76	98.83	99.40	98.92	99.15	98.99
Hosting phenocryst	Opx	Pla	Pla	Ol			Pla	Pla	Opx	Cpx
Trace elements (ppm)										
Li	22.02	23.77	24.06	24.68	25.21	na	23.08	23.24	25.45	23.61
B	32.60	46.40	46.34	192.77	37.49	na	35.63	22.78	42.01	36.42
Sc	41.12	31.64	32.65	30.73	27.42	na	20.20	33.83	26.47	36.51
Ti	5029.04	7195.51	8017.61	13364.0 7	6203.33	na	5775.49	5042.34	5167.94	7566.55
V	258.61	323.62	322.66	338.11	250.73	na	176.25	281.76	207.11	353.31
Cr	282.61	3.87	17.84	87.08	37.16	na	11.02	14.25	14.04	11.45
Mn	1280.92	829.14	796.15	1027.05	749.26	na	679.62	768.17	670.38	1090.64
Co	32.65	18.19	17.74	24.36	17.52	na	13.17	17.19	14.86	18.87
Ni	99.90	24.50	26.60	63.46	29.93	na	22.63	22.02	22.27	8.42
Cu	137.30	171.60	160.31	110.31	150.88	na	136.87	155.96	128.86	64.86
Zn	87.27	71.51	72.35	82.98	80.44	na	60.91	72.45	61.72	98.45
Ga	175.03	196.01	204.61	374.43	171.37	na	190.52	185.59	180.71	170.85
As	3.75	6.84	6.64	20.98	4.18	na	4.94	2.10	5.08	5.48
Se	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
Rb	62.26	87.26	86.83	138.76	79.81	na	58.15	70.25	107.27	83.59
Sr	165.86	156.32	164.51	200.51	169.99	na	181.13	172.38	132.91	166.80
Mo	1.06	1.29	1.86	10.17	1.40	na	1.73	0.39	1.22	1.10
Ag	0.18	nd	0.60	nd	nd	na	nd	0.74	0.26	0.13
Cd	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
Sn	3.18	1.16	nd	nd	1.73	na	0.22	2.24	nd	2.08
Sb	0.56	nd	nd	2.72	2.68	na	0.31	0.65	0.49	0.63
Ba	1016.24	1019.16	1113.67	1952.98	932.75	na	1080.52	1008.91	1010.83	981.22
Yb	4.44	2.88	4.17	4.59	2.50	na	4.11	3.73	2.79	5.41
W	1.50	2.16	2.42	10.41	1.23	na	1.42	0.65	2.40	1.44
Re	nd	0.16	nd	nd	0.24	na	nd	nd	nd	nd
Au	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
Tl	0.63	0.20	0.23	0.36	0.36	na	0.36	0.27	0.43	0.25
Pb	12.03	11.99	12.29	17.91	10.52	na	11.14	11.41	12.45	12.15
Bi	0.28	0.21	0.26	0.58	0.11	na	0.16	0.16	0.10	nd
U	2.19	2.75	2.39	8.84	1.69	na	2.56	1.09	2.10	2.09

Table A-2 (continued)

	WIDP1 1-IN06	WIDP11 -IN07	WIDP11 -IN08	WIDP11 -IN09	WIDP11 -IN10	WIDP11 -IN11	WIDP11 -IN13	WIDP11 -IN14	WIDP11 -IN15	WIDP11 - Matrix glass
Major elements (wt%)										
SiO ₂	63.91	63.64	64.00	63.33	63.97	64.60	64.55	64.91	65.14	63.18
TiO ₂	1.19	1.12	1.08	1.14	0.99	1.24	0.98	1.30	1.05	0.96
Al ₂ O ₃	13.55	13.47	14.40	14.32	14.41	13.48	14.45	12.74	13.79	14.62
FeO _t	7.93	8.03	6.28	6.29	6.26	7.48	5.91	7.30	6.50	6.15
MnO	0.13	0.15	0.11	0.12	0.08	0.13	0.12	0.15	0.11	0.11
MgO	1.92	1.93	2.17	2.20	2.13	1.88	1.94	1.93	1.97	2.55
CaO	5.23	5.47	5.27	5.38	5.26	5.56	5.00	5.19	4.86	5.95
Na ₂ O	2.55	2.92	2.38	2.44	2.96	1.70	3.15	2.75	1.96	3.18
K ₂ O	2.52	2.53	2.70	2.58	2.67	2.45	2.72	2.49	2.72	2.42
P ₂ O ₅	nd	nd	nd	nd	0.03	0.00	0.05	0.02	0.02	0.07
Cr ₂ O ₃	0.03	0.01	0.00	nd	0.05	nd	0.04	0.02	0.03	0.03
Cl (ppm)	1255	1112	1402	1393	1426	1433	1260	1219	1450	977
S (ppm)	124	83	108	125	59	268	52	166	37	55
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.09	99.39	98.54	97.95	98.96	98.69	99.05	98.94	98.29	99.33
Hosting phenocryst	Cpx	Cpx	Pla	Pla	Pla	Cpx	Pla	Cpx	Cpx	
Trace elements (ppm)										
Li	25.05	26.04	25.02	21.32	23.84	24.71	23.41	23.71	25.13	24.93
B	37.20	35.75	46.02	46.05	42.69	37.49	36.97	36.77	43.84	38.85
Sc	36.92	37.25	30.59	35.67	29.38	28.74	22.85	43.98	33.16	28.09
Ti	7243.94	7314.96	6368.33	7562.12	6502.85	8292.01	6534.22	8336.20	6835.10	6143.42
V	353.38	338.73	269.42	312.72	267.77	342.72	235.69	365.93	284.20	253.88
Cr	38.14	4.89	20.60	20.49	17.09	14.74	18.38	5.17	6.15	41.22
Mn	981.36	959.32	770.41	813.89	759.29	848.15	744.62	914.75	787.15	756.24
Co	19.08	17.51	16.92	15.97	17.49	15.78	14.77	18.20	16.01	17.64
Ni	17.72	8.83	31.33	25.83	29.03	6.31	26.37	11.38	11.74	31.36
Cu	139.09	154.82	146.86	147.86	150.24	57.58	145.23	87.85	122.28	142.53
Zn	90.33	89.06	62.48	65.78	70.56	69.68	66.53	76.50	69.44	64.72
Ga	170.32	168.81	172.94	193.68	185.87	180.32	178.57	173.90	202.59	164.18
As	5.16	4.70	5.20	6.03	5.86	4.18	5.40	4.98	5.60	4.27
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.18
Rb	75.31	77.43	98.01	96.85	97.26	82.18	77.25	85.02	87.73	77.38
Sr	155.82	162.50	148.90	162.17	161.13	197.60	161.62	135.62	182.82	172.68
Mo	1.36	1.32	1.27	1.38	1.25	1.45	1.63	1.10	1.47	1.22
Ag	nd	nd	0.43	nd	nd	nd	nd	nd	nd	nd
Cd	nd	nd	nd	nd	nd	nd	0.47	nd	nd	0.21
Sn	1.19	2.09	nd	0.98	2.19	1.27	nd	2.84	4.31	1.69
Sb	0.79	nd	0.99	0.57	0.43	0.62	0.40	0.40	0.38	0.57
Ba	943.19	947.31	1016.10	1133.09	1016.82	1019.70	1031.05	977.84	1203.25	924.30
Yb	3.49	4.38	2.93	3.76	4.08	5.12	2.95	5.98	2.29	3.03
W	1.43	1.14	1.74	1.17	1.28	1.17	1.57	1.40	1.41	1.24
Re	nd	nd	nd	nd	nd	nd	nd	0.27	nd	0.17
Au	nd	nd	nd	nd	0.48	nd	nd	nd	nd	0.30
Tl	0.36	0.46	0.42	0.26	0.20	0.44	0.27	0.47	0.48	0.33
Pb	13.01	11.91	12.36	14.20	13.88	14.85	11.34	11.68	14.48	10.99
Bi	nd	0.14	nd	0.29	nd	0.16	nd	0.15	0.17	0.15
U	2.00	1.95	1.87	1.89	1.92	2.58	2.45	2.06	2.75	1.62

Table A-2 (continued)

	WIDP1 3-IN03	WIDP13 -IN04	WIDP13 -IN05	WIDP13 -IN06	WIDP13 -IN07	WIDP13 -IN08	WIDP13 -IN09	WIDP13 -IN10	WIDP13 -IN13	WIDP13 -IN14
Major elements (wt%)										
SiO ₂	67.03	66.11	66.07	66.56	62.58	65.68	66.17	64.94	65.14	65.26
TiO ₂	1.00	1.08	1.02	1.02	1.66	1.00	1.04	1.08	1.02	0.91
Al ₂ O ₃	14.25	13.83	14.40	14.41	12.45	14.38	14.66	12.65	14.22	13.31
FeO _t	5.08	5.87	5.21	5.48	7.88	5.64	5.43	6.82	5.68	6.53
MnO	0.13	0.13	0.07	0.11	0.16	0.10	0.09	0.12	0.11	0.13
MgO	1.14	1.32	1.39	1.25	2.71	1.42	1.25	2.35	1.65	2.21
CaO	4.90	4.37	4.38	4.07	4.89	4.72	4.63	4.62	5.09	4.26
Na ₂ O	3.31	2.42	2.54	1.80	2.00	2.42	2.52	2.44	2.67	1.89
K ₂ O	1.98	2.58	2.61	2.70	2.70	2.63	2.60	2.89	2.58	2.98
P ₂ O ₅	0.03	nd	nd	0.03	0.25	0.03	0.03	0.01	0.03	nd
Cr ₂ O ₃	0.04	0.02	0.03	0.01	0.04	0.01	nd	nd	0.04	0.03
Cl (ppm)	1683	1645	1483	1473	1804	1336	1435	1533	1412	1416
S (ppm)	1391	371	113	97	88	67	85	100	87	39
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.22	97.94	97.89	97.60	97.50	98.17	98.57	98.08	98.37	97.66
Hosting phenocryst	Cpx	Cpx	Cpx	Cpx	Pla	Opx	Opx	Pla	Opx	Pla
Trace elements (ppm)										
Li	21.68	29.00	29.67	30.40	28.91	na	na	35.59	24.84	33.99
B	46.68	37.21	40.01	43.24	57.73	na	na	37.39	41.82	28.86
Sc	33.03	37.26	27.47	28.43	37.72	na	na	28.64	24.65	20.61
Ti	9575.07	6562.68	6949.38	7262.77	9777.56	na	na	5963.52	6239.37	5530.54
V	353.80	295.86	266.94	264.47	401.97	na	na	251.32	241.43	188.44
Cr	nd	43.34	nd	7.10	15.84	na	na	23.45	nd	21.90
Mn	980.29	889.13	674.62	666.38	918.61	na	na	712.95	763.13	751.06
Co	21.08	14.65	10.46	9.23	18.77	na	na	14.77	11.90	15.78
Ni	57.93	15.33	4.27	1.22	34.52	na	na	25.90	3.89	25.49
Cu	317.39	271.54	178.20	216.69	199.08	na	na	205.45	162.60	284.68
Zn	96.19	67.10	65.23	63.48	77.66	na	na	56.21	68.37	64.17
Ga	203.29	179.13	205.08	212.19	201.25	na	na	181.96	175.36	187.51
As	5.98	5.53	6.00	6.28	9.42	na	na	4.48	4.86	3.96
Se	nd	nd	nd	nd	nd	na	na	nd	nd	nd
Rb	76.87	85.75	94.45	93.06	97.40	na	na	86.21	90.24	68.63
Sr	219.43	155.23	193.24	196.61	161.42	na	na	201.71	162.21	160.98
Mo	1.33	1.35	1.92	1.93	2.24	na	na	0.26	1.52	0.95
Ag	nd	nd	nd	0.78	nd	na	na	nd	nd	nd
Cd	nd	nd	nd	nd	nd	na	na	0.59	0.53	nd
Sn	2.60	nd	2.20	nd	2.01	na	na	nd	1.45	nd
Sb	1.19	nd	nd	nd	nd	na	na	0.29	0.34	0.58
Ba	1327.59	1025.28	1144.86	1258.62	1131.71	na	na	994.60	924.08	1063.56
Yb	8.09	3.66	3.60	4.12	4.03	na	na	3.20	3.87	2.05
W	1.03	1.62	1.44	2.27	2.65	na	na	0.93	1.36	1.35
Re	nd	nd	nd	nd	nd	na	na	nd	nd	nd
Au	nd	0.15	nd	0.21	nd	na	na	nd	nd	nd
Tl	0.27	0.80	0.51	0.43	0.23	na	na	0.30	0.23	0.37
Pb	17.49	11.44	14.92	17.04	14.73	na	na	11.59	12.76	11.95
Bi	nd	nd	nd	nd	0.17	na	na	0.09	nd	nd
U	3.29	2.09	2.16	2.67	3.31	na	na	1.76	1.93	1.46

Table A-2 (continued)

	WIDP1 3-IN17	WIDP13 -IN18	WIDP13 - Matrix glass	WIDP9- IN01	WIDP9- IN02	WIDP9- IN03	WIDP9- IN04	WIDP9- IN05	WIDP9- IN06	WIDP9- IN08
Major elements (wt%)										
SiO ₂	65.40	65.80	66.90	65.66	66.38	63.88	66.32	65.51	64.96	67.96
TiO ₂	1.15	1.08	1.23	1.02	0.94	1.04	1.04	0.92	0.97	0.93
Al ₂ O ₃	14.72	14.63	13.62	14.59	15.02	15.25	14.93	14.98	14.77	14.95
FeO _t	6.04	6.05	6.02	5.80	5.85	6.42	6.78	5.83	6.62	5.34
MnO	0.07	0.13	0.08	0.10	0.11	0.11	0.11	0.11	0.10	0.10
MgO	1.22	1.26	1.38	1.62	1.37	1.72	1.36	1.74	1.45	0.88
CaO	4.86	4.92	3.78	5.08	5.10	4.94	3.85	4.88	5.09	4.18
Na ₂ O	3.11	1.58	3.10	3.28	2.65	3.39	3.16	3.06	3.43	3.00
K ₂ O	2.63	2.44	3.15	2.71	2.65	3.11	2.70	2.72	2.59	3.31
P ₂ O ₅	nd	0.04	0.07	nd	0.00	0.02	nd	0.01	nd	0.03
Cr ₂ O ₃	0.05	0.04	0.01	0.00	0.01	0.02	0.01	0.01	0.02	0.01
Cl (ppm)	1435	1554	1135	990	965	980	1133	963	1067	1137
S (ppm)	127	116	41	60	16	112	136	230	235	119
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.41	98.14	97.93	99.97	100.19	100.01	100.38	99.89	100.12	100.82
Hosting phenocryst	Opx	Opx		Cpx	Opx	Cpx	Cpx	Cpx	Opx	Opx
Trace elements (ppm)										
Li	30.70	21.15	26.49	23.78	15.18	44.64	33.43	28.21	21.34	10.65
B	41.19	39.77	39.93	41.18	21.82	43.59	43.42	38.61	35.42	11.56
Sc	25.47	25.41	25.64	28.35	49.28	23.53	27.29	24.76	28.19	61.75
Ti	7479.72	6922.56	6025.13	7004.86	3872.89	6206.79	6308.41	5294.71	6189.64	3972.66
V	291.67	267.07	241.28	272.83	239.86	231.02	263.35	203.59	302.93	320.86
Cr	9.02	37.48	33.61	7.21	579.34	3.30	37.17	7.00	4.70	674.17
Mn	633.85	721.53	688.46	739.10	2199.82	753.59	668.97	721.70	720.36	3204.91
Co	14.16	17.58	16.29	12.06	61.16	15.39	13.54	12.82	14.04	99.49
Ni	12.53	32.46	23.23	8.48	219.82	6.18	14.80	5.47	9.12	363.95
Cu	137.55	151.65	131.56	165.44	78.84	244.76	209.53	186.13	212.41	52.53
Zn	106.36	77.42	64.68	68.91	121.80	75.42	75.70	60.43	76.45	195.63
Ga	198.81	185.96	173.90	211.56	122.03	197.67	197.16	177.48	188.92	75.51
As	4.13	6.51	5.12	6.35	2.81	5.42	4.55	6.15	5.62	nd
Se	nd	nd	3.31	nd	nd	nd	nd	nd	nd	2.89
Rb	81.33	87.46	82.62	84.47	43.20	93.82	90.00	87.79	81.22	34.60
Sr	205.25	187.34	194.39	202.09	88.10	181.30	162.93	151.38	194.79	57.08
Mo	1.83	0.82	1.22	1.32	0.38	2.10	1.03	1.74	1.51	nd
Ag	nd	nd	0.37	nd	nd	0.23	0.43	nd	nd	0.31
Cd	nd	nd	0.63	nd	nd	nd	nd	nd	nd	nd
Sn	2.78	nd	2.25	1.79	1.94	1.01	nd	1.08	nd	2.44
Sb	5.36	0.35	0.70	nd	nd	0.04	1.12	0.22	0.94	nd
Ba	1114.16	1025.43	970.87	1192.63	514.43	1049.28	968.49	932.31	998.51	410.48
Yb	5.86	4.02	2.58	2.73	2.84	4.86	3.13	2.40	4.32	2.34
W	2.00	1.10	1.41	1.66	0.63	1.34	1.21	1.28	2.05	0.49
Re	nd	0.72	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	0.27	nd	0.87	0.25	nd	nd	nd	nd
Tl	0.58	nd	0.28	0.27	0.15	0.56	0.27	0.38	0.41	0.29
Pb	13.29	14.27	11.48	14.37	5.95	14.87	14.87	11.56	11.75	3.96
Bi	nd	nd	0.17	0.20	0.09	0.31	0.30	nd	0.18	nd
U	2.58	2.31	1.86	2.74	1.12	1.96	2.52	1.74	1.69	0.57

Table A-2 (continued)

	WIDP9- IN09	WIDP9- IN11	WIDP9- IN12	WIDP9- IN13	WIDP9- IN14	WIDP9- IN15	WIDP9- IN16	WIDP9- IN17	WIDP9- IN18	WIDP9- Matrix glass
Major elements (wt%)										
SiO ₂	67.03	64.55	64.95	65.35	67.76	63.52	64.59	65.77	66.03	65.92
TiO ₂	1.11	0.94	0.99	0.98	0.93	1.08	0.87	0.99	0.78	1.20
Al ₂ O ₃	14.40	13.43	13.54	13.96	14.06	15.66	14.99	14.44	14.85	13.91
FeO _t	5.63	6.33	7.36	6.98	6.03	7.22	6.38	7.02	6.42	6.18
MnO	0.12	0.12	0.11	0.07	0.06	0.15	0.13	0.12	0.13	0.09
MgO	1.55	3.17	1.78	1.48	1.18	1.56	1.76	1.39	1.26	1.74
CaO	4.46	6.32	5.26	5.28	4.33	5.38	5.16	5.38	4.88	4.68
Na ₂ O	3.31	2.84	3.37	2.81	2.58	2.59	3.32	2.60	3.15	3.19
K ₂ O	2.64	2.49	2.32	2.68	3.10	2.27	2.44	2.61	2.60	3.10
P ₂ O ₅	0.00	0.01	0.03	0.05	nd	0.03	0.03	0.05	0.01	0.02
Cr ₂ O ₃	0.00	0.02	nd	0.01	0.01	0.01	0.02	nd	0.02	0.04
Cl (ppm)	1060	922	1013	1297	940	1460	1018	1120	1117	647
S (ppm)	49	107	834	709	60	941	569	66	398	43
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	100.38	100.34	99.90	99.86	100.15	99.72	99.85	100.49	100.27	100.14
Hosting phenocryst	Cpx	Pla	Opx	Opx	Opx	Cpx	Cpx	Opx	Opx	
Trace elements (ppm)										
Li	30.20	53.60	29.89	21.04	15.57	24.36	27.65	21.92	20.42	33.49
B	44.01	51.23	39.76	37.52	19.61	29.95	34.04	38.06	27.68	43.07
Sc	28.11	64.42	29.07	34.33	51.49	61.29	28.40	29.36	36.99	29.46
Ti	7018.49	10335.0	6534.07	6109.26	4329.95	5500.31	5552.66	5832.76	4582.31	6873.64
V	315.55	587.51	323.23	296.68	277.99	319.78	207.63	254.20	254.07	273.01
Cr	nd	1.23	5.67	74.16	487.10	251.54	12.32	189.80	137.65	32.30
Mn	847.69	806.15	897.46	1140.43	2326.51	1350.54	818.38	1169.45	1497.24	834.30
Co	11.77	14.08	16.37	24.92	68.47	26.61	14.91	29.34	39.20	18.55
Ni	2.16	8.39	17.29	70.95	230.58	63.87	9.31	81.92	106.95	27.99
Cu	190.04	345.66	38.65	626.61	75.72	892.47	587.69	139.97	239.78	152.41
Zn	83.61	48.65	81.75	85.94	118.72	81.89	72.54	93.11	88.97	68.92
Ga	188.45	236.08	214.59	210.22	125.82	140.43	185.36	167.96	163.90	195.53
As	5.21	7.79	4.71	5.89	2.99	3.68	3.65	2.09	2.05	4.99
Se	3.13	nd	nd	nd	nd	nd	nd	2.24	4.05	nd
Rb	83.96	85.78	83.04	76.85	56.21	46.32	78.27	70.17	64.50	90.16
Sr	173.57	161.87	184.67	159.58	94.41	168.66	199.77	152.42	164.23	150.81
Mo	1.62	2.36	1.43	1.55	0.96	1.15	1.25	1.11	0.97	1.55
Ag	0.33	0.23	nd	nd	0.47	0.26	0.31	0.68	nd	0.27
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.58
Sn	nd	2.97	1.47	1.81	2.15	1.32	2.26	nd	nd	1.74
Sb	0.42	0.99	nd	0.42	0.37	0.78	0.12	nd	0.67	0.72
Ba	1045.95	1326.64	1171.80	1154.78	712.40	748.57	979.20	849.39	898.40	1046.48
Yb	4.05	4.37	3.97	4.21	2.51	2.67	3.22	4.16	4.49	3.13
W	1.62	3.21	1.16	1.39	1.95	2.50	1.44	0.95	1.96	1.38
Re	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	0.48	0.44	0.40	nd	nd	0.38	0.55	0.36
Tl	0.29	0.23	0.54	0.58	0.25	0.39	0.57	nd	0.36	0.29
Pb	13.72	16.26	13.32	11.96	6.88	11.19	11.90	9.98	6.59	11.86
Bi	0.16	nd	0.22	0.38	nd	0.17	0.07	0.16	0.18	0.22
U	2.12	3.21	1.95	1.57	1.59	2.27	2.19	1.44	1.09	2.07

Table A-2 (continued)

	WIDP8- IN02	WIDP8- IN03	WIDP8- IN04	WIDP8- IN05	WIDP8- IN06	WIDP8- IN07	WIDP8- IN08	WIDP8- IN09	WIDP8- IN10	WIDP8- IN11
Major elements (wt%)										
SiO ₂	66.36	59.96	64.40	65.05	66.86	65.37	64.71	64.69	65.26	64.87
TiO ₂	0.56	2.09	1.19	1.29	1.02	1.26	1.02	1.06	1.12	1.12
Al ₂ O ₃	15.00	12.98	13.33	13.49	13.60	13.53	14.33	14.35	14.05	13.32
FeO _t	5.59	7.73	6.64	6.27	5.97	5.86	6.32	6.54	6.25	6.32
MnO	0.07	0.15	0.10	0.09	0.09	0.11	0.12	0.08	0.10	0.11
MgO	1.46	3.21	2.58	1.56	1.34	1.63	1.61	1.61	1.55	2.49
CaO	4.64	5.54	4.72	4.36	3.92	4.29	4.67	4.63	4.58	4.60
Na ₂ O	3.59	2.68	3.04	3.36	3.27	3.32	3.36	3.28	3.19	3.07
K ₂ O	2.49	2.40	2.74	2.93	2.75	3.00	2.70	2.68	2.76	2.79
P ₂ O ₅	nd	0.55	0.11	0.08	0.02	0.06	0.01	0.01	0.03	0.02
Cr ₂ O ₃	0.00	0.00	0.01	0.03	0.01	0.01	0.01	0.02	0.01	0.01
Cl (ppm)	1340	1350	1080	1173	877	1187	973	1023	913	1140
S (ppm)	247	267	147	230	88	48	113	124	103	56
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.94	97.46	98.99	98.65	98.93	98.55	98.97	99.07	98.99	98.85
Hosting phenocryst	Opx	Pla	Pla	Pla	Cpx	Pla	Cpx	Cpx	Cpx	Pla
Trace elements (ppm)										
Li	20.34	30.30	34.51	36.35	22.25	25.72	23.02	23.86	24.63	26.56
B	22.74	43.04	42.97	45.03	30.34	45.78	41.12	40.41	42.04	37.55
Sc	42.81	44.47	34.17	29.90	21.79	31.06	24.52	26.75	27.43	26.62
Ti	2541.10	11813.48	7766.27	7663.25	4796.59	8446.95	6308.04	6805.22	6845.24	6556.49
V	233.55	492.52	324.22	343.05	178.74	307.89	244.30	261.50	275.28	257.88
Cr	816.46	nd	5.62	4.82	4.05	6.51	nd	nd	nd	23.69
Mn	2271.66	931.32	855.27	707.43	529.67	758.20	719.30	775.74	740.96	739.53
Co	60.89	20.75	19.81	15.14	10.99	14.46	14.93	14.04	14.76	17.56
Ni	201.86	17.15	13.74	13.31	6.14	13.98	9.06	6.63	12.35	11.03
Cu	41.93	248.92	189.39	210.08	114.65	144.71	157.78	166.37	154.37	132.73
Zn	156.57	92.32	81.40	75.02	59.10	62.79	71.19	87.05	70.15	65.53
Ga	130.89	192.31	199.07	196.61	162.83	240.52	189.57	199.90	195.05	189.00
As	3.14	8.24	4.67	5.93	3.68	5.41	5.71	6.97	4.83	5.55
Se	nd	nd	nd	nd	nd	nd	nd	nd	2.42	nd
Rb	39.83	62.86	86.81	91.37	77.26	91.64	88.01	89.57	88.29	81.77
Sr	106.92	163.10	151.03	146.69	210.57	163.38	155.04	174.49	150.58	144.67
Mo	0.90	3.97	1.73	1.79	1.52	1.84	1.14	1.98	2.11	1.67
Ag	nd	0.40	nd	nd	nd	0.47	0.39	nd	nd	nd
Cd	1.50	nd	nd	nd	nd	1.69	1.31	nd	nd	nd
Sn	nd	nd	2.44	2.02	2.35	0.01	2.33	0.73	nd	2.71
Sb	nd	nd	nd	nd	nd	1.02	0.43	0.64	1.29	nd
Ba	629.75	918.06	1059.51	1016.94	874.56	1341.72	972.00	1044.42	1081.51	1036.52
Yb	2.67	6.17	4.66	4.06	2.32	5.59	3.94	3.14	3.27	2.67
W	nd	4.73	1.56	1.92	0.59	1.47	1.41	1.07	1.55	1.75
Re	0.40	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	nd	0.47	nd	0.12	nd	nd	nd	nd
Tl	nd	nd	0.32	0.36	nd	0.69	0.57	0.32	0.40	0.21
Pb	9.14	12.82	13.62	13.28	8.76	14.49	12.20	12.91	13.42	13.64
Bi	0.17	nd	nd	nd	0.06	nd	0.31	nd	nd	0.25
U	1.00	5.45	1.77	2.34	1.39	2.32	2.15	2.39	1.82	1.73

Table A-2 (continued)

	WIDP8- -IN15	WIDP8- -IN16	WIDP8- -IN17	WIDP8- -IN18	WIDP8- -IN19	WIDP8- Matrix glass	WIDP17 -IN01	WIDP17 -IN02	WIDP17 -IN03	WIDP17 -IN04
Major elements (wt%)										
SiO ₂	65.48	63.33	60.89	70.21	71.47	67.68	64.52	64.40	63.05	64.04
TiO ₂	1.10	1.52	2.21	0.44	0.45	1.07	0.95	1.10	0.95	1.04
Al ₂ O ₃	13.29	13.49	13.31	11.24	11.57	13.34	14.77	14.78	13.91	15.03
FeO _t	5.93	6.56	7.55	5.58	5.45	5.45	5.67	5.31	6.84	5.64
MnO	0.10	0.13	0.11	0.13	0.09	0.08	0.08	0.02	0.10	0.07
MgO	2.19	2.30	2.50	1.13	0.79	1.39	2.25	2.29	2.55	2.01
CaO	4.55	5.03	5.45	3.11	2.60	3.95	5.28	5.39	5.29	5.03
Na ₂ O	3.05	2.70	2.73	2.71	2.73	3.10	2.76	2.49	2.73	3.19
K ₂ O	2.84	2.75	2.51	2.74	2.82	3.09	2.72	2.84	2.61	2.81
P ₂ O ₅	0.01	0.14	0.30	nd	nd	0.01	0.15	0.18	0.15	0.15
Cr ₂ O ₃	0.00	0.01	0.01	0.02	0.02	0.03	0.05	0.03	nd	0.04
Cl (ppm)	1003	1270	1260	1477	1593	1066	440	540	410	603
S (ppm)	156	242	247	99	77	58	122	28	103	109
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	98.66	98.12	97.72	97.47	98.15	99.30	99.25	98.90	98.24	99.10
Hosting phenocryst	Pla	Pla	Pla	Cpx	Cpx		Pla	Pla	Opx	Pla
Trace elements (ppm)										
Li	26.19	22.86	24.90	41.80	35.40	29.60	21.49	24.23	24.14	45.78
B	40.70	49.69	44.48	32.75	15.15	44.75	35.10	39.18	35.49	38.97
Sc	28.68	32.16	34.62	41.71	178.68	24.83	25.54	28.57	27.29	24.76
Ti	7167.83	8346.95	8488.09	2504.11	3093.12	6800.67	5659.44	7563.77	5597.69	6162.02
V	262.46	316.33	375.35	129.69	270.26	234.97	237.20	301.67	258.83	246.55
Cr	24.99	nd	14.36	3.08	nd	6.86	17.54	31.71	48.96	12.19
Mn	768.92	756.33	614.86	940.74	2598.39	655.11	666.10	777.98	832.20	714.81
Co	15.62	15.18	12.70	9.46	27.81	11.59	15.04	16.32	16.99	14.63
Ni	10.36	11.26	6.46	nd	4.71	7.23	23.54	36.07	34.61	23.18
Cu	139.46	190.68	94.49	85.32	38.48	131.71	134.62	136.44	137.35	184.73
Zn	66.92	61.54	53.95	66.53	107.63	62.74	57.04	63.44	77.44	60.36
Ga	202.68	213.03	176.57	169.67	104.95	214.72	171.98	205.86	170.51	164.43
As	7.18	6.06	9.05	4.71	4.30	5.77	4.04	6.38	4.69	3.66
Se	nd	nd	nd	0.33	nd	nd	nd	nd	nd	nd
Rb	94.00	92.23	63.59	92.70	50.28	100.25	78.79	86.77	76.07	86.41
Sr	159.98	189.86	333.08	88.70	71.69	151.39	181.70	203.95	168.75	152.60
Mo	1.61	2.27	1.42	1.25	0.61	1.28	1.05	1.03	1.14	1.13
Ag	nd	nd	nd	nd	nd	0.41	nd	0.60	0.25	nd
Cd	nd	0.24	nd	nd	nd	nd	nd	nd	nd	nd
Sn	1.85	3.50	1.07	2.16	3.23	2.22	3.30	nd	3.09	1.99
Sb	0.72	0.19	nd	0.87	nd	0.28	0.53	nd	nd	0.43
Ba	1136.28	1028.73	914.60	917.53	511.98	1198.65	975.96	1357.18	962.39	993.89
Yb	3.02	3.13	4.86	4.89	7.20	3.26	2.69	2.89	2.25	2.85
W	1.21	2.52	2.29	2.03	nd	1.64	1.11	2.13	1.78	1.53
Re	0.12	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	nd	nd	nd	0.45	nd	nd	nd	nd
Tl	0.38	nd	0.35	0.34	0.48	0.37	0.26	nd	nd	0.31
Pb	11.08	13.30	9.68	13.36	7.45	13.28	11.62	13.74	11.45	11.45
Bi	nd	nd	nd	0.21	nd	0.11	nd	nd	nd	0.09
U	2.35	2.29	3.39	1.92	1.06	2.29	1.54	2.41	1.80	1.70

Table A-2 (continued)

	WIDP1 7-IN05	WIDP17 -IN06	WIDP17 -IN07	WIDP17 -IN08	WIDP17 -IN09	WIDP17 -IN10	WIDP17 -IN11	WIDP17 -IN12	WIDP17 -IN13	WIDP17 -IN14
Major elements (wt%)										
SiO ₂	64.15	65.07	64.84	63.42	65.34	64.76	65.55	63.53	63.38	63.87
TiO ₂	1.29	1.13	1.15	1.06	1.11	0.80	0.85	0.97	0.97	0.94
Al ₂ O ₃	13.30	13.03	13.41	13.80	13.77	13.99	13.97	14.36	14.34	14.61
FeO _t	7.44	7.24	6.66	7.54	6.08	6.16	5.90	6.12	6.85	6.15
MnO	0.16	0.15	0.10	0.12	0.20	0.10	0.08	0.19	0.11	0.21
MgO	2.08	2.15	2.51	2.41	2.37	2.13	2.07	2.85	2.71	2.57
CaO	5.29	4.98	5.22	5.41	4.94	5.24	4.97	5.82	5.78	5.24
Na ₂ O	3.00	2.28	2.43	2.04	1.96	2.54	2.97	3.31	2.61	2.95
K ₂ O	2.62	2.65	2.63	2.50	2.87	3.26	3.29	2.54	2.50	2.64
P ₂ O ₅	0.14	0.12	0.15	0.17	0.15	0.18	0.16	0.12	0.11	0.16
Cr ₂ O ₃	0.02	0.02	0.07	0.01	0.03	0.07	0.02	0.05	0.01	0.10
Cl (ppm)	440	527	530	567	550	507	603	510	580	535
S (ppm)	28	174	172	368	36	88	129	142	126	26
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.53	98.88	99.24	98.56	98.86	99.28	99.91	99.94	99.43	99.49
Hosting phenocryst	Cpx	Cpx	Opx	Opx	Cpx	Cpx	Cpx	Opx	Opx	Opx
Trace elements (ppm)										
Li	23.83	19.87	22.06	25.17	24.56	25.87	23.98	28.16	22.59	23.68
B	37.11	33.01	37.23	33.39	38.03	38.77	39.26	38.37	31.91	39.91
Sc	39.73	62.28	29.23	28.81	34.15	25.64	26.98	28.07	28.07	26.46
Ti	8015.75	7012.89	7909.38	6035.91	7609.33	4759.33	5108.65	6445.56	5165.62	5488.67
V	315.04	420.32	319.83	282.36	306.36	180.35	191.83	263.14	228.41	205.57
Cr	14.12	290.57	17.61	6.92	36.06	20.32	9.57	22.91	149.93	96.52
Mn	914.60	1408.56	817.14	832.41	741.86	777.31	718.27	747.24	905.08	813.06
Co	17.71	28.85	15.96	16.00	17.02	13.68	14.12	15.03	28.70	20.96
Ni	11.05	55.65	19.72	16.09	24.10	10.41	11.65	18.96	89.68	51.89
Cu	125.48	110.18	151.80	52.57	151.52	141.57	144.91	162.56	135.01	146.10
Zn	82.81	82.16	73.41	91.77	61.94	75.24	64.54	67.39	74.97	71.49
Ga	165.81	136.96	192.53	157.88	183.85	189.41	205.40	172.96	140.62	169.39
As	4.73	4.57	3.97	2.86	5.50	5.46	5.41	6.16	4.58	3.53
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb	80.04	69.43	79.89	71.33	84.26	101.69	103.25	81.03	73.32	79.83
Sr	155.55	133.09	188.13	193.59	164.65	127.45	140.20	190.11	141.35	153.63
Mo	1.19	1.00	2.74	1.15	1.11	2.39	1.55	2.13	0.98	1.54
Ag	0.13	0.59	nd	0.29	nd	0.39	nd	0.40	nd	nd
Cd	nd	1.05	0.19	nd	nd	nd	nd	nd	nd	nd
Sn	3.80	1.36	3.51	2.25	7.24	2.50	1.28	nd	nd	1.57
Sb	nd	nd	0.92	0.25	0.64	0.02	0.59	0.12	0.50	0.40
Ba	966.42	800.04	1136.15	872.25	1027.86	1136.74	1234.41	985.33	790.09	998.76
Yb	4.19	4.46	3.24	2.98	3.45	3.21	2.45	3.33	2.32	2.85
W	1.41	0.92	2.02	1.08	1.20	0.84	1.78	0.95	1.06	1.20
Re	0.41	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	nd	nd	0.50	nd	0.09	nd	nd	nd
Tl	0.33	0.30	0.47	0.30	nd	0.29	0.51	0.23	0.25	0.47
Pb	12.41	9.36	11.97	11.45	12.40	12.52	12.71	12.81	9.30	11.48
Bi	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13
U	1.81	1.51	1.76	1.95	1.89	1.73	1.80	1.87	1.48	1.62

Table A-2 (continued)

	WIDP1 7_ Matrix glass	WIDP4- IN01	WIDP4- IN02	WIDP4- IN03	WIDP4- IN24-R2	WIDP4- IN25-R2	WIDP4- IN04	WIDP4- IN05	WIDP4- IN06	WIDP4- IN07-R2
Major elements (wt%)										
SiO ₂	62.94	64.68	62.97	66.29	57.14	56.71	62.83	65.84	65.75	56.65
TiO ₂	0.99	1.11	0.99	1.16	0.87	0.79	2.00	1.18	1.14	0.73
Al ₂ O ₃	14.73	14.30	15.42	13.80	15.13	15.93	14.01	14.38	14.28	16.33
FeO _t	5.94	5.99	7.57	5.91	7.94	7.01	6.76	6.54	6.33	5.59
MnO	0.08	0.08	0.12	0.09	0.15	0.14	0.10	0.12	0.08	0.11
MgO	2.89	1.95	2.01	1.67	4.89	3.54	2.46	1.71	1.74	2.85
CaO	5.78	5.03	5.99	4.73	9.10	11.03	5.45	4.79	4.79	12.17
Na ₂ O	3.58	2.75	2.17	2.25	2.12	2.52	2.23	1.77	2.04	2.28
K ₂ O	2.57	2.77	2.04	2.94	1.85	1.58	2.53	2.68	2.69	1.18
P ₂ O ₅	0.16	nd	nd	0.01	nd	nd	0.31	0.02	0.02	nd
Cr ₂ O ₃	0.05	0.01	0.01	0.04	0.02	0.00	0.01	0.01	nd	0.04
Cl (ppm)	429	1173	998	1325	1520	1118	1321	1270	1344	1022
S (ppm)	53	44	383	302	297	548	84	93	92	733
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.72	98.78	99.41	99.05	99.21	99.26	98.83	99.17	99.01	97.94
Hosting phenocryst		Cpx	Cpx	Opx	OI	OI	Pla	Cpx	Cpx	OI
Trace elements (ppm)										
Li	24.47	39.03	30.15	25.94	22.29	57.89	27.09	27.22	29.45	29.17
B	38.94	41.07	22.32	40.89	12.45	24.46	67.93	37.99	40.95	11.96
Sc	27.60	24.35	30.17	26.04	30.12	42.89	38.55	31.98	27.24	28.51
Ti	5966.68	6389.82	5650.74	7085.99	2346.23	4346.09	12791.4	7797.08	7420.35	2145.62
V	248.41	242.88	268.00	293.77	129.15	258.93	474.93	302.55	235.61	133.60
Cr	39.39	13.72	79.14	10.56	445.03	167.86	30.21	51.33	nd	615.66
Mn	747.04	729.05	914.61	714.85	2087.23	1130.80	905.27	820.68	753.42	1362.24
Co	17.98	15.75	22.82	14.86	140.68	35.15	19.61	15.75	16.27	103.84
Ni	31.22	14.34	29.26	9.99	1507.37	191.98	13.63	21.34	10.79	1850.01
Cu	150.96	149.81	90.17	23.79	42.88	227.00	191.15	176.26	169.38	101.96
Zn	64.55	65.03	93.92	65.62	136.42	72.61	83.59	63.03	75.48	73.46
Ga	160.06	189.49	149.49	255.05	73.09	121.08	210.34	210.40	204.41	57.67
As	4.64	4.79	2.04	5.85	1.72	3.04	8.62	5.46	5.00	nd
Se	3.44	nd	nd	nd	nd	nd	3.10	nd	nd	nd
Rb	77.62	89.24	64.41	93.77	29.14	40.41	79.01	85.32	86.61	16.53
Sr	167.66	165.68	198.41	165.82	77.70	194.25	183.77	183.44	186.08	97.70
Mo	1.22	1.05	1.05	1.58	0.67	1.32	2.98	1.51	1.30	nd
Ag	0.20	0.43	nd	nd	0.67	nd	nd	nd	nd	0.82
Cd	0.56	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sn	1.13	2.19	nd	2.21	nd	nd	1.95	nd	1.94	1.76
Sb	0.60	0.56	0.28	1.54	0.95	0.78	0.82	0.40	0.44	nd
Ba	932.22	932.85	801.43	1324.50	378.14	553.14	1096.89	1056.82	1045.48	289.25
Yb	3.04	3.00	5.29	2.92	0.57	1.64	7.67	5.22	3.80	2.42
W	1.26	1.23	1.22	1.91	nd	nd	3.76	2.36	2.05	0.51
Re	0.19	nd	nd	nd	0.69	nd	nd	0.53	nd	nd
Au	0.29	nd	nd	nd	nd	nd	0.37	0.48	nd	nd
Tl	0.35	0.45	nd	0.61	0.24	nd	nd	0.24	0.13	nd
Pb	11.30	11.82	10.20	13.94	7.11	9.78	12.84	14.10	13.22	3.25
Bi	0.24	0.22	0.24	nd	nd	0.18	nd	0.17	nd	0.17
U	1.65	2.09	1.29	2.26	0.37	0.99	5.14	2.13	2.10	0.53

Table A-2 (continued)

	WIDP4- IN08- R2	WIDP4- IN09-R2	WIDP4- IN10	WIDP4- IN13	WIDP4- IN14	WIDP4- IN15-R2	WIDP4- IN15b- R2	WIDP4- IN16	WIDP4- IN17	WIDP4- IN18-R2
Major elements (wt%)										
SiO ₂	55.30	56.72	66.31	63.46	62.61	52.44	53.04	65.37	64.23	55.60
TiO ₂	0.65	0.73	0.85	1.70	1.80	0.64	0.82	0.94	0.92	0.71
Al ₂ O ₃	15.05	16.17	13.97	13.99	13.74	16.13	18.05	14.21	14.30	15.29
FeO _t	6.84	6.96	5.65	6.52	7.08	4.86	4.68	6.36	6.86	6.61
MnO	0.14	0.14	0.09	0.10	0.11	0.08	0.10	0.10	0.10	0.12
MgO	6.12	3.43	1.90	2.34	2.59	7.06	4.00	1.75	1.80	6.89
CaO	11.14	9.70	4.58	5.65	5.76	12.16	13.99	5.34	5.62	10.88
Na ₂ O	2.54	2.72	2.30	2.87	2.62	2.07	2.46	1.82	2.43	1.84
K ₂ O	1.21	1.72	2.88	2.51	2.59	0.81	0.91	2.61	2.43	1.22
P ₂ O ₅	nd	nd	nd	0.11	0.28	nd	nd	nd	nd	nd
Cr ₂ O ₃	0.07	0.03	0.02	nd	0.02	0.03	0.00	0.00	0.01	0.06
Cl (ppm)	987	1068	1076	1193	1297	1310	1516	1092	1033	1038
S (ppm)	592	296	51	61	119	826	977	148	107	612
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	99.06	98.32	98.67	99.39	99.35	96.28	98.05	98.62	98.81	99.20
Hosting phenocryst	Ol	Ol	Pla	Pla	Pla	Ol	Ol	Cpx	Cpx	Ol
Trace elements (ppm)										
Li	33.02	34.36	27.26	27.20	24.81	4.78	7.85	24.52	27.90	21.98
B	14.11	15.17	27.48	44.79	42.07	12.68	14.75	38.32	35.82	9.87
Sc	27.87	32.42	21.69	61.06	48.20	32.41	39.29	24.11	25.67	27.16
Ti	2087.20	2885.68	5470.39	10672.1	11201.71	2474.21	2562.37	5716.61	5699.86	2054.45
V	125.54	169.14	190.25	616.61	462.82	197.90	187.17	245.29	272.33	134.45
Cr	410.53	387.29	12.91	19.40	33.93	518.03	362.71	9.61	15.23	528.64
Mn	1624.33	1604.98	695.18	826.95	882.37	1135.62	1163.08	733.71	800.63	1681.35
Co	113.09	94.62	15.31	18.23	19.43	105.83	87.14	15.05	16.76	138.23
Ni	1447.69	949.41	19.05	23.99	27.11	1564.10	1264.47	12.72	8.23	1933.66
Cu	114.80	134.89	152.07	179.54	187.32	45.40	35.93	161.22	157.96	78.95
Zn	98.36	98.72	59.68	75.55	76.39	58.09	59.57	68.26	75.69	88.12
Ga	50.42	83.55	199.36	219.79	220.90	46.02	47.58	188.29	184.90	51.08
As	2.45	2.74	3.42	7.94	8.75	nd	nd	5.41	4.45	1.01
Se	3.28	nd	nd	nd	nd	nd	nd	nd	4.20	nd
Rb	16.25	27.76	78.40	69.19	76.25	11.59	11.07	83.60	76.67	12.55
Sr	105.26	141.88	141.40	183.64	177.80	122.98	123.76	166.77	181.02	102.16
Mo	1.02	1.95	0.97	2.99	4.19	nd	nd	1.05	0.90	1.35
Ag	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cd	nd	nd	nd	nd	nd	nd	nd	nd	1.34	nd
Sn	nd	nd	3.03	1.81	nd	nd	nd	1.52	2.07	nd
Sb	1.10	nd	0.25	0.55	0.50	nd	nd	0.44	0.16	nd
Ba	220.02	391.33	1076.76	1181.28	1188.28	197.21	227.28	968.42	923.58	283.12
Yb	0.76	2.49	2.35	5.94	5.11	nd	5.92	3.17	2.68	1.65
W	0.51	1.67	0.87	2.51	4.32	nd	1.92	1.38	1.60	2.22
Re	0.71	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	0.66	nd	nd	0.29	1.63	0.92	nd	nd	0.37
Tl	nd	nd	0.26	0.33	0.42	0.59	nd	0.20	0.82	nd
Pb	2.85	4.21	12.32	13.03	16.00	3.88	2.21	12.23	11.93	4.13
Bi	nd	nd	nd	0.32	nd	nd	0.57	nd	0.11	nd
U	0.48	0.51	1.40	3.47	4.66	0.42	0.12	1.55	2.22	0.20

Table A-2 (continued)

	WIDP4- IN18b- R2	WIDP4- IN19	WIDP4- IN20-R2	WIDP4- IN21	WIDP4- IN22	WIDP4- IN23	WIDP4- Ctx18- IN01	WIDP4- Ctx18- IN02	WIDP4- Ctx15- IN01	WIDP4- Ctx15- IN02
Major elements (wt%)										
SiO ₂	57.23	65.67	52.18	67.70	63.53	65.54	67.31	65.23	64.88	65.16
TiO ₂	0.78	1.01	0.75	1.14	1.42	0.88	0.78	0.88	0.96	0.96
Al ₂ O ₃	16.04	14.35	18.06	13.04	13.82	14.51	14.08	14.21	14.16	14.20
FeO _t	6.92	6.70	5.18	6.51	6.91	6.17	5.63	6.37	6.20	5.94
MnO	0.14	0.09	0.10	0.12	0.12	0.10	0.07	0.09	0.11	0.11
MgO	4.37	1.79	3.51	1.58	2.48	1.71	1.39	1.88	2.03	1.66
CaO	10.37	5.50	14.67	4.27	5.26	5.31	4.42	5.21	5.17	5.04
Na ₂ O	2.57	1.19	1.91	1.68	2.27	2.18	2.08	2.63	2.71	2.39
K ₂ O	1.61	2.45	0.81	3.03	2.66	2.69	3.25	2.97	2.92	3.00
P ₂ O ₅	0.00	0.00	nd	0.01	0.11	0.03	0.03	0.04	0.00	0.01
Cr ₂ O ₃	0.04	nd	0.02	0.02	0.00	0.00	0.02	0.04	0.06	0.00
Cl (ppm)	1078	1200	1580	983	1243	1243	1816	1275	1181	1230
S (ppm)	339	176	1020	107	100	131	231	247	81	95
H ₂ O (wt%)	na	na	na	na	na	na	0.30	0.49	0.33	0.63
Total	100.06	98.88	97.19	99.20	98.72	99.26	99.28	99.70	99.33	98.61
Hosting phenocryst	Ol	Opx	Ol	Cpx	Pla	Opx	Opx	Opx	Cpx	Cpx
Trace elements (ppm)										
Li	39.44	26.24	9.25	26.72	20.91	25.63	27.29	28.27	26.09	26.50
B	17.80	37.31	13.36	38.39	47.21	42.08	41.96	38.56	39.99	41.92
Sc	31.02	24.84	46.65	35.73	27.16	26.22	21.97	24.21	23.97	25.42
Ti	3338.01	5807.08	3625.96	6924.44	7298.41	5270.61	4811.83	5798.24	6183.35	6606.36
V	194.71	258.38	258.65	265.47	292.55	225.98	205.43	249.52	261.57	260.14
Cr	236.06	15.44	460.89	14.68	16.07	8.11	13.24	26.88	11.54	3.13
Mn	1315.64	753.19	1165.09	823.61	763.05	738.37	643.79	784.43	765.17	748.62
Co	76.53	16.95	65.26	14.01	16.37	15.03	15.38	15.10	15.00	15.58
Ni	666.76	14.75	867.60	6.49	20.14	11.78	15.43	8.81	13.71	9.22
Cu	51.68	172.05	31.33	108.41	139.59	156.87	76.65	77.06	151.23	144.39
Zn	94.29	66.46	72.06	69.02	59.44	65.18	63.55	73.23	69.63	68.18
Ga	99.71	175.44	68.74	188.02	185.22	218.67	216.13	195.46	192.33	201.27
As	3.73	5.08	3.06	4.48	4.97	7.03	5.79	3.99	5.05	5.67
Se	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Rb	41.18	78.38	19.12	104.61	85.34	88.60	103.89	85.72	89.64	89.79
Sr	147.52	172.54	175.16	134.79	172.39	175.10	150.53	159.13	167.21	174.45
Mo	0.78	1.48	0.03	1.49	2.10	1.45	1.29	0.75	1.25	1.04
Ag	nd	nd	nd	nd	nd	0.40	nd	nd	0.36	nd
Cd	nd	nd	3.06	nd	nd	nd	nd	0.65	nd	nd
Sn	nd	nd	nd	nd	4.08	nd	2.29	4.15	1.93	1.42
Sb	0.92	nd	nd	0.48	0.59	0.28	nd	nd	nd	0.75
Ba	512.82	887.41	265.20	1023.63	867.27	1119.19	1138.34	1012.82	1054.08	1054.89
Yb	0.66	2.96	0.47	4.12	3.98	2.15	2.46	2.99	3.86	2.98
W	nd	1.51	0.43	2.55	2.69	2.61	1.41	0.94	1.48	1.12
Re	1.17	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	0.82	nd	nd	0.38	nd	0.12	nd	nd	nd	nd
Tl	nd	0.21	nd	0.37	0.50	0.21	0.47	0.73	0.18	0.23
Pb	8.78	11.29	3.44	12.48	11.93	15.72	13.47	14.14	12.40	12.95
Bi	0.24	nd	nd	nd	0.16	nd	nd	nd	nd	nd
U	0.85	1.56	0.39	1.90	1.96	2.04	1.93	2.07	2.15	1.86

Table A-2 (continued)

	WIDP4- -Ctx13- IN03	WIDP4- Ctx13- IN02	WIDP4- Ctx17- IN01	WIDP4- Ctx17- IN02	WIDP4- Ctx9- IN01	WIDP4- Ctx9- IN03	WIDP4- Ctx9- IN04	WIDP4- Ctx4- IN01	WIDP4- Ctx2- IN01	WIDP4- Ctx16b- IN01
Major elements (wt%)										
SiO ₂	63.12	64.96	64.56	64.05	63.73	62.80	63.92	64.17	65.85	62.53
TiO ₂	1.01	0.82	0.89	0.88	1.25	1.31	1.06	1.07	0.93	1.34
Al ₂ O ₃	14.11	14.26	13.95	13.65	13.95	13.72	13.88	14.06	14.06	14.02
FeO _t	6.23	6.19	6.13	6.26	6.11	6.06	5.78	6.28	5.79	7.55
MnO	0.09	0.09	0.10	0.08	0.09	0.11	0.08	0.09	0.08	0.13
MgO	1.67	1.39	1.96	1.90	2.24	2.26	2.15	1.66	1.81	1.97
CaO	5.71	5.10	5.08	4.93	4.92	4.75	4.69	4.91	4.90	5.49
Na ₂ O	2.56	2.32	2.83	2.54	2.61	2.69	2.72	2.43	2.48	2.71
K ₂ O	2.82	2.89	2.75	2.73	2.76	2.73	2.83	2.68	2.82	2.34
P ₂ O ₅	nd	0.05	0.00	0.05	0.06	0.08	nd	nd	0.00	0.01
Cr ₂ O ₃	0.03	nd	0.06	0.08	0.00	0.04	0.01	0.03	nd	nd
Cl (ppm)	1415	1510	1049	1420	1326	1284	1249	1091	1207	1474
S (ppm)	78	332	188	290	60	119	80	31	51	535
H ₂ O (wt%)	0.47	0.34	0.71	0.93	0.59	na	na	0.76	0.29	0.80
Total	97.49	98.26	98.43	97.32	97.86	96.67	97.26	97.48	98.85	98.30
Hosting phenocryst	Opx	Opx	Opx	Opx	Pla	Pla	Pla	Cpx	Opx	Opx
Trace elements (ppm)										
Li	20.71	29.01	27.40	21.83	22.28	21.89	21.15	27.17	25.19	26.61
B	33.70	45.24	37.01	39.66	42.34	44.04	39.17	39.91	36.94	36.36
Sc	26.23	24.24	24.05	24.92	26.29	27.72	24.61	26.00	22.88	31.60
Ti	5767.32	4887.97	5715.15	5756.64	6862.57	7977.22	6270.83	6902.33	5736.15	8111.71
V	236.83	240.22	239.29	245.31	283.72	320.27	259.35	256.43	245.43	339.62
Cr	191.00	16.67	14.11	13.23	15.14	10.86	12.81	nd	9.00	10.13
Mn	998.72	751.46	764.38	766.38	725.74	792.03	745.75	792.46	709.15	971.42
Co	32.17	15.68	15.41	15.07	16.89	16.01	14.84	15.49	12.67	19.60
Ni	114.60	8.57	10.80	13.59	22.72	24.32	19.92	9.80	9.08	11.61
Cu	140.54	20.95	124.74	234.23	156.46	158.96	145.66	159.22	148.23	23.16
Zn	78.91	73.80	69.24	72.22	58.35	73.18	57.83	70.94	76.87	90.44
Ga	151.51	168.27	195.54	196.34	182.01	187.07	190.13	188.54	190.98	176.08
As	6.03	5.16	4.55	5.10	6.07	5.96	4.69	5.07	4.65	3.93
Se	nd	nd	nd	nd	0.02	nd	nd	nd	nd	nd
Rb	73.12	86.39	89.01	91.09	83.95	83.02	81.96	87.77	89.12	70.97
Sr	134.77	156.28	174.89	167.31	132.95	138.54	130.74	168.32	160.70	182.43
Mo	1.68	0.14	1.34	1.81	1.79	1.27	1.15	1.05	1.55	1.20
Ag	nd	nd	0.60	nd	nd	nd	nd	nd	nd	nd
Cd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Sn	2.45	3.37	nd	1.48	1.28	nd	nd	nd	nd	1.91
Sb	nd	nd	nd	0.40	0.53	0.54	0.36	0.72	nd	0.51
Ba	688.62	903.83	1046.31	1062.75	938.54	964.61	1020.52	1034.51	1004.46	942.68
Yb	1.76	2.64	2.66	3.10	2.73	3.79	3.26	3.33	2.60	3.85
W	0.79	1.99	1.26	1.07	1.68	2.52	1.73	1.58	2.51	0.89
Re	0.81	nd	0.33	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	0.15	nd	nd	nd	nd	0.24	nd	nd
Tl	0.47	0.25	0.35	0.37	nd	0.44	0.31	0.36	0.55	0.43
Pb	13.52	12.58	11.08	12.95	12.51	13.39	12.40	12.33	12.73	11.89
Bi	nd	0.31	nd	0.19	nd	0.09	nd	nd	nd	nd
U	1.34	2.16	2.02	1.85	2.19	2.30	1.56	1.63	1.69	1.69

Table A-2 (continued)

	WIDP4- Ctx16- IN01	WIDP4- Ctx16- IN02	WIDP4- Ctx14- IN01	WIDP4- Ctx14- IN03	WIDP4- Matrix glass	WIDP4- Matrix glass enclave	WIDP7- IN06	WIDP7- IN24	WIDP7- IN08	WIDP7- IN08b
Major elements (wt%)										
SiO ₂	64.31	61.45	64.95	65.12	61.44	61.73	67.61	67.38	69.55	71.38
TiO ₂	1.08	1.20	0.85	0.86	0.92	0.92	0.69	1.03	1.14	1.07
Al ₂ O ₃	14.33	14.39	13.84	13.78	15.15	14.77	15.03	16.93	15.81	15.99
FeO _t	6.35	8.40	6.05	5.99	5.89	5.13	1.55	3.80	1.24	1.57
MnO	0.10	0.16	0.09	0.09	0.09	0.11	0.03	0.04	0.04	0.03
MgO	1.81	2.44	1.96	1.75	2.91	2.39	0.29	0.40	0.20	0.36
CaO	4.91	6.34	4.69	4.74	6.32	6.20	2.87	4.79	2.78	3.05
Na ₂ O	2.88	2.58	3.12	2.97	4.56	5.62	2.61	3.68	2.96	3.34
K ₂ O	2.72	1.79	2.61	2.70	2.55	1.93	3.43	3.14	5.56	3.38
P ₂ O ₅	nd	nd	0.01	0.05	0.04	0.02	0.01	0.04	0.01	0.02
Cr ₂ O ₃	0.02	0.04	0.03	0.00	0.05	0.03	0.01	0.01	0.00	0.03
Cl (ppm)	1291	1154	1342	1619	1918	3659	1585	1189	1445	1499
S (ppm)	164	513	304	310	52	79	112	87	104	75
H ₂ O (wt%)	0.75	na	0.33	0.47	na	na	na	na	na	na
Total	98.64	98.95	98.37	98.23	100.09	99.23	94.31	101.39	99.48	100.37
Hosting phenocryst	Opx	Opx	Opx	Opx			Opx	Cpx	Opx	Opx
Trace elements (ppm)										
Li	27.40	29.16	26.62	26.22	32.58	na	12.25	16.13	44.56	25.91
B	40.59	29.67	41.09	40.46	34.51	na	19.24	0.21	48.27	49.31
Sc	25.11	37.24	23.69	23.66	31.33	na	49.23	8.06	14.11	23.26
Ti	6147.87	7708.03	5414.87	5529.71	5837.59	na	3701.14	533.94	6339.55	7321.92
V	235.98	370.24	228.25	237.53	248.98	na	253.34	6.12	172.09	258.08
Cr	26.41	0.05	16.05	5.80	89.25	na	660.53	nd	nd	nd
Mn	723.31	1104.02	721.67	707.23	873.79	na	2600.73	75.40	290.48	504.96
Co	31.41	21.20	15.02	14.41	20.99	na	73.15	2.58	0.36	6.29
Ni	9.38	13.69	13.53	10.46	31.10	na	292.00	nd	3.85	nd
Cu	214.32	9.33	72.70	53.65	81.44	na	24.46	3.72	21.26	130.44
Zn	63.17	94.74	61.96	67.20	66.22	na	145.59	14.54	22.46	31.09
Ga	182.19	145.66	200.67	202.01	155.96	na	95.73	77.77	212.98	256.44
As	4.52	3.67	5.05	4.26	4.11	na	1.53	nd	2.66	4.58
Se	1.86	nd	nd	nd	nd	na	nd	nd	nd	nd
Rb	86.13	59.31	92.47	87.90	71.50	na	39.87	4.36	116.80	105.93
Sr	157.31	206.56	165.35	160.56	177.18	na	80.07	427.98	205.30	229.30
Mo	1.57	1.09	1.93	1.45	1.22	na	0.66	1.41	1.16	1.17
Ag	nd	nd	nd	nd	0.34	na	nd	nd	nd	0.20
Cd	nd	nd	nd	nd	nd	na	nd	1.57	nd	nd
Sn	2.44	nd	nd	2.68	1.43	na	3.94	10.04	nd	nd
Sb	0.73	0.32	0.19	0.27	0.71	na	0.84	0.40	nd	nd
Ba	1006.28	794.40	1054.74	1047.37	822.11	na	489.98	277.18	1232.50	1375.07
Yb	2.70	3.15	2.61	2.46	2.82	na	1.65	nd	4.39	3.13
W	1.23	1.20	1.34	1.49	1.19	na	1.03	0.45	2.48	1.64
Re	nd	nd	nd	nd	nd	na	nd	nd	nd	nd
Au	nd	nd	nd	nd	0.19	na	nd	nd	nd	0.13
Tl	0.56	0.25	0.50	0.32	0.15	na	nd	nd	0.97	0.68
Pb	13.67	10.23	12.76	13.06	9.77	na	4.77	3.42	12.99	14.82
Bi	nd	nd	0.15	0.33	0.14	na	nd	0.74	0.14	nd
U	2.35	1.56	1.98	1.79	1.44	na	0.67	nd	2.64	2.88

Table A-2 (continued)

	WIDP7- IN13b	WIDP7- IN14b	WIDP7- IN15b	WIDP7- IN16	WIDP7- IN20	WIDP7- Matrix glass	WIDP3- IN01	WIDP3- IN02	WIDP3- IN04	WIDP3- IN05
Major elements (wt%)										
SiO ₂	70.96	70.82	71.00	71.55	70.81	64.36	65.41	66.12	65.39	65.14
TiO ₂	1.10	1.29	1.10	1.22	1.14	1.03	0.76	0.88	1.07	1.30
Al ₂ O ₃	15.59	15.89	15.52	15.49	15.77	15.47	14.09	13.65	13.81	13.85
FeO _t	1.33	1.34	1.35	1.38	1.22	5.54	6.64	6.16	6.54	7.08
MnO	0.03	0.04	0.05	0.04	0.04	0.07	0.09	0.08	0.10	0.10
MgO	0.10	0.17	0.15	0.15	0.15	2.18	1.11	1.35	1.23	1.47
CaO	1.82	2.84	2.32	2.40	2.62	5.98	4.61	4.64	5.12	5.09
Na ₂ O	3.35	3.07	3.09	2.95	3.04	3.39	2.34	2.40	1.67	1.16
K ₂ O	6.09	5.84	6.02	5.67	5.44	2.70	2.64	3.26	3.06	2.60
P ₂ O ₅	nd	nd	0.01	0.03	0.03	0.02	nd	0.03	0.01	0.00
Cr ₂ O ₃	0.01	0.01	0.01	0.01	0.01	0.05	0.03	0.02	nd	0.04
Cl (ppm)	1402	1519	1402	1371	1433	873	1531	1278	1165	1231
S (ppm)	93	196	135	105	220	50	359	299	81	290
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	100.53	101.48	100.77	101.03	100.43	100.88	97.91	98.72	98.11	97.98
Hosting phenocryst	Opx	Opx	Opx	Opx	Opx		Opx	Opx	Opx	Opx
Trace elements (ppm)										
Li	39.65	34.62	30.09	38.63	43.57	18.53	24.44	19.68	24.90	25.12
B	48.66	40.62	44.58	46.59	40.11	40.86	36.12	42.64	40.51	38.64
Sc	15.76	19.94	16.63	17.93	28.83	26.84	25.94	24.71	25.09	29.54
Ti	7884.00	7541.43	6560.22	7645.37	7776.43	6195.91	4241.34	5762.77	6393.22	7703.93
V	287.17	261.44	229.62	250.45	310.93	258.07	249.00	240.58	270.29	302.93
Cr	nd	80.10	nd	1.78	nd	39.37	20.87	26.76	22.20	20.01
Mn	308.38	814.66	382.33	356.45	891.82	772.56	698.76	644.10	724.28	761.12
Co	3.21	22.82	3.49	2.81	12.64	19.10	13.24	13.25	10.51	14.41
Ni	1.58	48.69	4.98	nd	10.04	34.30	4.74	4.19	2.90	1.19
Cu	91.61	292.13	126.64	71.38	77.76	14.35	169.98	68.53	85.54	77.08
Zn	43.12	77.70	41.07	25.59	43.55	63.81	60.74	68.03	74.74	69.96
Ga	226.28	222.19	281.60	253.63	191.03	171.57	180.72	209.51	181.59	193.13
As	5.11	5.79	6.65	6.99	3.48	4.15	4.20	6.57	4.68	4.37
Se	nd	nd	3.28	nd	nd	1.52	nd	nd	nd	3.42
Rb	174.77	160.79	201.87	156.50	107.37	85.48	72.04	98.15	95.54	79.35
Sr	201.23	209.60	182.85	199.98	195.37	178.29	225.47	148.03	163.00	182.58
Mo	1.55	1.32	1.16	2.25	0.17	1.00	0.59	1.30	1.07	1.39
Ag	nd	0.32	nd	nd	0.30	0.11	nd	0.57	nd	nd
Cd	nd	nd	nd	0.89	1.36	nd	nd	nd	nd	1.69
Sn	nd	0.08	1.84	5.05	nd	2.07	1.04	1.08	1.49	3.05
Sb	nd	0.54	nd	nd	nd	0.72	nd	0.04	nd	0.71
Ba	1217.14	1224.68	1665.69	1399.28	982.30	907.35	1001.56	980.71	961.83	996.42
Yb	2.81	2.20	2.86	2.63	5.83	2.85	4.02	2.07	2.38	4.09
W	1.18	2.08	2.26	1.81	1.85	1.25	0.92	2.03	2.53	1.57
Re	nd	nd	nd	nd	nd	nd	0.14	nd	nd	1.28
Au	nd	nd	nd	nd	nd	nd	nd	0.62	0.46	nd
Tl	1.84	1.15	1.49	1.18	1.95	0.52	0.77	0.67		0.37
Pb	22.62	16.43	17.95	12.92	12.44	10.20	13.41	19.54	14.31	14.17
Bi	nd	0.07	0.59	nd	nd	0.26	0.31	nd	0.21	nd
U	2.19	2.46	3.11	2.38	2.01	1.83	2.08	2.05	1.52	2.32

Table A-2 (continued)

	WIDP3- IN06	WIDP3- IN07	WIDP3- IN08	WIDP3- IN09	WIDP3- IN10	WIDP3- IN11	WIDP3- IN12	WIDP3- IN13	WIDP3- IN14	WIDP3- IN15
Major elements (wt%)										
SiO ₂	63.54	65.06	66.25	67.02	63.47	65.08	66.38	60.63	64.74	65.72
TiO ₂	1.17	0.94	1.05	1.11	1.17	1.09	1.07	2.27	1.14	1.12
Al ₂ O ₃	14.28	14.20	13.95	14.09	13.76	14.13	13.61	13.66	14.20	13.87
FeO _t	6.13	6.02	6.55	6.47	7.49	5.69	6.56	7.26	5.79	6.49
MnO	0.09	0.08	0.10	0.10	0.09	0.09	0.09	0.12	0.09	0.09
MgO	2.28	2.32	1.36	1.14	1.92	2.05	1.40	3.00	2.20	1.34
CaO	5.14	5.05	5.06	4.88	5.76	4.92	4.93	5.98	5.13	5.19
Na ₂ O	2.53	1.68	2.16	1.37	1.73	2.88	1.66	1.67	2.26	1.49
K ₂ O	3.05	3.19	2.95	2.88	2.31	2.84	2.77	2.57	2.75	2.53
P ₂ O ₅	0.04	0.01	0.02	0.04	0.01	0.00	0.04	0.51	0.01	nd
Cr ₂ O ₃	0.04	0.00	0.00	0.03	0.03	0.02	0.03	0.02	0.00	0.01
Cl (ppm)	1041	1150	1274	1220	1228	1022	1181	1398	963	1313
S (ppm)	81	80	69	89	296	76	111	123	32	63
H ₂ O (wt%)	na	na	na	na	na	na	na	na	na	na
Total	98.38	98.66	99.58	99.27	97.90	98.90	98.66	97.85	98.42	97.99
Hosting phenocryst	Pla	Pla	Opx	Opx	Opx	Pla	Opx	Pla	Pla	Opx
Trace elements (ppm)										
Li	24.28	31.06	28.34	17.46	23.43	24.90	25.49	17.56	20.46	24.47
B	39.58	36.67	41.88	43.78	35.66	43.24	38.13	43.78	42.69	37.83
Sc	27.22	24.98	26.28	26.74	27.37	22.74	25.51	47.93	24.80	25.46
Ti	6884.28	5650.00	6184.67	6837.40	6833.89	6375.33	6626.43	13271.3	6954.82	6674.72
V	280.09	245.95	275.34	282.95	302.57	234.71	267.24	481.23	270.83	271.02
Cr	23.28	8.14	1.72	4.28	19.78	14.04	3.06	21.80	16.83	18.93
Mn	776.96	781.14	754.37	675.10	831.25	742.36	715.22	909.11	721.84	774.46
Co	16.41	17.72	13.28	12.12	16.15	14.89	12.61	20.04	14.77	15.01
Ni	24.48	28.36	3.14	2.87	9.92	19.58	4.03	34.92	23.67	19.94
Cu	140.21	150.72	105.96	88.21	44.01	160.09	45.80	147.49	148.75	107.34
Zn	72.99	73.56	66.85	77.32	79.33	66.68	61.73	83.03	60.33	82.23
Ga	198.94	204.38	203.89	220.23	158.07	198.73	196.86	220.97	188.23	199.79
As	5.75	5.55	4.14	5.07	4.95	4.96	4.09	15.24	4.28	3.59
Se	nd	nd	nd	nd	nd	4.52	nd	2.72	nd	nd
Rb	86.35	89.77	88.11	100.91	68.02	86.93	90.31	66.30	82.52	86.03
Sr	152.03	142.71	164.26	174.80	178.73	150.22	154.36	193.04	149.10	158.34
Mo	1.23	1.68	1.50	1.12	1.10	1.20	1.06	5.91	0.96	1.35
Ag	0.37	nd	nd	nd	nd	nd	nd	nd	nd	nd
Cd	nd	nd	nd	nd	nd	1.48	nd	nd	nd	0.59
Sn	nd	nd	2.55	2.35	nd	1.68	1.17	nd	nd	1.53
Sb	0.80	0.84	0.26	0.48	0.73	0.53	0.28	0.72	1.29	0.67
Ba	980.63	1063.31	1053.13	1209.16	824.53	1080.40	1075.41	1164.17	1008.15	960.86
Yb	3.66	3.09	2.91	2.68	3.67	2.62	1.81	6.41	4.39	3.20
W	1.56	1.14	1.06	1.38	0.66	1.33	1.22	6.77	1.75	1.49
Re	nd	nd	nd	nd	nd	0.52	nd	nd	nd	nd
Au	nd	nd	nd	nd	nd	nd	nd	0.31	nd	nd
Tl	0.60	0.48	0.36	0.30	0.44	0.41	0.39	0.06	0.43	0.45
Pb	11.89	12.20	14.11	15.18	14.07	11.98	17.09	13.10	10.38	14.13
Bi	nd	0.21	nd	0.20	0.19	0.22	0.26	0.24	nd	0.23
U	2.20	2.01	2.28	2.70	2.34	1.86	1.75	8.53	1.92	1.91

Table A-2 (continued)

	WIDP3- IN16	WIDP3- IN17	WIDP3- IN18	WIDP3- IN19	WIDP3- IN21-R2	WIDP3- Ctx17- IN01	WIDP3- Ctx2- IN01	WIDP3- Ctx2- IN02	WIDP3_ Matrix glass
Major elements (wt%)									
SiO ₂	63.62	64.35	64.33	64.98	59.89	66.80	66.93	65.66	64.04
TiO ₂	1.35	1.16	1.21	1.19	1.34	1.12	0.95	0.94	1.04
Al ₂ O ₃	14.24	14.25	13.75	13.73	15.55	15.08	15.11	14.49	14.58
FeO _t	6.16	6.11	6.65	7.44	6.39	5.25	4.66	5.84	5.95
MnO	0.09	0.11	0.11	0.11	0.10	0.07	0.06	0.08	0.09
MgO	2.34	2.24	2.06	1.76	2.38	0.73	0.72	1.21	2.64
CaO	5.29	5.07	5.10	4.68	7.09	3.02	4.22	5.00	5.78
Na ₂ O	2.11	2.82	2.76	1.64	1.16	1.55	1.38	1.86	3.05
K ₂ O	2.76	2.77	2.54	2.49	3.51	3.58	3.06	2.98	2.63
P ₂ O ₅	0.08	0.03	0.05	0.01	0.70	0.05	nd	0.01	nd
Cr ₂ O ₃	0.03	nd	0.00	0.01	0.04	0.04	nd	nd	0.03
Cl (ppm)	1103	1057	1053	1173	4388	1671	1386	1365	1048
S (ppm)	97	89	112	183	559	129	162	139	47
H ₂ O (wt%)	na	na	na	na	na	0.94	0.42	0.34	na
Total	98.19	99.03	98.68	98.19	97.44	97.47	97.25	98.23	99.94
Hosting phenocryst	Pla	Pla	Cpx	Cpx	Ol	Opx	Opx	Opx	
Trace elements (ppm)									
Li	21.51	18.65	25.28	26.27	24.43	21.56	26.92	26.31	19.76
B	51.19	41.08	41.04	41.99	197.90	28.48	42.49	39.74	39.41
Sc	27.33	25.79	30.41	28.54	25.36	81.94	22.71	24.10	26.52
Ti	8223.73	6834.16	7478.77	7428.61	6519.01	7150.71	5631.52	5578.22	6267.02
V	332.98	259.00	291.60	282.39	268.18	484.08	242.89	243.49	249.91
Cr	19.28	16.85	23.40	11.24	2.81	408.32	2.99	20.19	54.35
Mn	810.53	733.39	880.39	829.42	1571.58	1569.99	648.90	713.84	771.71
Co	18.48	16.04	16.21	16.06	106.63	39.62	13.52	13.61	18.39
Ni	26.74	28.56	11.14	6.01	987.73	97.51	7.49	3.12	34.84
Cu	151.09	159.66	78.13	110.94	183.96	138.85	168.81	127.20	44.11
Zn	67.77	56.62	73.03	77.97	150.30	93.59	64.84	82.52	66.88
Ga	198.66	191.03	189.94	190.75	426.61	184.03	188.96	184.91	176.87
As	5.68	5.22	4.27	4.58	15.52	3.69	5.17	5.38	5.38
Se	nd	nd	nd	nd	nd	nd	nd	nd	2.60
Rb	76.24	80.46	81.73	88.47	141.19	59.06	94.36	83.77	84.81
Sr	144.94	132.18	168.23	158.79	240.03	140.93	157.96	159.65	168.24
Mo	2.10	1.25	1.20	0.98	10.21	1.97	2.03	2.01	1.53
Ag	nd	nd	nd	0.66	nd	0.62	nd	nd	nd
Cd	nd	nd	nd	nd	nd	0.65	nd	nd	nd
Sn	nd	3.58	1.61	nd	nd	2.65	nd	3.39	1.99
Sb	0.50	nd	0.69	0.64	3.32	nd	nd	0.14	0.75
Ba	1072.10	1073.17	979.15	1004.59	2304.92	1020.52	993.09	969.10	967.10
Yb	4.43	3.08	3.87	2.81	3.93	4.08	2.58	3.94	3.09
W	1.87	2.13	1.55	1.37	6.16	1.37	1.25	1.81	1.20
Re	nd	nd	nd	nd	nd	nd	nd	nd	nd
Au	nd	nd	nd	nd	nd	nd	nd	nd	nd
Tl	0.84	nd	0.24	0.25	nd	nd	0.88	0.01	0.33
Pb	13.07	11.50	13.67	15.22	25.80	12.72	11.71	13.33	11.44
Bi	0.15	0.11	0.30	0.11	nd	0.26	0.23	nd	0.20
U	2.35	2.13	1.82	2.20	8.84	2.11	2.00	2.15	1.79

Notes: na: Not analyzed. nd: Below detection limit. Pla: Plagioclase. Cpx: Clinopyroxene. Ol: Olivine. Opx: Orthopyroxene.

A.3 Cu-Fe sulphide composition maps

a) WIDP 13 _ 12-25 March 1977 _ Sulfide 2

b) WIDP 8 _ 27 July-3 August 1977 _ Sulfide 1

c) WIDP 8 _ 27 July-3 August 1977 _ Sulfide 3

Figure A-1: Cu-Fe sulphide composition maps 2. The reflected light image on top left corner shows the position of quantitative point analyses. The other images are composition maps acquired using WDS detectors and show the distribution of each species within the sulphide. a) Sulphide in plagioclase phenocryst from WIDP 13, March 1977. b) Sulphide in plagioclase phenocryst from WIDP 8, July-August 1977. c) Sulphide in plagioclase phenocryst from WIDP 8, July-August 1977.

a) WIDP 4 _ 19 Octobre 1977

b) WIDP 3 _ 27 July 2000 _ Sulfide 2

c) WIDP 3_ 27 July 2000 _ Sulfide 3

Figure A-2: Cu-Fe sulphide composition maps 3. The reflected light image on top left corner shows the position of quantitative point analyses. The other images are composition maps acquired using WDS detectors and show the distribution of each species within the sulphide. a) Sulphide in a melt inclusion hosted in an orthopyroxene phenocryst from WIDP 4, October 1993. b) Sulphide in a melt inclusion hosted in an orthopyroxene phenocryst from WIDP 3, July 2000. c) Sulphide in an orthopyroxene phenocryst from WIDP 3, July 2000.

A.4 Sediment core and sulfur globule compositions

Table A-3: Sediment cores composition, black and yellow sulfur globules composition.

	Core 1a-1	Core 1a-2	Core 1a-3	Core 1a-4	Core 1a-5	Core 1a-6	Sulfur globules yellow	Sulfur globules black
Date	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15
Na (ppm)	10061	4745	8280	4780	4380	5005	326.4	91.93
Ca	150820	172908	50801	35399	62259	53901	609.8	553.7
Mg	5401	2286	9352	3164	2603	3103	158.2	36.70
Al	12641	7197	28442	19739	19656	22098	268.3	82.83
Fe	6799	2914	17364	11693	11741	11946	442.1	20582
K	4235	2223	10338	6311	6479	7160	91.71	32.51
B	45.56	5.21	78.91	11.63	36.44	10.03	4.51	1.68
Rb	14.55	8.46	39.81	32.33	29.95	33.99	0.26	0.06
Sr	313.4	295.0	217.6	131.9	191.4	175.0	0.83	0.67
Zr	10.67	14.39	91.96	106.1	85.07	96.11	0.24	0.41
Mo	0.48	0.46	1.38	1.50	1.50	1.40	0.37	1.40
Ba	62.97	181.6	531.1	604.6	545.6	605.9	0.52	1.57
Tl	7.05	2.61	4.08	3.59	2.58	2.50	0.17	1.31
Pb	16.36	6.94	20.54	11.15	10.43	11.04	0.35	3.30
Bi	5.86	2.00	2.01	1.59	1.52	1.45	0.15	1.71
Sc	20.68	26.94	12.79	7.18	6.82	7.78	0.05	0.07
Ti	498.8	792.1	3468	4288	3365	3703	4.71	30.06
V	38.19	20.87	88.48	59.56	55.77	63.45	0.43	0.64
Cr	44.20	26.23	132.8	65.16	55.77	59.25	0.69	6.29
Mn	356.7	63.69	249.0	125.2	102.3	122.5	3.59	2.59
Co	3.17	1.45	8.31	6.05	5.27	5.31	0.20	27.14
Ni	9.38	4.86	25.36	15.75	13.56	12.73	0.34	62.20
Cu	14.56	7.34	31.86	80.00	34.51	36.52	0.79	98.97
Zn	24.74	8.43	17.17	10.44	10.52	11.78	0.51	1.37
Ga	2.64	1.41	6.64	4.59	4.53	4.99	0.03	0.03
As	47.83	31.89	26.74	21.98	17.73	18.14	na	345.0
Se	nd	nd	39.15	26.12	25.88	21.82	305.8	701.2
Ag (ppb)	263.1	140.2	817.7	975.5	764.6	1088	8.52	96.09
Cd	245.9	124.5	160.3	128.8	129.6	124.7	7.34	32.48
In	165.6	69.13	76.44	51.25	50.16	48.31	4.61	9.26
Sn	984.3	507.8	1057	929.1	920.6	904.9	138.0	96.71
Sb	2410	1067	2394	1768	1594	1713	151.3	315.3
Te	nd	nd	120.99	66.89	74.16	63.63	186982	128643
Sm	2692	2993	3350	1678	2285	2152	4.01	5.58
Yb	533.6	480.2	1345	732.7	771.0	848.1	5.92	3.27
W	360.2	460.8	1436	1482	1417	1228	103.7	145.6
Re	8.31	8.36	11.79	18.52	22.79	23.62	3.12	294.0
Au	19.62	36.94	124.5	158.7	192.7	167.3	9.99	124.4
Hg	21.91	nd	28.87	nd	nd	nd	nd	59.39

Table A-3 (continued)

	Core 1b- 1	Core 1b- 2	Core 1b- 3	Core 1b- 4	Core 1b- 5	Core 1b- 6	Core 1b- 7	Core 1b- 8
Date	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15	5/06/15
Na (ppm)	9516	6718	6866	5352	5308	3614	5780	4982
Ca	137766	157499	35770	164527	147374	39832	30364	24188
Mg	4795	3231	8137	2861	3072	3672	3000	3360
Al	13335	9455	24468	8339	7821	8227	31878	22850
Fe	6887	3833	14254	4004	4008	9792	15693	15226
K	4266	2878	2857	2637	2287	2757	2573	7269
B	27.37	86.93	125.63	49.65	18.80	12.27	85.58	nd
Rb	14.50	10.79	34.69	9.28	10.32	11.87	32.94	36.48
Sr	264.8	272.1	118.5	272.6	220.6	75.94	134.3	107.4
Zr	16.12	15.80	91.37	12.40	17.83	27.84	98.86	89.83
Mo	0.64	0.58	1.23	0.34	0.46	0.85	1.67	1.41
Ba	120.8	175.6	314.2	224.0	256.4	225.1	531.4	527.5
Tl	6.28	3.43	3.93	2.97	3.18	1.93	2.77	2.65
Pb	14.71	9.88	11.23	9.06	8.57	5.15	13.48	10.67
Bi	5.19	2.74	1.84	2.32	2.66	1.63	1.48	1.34
Sc	20.25	21.34	10.64	10.95	16.38	4.13	10.21	7.61
Ti	753.3	811.0	3171	572.0	904.4	1097	3651	3412
V	40.69	27.17	70.54	25.69	23.54	26.49	92.46	63.49
Cr	49.50	33.66	88.44	32.67	26.97	35.33	116.2	62.46
Mn	141.4	89.12	198.3	79.76	86.11	88.76	108.8	126.4
Co	3.48	1.77	6.72	1.75	1.83	6.54	7.58	6.38
Ni	10.33	5.81	20.34	5.46	5.23	17.12	18.08	16.13
Cu	17.16	8.98	35.49	8.08	8.85	27.47	43.68	38.49
Zn	24.11	12.32	18.81	9.07	9.78	7.43	11.63	12.05
Ga	2.90	1.90	5.10	1.94	1.56	1.72	7.07	4.97
As	52.26	33.60	16.70	17.78	19.26	138.4	17.71	45.67
Se	nd	nd	17.32	nd	nd	296.3	34.41	73.89
Ag (ppb)	180.6	236.3	829.9	127.9	166.5	225.8	892.5	734.7
Cd	229.1	162.5	144.7	108.4	123.5	66.46	125.5	115.8
In	148.4	92.32	65.45	77.02	90.73	43.25	55.24	46.58
Sn	977.6	706.2	989.0	570.7	573.3	484.1	805.5	902.3
Sb	2246	1540	2214	1354	1480	1016	1777	1655
Te	nd	nd	49.37	nd	nd	1229	67.78	244.9
Sm	2398	2538	1512	2502	2526	1025	1352	1178
Yb	478.2	442.2	860.3	381.2	448.6	378.7	655.9	668.8
W	495.2	448.8	1303	313.7	497.1	533.8	1275	1193
Re	9.91	5.88	14.09	4.45	8.58	29.62	30.52	19.13
Au	43.47	25.96	136.7	10.21	17.66	28.05	112.6	138.8
Hg	13.62	13.92	17.82	16.06	nd	nd	nd	nd

Table A-3 (continued)

	Core 1b-9	Core 2-1	Core 2-2	Core 2-3	Core 2-4	Core 2-5	Core 2-6	Core 2-7
Sampling date	5/06/15	23/12/15	23/12/15	23/12/15	23/12/15	23/12/15	23/12/15	23/12/15
Na (ppm)	5596	3525	2405	3332	1158	4107	4445	4568
Ca	35178	22008	16304	5193	1295	9618	30663	36802
Mg	4006	1842	1119	1708	531.1	2014	2232	2307
Al	24378	5785	4339	5300	1800	7666	11878	13498
Fe	13100	15594	21186	15167	11713	12825	8695	8569
K	7115	1570	1268	1411	625.7	1896	2953	3377
B	89.30	nd	nd	nd	nd	nd	nd	nd
Rb	33.05	6.08	5.83	5.92	2.08	10.62	20.45	24.83
Sr	131.2	285.0	315.3	213.0	52.08	313.1	492.1	548.2
Zr	91.10	22.04	20.74	19.93	5.11	30.79	56.74	69.51
Mo	1.36	1.15	1.25	1.24	0.60	1.11	1.13	1.23
Ba	508.4	300.8	283.1	252.3	102.3	479.0	563.6	919.1
Tl	2.32	3.10	2.83	3.11	1.30	3.48	3.81	4.11
Pb	10.52	5.43	4.77	5.16	2.00	5.31	5.29	5.52
Bi	1.30	3.01	2.63	2.83	1.44	2.98	2.39	2.27
Sc	8.66	2.48	1.89	2.36	0.80	3.19	4.81	5.32
Ti	3474	967.1	873.0	891.8	254.7	1515	3006	3707
V	70.05	17.60	13.00	16.01	5.56	21.24	31.91	36.11
Cr	71.99	23.28	17.14	21.49	9.01	24.61	29.02	30.23
Mn	143.4	64.00	43.41	60.09	20.18	78.83	105.7	117.4
Co	5.87	13.20	17.65	12.01	9.11	8.93	5.99	5.66
Ni	14.34	34.35	44.24	31.81	24.46	23.20	14.40	13.65
Cu	36.30	76.18	117.3	79.52	49.60	49.17	37.73	38.90
Zn	12.09	18.43	6.62	8.04	2.84	10.44	10.78	11.90
Ga	5.27	1.21	0.85	1.04	0.37	1.42	2.06	2.37
As	21.07	549.5	431.3	692.5	257.1	737.2	333.3	187.3
Se	29.61	540.4	558.9	534.5	709.8	424.1	169.3	84.27
Ag (ppb)	795.3	214.0	233.7	205.0	73.4	320.2	644.2	860.5
Cd	125.1	94.22	82.71	89.28	35.50	83.81	103.2	129.8
In	50.39	74.76	53.44	67.11	25.91	81.98	81.17	85.49
Sn	879.3	868.0	639.6	898.5	299.2	1093	8855	1557
Sb	1819	1211	1025	1161	397.3	1283	1753	2103
Te	147.5	52974	52724	49866	54683	40153	15100	7585
Sm	1338	599.2	704.7	481.9	141.2	752.1	1389	1493
Yb	700.5	248.2	243.5	250.8	82.2	375.7	659.8	766.2
W	1139	290.1	291.7	301.5	117.1	422.1	854.8	1034
Re	20.96	221.9	274.2	243.4	160.0	198.8	124.0	107.4
Au	99.38	22.99	34.06	46.55	11.86	25.54	31.92	41.42
Hg	nd	6.83	10.27	4.94	5.60	42.45	49.65	11.31

Table A-3 (continued)

	Core 2-8	Core 2-9	Core 2-10	Core 2-11	Core 2-12	Core 2-13
Sampling date	23/12/15	23/12/15	23/12/15	23/12/15	23/12/15	23/12/15
Na (ppm)	2883	4000	4498	3280	3552	3512
Ca	6238	6415	4224	2745	3116	8999
Mg	1721	2048	2153	1754	1892	1863
Al	12143	10280	16298	8560	9322	10833
Fe	11074	8988	12747	11471	8955	8984
K	3126	2546	4543	2106	2254	2499
B	nd	nd	nd	nd	nd	nd
Rb	24.36	17.33	30.35	15.43	16.32	18.46
Sr	156.6	232.6	147.5	239.6	229.5	186.0
Zr	60.16	48.15	66.64	42.17	40.33	43.64
Mo	0.98	1.27	1.07	1.27	1.12	1.25
Ba	435.6	619.6	384.6	1102	823.7	597.1
Tl	2.47	3.72	4.48	3.41	3.50	3.22
Pb	4.30	4.69	5.73	4.29	4.11	3.83
Bi	1.81	2.51	2.08	2.40	2.37	1.89
Sc	3.78	3.68	4.91	3.09	3.23	3.52
Ti	3130	2907	3269	2666	2738	3196
V	29.16	27.65	37.95	23.88	24.86	28.07
Cr	20.53	25.92	26.99	22.47	21.85	25.17
Mn	89.92	85.51	126.0	72.39	80.17	86.92
Co	7.67	6.72	9.72	8.67	6.86	6.17
Ni	19.25	17.06	24.48	22.28	16.61	14.98
Cu	42.03	38.39	54.41	46.29	45.22	47.88
Zn	9.56	9.18	12.35	8.74	8.24	9.27
Ga	2.11	1.74	2.88	1.53	1.57	1.77
As	101.7	465.5	86.11	344.2	310.8	238.2
Se	341.9	239.0	227.1	320.6	257.5	202.6
Ag (ppb)	777.0	654.8	965.3	587.0	593.2	696.7
Cd	98.95	104.3	125.5	103.2	89.26	89.17
In	53.17	79.57	64.36	67.30	71.48	62.81
Sn	2221	1238	1290	1211	1095	1106
Sb	1227	1695	1727	1472	1550	1622
Te	31452	23161	21514	31590	26600	16756
Sm	812.3	567.7	926.2	407.6	430.0	527.0
Yb	623.4	436.4	845.8	369.3	378.3	429.2
W	844.9	856.5	969.4	799.8	790.4	896.7
Re	119.8	157.3	106.2	193.5	145.0	123.9
Au	43.63	38.46	52.98	29.94	31.30	29.61
Hg	8.46	31.30	29.25	8.00	10.67	12.27

Notes: nd: Note determined.

Core 1a and 1b were collected on 5 June 2015. Core 2 was collected on 23 December 2015.

A.5 XRD diffractograms

Figure A-3: XRD diffractograms of ash and suspended particles.

Figure A-4: XRD diffractograms of sediment cores. Layer 1b-8 was analysed in the sediment core collected on 5 June 2015. Layer 2-6 was analysed in the sediment core collected on 23 December 2015.

Figure A-5: XRD diffractogram of Core 1b-1. Analysis performed at Callaghan Innovation, Lower Hutt, New Zealand.

A.6 Sediment core 1a collected on 5 June 2015

Figure A-6: Picture of one of the core sediments collected on 5 June 2015, Core 1a.

A.7 ICP-MS detection limit, accuracy and precision

Table A-4: ICP-MS detection limit (3 SD), secondary standards (SLRS-4, JB1, BIR-1) measurement values, errors (1 SD) and bias.

	DL (ng/g)	SLRS-4 CRM (µg/l)	MV (µg/l)	Bias (%)	JB1 CRM (µg/g)	MV (µg/g)	Bias (%)	BIR-1 CRM (µg/g)	MV (µg/g)	Bias (%)
B	0.84	5.95*	6.15 ± 0.67	3.3						
Na	1.66	2400 ± 200	3083 ± 1169	28.5	20393 ± 490	22048 ± 506	8.1	13591 ± 1632	14082	3.6
Ca	15.15	6200 ± 200	6309 ± 364.7	1.8	66681 ± 1144	63840 ± 1066	-4.3	94983 ± 429	126506 ± 98	33.2
Rb	0.006	1.53* ± 0.05	1.61 ± 0.14	5.5	39.8 ± 1.1	36.3 ± 0.9	-8.8	0.21 ± 0.0081	0.18 ± 0.03	-12.1
Sr	0.21	26.3 ± 3.2	27.39 ± 0.72	4.1	440.5 ± 5.9	409.3 ± 0.9	-7.1	108.6 ± 0.7	108.7 ± 0.4	0.1
Zr	0.001	0.12* ± 0.015	0.1 ± 0.01	-15.2	137.9 ± 4.3	130.3 ± 2.7	-5.5	14.8 ± 0.22	15.7 ± 0.7	6.3
Mo	0.006	0.21 ± 0.02	0.22 ± 0.02	6.3	31.6 ± 2.6	23 ± 1.6	-27.3	0.068 ± 0.021	0.49 ± 0.1	621.1
Ag	0.0004	0.035*	0.001 ± 0.0003	-96.8	0.049	1.1 ± 0.1	2148.5	0.041	0.006 ± 0.002	-84.3
Cd	0.002	0.012	0.014 ± 0.002	18.3	0.11	0.22	97.2	0.077 ± 0.017	0.067 ± 0.03	-12.5
In	0.0002				0.054 ± 0.007	0.049 ± 0.037	-9.3	0.0576 ± 0.0028	0.044 ± 0.008	-23.2
Sn	0.019	0.008-0.01*	0.013 ± 0.008		2	4.1 ± 3.4	103.4	0.701 ± 0.067	0.65 ± 0.06	-7.6
Sb	0.002	0.23 ± 0.04	0.28 ± 0.04	20.7	0.295 ± 0.027	0.31 ± 0.07	6.1	0.462 ± 0.032	0.45 ± 0.03	-2.1
Te	0.008	0.004*	0.008 ± 0.006	98.3	0.0018	2.9 ± 4	159735.4	0.0057 ± 0.0024	0.0003	-95.0
Ba	0.035	12.22 ± 0.6	13.33 ± 1.12	9.1	501.2 ± 7.2	445.3 ± 24.7	-11.2	6.75 ± 0.13	6.96 ± 0.67	3.1
Sm	0.0002	0.0574* ± 0.0028	0.059 ± 0.004	2.8	5.08 ± 0.1	4.7 ± 0.3	-7.7	1.113 ± 0.018	1.08 ± 0.02	-2.8
Yb	0.00004	0.012* ± 0.0004	0.013 ± 0.001	7.9	2.108 ± 0.052	2 ± 0.2	-6.5	1.631 ± 0.015	1.58 ± 0.1	-3.1
W	0.002	0.0133* ± 0.001	0.011 ± 0.004	-16.2	18	10.5 ± 0.8	-41.8	0.027 ± 0.015	1.27 ± 0.78	4585.4
Re	0.0001	0.0072*	0.007 ± 0.001	0.3	0.0038	0.01 ± 0.006	161.4	0.00065	0.001 ± 0.000004	85.1
Au	0.001	0.0009-0.00277*	0.009 ± 0.003		0.00079	0.96 ± 0.36	121317.8	0.0025	0.0001 ± 0.0001	-95.9
Hg	0.006	0.032-0.051*	0.022 ± 0.025		0.0299	0.23 ± 0.13	670.1	0.0073	0.001	-81.2
Tl	0.001	0.0068* ± 0.0013	0.008 ± 0.002	13.6	0.1	0.13 ± 0.09	31.7	0.0021 ± 0.0007	0.002	-18.5
Pb	0.001	0.086 ± 0.007	0.092 ± 0.011	6.4	7.13 ± 0.33	9.2 ± 1.5	29.4	3.037 ± 0.049	2.89 ± 0.11	-4.7
Bi	0.0001	0.0021* ± 0.0001	0.002 ± 0.0004	2.0	0.03	0.03 ± 0.009	0.2	0.0051 ± 0.0014	0.014 ± 0.009	168.9
Mg	0.22	1600 ± 100	1629 ± 172	1.8	47081 ± 531	57622 ± 537	22.4	58431 ± 314	59926 ± 1938	2.6

Table A-4 (continued)

	DL	SLRS-4			JB1			BIR-1		
	(ng/g)	CRM (µg/l)	MV (µg/l)	Bias (%)	CRM (µg/g)	MV (µg/g)	Bias (%)	CRM (µg/g)	MV (µg/g)	Bias (%)
Al	0.26	54 ± 4	57.59 ± 4.73	6.7	76899 ± 741	67679 ± 822	-12.0	82085 ± 370	85124	3.7
Sc	0.0002	0.0113* ± 0.0006	0.011 ± 0.002	1.3	27.3 ± 3.8	25.8 ± 0.4	-5.3	43.21 ± 0.59	43.7 ± 1.2	1.2
Ti	0.11	1.46* ± 0.08	1.33 ± 0.19	-9.1	7787 ± 126	7649 ± 74	-1.8	5747 ± 40	6033 ± 35	5.0
V	0.001	0.32 ± 0.03	0.35 ± 0.03	10.5	213 ± 13	201 ± 3	-5.5	320.6 ± 2.9	346.4 ± 1.4	8.0
Cr	0.013	0.33 ± 0.02	0.33 ± 0.03	1.2	430 ± 31	459 ± 4	6.8	392.9 ± 3.9	392.8 ± 5.9	0.0
Mn	0.030	3.37 ± 0.18	3.72 ± 0.29	10.4	1157 ± 45	1153 ± 55	-0.4	1341 ± 12	1420 ± 33	5.9
Fe	0.10	103 ± 5	105.2 ± 8	2.1	62880 ± 909	58152 ± 559	-7.5	79737 ± 350	83229 ± 2297	4.4
Co	0.001	0.033 ± 0.006	0.037 ± 0.003	12.5	37.8 ± 2.4	36 ± 1.2	-4.7	52.22 ± 0.57	53.7 ± 1.5	2.8
Ni	0.041	0.67 ± 0.08	0.74 ± 0.06	9.9	138.6 ± 5.9	133 ± 8	-3.7	168.9 ± 1.9	181.5 ± 8.1	7.5
Cu	0.006	1.81 ± 0.08	1.93 ± 0.13	6.4	54.9 ± 1.3	50.5 ± 3.6	-8.0	120.7 ± 1.6	132 ± 10	9.4
Zn	0.054	0.93 ± 0.1	1.58 ± 0.16	69.7	83.7 ± 5.4	89.8 ± 13.4	7.3	70.4 ± 1.1	75.5 ± 34.5	7.2
Ga	0.0003	0.0119* ± 0.0004	0.01 ± 0.001	-14.8	17.3 ± 1.8	17.4 ± 1	0.8	15.46 ± 0.23	16 ± 0.3	3.5
K	1.28	680 ± 20	708.3 ± 67	4.2	11788 ± 224	11181 ± 309	-5.2	241 ± 25	233.1 ± 62.4	-3.3
As	0.012	0.68 ± 0.06	0.81 ± 0.06	19.1	2.5 ± 0.5	2.1 ± 0.1	-14.4	0.17 ± 0.14	0.094 ± 0.066	-45.0
Se	0.15	0.23* ± 0.03	0.27 ± 0.11	19.0	0.02	1.4 ± 1.3	7144.1	0.019 ± 0.012	0.12 ± 0.16	545.4

Notes: DL: Detection Limit (3 standard deviations 1% HNO₃). CRM: Certified Reference Material. MV: Measured value and standard deviation. Bias: Deviation between the certified and measured values. * Compiled values.

A.8 Plume enrichment factors, rock compositions (White Island, Yasur, Etna)

Table A-5: Enrichment factors in the aerosol and rock composition for White Island, Yasur and Etna

	Enrichment factors					Rock composition ($\mu\text{g.g}^{-1}$)		
	White Island	White Island	White Island	Yasur	Etna	White Island	Yasur	Etna
	26/06/15	17/06/16	20/12/16	18/10/16	3/08/16	Andesite	Ash	Lava
B	214.2		325.5			25	39	na
Na		2.8	0.3	2.0	86.9	16988	23534	27100
Ca	3.1	5.8	2.0	2.0		57819	55131	74200
Rb	0.5	1.5	0.2	1.9	295.7	47	40	40
Sr	1.0	12.7				161	na	1270
Zr	0.4		1.6	0.7	2.2	98	107	210
Mo	204.7		160.5	28.1	971.6	1.0	3.0	3.7
Ag	281.5		1280.6	9.5	5.8	0.04	0.7	0.9
Cd	143.1	1410.0		1196.5	8175.8	0.05	0.12	0.9
In	41.3			4107.1		0.05	0.04	0.08
Sn	43.2					1.5	1.1	1.5
Sb	1063.6	13878.6	200.1	66.0	8382.7	0.19	0.19	0.12
Te	312451.2	1271470.7			8707.6	0.0011	-	1.9
Ba	0.4	7.6	1.2	1.0	5.5	510	531	680
Sm	0.4	1.5	1.8	0.9	2.5	2.4	4.7	9.2
Yb	0.2	1.0	0.6	0.9	3.6	2.0	2.6	1.3
W	269.5	1.5		29.9		1.3	0.33	1.0
Re	1044.9				298103.4	0.0012	-	0.0004
Au	62128.0		37709.7			0.0001	0.05	0.10
Tl	2372.6	11988.7	78.7	3830.8	253601.5	0.19	0.05	0.09
Pb	100.1	703.6	5.1	82.6	7369.7	7.7	11.8	8.0
Bi	382.2	449.1	47.8	2433.7	390531.2	0.76	0.02	0.02
Mg	0.1	0.6	0.1	3.7		48185	16284	30700
Al	1.0	1.0	1.0	1.0	1.0	69966	84172	96000
Sc	0.3	0.6	0.3	0.7	1.1	30	20	20
Ti	0.4	0.8	0.5	1.7	8.0	3657	4808	6300
V	0.4	1.4	0.1	0.9	10.4	211	254	305
Cr	23.6		40.7	0.7		356	27	32
Mn			0.2	0.8	0.5	929	1285	1000
Fe	0.4	0.5	0.1	0.9	3.9	56096	55783	77200
Co	0.2	1.5	0.2	0.9	26.1	32	19	30
Ni	0.4		3.1	2.7		114	17	54
Cu	4.4	17.6	9.1	16.5	2746.7	81	277	90
Zn	21.6	6847.4		7.4	2225.6	47	98	110
Ga	1.0	5.6	1.4	1.0	3.4	13	19	16
K	0.6	5.8	0.6	12.9	128.0	11871	3582	15400
As	855.7	7222.4	13.2	378.2	38502.5	4.8	2.9	1.0
Se	1524.9	74031.8		418.1	2159524.3	0.9*	0.9	0.05

White Island 1977 andesite (this study), Yasur ash (this study), Etna lava (Aiuppa et al., 2003)

*: Se value for White Island andesite from Wells (1967).

A.9 HSC input files

Table A-6: Gas composition in mol% used as input for HSC thermochemical modeling

Sample	Donald Mound ^a	F0	F0	F0	Yasur ^b	Kudriav ^b	White Island ^d
Date	Feb 1988	23 Dec 2014	5 Jun 2015	30 Sep 2015	Oct 2007	1995	Feb 1984
(°C)	495	160.7	160	174	na	984	772
$\log f_{\text{O}_2}$ (bar) ¹	-20.53	-53	-45.95	-44.07	na	-10.99	-13.18
ΔNNO^1	+2.56	-4.90	+2.25	+2.32	na	-0.52	+1.31
$\log f_{\text{O}_2}$ (bar) ²	-20.74	-48.72	-47.83	-39.48			
ΔNNO^2	+2.35	-0.62	+0.36	+6.91			
H ₂ O	94.44	92.22	89.18	85.47	97.17	94.79	94.50
CO ₂	4.00	6.18	8.78	12.34	1.50	1.72	3.85
SO ₂	0.59	0.074	0.82	1.47	0.83	1.83	0.86*
H ₂ S	0.17	0.35	0.24	0.12	4.16E-03	0.19	na
HCl	0.60	0.82	0.80	0.52	0.36	0.17	0.63
HF	9.80E-03	3.65E-04	1.42E-04	6.07E-04	0.097	0.075	0.03
NH ₃	na	8.37E-05	3.32E-05	1.85E-04	na	na	0.003
H ₂	0.025	0.32	0.10	5.3E-05	0.042	1.17	0.23
N ₂	0.017	0.033	0.077	0.084	na	na	0.02
CH ₄	4.60E-04	1.50E-03	8.96E-04	7.50E-04	na	8.15E-12	0.001
CO	1.50E-04	5.82E-03	2.48E-06	4.17E-06	na	0.033	0.004
HBr	na	4.91E-05	1.23E-04	2.37E-04	na	1.54E-04	na
Tl	6.62E-07	8.64E-11	9.11E-11	2.2E-09	8.82E-08	6.69E-07	6.50E-07
Pb	1.68E-06	9.05E-09	1.5E-08	2.4E-07	5.45E-07	6.76E-06	1.65E-06
Bi	6.48E-07	3.48E-09	5.82E-09	5.5E-08	3.07E-08	5.46E-07	6.36E-07
Fe	3.29E-05	2.11E-06	3.26E-07	2.2E-05	2.64E-05	1.52E-04	3.23E-05
Cu	9.13E-07	1.53E-07	1.37E-07	3.2E-06	1.27E-05	1.52E-06	8.97E-07
Zn	3.55E-05	1.48E-06	2.66E-07	8.4E-06	2.58E-06	3.46E-05	3.49E-05
As	6.97E-05	3.22E-06	3.01E-05	1.4E-05	1.94E-06	4.39E-05	6.84E-05

Note: na: Not analysed.

^a: From Tedesco & Toutain, 1991

^b: Major elements from Metrich et al., 2011, trace metals from our filter pack study

^c: From Wahrenberg et al., 2002

^d: Major elements from Giggenbach & Sheppard, 1989, trace metals from Tedesco & Toutain, 1991

*: sulfur total

¹: f_{O_2} calculated from CO/CO₂

²: f_{O_2} calculated from H₂/H₂O