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Arc Crust-Magma Interaction in the Andean Southern Volcanic Zone from Thermobarometry, Mineral Composition, Radiogenic Isotope and Rare Earth Element Systematics of the Azufre-Planchon-Peteroa Volcanic Complex, Chile

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

ARC CRUST-MAGMA INTERACTION IN THE ANDEAN SOUTHERN VOLCANIC ZONE
FROM THERMOBAROMETRY, MINERAL COMPOSITION, RADIOGENIC ISOTOPE AND
RARE EARTH ELEMENT SYSTEMATICS OF THE AZUFRE-PLANCHON-PETEROA
VOLCANIC COMPLEX, CHILE

A dissertation submitted in partial fulfillment of the

requirements for the degree of

DOCTOR OF PHILOSOPHY

in

GEOSCIENCES

by

Sven Paul Holbik

2014

To: Interim Dean Michael R. Heithaus
College of Arts and Sciences

This dissertation, written by Sven Paul Holbik and entitled, Arc Crust-Magma Interaction in the Andean Southern Volcanic Zone from Thermobarometry, Mineral Composition, Radiogenic Isotope and Rare Earth Element Systematics of the Azufre-Planchon-Peteroa Volcanic Complex, Chile, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this dissertation and recommend that it be approved.

-

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The dissertation of Sven Paul Holbik is approved.

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Florida International University, 2014

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DEDICATION

I dedicate this dissertation to my wife Annie Palya, to my parents Sigrid Bataille and Goffredo Holbik and family and friends who offered support and encouragement. This work would not have been possible without their patience, love, support and inspiration.

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ABSTRACT OF THE DISSERTATION

ARC CRUST-MAGMA INTERACTION FROM MINERAL COMPOSITION, RADIOGENIC AND RARE EARTH ELEMENT SYSTEMATICS OF THE AZUFRE-PLANCHON-PETEROA VOLCANIC COMPLEX, CHILE

By

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Florida International University, 2014

Miami, Florida

Professor Rosemary Hickey-Vargas, Major Professor

The Andean Southern Volcanic Zone (SVZ) is a vast and complex continental arc that has been studied extensively to provide an understanding of arc-magma genesis, the origin and chemical evolution of the continental crust, and geochemical compositions of volcanic products. The present study focuses on distinguishing the magma/sub-arc crustal interaction of eruptive products from the Azufre-Planchon-Peteroa (APP 35°15'S) volcanic center and other major centers in the Central SVZ (CSVZ 37°S - 42°S), Transitional SVZ (TSVZ 34.3-37.0°S), and Northern SVZ (NSVZ 33°S - 34°30'S). New Hf and Nd isotopic and trace element data for SVZ centers are consistent with former studies that these magmas experienced variable depths of crystal fractionation, and that crustal assimilation is restricted to the lower crustal depths with an apparent role of garnet. Thermobarometric calculations applied to magma compositions constrain the depth of magma separation from mantle sources in all segments of the SVZ to <60 km thus out of the predicted stability range of garnet in mantle peridotite (70-90 km). Magmatic separation at the APP complex occurs at an average depth of ~50 km which is confined to the mantle lithosphere and the base of the crust suggesting localized thermal abrasion both reservoirs. Thermobarometric calculations indicate that CSVZ primary magmas arise from a similar average

depth of (~54 km) which confines magma separation to the asthenospheric mantle. The northwards along-arc Sr-Nd-Hf isotopic data and LREE enrichment accompanied with HREE depletion of SVZ mafic magmas correlates well with northward increasing crustal thickness and decreasing primary melt separation from mantle source regions indicating an increased involvement of lower crustal components in SVZ magma petrogenesis.

The study concludes that the development of mature subduction zones over millions of years of continuous magmatism requires that mafic arc derived melts stagnate at lower crustal levels due to density similarities and emplace at lower crustal depths. Basaltic underplating creates localized hot zone environments below major magmatic centers. These regions of high temperature/partial melting, and equilibration with underplated mafic rocks provides the mechanism that controls trace element and isotopic variability of primary magmas of the TSVZ and NSVZ from their baseline CSVZ-like precursors.

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1. INTRODUCTION

Subduction zones are areas at convergent boundaries where dense lithospheric plates plunge into the hot and structurally weak asthenospheric mantle as a result of converging on a buoyant lithospheric plate. The driving force for the motion of the large scale form of crust-mantle recycling is the negative buoyancy of the dense lithospheric plate (Carlson et al. 1983; Stern 2004). The crustal features produced as a result of subduction zones are the trench, the forearc with or without an accretionary wedge, the volcanic arc where most subduction volcanism occurs, and the back arc region which is mostly associated with local faulting, extension and magmatism (Stern, 1991). Oceanic and continental magmatic arcs are the two principal types of arcs found at convergent plate boundaries. Oceanic arcs involve two oceanic lithospheric plates converging and forming volcanic island arcs. Continental magmatic arcs are defined as an oceanic lithospheric plate converging and subducting underneath continental lithosphere. The processes of magma generation in these environments is similar, however, continental arc magmas evolve through interaction with the thick overlying continental crust.

Magma genesis and subsequent magma-crust interaction in continental arcs is exceptionally complicated and includes processes such as the release of fluid during dehydration reactions, assimilation of diverse continental lithologies, and various petrologic differentiation processes. Unraveling these intricate magma histories is essential to understanding and modeling the chemical evolution of subduction volcanism and determining the chemical makeup of the continental crust. Recognizing the sources that contribute to subduction zone magmas can also serve as a proxy on how continental arc crust changes over time. For example, magmas generated at subduction zones are enriched in K, Rb, and Cs relative to Nb, Ta, Zr and Hf when compared to magmas generated at mid-ocean ridges (Stern 2004). Geochemical data like these provide useful insights and link to processes at work in subduction zones.

The southern Andean continental arc is a prime example of just how complex the interactions of ascending magma with the continental crust can be in subduction zone settings. The Southern Volcanic Zone (SVZ: 33-46°S) spans approximately 1,450 km and is the result of the subduction of the Nazca oceanic plate beneath the continental part of the South American plate. The Southern Volcanic Zone records along-arc differences in evolved magma compositions, geochemical trends, and variable proportions of erupted mafic and silicic magmas at volcanic centers. Continental crust thickness varies in the SVZ, which correlates with different internal magmatic domains referred to as the Northern SVZ (NSVZ), the Transitional SVZ (TSVZ), the Central SVZ (CSVZ), and the Southern SVZ (SSVZ) (Figures 2.3 and 2.4; Tormey et al. 1991; Lopez-Escobar et al. 1995; Stern 2004). The Pleistocene and Holocene volcanoes of the southern Chilean Andes provide a unique natural laboratory for the study of the mechanisms of volcanism, magma genesis, and the interaction of magma with the continental lithosphere. Recent advances in this field focus on how elements are transported from the subducting crust to the mantle source via dehydration and possible sediment melting, and how these hydrous fluids and melts ultimately leave their source regions to crustal regions. Current work of subduction volcanism view the source of magma generation as melting of mantle wedge peridotite metasomatized by fluids and/or melts from the subducted ocean crust and sediments present. In addition to these sources the SVZ magmas may have also been modified during their ascent through the continental crust from processes like crustal fractionation, melting, assimilation, storage and homogenization as described by Hildreth and Moorbath (1988). Numerous studies have sought to explain and quantify magmatic inputs from subduction zone, mantle wedge, lower and upper continental crust in the SVZ (Stern, 1991; Kay et al. 2005; Hickey et al., 1986; Hildreth and Moorbath 1998; Tormey et al., 1991; Dungan et al. 2001; Hickey-Vargas et al.

1989; 2002; Jacques et al. 2013; Dungan and Davidson 2004). Nonetheless, many aspects of the magmatic diversity present in the SVZ remain incompletely understood.

The goal of the present research is to address some unanswered questions, and to test existing hypotheses about the origin of magma in continental arcs, using the unique aspects of the SVZ including its chemical diversity. The current study focuses on one volcanic center, the Azufre-Planchon-Peteroa (APP) volcanic center located in the Transitional SVZ, with the purpose of defining the processes that create the broad chemical trends present in the SVZ, and continental arcs generally. Some outstanding questions include:

- 1. To what degree and how has the continental crust changed the chemical composition of primary magmas generated at continental convergent margins?*

Magmas generated in the mantle wedge at convergent margin subduction zones must pass through a thick layer of sialic and incompatible element enriched crust before it reaches the surface, thus the potential for crustal contamination of these rising parental magmas is great. The low density of the sialic upper crust may act as a density filter and significantly impede the upward movement of mafic to intermediate magmas resulting in assimilation of crustal materials and/or differentiation at variable crustal depths. Additionally, the melting point of continental crust may be low enough to be partially melted by the increase in heat associated with subduction magmatism which would alter the chemical composition of mafic magmas. Studies have envisioned the process of crustal contributions to mafic subduction magmas deep beneath large magmatic centers as a zone of melting, assimilation, storage and homogenization (MASH) (Hildreth and Moorbath 1988), whereas others have called upon intracrustal assimilation to produce greater geochemical variability (Hickey-Vargas et al. 2002; Dungan et al. 2001; Dungan and Davidson 2004). In the lowermost crust-mantle

transition, the neutrally buoyant basaltic magmas may induce local melting, assimilate and extensively mix then fractionate to a degree necessary for continued ascent.

Alternatively, others have suggested that basaltic magmas generated at the Chilean convergent margin may contain sediment and upper plate lithospheric remnants pulled into the source region via subduction erosion (Stern 1991; Kay et al. 2005). Here the subducting Nazca plate, in its descent towards the mantle, scrapes slivers of continental crust and delivers these eroded features to mantle source regions. These processes are reflected by the chemical variation exhibited by erupted products along the volcanic arc in the SVZ and could possibly be differentiated with further study.

2. *Can assimilation of upper and lower crustal sources be distinguished in mafic magmas at convergent margins?*

The continental crustal reservoir consists of two main layers; the upper and lower crust and can be distinguished by their P-wave velocities from less than or greater than 6.5 km/s, respectively (Wedepohl, 1995; Rudnick and Fountain 1995). This interface most often occurs at ~ 20 km of depth; however, the upper crustal thickness is more variable and the interface depth may range from 20 km to 50 km. The standard profile for the upper continental crust (total thickness ~ 21 km) is divided into thin (~3 km) layer of sedimentary rocks (shales, siltstones, sandstones, volcanics, carbonates) on top of a much thicker ~ 18 km layer composed of felsic intrusives, gabbros, and low to medium grade metamorphic rocks (Wedepohl 1995; Taylor and McLennan 1985). The lower crust in a standard profile is ~ 20 km thick and is separated into an upper layer of felsic granulites (~ 12 km) and a ~ 8 km lower layer of mafic granulites (Wedepohl 1995; Taylor and McLennan 1985). Major, trace, and isotopic compositions of the upper as

compared to the lower crust vary significantly. For example, the upper crust is enriched in volatile compounds and highly incompatible elements like K, Rb, U, Cs, B, Th, Na and is composed of highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$, high $^{18}\text{O}/^{16}\text{O}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios. The extent of ^{18}O enrichment can vary but upper crustal rocks have $\delta^{18}\text{O}$ ‰ values ranging from 10 to 35 ‰ and are a result of low temperature isotope fractionation between surface water and rock-forming minerals producing ^{18}O enrichment (Harmon and Hoefs 1984). Contrastingly, the lower crustal reservoir has low $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios (0.702 to 0.705), MORB-like $\delta^{18}\text{O}$ values of $5.7 \pm 0.5\text{‰}$, and higher $^{143}\text{Nd}/^{144}\text{Nd}$ (Harmon and Hoeffs, 1984; Rollinson, 1993).

On the basis of the geochemistry of upper and lower crustal lithologies, the lower crust is believed to be residue left after melt extraction of granodioritic upper crust along with additions of underplating basaltic magmas (Taylor and McLennan, 1995). Basaltic underplating at convergent margins has been proposed as a mechanism for the growth of continental crust (Kempton and Harmon, 1992) and also a major process for crust building in oceanic arcs (Tatsumi et al., 2008). Convergent arc magmatic environments are ideal environments for basalt magma genesis and emplacement at lower levels of continental crust. If arc derived magma has significantly incorporated any of these crustal reservoirs, it will be apparent in the isotopic signatures and chemistry of the magma which crustal reservoir was dominantly involved.

3. *How and to what extent does complex multi-level poly-baric crystallization and fractionation affect chemical trends of basaltic magmas at convergent margins?*

Continental arc magmatism is a complex tectonic and petrologic system consisting of multi-source and multi-stage processes. The magmatism has its principal

origins from partial melts of peridotite mantle producing olivine tholeiitic basalts. These melts rarely transit directly to the surface but rather are impeded by the lower density thick continental crust above. As these primary melts stagnate and pond at depth they will likely undergo extensive fractional crystallization. Fractional crystallization of olivine and augite (without plagioclase) of H₂O rich magmas at depth can produce low Mg and high-alumina basalts which are typical in subduction zone magmas (Sisson and Grove, 1993; Kay and Kay, 1994). High alumina basalts (>17 wt. % Al₂O₃) therefore may not be primary but derivative of tholeiitic magma undergoing a degree of fractional crystallization. Other phases like amphibole can result in crystallization at intermediate crustal depths and high water contents (Wallace, 2005; Fischer and Marty, 2005). Amphibole has a limited stability range it is often resorbed quickly near the surface of the earth prior to eruption and not found in the resultant rocks (Rutherford and Hill, 1993). However, fractionation of “cryptic” amphibole can impart controls on the chemical evolution of magmas (Davidson et al. 2007). The continued rise of these hydrous basalts to lower pressures leads to more crystallization, volatile loss, and emplacement in shallow magma chambers. In these lower pressure environments fractionation of magnetite, Cr-spinel, and anorthitic plagioclase and/or hornblende may take place producing the calc-alkaline trend. It is clear that fractional crystallization takes place at a number of levels and evidence of this may be recorded in the character and composition of the phenocryst “cargo” these magmatic liquids carry. High pressure crystallizing phases or even xenocrysts may be present as remnants or vestiges and may provide insight on depth, temperature, oxygen fugacity, H₂O composition, of early magmatic environments. Detailed information on these phases can discern the processes involved in the evolution of magmatic compositions in convergent margins.

4. *What processes are involved and to what extent does the asthenospheric mantle melt to produce the magmas at convergent margins?*

The melting process in subduction zones is triggered by the release of fluids and melts from hydrous phases (flux melting) from the down going slab into the asthenospheric mantle wedge (Ulmer 2001; Pearce and Peate 1995). In some unique cases direct melting of the altered ocean crust is possible and are only found in situations where young (< 25 Ma) oceanic lithosphere is being subducted creating a thermal regime hot enough for slab melting (Peacock 1990). The resultant arc magmas produced are high in Na, Al, and have high La/Yb and Sr/Y ratios which have been named adakites (Kay et al. 1978). However, the majority of melts generated at subduction zones are not adakitic and are magmas with enriched K, Rb, and Cs relative to Nb, Ta, Zr and Hf. The unique geochemical signature is the result of the breakdown of hydrous minerals in the subducting lithosphere such as amphibole, chlorite, lawsonite, serpentine, and zoisite at pressures of ~ 2 GPa then subsequent partial melting of the metasomatized mantle wedge (Peacock, 1990; Arculus, 1994). The extent of the partial melting can vary depending on the amount of hydrous fluids added to the mantle wedge, for example, large extents of melting require a larger input of fluids and lead to voluminous magma generation. Smaller extents of melting lead to less voluminous magma production and more enriched melts assuming melting of the same mantle source (Carr et al. 1990). Additionally, studies suggest that sediments subducted to these depths may undergo melting rather than just dehydration of fluid phases which adds another level of complexity to basalt magma generation at subduction zones (Johnson and Plank, 2000).

The purpose of the project is to investigate, compare and distinguish mantle, lower and upper crustal geochemical fingerprints in a well-characterized suite of rocks from a volcanic

center in the section of the SVZ where lower crustal influences have been hypothesized and delineated by several researchers (Hildreth and Moorbath, 1988; Tormey et al. 1991; Tormey et al. 1995; Dungan et al., 2001; Davidson et al. 1987, 1988; Jacques et al. 2013). To approach the hypothesis I will use: 1) detailed mineral/phenocryst chemistry; 2) major and trace element modeling; and 3) radiogenic isotopic systems in bulk rock samples from the APP center in comparison with published data for the NSVZ, TSVZ and SSVZ. Chapter 2 of the dissertation lays out the geologic and petrologic background of SVZ subduction related magmatism, detailed information and prior work about the Transitional SVZ, and on the APP volcanic center. A summary of specific questions and hypotheses to be tested are given in the final section of Chapter 2. Chapters 3, 4, 5 and 6 describe tests of those hypotheses using mineral chemistry, bulk rock major element geochemistry; trace element geochemistry, and radiogenic isotope geochemistry, respectively. Chapter 7 is a synthesis of results and conclusions.

2. BACKGROUND

2.1 Subduction Volcanism

Subduction is a geologic process that exclusively takes place at convergent boundaries of lithospheric plates. Excess density of the sinking oceanic lithosphere provides enough force to move plates and induce mantle downwellings. When two lithospheric plates converge the dense plate subducts and slides beneath the buoyant plate. It is overwhelmingly understood that subduction of the mechanically stronger lithospheric plate (slab) plays a critical role in driving the motion of tectonic plates because of its negative buoyancy (Forsyth and Uyeda, 1975; Carlson et al., 1983). In the subduction medium; sediment, ocean crust and mantle lithosphere return to the Earth's mantle to re-equilibrate (Stern 2004). The cold down-going oceanic plate encourages mantle convection of the overlying mantle wedge pulling the asthenospheric mantle towards it. At approximately 100 km, water from hydrous minerals in the down-going plate are released from the sinking slab as it heats up and interacts with the mantle wedge by depressing the mantle solidus and induces partial melting (Stolper and Newman, 1994; Kelly et al. 2006; Ulmer 2001). These melts buoyantly pass through the overriding mantle wedge and the leading edge of the continental or oceanic lithosphere to erupt at the surface of the Earth or remain stagnated in the crust as a plutonic body. This process is reflected geochemically in the arc lavas by showing significant enrichments in large ion lithophile elements (LILE), such as Rb, Cs, K, Sr, and Ba compared to high field strength elements (HFSE) such as Zr, Nb, Hf, and Ta, and distinguishes subduction zone geochemical signatures from mid ocean ridge and ocean island volcanics (Perfit et al. 1980). Large ion lithophile elements (LILE) are defined as elements characterized by a small charge to ionic radius ratio (mostly because of large ionic radii) making these elements highly incompatible meaning it is an unsuitable fit in cation sites of minerals and concentrate instead into melt phases. High field strength elements (HFSE) are also highly incompatible;

however, due to their large ionic valences (high charge). Igneous activity at subduction zones is responsible for creating island arcs which are a chain of volcanic islands situated parallel to the boundary of two converging plates, many ore deposits and the continental crust. The subduction process is the main source of magmatic activity and creation of volcanic terrain at convergent boundaries as well as introducing lithospheric materials into the mantle.

2.2 Andean Volcanism

Andean volcanism stretches over 4,000 km along the west coast of the South American continent and is divided into the Northern Volcanic Zone (5°N - 2°S), Central Volcanic Zone (16°S - 28°S), Southern Volcanic Zone (33°S - 46°S), and Austral Volcanic Zone (49°S - 55°S) (Figure 2.1). In these four regions there are over 200 Pleistocene and Holocene arc volcanoes. These volcanic zones are demarked by physiographic features on the Nazca oceanic plate. The Northern Volcanic Zone (NVZ) begins from the Cordillera Central area of Colombia and extends to its southern edge at the Carnegie Ridge. The Central Volcanic Zone (CVZ) is located between the Nazca ridge and the volcanic oceanic islands of the Juan Fernandez Ridge. The Southern Volcanic Zone (SVZ) is bounded by the Juan Fernandez Ridge at its northern edge and the Chile Rise to the south and the Austral Volcanic Zone (AVZ) is just south of the Chile Rise. Volcanism in the Andes is the result of the subduction of the Nazca and Antarctic oceanic plates beneath the South American continental plate (Figure 2.2). The Antarctic plate is being subducted south of 48°S at approximately 2-3_{cm/yr} and is responsible for the volcanism at the AVZ (Minster et al., 1974; Stern 2004). The Nazca plate's motion is oblique (c. 20-30°; Jarrard 1986; Dewey & Lamb 1992) in a northeast direction and is subducting underneath the South American plate at approximately 7-9_{cm/yr} (DeMets *et al.* 1990). The approximate age of the Nazca oceanic plate at the trench varies from 12 Ma to 20 Ma in the NVZ, 60 Ma to 45 Ma in the CVZ, and 45 Ma to 0 Ma in the SVZ (Figure 2.2 & 2.3). The age of the subducting Antarctic Plate beneath the South American Plate ranges from 6 Ma to 24 Ma (Figure 2.2 & 2.3). The

volcanism in the CVZ and the SVZ correspond to relatively steep subduction angles (defined by Wadati-Benioff zone; $>25^\circ$) at depth of $> 90\text{km}$ of the Nazca oceanic plate.

The CVZ and the SVZ are separated by the Pampean flat-slab segment ($28\text{-}33^\circ\text{S}$) in which the subduction angle of the down going Nazca oceanic plate is $< 10^\circ$ at depths $> 90\text{km}$. The NVZ and CVZ are also separated by shallow dipping portion of the down going slab known as the Peruvian flat-slab segment ($3\text{-}15^\circ\text{S}$). As a result of the shallow subduction angle these segments of the Andean arc are devoid of volcanic activity. Worldwide shallow inactive subduction arcs are associated with subduction of thickened ocean crust (seamounts or oceanic plateaux) and/or with the subduction of ocean ridges. The subduction of the Juan Fernandez Ridge and the Nazca Ridge are thought to cause the volcanic inactivity of the Pampean and Peruvian flat-slab segments (Kirby et al. 1996; Gutscher et al. 2000; Yañez et al. 2001, 2002). The Patagonian volcanic gap ($46\text{-}49^\circ\text{S}$) separates the SVZ from the AVZ and its volcanic inactivity can be attributed by the subduction of the Chile Rise. The varying ages of the Nazca plate and local regional tectonic settings lead to varying buoyancies of the subducting plate thus creating the subducting slope variability along the entire arc. The presence of asthenospheric mantle below an active arc plays a pivotal role in the synthesis and evolution of active arcs because of the observation that regions of the arc where the subducting slab angle is low coincides with the absence of volcanism and asthenospheric mantle between the subducting slab and overriding lithospheric plate (Thorpe et al., 1981).

Figure 2.1: Terrain map of the four active volcanic zones of South America. All volcanic centers referenced in this study are found in the Southern Volcanic Zone (33°S - 46°S).

Figure 2.2: Schematic map of the four active volcanic zones in South America. Benioff zone locations are contoured by depth in kilometers, convergence directions and rates of the subducting ocean plates are given in cm/yr. The approximate ages of the ocean plates are also indicated on the diagram adopted from Stern (2004).

Figure 2.3: Schematic diagram of the locations of some of the major volcanic centers and large caldera systems in the Southern Volcanic Zone. The ages of the subducting Nazca plate are shown in more detail along with the locations of major fracture zones. The north-south dashed line labeled “NOFS” is the Liqueine-Ofqui Fault System. This diagram was adopted from Stern (1990).

2.3 The Southern Volcanic Zone

The volcanoes of the SVZ are located along a 1,400 km long continuous arc segment from 33.3° to 46°S in both Argentina and Chile and comprise > 70 Pleistocene and Holocene composite stratovolcanoes, large volcanic fields, at least nine caldera complexes, and hundreds of minor eruptive centers (Moreno et al. 2007). The axis of the Holocene volcanic front is located at approximately 280km from the Chile-Peru trench and has an average width of 40km although at 39°S the volcanic front widens to around 80km (Moreno et al. 2007). Researchers divide the SVZ into the Northern SVZ or NSVZ (33°S - 34°30'S), the Transitional SVZ or TSVZ (34°30'S - 37°S), the Central SVZ or CSVZ (37°S - 42°S), and the Southern SVZ or SSVZ (42°S - 46°S; Figure 2.3 & 2.4) (Tormey et al. 1991; Lopez Escobar et al. 1995; Stern 2004). The NSVZ is a narrow chain of volcanoes where the down going Nazca plate is approximately 45 Ma and is subducting at an angle of 20°. The volcanic arc widens to approximately > 200km from 34.4°S to 39.5°S and the subduction angle increases to > 25° (Figure 2.3 & 2.4). As a result the distance of the volcanic front from the trench decreases from > 290km in the north end to < 270km in the south. The decrease in distance has caused the location of the volcanoes in the northern end of the SVZ to be along the Andes continental drainage divide at high basal elevations. To the south the volcanoes are predominantly found on the western margin of the Andean Cordillera closer to the Central Valley region, which is an extensional basin of beginning to late Oligocene age (Charrier et al. 2002). The crustal thickness in the SVZ also varies from 55-60 km in the NSVZ to < 35km in the CSVZ and SSVZ (Tassara & Yanez, 2003; Tassara, 2006; Figure 2.6 & 4.13). The crust below the SVZ segment mainly consists of Paleozoic pre-Andean basement and Mesozoic-Cenozoic igneous rocks (Stern 2004). In the southern segment of the SVZ oblique (20 to 30°) convergence causes slip parallel to the active arc creating the Liquine-Ofqui Fault System (LOFS in Figure 2.3 & 2.5; Lavenu & Cembrano 1999; Cembrano *et al.* 2000). The LOFS fault

system largely controls the locations of many larger volcanic centers as well as small eruptive centers (Lopez-Escobar *et al.* 1995). The northern end of the SVZ (33.3-34° S) experiences crustal shortening and there is only minor slip on arc-parallel faults (Dewey & Lamb 1992). The area including the TSVZ of (34-39°S) is the widest portion of the entire southern volcanic arc and the locations of the stratovolcanoes and calderas are controlled largely by NW-SE and NE-SW fault structures.

Volcanic rocks from the NSVZ segment range in composition from basaltic andesite to dacites with a mineralogy that mainly includes plagioclase + clinopyroxene + orthopyroxene + magnetite ± hornblende and rocks with $\text{SiO}_2 < 57\% \pm$ biotite and rocks with $\text{SiO}_2 > 60\% \pm$ olivine (Hildreth and Moorbath 1988; Sruoga et al. 2005). Rhyolites are rare in the NSVZ and basalts have not yet been reported or are completely absent. Geochemically the NSVZ rocks are higher in K, Rb, Sr, Ba, La, Th, and U and higher La/Yb and $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ but lower $^{143}\text{Nd}/^{144}\text{Nd}$ isotope values as compared to the rest of the SVZ (Figures 2.7 and 2.8).

The rocks from the TSVZ vary considerably from one volcanic center to another. The Tatara-San Pedro-Pellado volcanic complex ranges in composition from basaltic andesites to rhyolites, however, most erupted materials are porphyritic dacite flows (Dungan et al. 2001). Nevados de Longavi volcanic products are basalts to andesites while Nevados de Chillan lavas are calc-alkaline basaltic andesites to rhyolites (Selles et al. 2004). Laguna del Maule is a bimodal center erupting basaltic andesite and rhyolites (Frey et al. 1984). Geochemically the TSVZ rocks are variable and complex. They have lower La/Yb than NSVZ rocks but higher than the CSVZ and have lower $^{87}\text{Sr}/^{86}\text{Sr}$ and higher $^{143}\text{Nd}/^{144}\text{Nd}$ than the NSVZ. Nevados de Chillan have Sr and Nd isotopic ratios among the most primitive in the SVZ; however, in most cases $^{87}\text{Sr}/^{86}\text{Sr}$ of the TSVZ volcanoes are equal to or lower than volcanoes of the CSVZ (Figures 2.7 and 2.8)

Central southern volcanic zone rocks predominantly consist of basalts with smaller volumes of rhyolites. These basalts are considered the most primitive kind in the volcanic arc. Olivine phenocrysts are present in the entire zone including some rhyolites. Plagioclase is also ubiquitous even though in lower modal abundances and orthopyroxene appears in rocks with > 57% SiO₂ (Moreno et al. 2007). The central southern volcanic zone has few examples of rocks containing hornblende and it is largely absent. Sr, Nd, and O isotopic data for the CSVZ reflect minimal assimilation of continental crust with lower ⁸⁷Sr/⁸⁶Sr and δ¹⁸O and higher ¹⁴³Nd/¹⁴⁴Nd relative to the NSVZ and TSVZ. Additionally the CSVZ have higher Ba/La, Ba/Nb, and La/Nb and lower La/Yb than rocks in the TSVZ and NSVZ (Figures 2.7 & 2.8)

Figure 2.4: Terrain map of the Southern Volcanic Zones with the approximate locations of the major volcanic centers referenced in this study. The SVZ is divided into four distinct magmatic regions three of which are shown above; Northern Southern Volcanic Zone, Transitional Southern Volcanic Zone, and Central Southern Volcanic Zone.

Figure 2.5: A schematic sequential diagram (A-D) showing three states of deformation of the active margin in the SVZ. (2) Block diagram of how heterogeneous compressional and transpressional deformation accommodates oblique convergence of the Nazca plate. These tectonic regimes lead to the Liquine Ofqui fault zone. Figure from Cembrano et al. (1996).

Figure 2.6: Map view of the Andean mountain chain accompanied by a cross section of proposed crustal thickness and crustal reservoirs constructed from seismic data and adopted from Tassara & Yanez, 2003. The Azufre-Planchon-Peteroa complex is ~ located on the gold star in the TSVZ. The white and red star shows the approximate locations of Llaima, Villarrica and the SEC's in the CSVZ.

Figure 2.7: The La/Yb ratios of basalt and basaltic andesites magmas from multiple centers along the SVZ volcanic front. Segments of the SVZ (CSVZ, TSVZ, and NSVZ) are plotted against their latitude locations. Data sources were collected from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey 1989; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001).

Figure 2.8: Neodymium isotopic data of basalt and basaltic andesite magmas from many centers along the SVZ volcanic front. Segments of the SVZ (CSVZ, TSVZ, and NSVZ) are plotted against their latitude locations. Data sources were collected from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey 1989; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished.

2.4 Azufre-Planchon-Peteroa Volcanic Complex & Regional Geology

The Pleistocene and Holocene volcanic front from the TSVZ (34.3-37.0°S) trends approximately N 20°E. The TSVZ volcanic front also widens eastward to around 80km well into western Argentina. Tectonic forces control the locations of several volcanic centers within the arc trending NW-SE on uplifted blocks separated by intra-arc extensional basins such as Nevado de Longavi and Nevados de Chillan and just south of 35°15'S volcanic complexes such as Descabezado Chico and San-Pedro-Tatara-Pellado are trending NE-SW (Muñoz & Stern 1988). The TSVZ characterized by many large volcanic complexes and compound stratovolcanoes that overlie older calderas, basaltic shield volcanoes and volcanic fields. The basal elevation of the volcanic front decreases from north to south because the volcanic front moves eastward into Argentina and the Andes elevation generally decreases to the south (Hildreth and Moorbath 1988).

The sub-arc crust at TSVZ is approximately 35-40 km thick and continues to thicken northward (33-34.5°S) to 55-60 km and thin southward (42-46°S) to <30 km (Tassara & Yanez, 2003; Tassara et al., 2006). The effects of these parameters on magma genesis and subsequent magma evolution can be tested in the Azufre-Planchon-Peteroa volcanic complex and may elucidate the nature of sub-arc crust of the TSVZ. Detailed studies of volcanic centers in TSVZ and CSVZ have proposed that low pressure processes control the compositional range from andesite to rhyolite (Davidson et al., 1987; Gerlach et al. 1988; Tormey, 1989). Therefore the Azufre-Planchon-Peteroa complex offers a unique setting to study lower crustal processes because Planchon is the northernmost volcano in the SVZ that has mostly erupted basaltic magmas.

The Azufre-Planchon-Peteroa volcanic complex comprises of three volcanoes located in the TSVZ (35°15'S) which are less than 0.55 m.y. old on the basis of a K-Ar whole rock date from a pre-Azufre mafic andesite (Hildreth et al. 1984) (Figure 2.4 & 2.6). Azufre, at an

elevation of 3603m, is the oldest and largest volcano in the area and it has erupted around 30km³ of lavas, pyroclastics, and lahars composed of mostly basaltic andesite (70%) and dacites (30%), which have been glaciated (Tormey, 1989). Eruptive products from Azufre have a compositional gap from 57% to 63% SiO₂ and have had at least two intervals of dacitic eruption. The first interval of dacite activity consists of six massive flows totaling approximately 0.006 km³, with no evidence of sedimentary deposits between flows indicating short time intervals in extrusive activity (Tormey 1989). The final dacitic phase is preserved as a dome on the top of Cerro Azufre (Figure 2.6). The basaltic andesites from Azufre are also small in volume like the dacites but the flows are longer and continuous sections are rare because of frequent interruptions form lahars.

As the activity at Azufre decreased the Planchon center emerged six km north of Azufre and is composed of approximately 25 km³ of basalt and basaltic andesite lavas (Tormey 1989). Planchon is the northernmost basaltic volcano along the Southern Volcanic Zone. Planchon's eruptive products consists of ~ 25 km³ of basalt and basaltic andesite lavas that are transitional between tholeiitic and calc-alkaline magmatic series (Figure 4.3). At the edifice of Planchon there is significant degree of glacial and volcanic dissection which allowed for stratigraphic sampling by relative age of Planchon lavas. Tormey (1989) thus denoted his Planchon samples starting from 1 (PL-1 for example-youngest) to PL-35 (oldest) in relative age and this nomenclature will continue in this study. Planchon lava flows are flat and sheet-like and lack sedimentary horizons suggesting the Planchon edifice construction was fast enough to prevent deep erosion and slow enough to completely cool individual lava flows and ensure compositional variability (Tormey 1989).

Figure 2.9: Geologic map of Azufre, Planchon, and Peteroa volcanic complex from Tormey (1991). The white regions at the summit are regions of snow and ice. In between Planchon and Peteroa are a steaming crater lake (L) and a fumarole field (F).

Approximately 10,000 years before present, Planchon and a portion of Azufre underwent a sector collapse which created a debris avalanche that traveled 75 km down the Rio Claro and Rio Teno valleys before spreading out in the Central Chilean Valley and forming a hummocky deposit (Tormey 1989). After the sector collapse a second edifice formed (Planchon II) within the Planchon summit amphitheater created by the sector collapse. Planchon II has erupted an approximate volume of 5 km³ of basalt and basaltic andesite lavas compositionally similar to Planchon. These lavas have been dissected by summit glaciers and later eruptions by the scattered Peteroa vents.

The most recently active center, called Peteroa, consists of scattered vents between the Azufre and Planchon volcanoes with less than 1 km³ of preserved lavas and pyroclastic materials (Tormey 1989). Four andesitic Peteroa flows have emerged from a cone near the Azufre crater (Figure 2.9). Samples PT-6 and PT-6B are Holocene biotite dacite pumice that was found on the eastern flank of Azufre. Sample PT-7 is a biotite dacite plug found in the amphitheater between Azufre and Planchon. In 1937 there was an eruption that produced a small lava flow (PT-9) which was part of a small pyroclastic cone within the summit of Planchon. Tormey also collected tephra samples PT-91A and PT-91B from eruptions in February of 1991, and additional tephra samples (PT-101 and PT-102) and a volcanic bomb sample (PT-100) from eruptions in September of 2010, which he provided for this study. The recent continuous eruptions and the presence of fumarolic activity attest that this magmatic system is still active.

2.5 Summary of Mineralogy at Azufre-Planchon-Peteroa

On the basis of mineral assemblages, mineral compositions, and textures Tormey (1989) concluded that Planchon and Azufre magmas evolved at shallow levels in the crust, and did not undergo magma mixing, although there was some evidence for thermal perturbation. Tormey (1989) also inferred an upper limit to H₂O content (less than 5%) in Planchon magmas from an amphibole bearing inclusion in an olivine.

According to Tormey (1989) Peteroa is petrologically distinct from Azufre and Planchon because of an abundance of disequilibrium textures and complex zoning. Tormey also reported a lack of xenolith and xenocryst materials in Peteroa samples suggesting disequilibrium textures are a product of mixing magmas rather than crustal partial melts. Additionally, some Peteroa samples contain biotite indicating higher volatile contents than Planchon and Azufre.

2.6 Summary of the Geochemistry of Azufre-Planchon-Peteroa

Major and some trace elements, together with 17 strontium and 9 neodymium radiogenic isotopes analyses, and 6 oxygen isotope analyses were acquired by Tormey, (1989) on samples that he collected from the Azufre-Planchon-Peteroa.

According to the work by Tormey et al. (1995), the geochemical data from the Azufre-Planchon-Peteroa complex reflect both lower and upper crustal contamination and an apparent role of garnet as a residual phase in the lower crust. The invariable $^{87}\text{Sr}/^{86}\text{Sr}$ values, wide range in La/Yb and enrichment of incompatible element contents in Planchon basalts were attributed to assimilation of a lower crustal component that is young and arc derived because these geochemical features could not be reconciled with fractionation crystallization alone (Tormey et al. 1995). Additionally, Planchon lavas show a slight negative correlation with La/Yb with respect to Yb concentration. The gradient of low heavy rare earth element contents suggests a possible role of residual garnet in crustal melting, partitioning those elements accordingly. The distinctive $^{87}\text{Sr}/^{86}\text{Sr}$ and δO^{18} values of Azufre Dacites are a product of $\sim 12\%$ upper crustal assimilation of a possible limestone source in combination with fractional crystallization at low pressures (Tormey 1989). Peteroa lavas are predominantly calc-alkaline andesites and dacites with petrographic textures suggesting magma mixing at shallow crustal levels. Peteroa samples define a mixing trend between basaltic andesites and rhyodacite and abundances of Rb, Cs, and Th are also enriched and suggest involvement of upper crustal materials; however, isotopic values fall in between Azufre and Planchon.

2.7 Summary of the Geochemistry of Volcanic Centers in the TSVZ

In the Tatara-San Pedro-Pellado complex, a number of studies have concluded that asthenospheric mantle, slab-derived fluids, and continental lithosphere including mantle and/or lower crust were the three main source components contributing to parental magmas (Feeley & Dungan 1996; Dungan et al. 2001). They interpreted the variability in the most mafic rocks as a result of deep level processes and source heterogeneity. Additionally Dungan et al. (2001) concluded that basaltic andesites to andesite lavas show evidence of magma mixing with repeated replenishment and incorporation of silicic melts in an open-system processes which may account for the trace element variability along the SVZ arc.

Studies from the Nevados de Longavi volcanic center have proposed a polybaric two stage crystal fractionation model to explain the whole rock major and trace element trends in water rich magmas erupted there (Rodriguez et al. 2007). Dacites from this center have among the highest La/Yb ratios (15-20) and Sr/Y (60-90) in the TSVZ, which are attributed to high pressure crystal fractionation of modally dominant amphibole and minor garnet (Rodriguez et al. 2007). These authors use the deep crustal hot zone thermodynamic model of Annen et al. (2006) as a framework for the generation of these water-rich magmas by high pressure crystal fractionation.

Geochemical work done at the Laguna del Maule volcanic complex in the TSVZ has shown that rhyolites erupted are genetically related by fractional crystallization or partial melting to older basaltic rocks from the complex (Frey et al. 1984). Additionally it was concluded that the basic magmas evolved to more silicic differentiates with no significant contamination by upper crustal rocks (Frey et al. 1984).

The causes of geochemical variability in the TSVZ and the geochemical trends further north in the NSVZ are still under debate. Hildreth & Moorbath proposed a model termed MASH where primary mantle derived basalt magmas stall at intra-crustal levels, mix, assimilate, stagnate

or remain in storage and homogenize in magmatic chambers. The MASH model explains why basalts from the NSVZ and TSVZ with similar SiO₂ compositions to basalts from the CSVZ have higher ⁸⁷Sr/⁸⁶Sr, Ba/La, and La/Yb and lower ¹⁴³Nd/¹⁴⁴Nd geochemical signatures. However, Stern & Skews (1995, 2005) and Kay et al. (2005) attributed these geochemical differences of the NSVZ relative to the CSVZ to an increase in mantle source region contamination by subducted continental components due to either a smaller volume of mantle wedge generated magma because of a smaller melting column and/or increased subduction erosion caused by the southward migration of the locus of subduction of the Juan Fernandez ridge. Tormey et al. (1991, 1995) attributed the regional trends from the CSVZ to the TSVZ as a combination of both decreasing degree of mantle partial melting and an increase in the proportion of slab-derived fluids as the subarc mantle thins northward.

2.8 Specific Objectives in this Study

The purpose of this project is to investigate, compare and distinguish mantle, lower and upper crustal geochemical fingerprints in a well-characterized volcanic center in a section of the SVZ where previous studies have found apparent lower crustal influences. To resolve this multifaceted problem, I will approach with the following techniques:

1. Tormey et al. (1991) and many other workers in the TSVZ (Hildreth and Moorbath 1989; Rodriguez et al., 2007; Davidson et al. 1987; Dungan et al. 2001) hypothesize lower crustal assimilation and/or polybaric crystallization as a cause for unique geochemical features of TSVZ basalts. In Chapter 3, I approach this hypothesis using detailed mineral chemistry, including grain transects and BSE imaging, and address the following questions:

A. Are there chemical variations in phenocryst compositions indicative of lower crustal processes?

B. Do phenocryst compositions reflect high pressure crystallization?

C. Are there any remnants, vestiges or any evidence of high pressure crystallizing phases?

D. Are there xenocrysts that may show the nature of the deep crust?

2. Many TSVZ researchers attribute geochemical features of TSVZ lavas to the thickening of continental crust there, either by allowing for greater assimilation of crust through its longer path and higher lower crustal temperatures, or by shortening the mantle melting column (Tormey et al. 1991; Hildreth and Moorbath 1989; Davidson et al. 1988; Dungan and Davidson 2004). In Chapter 4, I address these hypotheses by modelling major element data for volcanic centers using the thermodynamically and experimentally based model and program of Lee et al (2009) to determine melting depths and temperatures for primary magmas to answer the following questions.

A. Does basaltic melt extraction from the mantle occur at the same depths across the SVZ?

B. Are melting temperatures the same across the SVZ and in large and small eruptive centers?

C. Can the effect of initial magmatic water contents on melting be discerned and how does it vary across the SVZ?

3. Rare earth elements are useful trace elements in igneous rocks and their compositional patterns are controlled by the REE chemistry of its source and crystal-melt equilibria. Modelling the changing compositions of REE in differentiating volcanic rocks can identify the roles of individual minerals during magmatic evolution. Tormey (1989) concluded that garnet was present in the mantle source and as a residual phase of partial melting at lower crustal depths, but his work did not cover the HREE in detail. In chapter 5 I obtained data for 12 REE elements,

showing the complete shape of the REE patterns, together with data for other trace elements I intend to address these questions:

- A. Can the partial melting of a mantle source with or without garnet produce parental magmas with the REE trends exhibited in APP magmas?*
- B. Is garnet and/or hornblende involved in melting and/or crystallization?*
- C. What are the main igneous phases that control the trace element patterns in APP magmas?*
- D. Can APP magmatic REE compositions be the result of distinct batches of parental magmas of the same source but with differing extents of melting?*

4. Isotopic ratios in magmas are characteristic of the source region from which it came from and these ratios remain unchanged during subsequent fractionation. As a result, distinct source regions can be recognized with their unique isotopic compositions and mixing relationships can be recognized between isotopically distinct sources. In this project I obtained new data for neodymium and hafnium isotopes, for APP and other SVZ centers along with oxygen stable isotopic values for a number of volcanic samples from the APP (Chapter 6). With this isotopic data I hope answer the following questions:

- A. Can mantle, lower crustal and upper crustal sources be distinguished in different APP magmas using radiogenic isotopes?*
- B. To what extent have Azufre dacites assimilated upper crustal contaminants?*
- C. What possible sources could account for along arc isotopic trends in the SVZ?*
- D. Can underplating of arc derived underplated basaltic magma over the history of subduction at this plate margin affect the isotopic compositions of younger arc magmas?*

These sets of hypotheses are addressed in chapters 3 through 5 respectively, and a synthesis of probable magmatic processes involved in the SVZ and the APP center is presented in chapter 7.

Methods used in this dissertation and data collected are reported in detail in Appendices 1-5. Mineral analyses were performed using the JEOL 8900 EPMA at the Florida Center for Analytical Electron Microscopy at FIU. A complete suite of trace elements (Rb, Sr, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu, Hf, Ta, Pb, Th, and U) on Azufre-Planchon-Peteroa samples was acquired by inductively coupled mass spectrometry equipped with a dynamic reaction cell (ELAN DRC ICP-MS) at the Trace Evidence Analysis Facility (TEAF) in the Department of Chemistry at Florida International University. The analysis of this suite of elements was done to complement the existing data gathered by Tormey (1989) on the APP center. The same suite of elements were analyzed for volcanic centers Maipo, Laguna del Maule, Descabezado, Nevados de Longavi, Nevados de Chillan, Antuco and Callequen representing major centers along the SVZ. Newly acquired tephra samples from a Peteroa eruption in September of 2010 were collected by Daniel Tormey and analyzed for major, trace and rare earth elements (same suite as above). Isotopic ratios of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ were determined for the Azufre-Planchon-Peteroa complex, Villarrica, Villarrica small eruptive centers, Calbuco, Osorno, Antuco, Nevados de Chillan, Descabezado, Laguna del Maule, and Maipo in order to delineate potential sources and processes that cause the geochemical differences between the centers along the SVZ arc.

3. MINERAL CHEMISTRY

Research on magmatism in continental arcs has led to the hypothesis that magma ascent can be gradual and episodic, leading to crystallization of distinct phenocryst assemblages reflecting high and lower pressure regimes (Ginibre et al., 2002; Singer et al., 1995; Selles et al. 2004). Further work has suggested that chemical evidence for early, deeper stages of crystallization may be erased by storage and equilibration of magma in mid to upper crust (Annen et al. 2006). For the current project, my first effort was to examine mineral assemblages, mineral composition, and variations in the composition of individual phenocrysts in mafic lavas from Planchon, Peteroa and Azufre in order to discern evidence for crystallization in the lower crust, and/or polybaric crystallization. Phenocryst assemblages and their compositions can be used to constrain pressure conditions with comparisons of experimental results and these chemical features may record early crystallization processes at mid-crustal to lower crustal levels (Bartels et al., 1991; Grove et al., 1982).

Amphibole crystallization, amphibole breakdown textures, and/or the presence of xenocrystic amphibole-bearing cumulates in continental arc magmas can indicate crystallization/assimilation at deeper crustal conditions. Amphibole is a pressure sensitive mineral which crystallizes at intermediate crustal depths and high water contents typical of primitive magmas at subduction zones (Wallace, 2005; Fischer and Marty, 2005; Allen and Boettcher, 2009). Additionally, experiments have shown that amphibole crystallization is abundant when basaltic liquids cross the amphibole-in phase boundaries (Barclay and Carmichael, 2004). However, amphibole in arc magmas is not common because amphibole is resorbed quickly near the surface of the earth prior to eruption (Rutherford and Hill, 1993). Due to the instability of amphibole in near-surface magmatic conditions, heavily resorbed amphiboles and breakdown textures may be remnant. Are there any remnants or vestiges of crystallizing phases present in Planchon or Peteroa lavas?

Abrupt crosscutting and resorption textures in other common arc-magmatic minerals like plagioclase, olivine and clinopyroxene may also yield evidence for complex multi-stage polybaric evolution of crystallization. Magma chamber processes like bulk melt differentiation, convection, and magma recharge can be studied using plagioclase as a record for crystallizing conditions and magma compositions (Ginibre et al. 2002). Olivine composition and zoning patterns are responses to changes in temperature, pressure, oxygen fugacity and co-precipitating phases in magmatic environments (Van Koosen and Buseck, 1978). The major rock forming minerals olivine, plagioclase, and clinopyroxene present in Planchon and Peteroa lavas have been examined in detail in order to identify their crystallization conditions.

Detailed work on the mineral chemistry of samples from Azufre-Planchon-Peteroa (APP) was performed at the Florida Center for Analytical Electron Microscopy (FCEAM) in order to reveal any internal chemical features found in phenocryst phases indicating crystallization at depth. Samples were carefully chosen for analysis on the EPMA on the basis of high MgO wt. % compositions and abundance of phenocryst phases. All analytical measurements and results from this chapter can be seen in Appendix 2.

3.1 Mineralogy of Planchon

Planchon lavas compositionally consist of basalts and basaltic andesites (Figure 3.1), with total phenocryst contents of 10 to 75%. The phenocrysts present in both episodes of Planchon's eruptive activity, Planchon I and II, are plagioclase, olivine, clinopyroxene and oxides. Plagioclase makes up the majority of phenocrysts present (60-80%) in all mineral assemblages. Olivine is the second most abundant phenocrysts phase in assemblages and makes up approximately 6 to 40% of total phenocrysts phases, however, in four samples the presence of olivine increases to 40- 63% of phenocrysts which may indicate accumulation. Clinopyroxene phenocryst abundances range from trace amounts to 4% of total phenocrysts. The groundmass textures are mostly small laths of plagioclase with interstitial oxides, olivine, clinopyroxene and

occasional pigeonite. In some cases glomerocrysts of plagioclase, olivine and clinopyroxene are present.

3.1.1 Plagioclase Phenocrysts

I analyzed of over 48 phenocryst core and rim spots in 11 different samples (complete microprobe data on plagioclase can be found in Appendix 2). Plagioclase phases in Planchon lavas are mostly euhedral to subhedral, 0.5 to 6 mm in diameter and lengths ranging from 1 to 12 mm. Plagioclase mostly crystallizes as a single phase but is sometimes found in glomerocrystic clusters with olivine, other plagioclases, and small Fe and Ti oxides. Most of the micro-phenocrysts are normally zoned or unzoned and show little disequilibrium textures but the larger phenocrysts are often sieve textured, contain abundant inclusions, and have complex zoning patterns (Figure 3.2). The overall range of plagioclase compositions are from An_{48} to An_{86} . A few normally zoned profiles of large crystals show the entire range, but phenocryst core compositions fall within the An_{56} to An_{66} and An_{72} to An_{78} ranges (Figure 3.3). The bimodal compositional population of plagioclase cores may indicate the occurrence of two dominant magmatic environments in which these phases occurred and/or two dominant mixing magmatic compositions.

It has been well established that plagioclase zoning patterns record magmatic events during crystallization (Singer and Pearce, 1993; Vance 1962). The zonation of plagioclase is caused by Ca and Na variations in the magma while the crystal is growing. Plagioclase records perturbations in crystallization conditions better than olivine because of the slower diffusion of NaSi for CaAl in plagioclase versus the Fe-Mg diffusion in olivine (Grove et al., 1984; Misner 1977). Plagioclase phenocrysts in Planchon lavas often show oscillatory zoning, reverse zoning, and zones that are rich in melt inclusions and oxide inclusions. The melt inclusion-rich zones most likely represent rapid growth and crystal resorption during ascent causing entrainment of magma in the plagioclase growth rims. Changes in zoning patterns and An mol% in plagioclase

phases can be affected by thermal perturbations, decompression, differing dissolved water contents in magma, magma mixing and crystal growth rates (Singer et al., 1997; Holten et al., 1997; Allegre et al., 1981). At higher pressure and water content, like a lower crustal setting, plagioclase will crystallize with higher anorthite compositions and richer trace magnesium and iron. In a lower pressure environment, the same crystallizing magma would yield more albitic plagioclase phenocrysts with lower magnesium and iron contents. The majority of plagioclase phenocrysts present in Planchon lavas are more albitic, indicating that they crystallized in a lower pressure environment.

3.1.2 Olivine Phenocrysts

Olivine grains are euhedral to subhedral with a 0.5 to 3mm diameter and length reaching 5mm in some samples. The olivines mostly crystallize as single crystals or occasionally as glomerocrysts with plagioclase and clinopyroxene (Figure 3.4). Some olivines display embayed crystal margins indicating reactions with the liquid phases. I measured a compositional range in olivines of Fo₄₄ to Fo₈₅ in normally zoned profiles from core to rim. The majority of the olivine core compositions range from Fo₇₀ to Fo₈₂ and rim compositions mostly falls in the Fo₆₈ to Fo₇₈ range. The changing composition indicates the rims of the olivines were reacting with the evolving groundmass and liquid compositions of the magma (differentiation). The apparent Fe-Mg exchange coefficients defined as $(K_d = (Fe^{crystal} \times Mg^{Liquid}) / (Fe^{whole\ rock} \times Mg^{crystal}))$ range from 0.25 to 0.96 (Figure 3.6) which is a high upper range for exchange coefficients in olivine and suggests that olivine cores formed in a liquid with higher Fe than the liquid composition inferred from the whole rock (equilibrium ~ 0.25 to 0.34, Roeder and Emslie, 1976; Baker and Eggler 1983). Samples PL-16 and PL-25 have unusually high apparent Fe-Mg exchange coefficients ranging from 0.38 to 0.96 which may indicate that these samples have an excess of olivine (accumulating olivine in a sample will increase the Mg # of the whole rock or liquid). Another way to test for olivine equilibrium with whole rock compositions is in the Rhodes diagram

(Figure 3.7; Dungan et al. 1978; Rhodes et al. 1979). In the Rhodes diagram it is apparent that samples with suites of olivines analyzed show differentiation trends and samples PL-16 and PL-25 both plot to the right of the equilibrium line which is consistent with olivine accumulation. From the modal analysis it is also apparent that sample PL-16 and PL-25 have higher proportions of olivine than most other samples. Additionally, I calculated the average olivine phenocryst composition in each respective sample (Appendix 2) and subtracted the modal amount of olivine present from each of the whole rock compositions and as a result the Mg #'s of the whole rock composition was reduced to ~ 55 for PL-16 and 57 for PL-25 (from Mg #'s of 64 for PL-16 and 62 for PL-25) and plot within the equilibrium line. In contrast, the other 9 samples contained olivine core exchange coefficient values indicating crystal growth in equilibrium with whole rock values (0.25-.34). The corresponding olivine rims in these samples have mineral-whole rock apparent Kd's of up to 1.39 and can be explained through within sample differentiation with closed-system crystallization during late stage of crystallization where the liquid surrounding the olivine becomes very Fe rich corresponding to Fe rich rims and does not affect the whole rock composition (Bryan et al. 1981). The within sample differentiation trend can be seen in Planchon samples in Figure 3.7.

3.1.3 Olivine Transects

Four samples (PL-8, PL-16, PL-25, and PL-27) and 10 phenocrysts from the Planchon lava series were studied in more detail by conducting transects along the growth axis in olivine phases. Transect compositional data can be seen in Appendix 2. Most olivines exhibit Fe-Mg zoning and such zoning reflects a disequilibrium state representing the crystallization history of the mineral (Van Kooten and Busek, 1978). The crystallization of olivine is affected by changes in temperature, pressure, time involved in crystallization, f_{H_2O} , f_{O_2} and co-crystallizing phases (Van Kooten and Busek, 1978). These changes in magmatic environment or perhaps stable environments can be understood by examining the compositional profiles of olivine phenocrysts.

Sample PL-8, from the core and rim analysis reported in the previous section, displays apparent Mg-Fe crystal to liquid exchange coefficients falling in the equilibrium range of Roeder and Emslie (1976). These same three phenocrysts were analyzed on rim to rim traverses with spot spacing of 20 μ m and 15 μ m with a crystal size range of 240 μ m to 660 μ m (Figure 3.8-3.10). Certain spots were not included in the compositional profiles because they yielded unreasonable data due to crystal voids, cracks, or small inclusions. The compositional profiles of PL-8-OL1, OL-2, and OL-3 all show relatively homogenous distribution of Mg-Fe in most of the exposed crystal surface (Figure 3.11 to 3.13). Phenocryst PL-8OL-2 has an average forsterite composition of 81.6 with a sigma of 0.34 which represents around 80% of the mineral. PL-8OL-3 has an identical forsteritic average as OL-2 at 81.6 but a slightly higher standard deviation of 0.41 in ~97% of the analyzed profile. Sample PL-OL-1 has larger core to rim variation (sigma 0.48) and is not largely zoned. The homogeneity in PL-8 olivine profiles suggests very slow crystallization at depth allowing diffusion between crystal and the melt in order to maintain homogeneity in stable magmatic conditions (Van Kooten and Busek, 1978). Additionally PL-8-OL2 at the rim of the phase shows a quick and dramatic change in composition (Fo₈₁ to Fo₆₈) in less than 30 μ m indicating that after the long period of stable magmatic conditions with homogeneous growth there was abrupt crystallizing and cooling presumably as magma rose up to surface with ensuing eruption (Pearce, 1984; Costa and Dungan, 2005; Costa and Chakraborty, 2004).

PL-27 is an interesting sample because the core and rim analysis show crystal-liquid bimodal Fe-Mg exchange values; about half of the 9 phenocrysts seem to be out of equilibrium with the whole rock values and half are in equilibrium (Figures 3.6 & 3.7). Additionally, the compositional profiles of three olivine phases (PL-27-OL4, OL-8, and OL-9) show reverse zoning in Fe-Mg diffusion profiles (Figures 3.14 to 3.16). The transects were analyzed from rim to rim using 15 μ m and 20 μ m spot spacing with phases ranging in size from 320 μ m to 670 μ m (Figures 3.17 to 3.19). Around half (225 μ m of the total length of phase 450 μ m) of PL-27-OL9

shows a somewhat stable core composition of Fo₇₀ then closer to each rim of the phase the composition slowly enriches in Mg to a maximum of Fo₇₆. Subsequently the olivine returns to a normal zoning profile and at the very edge of the rims and Fe enrichment ensues back to Fo₇₀. The remarkable symmetry of the profile extends from either end of the core and the reverse zoning is clearly noticeable in a BSE image in Figure 21 where there is a darker layer surrounding the phase indicating the Mg enrichment. PL-27OL-4 shows an asymmetric profile where the core composition is Fo₇₂ and one side enriches in Mg to Fo₇₄ and the other rim contrastingly enriches in Fe to Fo₆₉ (Figure 3.14). PL-27-OL8 mimics the profile of OL-9 but to a lesser extent. The core composition is stable at Fo₆₈ for around 90% of the crystal then approaching both rims the composition changes to Fo₇₂. A possible explanation of this oscillatory zoning in olivine could be an isothermal decrease in pressure in an H₂O-saturated magma. The increased f_{O_2} would decrease the Fe^{2+}/Fe^{3+} in the melt and shift the liquid composition toward the forsterite end member (Van Kooten and Busek, 1978). The supercooled liquid would then crystallize (because of the rise in liquidus and solidus curves) olivine with higher forsteritic values. Another possible explanation is that the diffusion profiles from the olivine phenocrysts from PL-27 are recording an influx of a more magnesium rich magma into the chamber causing a mixing affect and thus crystallizing a more forsteritic edge on the phenocrysts. PL-27OL-4's asymmetry may mean that the transect line did not pass through the core of the mineral or that adjacent olivine crystals shielded the facing surfaces from the melt (Van Kooten and Busek, 1978).

Samples PL-16 and PL-25 were investigated with very widely spaced spots so transects are not as detailed as the phenocrysts in samples PL-27 and PL-8 (Figures 3.20 – 3.23). Only one olivine transect was measured in PL-16, with seven points along rim to rim distance of ~ 1460µm. That gives an average spacing between analyzed spots of 208µm. PL-16 shows some symmetrical variation from core towards the rim with values of Fo₈₀ to Fo₈₁ then shows a typical

quick Fe enrichment towards the rims to values of Fo₇₈ (Figure 3.24). Three different olivines were analyzed along a line from core to rim in PL-25 (PL-25-OL8, OL10, and OL13). The analyzed spots were spaced from 33µm apart in sample OL13 to 218µm in sample OL13. PL-25-OL8 and OL10 have similar core compositions of ~ Fo₆₉ and become more Fe rich towards the rim to Fo₆₀. These olivines have crystal-whole rock exchange coefficients of 0.80 to 0.89 which means they are out of equilibrium with the liquid. PL-25-OL-13 has a stable core composition of Fo₈₁ and becomes more Fe rich at the rims to Fo₄₀. OL-13 has a crystal-whole rock exchange coefficient core value at ~0.37 within the range of crystal liquid equilibrium (Figures 3.24 & 3.25).

3.1.4 Pyroxene Phenocrysts

Clinopyroxenes and rare orthopyroxenes consist of subhedral phenocrysts ~ 2mm in diameter or less and are mostly unzoned (Figure 3.26). Clinopyroxenes are mostly augites with occasional groundmass pigeonite (Figure 3.27). Forty nine phenocrysts in nine different samples were analyzed with the electron microprobe and the data are presented in Appendix 2. Tormey (1989) reported coexisting augite and groundmass pigeonite recording temperatures of approximately 1100°C. With further analysis of the 49 phenocryst augites cores the magmatic temperatures are confirmed with only small variations of 1050°C to 1100°C at 1 atmosphere (Lindsley, 1983). The small variability in recorded temperature in augites phenocrysts most likely represents a range of eruption temperatures from different lava flows. It seems that the variation in clinopyroxene abundance in samples and appearance is largely dependent on lava cooling times and low pressure crystallization rather than initial bulk composition of the lavas because Planchon lava's are compositionally similar. Additionally, the presence of clinopyroxene is independent of sample composition and differentiation as shown by MgO content and its abundance increases when lavas have ~ 20% crystals (Tormey 1989, Figure 3.28).

The relatively smaller grain sizes of the augite phenocrysts, their presence in the groundmass, and their subhedral grain shapes suggests they formed in the later stages of crystallization.

Augite compositional core to rim transects of two phenocrysts from samples PL-27 and PL-28 show a general decrease in Fe and Ca with little variation in Mg from the core of the phase to the rim (Figure 3.29). Sample PL-28-CPX-1 is ~ 190µm in length with six analyzed points spaced at ~ 15µm from its core to approximate rim (Figure 3.30). This sample shows a gradual decrease in Fe and Ca approaching the rim however at the rim of the phase there is a drastic increase in Fe and decrease in Ca. Fe enrichment at the rim is likely the result of reacting with evolving groundmass and liquid compositions. Sample PL-27-CPX-12 is ~ 190µm in length with 7 analyzed points spaced at ~ 27µm spanning the length of the entire crystal rim to rim (Figure 3.31). Oddly enough each side of the crystal shows two differentiation trends. Points 1 to 4 show a slight decrease in Mg and increase in Ca and Fe from core to rim (Figure 3.29). Points 4 to 7 show a decrease in Mg and Ca and a large increase in Fe from core to rim. The increase in Fe towards the rim is likely due to reaction with the groundmass and remaining liquid compositions which is typical of pyroxenes grains that are in the later stages of crystallization. Early forming augite will compositionally plot close to the diopside (higher Ca) end member and later forming sub-calcic augite and corresponding pigeonite form later in more fractionated iron rich samples. Additionally, the apparent exchange coefficients for Fe-Mg for analyzed augites fall above the equilibrium ranges and are much more Fe rich than the corresponding whole rock liquid values also suggesting late stage crystallization mostly likely at shallow pressure prior to eruption (Figure 3.32).

3.1.5 Oxides

The oxides present in Planchon lavas are predominantly magnetite (spinel) forming small (typically no longer than 50µm) euhedral cubes and anhedral shapes in the groundmass and is present in the groundmass of all Planchon. Chromian spinel was identified in many samples

using the energy dispersive spectrometer on the EPMA and often occurs as inclusions in olivine phenocrysts. Low Cr #'s of 51 to 54 (found in Planchon samples) Chromian spinels from Planchon samples have low Cr #'s of 51 to 54 and $Mg/Mg+Fe^{2+} = .30$ to $.34$, which Dick and Bullen (1984) suggest indicates crystallization under oxidizing conditions. The relatively low Cr # and low TiO_2 wt% (1.38 and 0.91 in two samples) also suggest oxidizing magmatic conditions (Shoji, 1992). The co-precipitation of olivine and magnetite indicate oxidizing conditions near the nickel-nickel oxide (NNO) buffer (Gust and Perfit, 1987).

3.1.6 Amphibole

Amphibole or hornblende phases were not found and were not identified using the EPMA and optical microscope in Planchon samples. Glomerocrysts are rare in Planchon samples and mostly consist of olivine and clinopyroxene or multiple plagioclase phases bound together. No xenocrystic material was found entrained in the samples which would be a likely location to find amphibole. It is clear that Planchon magmas did not crystallize amphibole phases or these magmas stagnated at upper crustal levels long enough for amphibole to be resorbed completely.

3.2 Mineralogy of Peteroa

Tormey (1989) defined two distinct petrographic varieties among volcanic samples from Peteroa. The first is a somewhat homogenous set of andesite flows located near the now inactive Azufre crater that contains phenocrysts of olivine, plagioclase, clinopyroxene, and oxides. Plagioclase phenocrysts display three types of plagioclase zoning (normal, reverse, and oscillatory) in these andesite flows. The second petrographic type from Peteroa is variable and located near the summit amphitheater region of the complex. The most compositionally evolved samples are PT-6 (a biotite rhyodacite pumice) and PT-7 which is a biotite-bearing dome fragment. These samples have unique phenocryst assemblages of olivine, biotite, two pyroxenes, and zoned plagioclase. Disequilibrium textures and mineral zoning are ubiquitous in both petrographic types in all samples from Peteroa (Figure 3.33).

3.2.1 Transects of Plagioclase and Olivine

Core to rim transects were performed on five different plagioclase phenocrysts found in sample PT-15. The phenocryst widths range from 200-480 μ m and the EPMA data on these profiles can be seen in Appendix 2. Phenocrysts PT-15A-1, 1A, 2, 3, and 4 all show similar chemical compositional trends towards the rim of the phase with fluctuations up to 20 An mol% (Figures 3.35-3.39). Samples PT-15A-1, 1A, 2, and 4 have stable core albitic compositions of An₅₂ to An₅₉ and continue outwards from the core until there is a drastic enrichment in Ca (reverse zoning) to An₆₃ to An₇₀ (figures 3.35-3.37 & 3.39). The PT-15A-3 core composition is An₆₀ then it slowly shows a step-wise decrease to An₅₀ remaining relatively stable until a huge spike in Ca to An₇₀ (Figure 3.38). Although phenocryst PT-15A-4 shows a slightly different compositional pattern than the other four phenocrysts, the same anorthitic enrichment is clearly visible. After the spike in Ca all phenocrysts evolve to intermediate compositions from their more albitic cores and the anorthitic spike high. It is clear that all these sudden changes in anorthitic compositions are correlated and seem to suggest that Peteroa lavas are the result of magma mixing of one end member being a dacitic liquid (albitic cores) and a sudden influx of another endmember of a mixed andesite (sieve textured anorthitic cores). Additionally the FeO concentration generally increases as the phenocrysts grow from core to the rim correlating negatively with An mol% which is in agreement with Fe incorporation into plagioclase as observed by Bindeman et al. (1998; Figures 3.40-3.44). Although the overall negative correlation between An mol% and Fe concentration for plagioclase in PT-15 is observed, within transects of these phenocrysts sharp increases in An mol% are accompanied by increases in Fe concentrations. The partitioning of Fe into plagioclase is sensitive to oxygen fugacity because of the increase in partition coefficients with increasing fO_2 (Bindeman et al., 1998; Ginibre et al., 2002; Phinney, 1992; Sugawara, 2001; Huebner et al., 1989; Wilke and Behrens, 1999). An increase in Fe alone could indicate an increase in fO_2 of the magma or magma mixing with a Ca

and Fe rich magma and since anorthite composition is not directly affected by fO_2 it seems that only mixing of magmas could explain the correlative spikes in Ca and Fe in plagioclase phenocrysts.

Four olivine phenocrysts (PT-3A-OL1, OL2, OL3, and OL4) were analyzed along their growth axis from rim to rim (Figures 3.45-3.48). The phenocrysts ranged in length from 400 to 440 μ m and transect lines were placed to avoid voids, cracks, and inclusions with points spaced 20 μ m apart; the results can be seen in appendix 2. Phenocrysts PT-3A-OL1 and OL3 show homogenous diffusion of Mg-Fe throughout the crystal faces. The PT-3AOL1 phenocryst has an average composition of Fo₆₉ with a core composition of Fo₇₀ and slight normal zoning towards the rim to Fo₆₈ (Figures 3.49-3.52). Similarly PT-3A-OL3 has an average composition of Fo₆₈ with a core composition of Fo₇₀, tapering to Fo₆₈ at one rim and Fo₅₅ at the other. The homogeneity in PT-3A-OL1 and OL3 olivine profiles suggests very slow crystallization allowing diffusion between crystal and the melt in order to maintain homogeneity in stable magmatic conditions (Van Kooten and Busek, 1978). The rim of phenocryst PT-3A-OL3 shows a quick change in composition (Fo₇₀ to Fo₅₄) in less than 40 μ m, indicating that after the long period of stable magmatic conditions with homogeneous growth there was abrupt crystallization and cooling reflecting a change in pressure of magmatic regime (Pearce, 1984; Costa and Dungan, 2005; Costa and Chakraborty, 2004). Phenocrysts PT-3A-OL2 and OL4 show larger variability in forsteritic composition throughout the length of the phases. Phenocryst PT-3A-OL2 has a core composition of ~Fo₇₂ and slowly enriches in Mg as you approach the rims in either direction to a maximum of Fo₇₇. After the forsterite maximum, the Fe enrichment growth ensues to the rim of the crystal to Fo₆₅. PT-3A-OL-4 has a core composition of ~Fo₆₉ and asymmetrically increases to Fo₇₂ before it resumes a normal diffusion trend at the rim back to Fo₆₃. The other side of OL-4 is normally zoned and the rim composition is ~Fo₅₈. The variability shown by phenocrysts PT-3A-

OL2 and OL4 could possibly be explained by changes in temperature, $f_{\text{H}_2\text{O}}$, pressure, f_{O_2} , and/or magma mixing.

3.3 Mineralogy and Petrography of Azufre

The olivine phases are euhedral to subhedral and occur as single crystals or as part of crystal clusters with plagioclase, clinopyroxene and oxides. The plagioclase phases are euhedral to subhedral with size ranges from 1mm to 8mm. The plagioclase phenocrysts show complex zoning and sieve textures much like the plagioclase found in Planchon. The basaltic andesites from Azufre are petrographically very similar to Planchon basaltic andesites.

The dacites from Azufre are the most differentiated samples collected from the entire complex and contain less than 10% unzoned phenocrysts of plagioclase, clinopyroxene, orthopyroxene, magnetite, ilmenite, and apatite in a glassy groundmass. The phases generally occur in glomerocrysts of approximately 1cm in diameter that contain trapped melt and are plagioclase rich which is consistent with low pressure crystallization (Grove et al. 1982, Grove and Baker 1984; Tormey, 1989). The presence of apatite in the glassy groundmass in more silicic samples is important because it may account for later stages of P_2O_5 decreases from fractionation and may account for changes in rare earth element composition because REE partition coefficients are high for apatite. The glomerocrysts of plagioclase clinopyroxene orthopyroxene and oxides present in silicic Azufre rocks could possibly represent vestiges of hornblende phenocrysts. Hornblende can be an early forming mineral in water-bearing mafic magmas and stagnation at lower crustal levels for long periods of time will resorb the mineral (Beard & Borgia 1989; Conrad and Kay, 1984).

3.4 Summary of Conclusions

It is evident that plagioclase phenocrysts in Planchon lavas record the changing crystallization conditions during their growth and the variety of textures exhibited speak to the complexity of their formation. Large phenocrysts often show disequilibrium textures like

compositional zoning, resorption zones, inclusions, and sieved texture. Smaller micro-phenocrysts are in large part normally zoned and show little evidence for disequilibrium textures. The bimodal core and rim compositional character of the phenocryst are likely due to multiple crystallizing environments or an influx of two compositionally distinct magmas mixing. The newly compiled data conflict with Tormey's findings that Planchon lavas did not require an influx of different magmas. Magma mixing, as well as thermal and pressure perturbations can account for the variety of textures observed in Planchon phenocrysts and explain the bimodal nature of their composition.

The absence of highly anorthitic plagioclase phenocrysts, indicative of higher pressure and water content crystallizing conditions, suggests that the majority of plagioclase phenocrysts crystallized at lower pressure upper crustal levels. The disequilibrium textures and complex zoning in the plagioclase phenocrysts can also reflect the rapid ascension prior to eruption and possible mixing of multiple ejections of basaltic liquids into a shallow magmatic chamber.

Olivine phenocrysts were the first forming phases in Planchon, determined by the large grain size and euhedral to subhedral shape. Like the plagioclase phenocrysts, the olivine core compositions also show a bimodal character with most falling into the Fo₇₀ to Fo₇₄ and Fo₈₂ to Fo₈₆. Similarly, this bimodal composition could be attributed to mixing of two compositionally distinct parental magmas. Olivines from sample PL-27 show direct evidence of drastic reverse zoning which could be explained via magma mixing. The majority of olivines are normally zoned with very stable compositional profiles from core to rim suggesting initial long periods of slow cooling and stable magmatic conditions that induce crystal growth. The high magnesium composition of many olivine cores (Fo₈₂ to Fo₈₈) are close to mantle equilibrated olivine (~Fo₉₀) which could mean they may have begun crystallization in mantle like conditions at high pressures. Some of the magnesium-rich olivine phenocrysts present in Planchon lavas may be remnants of high pressure crystallization.

Compositional transects of plagioclase phenocrysts in Peteroa samples show correlations in Ca and Fe along the growth axis. These trends can be explained by magma mixing of sources with varying amounts of FeO. The abundance of resorption zones, inclusions, oscillatory-reverse-normally zones phenocrysts, and sieve textured nature of all Peteroa plagioclase reveals a complex growth and resorption history which is in accord with the conclusions from Tormey (1989). These perturbations in plagioclase growth are likely a consequence of changing magmatic conditions and magma mixing in a shallow chamber.

The complete absence of amphibole minerals, amphibole bearing vestiges and xenocrystic material indicates that it either was not an important phase in the evolution of Planchon and Peteroa magmas or these magmas stagnated at near surface conditions for a long enough period of time for amphibole to be completely resorbed and nonexistent. The magmatic stagnation at upper crustal pressures is consistent with the late stage crystallization of clinopyroxene phenocrysts and their presence in groundmass. Additionally, the low anorthitic plagioclase core compositions may also represent low pressure crystallizing conditions. Even though Planchon basalts are primitive from a whole rock chemical perspective, the corresponding mineral phases or “cargo” carried in these liquids represent development under upper crustal conditions. There is a mineralogical upper crustal imprint imposed on these magmas and any evidence of lower crustal crystallization has been obliterated, efficiently fractionated, or may not have occurred.

A likely explanation of the lack of high pressure crystallographic evidence could be the concept of basaltic underplating and the development of crustal hot zones in mature volcanic arcs (Raia & Spera 1997; Annen et al. 2006). Simulations of heat transfer as well as high-temperature experiments suggest a model where intermediate and silica rich magmas can be generated by incomplete crystallization of hydrous basalt at upper mantle and/or lower crustal levels (Annen and Sparks 2002; Muntener et al. 2001). In the model proposed by Annen et al. 2006, mantle

derived hydrous basalts are emplaced as a succession of sills into the lower crust that partially crystallize creating H₂O rich residual melts and/or partial melting of pre-existing crustal rocks. The mixing of residual and crustal partial melts leads to the diversity in isotope and trace element chemistry. The resultant residual and crustal partial melts in the Annen et al. (2006) model will become more silicic than the primary basalts generated; however, that is under the assumption that the crustal partial melts are compositionally different than the subduction zone primary melts. A mantle melt-derived mafic lower crust formed by underplating would be very similar in composition to the newly arrived H₂O rich primary mantle melts. As a result of the compositional similarity, crustal partial melts and residual H₂O magmas in these crustal hot zones can remain basaltic. These basaltic hot zone melts are H₂O rich and consequently have low viscosity allowing for rapid ascension (Annen et al. 2006). In the case of adiabatic ascent, the magma attains a super-liquidus state which leads to resorption and loss of any entrained high pressure crystals or country rock xenoliths (Annen et al. 2006). For example, amphibole becomes unstable at pressures less than 0.1 GPa and will either become resorbed or be pseudo-morphed by anhydrous reactions products (Rutherford and Hill 1993). Once these H₂O rich magmas ascend to shallow depth they will intersect their H₂O-saturated liquidus and crystallization begins. Crystallization is therefore driven by decompression and degassing at shallow depths consistent with the compositional character of the phenocrysts from Azufre, Planchon, and Peteroa. Subsequent shallow crystallization is dominated by plagioclase and the proportion increases with decreasing pressure.

Figure 3.1: Samples from the Azufre-Planchon-Peteroa volcanic complex plotted on the Total Alkali Silica (TAS) classification for igneous rocks diagram. Data were compiled from Tormey 1989 and recent analysis.

B

D

Figure 3.2: (A) Photomicrograph in cross polarized light of unzoned plagioclase laths. (B) Backscattered electron microprobe image of plagioclase phenocrysts displaying unzoned core with disequilibrium textures (inclusions, resorption zones, and sieve textures) towards the rim. (C) Photomicrograph in cross polarized light of sieve textured plagioclase in a Planchon lava. (D) BSE image of plagioclase showing sieve texture and various inclusions throughout the crystal.

Figure 3.3: Histogram of plagioclase core and rim compositions found in Planchon lavas. Data comprises of 48 different plagioclase phenocrysts in 11 different samples including data compiled by Tormey et al. (1989).

Figure 3.4: (A) Photomicrograph in cross polarized light of an olivine phenocryst existing within a glomerocryst in a Planchon sample. (B) Photomicrograph of a single olivine phenocryst in a Planchon lava.

Figure 3.5: A histogram of olivine phenocryst core and rim forsterite compositions in Planchon lavas. Data consists of 55 different olivine phenocrysts in 11 different samples including data compiled by Tormey (1989).

Figure 3.6: Fe-Mg exchange coefficients from olivine cores from 11 different samples in Planchon. The highlighted area is the approximate range for equilibrium ~ 0.25 to 0.34 , Roeder and Emslie, 1976; Baker and Eggler 1983.

Figure 3.7: Rhodes diagram tests olivine equilibrium with coexisting whole rock compositions (Dungan et al. 1978; Rhodes et al. 1979). Olivine core compositions are plotted from 11 different samples from the Planchon volcanic center. The curved solid line is the olivine-liquid equilibrium line with the dashed lines surrounding as error bounds. The arrows on the plot are explanations for deviations from the equilibrium line.

Figure 3.8: Backscattered electron microprobe image of olivine phenocrysts PL-8-OL-1 with yellow transect line ~ 560 μ m in length with spot spacing of 20 μ m.

Figure 3.9: Backscattered electron microprobe image of olivine phenocrysts PL-8-OL-2 with yellow transect line ~ 240μm in length with spot spacing of 15μm.

Figure 3.10: Backscattered electron microprobe image of olivine phenocrysts PL-8-OL-3 with yellow transect line ~ 660 μ m in length with spot spacing of 20 μ m.

Figure 3.11: Forsteritic (100Mg/Mg + Fe) compositional profile for sample PL-8OL-1 from rim to rim with spot spacing of 20 μ m.

Figure 3.12: Compositional profile for sample PL-8OL-2 from rim to rim with spot spacing of 15 μ m. Forsterite mol % = $(100\text{Mg}/\text{Mg} + \text{Fe})$.

Figure 3.13: Compositional profile for sample PL-8OL-3 from rim to rim with spot spacing of 20 μ m. Forsterite mol % = $(100\text{Mg}/\text{Mg} + \text{Fe})$.

Figure 3.14: Compositional profile for sample PL-17-OL-4 from rim to rim with spot spacing of 15 μ m.

Figure 3.15: Forsteritic mol % compositional profile for sample PL-17-OL-8 from rim to rim with spot spacing of 20 μ m.

Figure 3.16: Compositional profile for sample PL-17-OL-9 from rim to rim with spot spacing of 15 μ m showing the unique reverse zoning disequilibrium.

Figure 3.17: Backscattered electron microprobe image of olivine phenocrysts PL-27-OL-4 with yellow transect line ~ 315 μ m in length with spot spacing of 15 μ m.

Figure 3.18: Backscattered electron microprobe image of olivine phenocrysts PL-27-OL-8 with yellow transect line ~ 560 μ m in length with spot spacing of 20 μ m

Figure 3.19: Backscattered electron microprobe image of olivine phenocrysts PL-27-OL-9 with yellow transect line ~ 450 μ m in length with spot spacing of 15 μ m

Figure 3.20: Backscattered electron microprobe image of olivine phenocryst PL-16-OL-8 with locations of analyzed points along growth axis of the crystal.

Figure 3.21: Backscattered electron microprobe image of olivine phenocryst PL-25-OL-8 with locations of analyzed points along growth axis of the crystal. This olivine also contains a large melt inclusion in the south eastern portion of the image.

Figure 3.22: Backscattered electron microprobe image of olivine phenocryst PL-25-OL-10 with locations of analyzed points along growth axis of the crystal.

Figure 3.23: Backscattered electron microprobe image of olivine phenocryst PL-27-OL-13 with locations of analyzed points along growth axis of the crystal.

Figure 3.24: (A) Compositional profile for sample PL-16-OL-8 from rim to rim. (B) Compositional profile for sample PL-25-OL-8 from core to rim.

Figure 3.25: (A) Compositional profile for sample PL-25-OL-10 from core to rim. (B) Compositional profile for sample PL-25-OL-13 from core to rim.

Figure 3.26: Backscattered electron microprobe image of clinopyroxene (Augite) phenocryst in sample PL-27.

Figure 3.27: Ternary diagram of the pyroxene quadrilateral showing over 49 different phenocrysts analyzed in 9 different samples from the Planchon volcanic center.

Figure 3.28: (A) Percent clinopyroxene vs. MgO of samples from Planchon. (B) Percent CPX vs. total phenocrysts in sampled from Planchon Modal analysis from Tormey (1989).

Figure 3.29: Ternary plot of the pyroxene quadrilateral of Augite phenocrysts in PL-28 and PL-29 transects from core to rim. The black arrow denotes the composition of the core and the direction is the changing composition towards the rim.

Figure 3.30: Backscattered electron microprobe image of Augite phenocryst in sample PL-28. Analyzed points are labeled from point 1 to 6 (core to rim).

Figure 3.31: Backscattered electron microprobe image of Augite phenocryst in sample PL-27. Analyzed points are labeled from point 5 to 1 (core to rim).

Figure 3.32: Apparent exchange coefficients for augite core compositions in selected Planchon samples. The yellow shaded region is the 1 atm QFM experimental equilibrium range from Grove and Baker 1984).

Figure 3.33: Examples of different plagioclase phenocryst populations found in Peteroa lavas. **(A)** on the left is a photomicrograph in crossed polarized light of plagioclase with sieve textured core and outwardly zoned rims. To the right is a backscattered electron microprobe image of a plagioclase phenocryst with sieve textured anorthitic core and a relatively unzoned albitic rim/edge. **(B)** On the left is a photomicrograph in crossed polarized light displaying a wide variety of disequilibrium textures. On the right is a backscattered image of a plagioclase phenocryst with an albitic core relatively unzoned surrounded by many resorption zones littered with inclusions and a more anorthitic rim.

Figure 3.34: Histogram of anorthite mole percent of 43 different phenocryst phases in 8 samples from Peteroa lavas. Notice the large variability of plagioclase compositions and seemingly trimodal population of plagioclase cores.

Figure 3.35: Anorthitic compositional profile for sample PT-15A-1 from core to rim with spot spacing of 5μm.

Figure 3.36: Compositional profile for sample PT-15A-1A from core to rim with spot spacing of 5μm.

Figure 3.37: Anorthite compositional profile for sample PT-15A-2 from core to rim with spot spacing of 5μm.

Figure 3.38: Anorthitic compositional profile for sample PT-15A-3 from core to rim with spot spacing of 5μm.

Figure 3.39: Anorthitic compositional profile for sample PT-15A-4 from core to rim with spot spacing of 10μm.

Figure 3.40: Fe wt. %compositional profile from core to rim of a plagioclase phenocryst in sample PT-15A-1 from Peteroa.

Figure 3.41: Fe wt. % compositional profile from core to rim of a plagioclase phenocryst PT-15A-1A from Peteroa.

Figure 3.42: Fe wt. % compositional profile from core to rim of a plagioclase phenocryst PT-15A-2 from Peteroa.

Figure 3.43: Fe wt. % compositional profile from core to rim of a plagioclase phenocryst PT-15A-3 from Peteroa.

Figure 3.44: Fe wt. % compositional profile from core to rim of a plagioclase phenocryst PT-15A-4 from Peteroa.

Figure 3.45: Backscattered electron microprobe image of olivine phenocrysts PT-3-OL-1 with yellow transect line ~ 400 μ m in length with spot spacing of 20 μ m.

Figure 3.46: Backscattered electron microprobe image of olivine phenocrysts PT-3-OL-2 with yellow transect line $\sim 380\mu\text{m}$ in length with spot spacing of $20\mu\text{m}$.

Figure 3.47: Backscattered electron microprobe image of olivine phenocrysts PT-3-OL-3 with yellow transect line ~ 400 μ m in length with spot spacing of 20 μ m.

Figure 3.48: Backscattered electron microprobe image of olivine phenocrysts PT-3-OL-4 with yellow transect line ~ 420 μ m in length with spot spacing of 20 μ m.

Figure 3.49: Forsterite compositional profile for sample PT-3-OL-1 from rim to rim with spot spacing of 20 μ m.

Figure 3.50: Forsterite mol. % compositional profile for sample PT-3-OL-2 from rim to rim with spot spacing of 20 μ m.

Figure 3.51: Forsterite compositional profile for sample PT-3-OL-3 from rim to rim with spot spacing of 20 μ m.

Figure 3.52: Forsterite compositional profile for sample PT-3-OL-4 from rim to rim with spot spacing of 20 μ m.

4. MAJOR ELEMENT CHEMISTRY

The major and trace element data were collected from the ICP-MS at Harvard University, ICP-MS at TEAF in FIU, and published data from the Azufre-Planchon-Peteroa complex (Tormey et al, 1991; Tormey et al., 1995) are given in Appendix 3. Analytical techniques and uncertainties are discussed in Appendix 1 and all data presented in this chapter are available in Appendix 3.

4.1 Whole Rock Major Element Chemistry

The major element composition of volcanic rocks is frequently used as a proxy for the composition of the magma from which they solidified. As such, major element composition can be used to infer the crystallization history of the magma, various differentiation processes, such as crystal settling and accumulation, and assimilation of crust. Experimentally determined mineral stabilities in synthetic melts and associated phase diagrams can be used to compare with natural melt compositions and determine their likely crystallization paths. Characterizing the crystallization behavior of multiple samples can lead to determining compositional trends called liquid lines of descent (LLD). These trends of liquid composition can not only show the compositional path of all associated liquids, it also can lead to the composition of likely parent or primary magmas. Understanding the primary composition of melts can help understand how they have evolved and changed en route to eruption at the surface. The composition of a primary magma formed by mantle melting can also be calculated and used to infer melting conditions such as melting temperatures and pressures (depth). Many variables are responsible for melting conditions of magmas like initial magmatic H₂O contents, composition, and oxygen fugacity. This chapter will explore the whole rock variability of the APP volcanic center, compare this data to experimentally determined crystallization paths, and calculate primary melting compositions and conditions of the APP complex in comparison to the melting conditions at other regions of the SVZ.

4.1.1 Classification and Compositional Range

The compositional ranges of lavas from the Azufre-Planchon-Peteroa complex are from basalt to dacite with an almost complete absence of andesitic lavas (Figure 4.1). There are only two tephra samples from Peteroa that were collected from an eruption in September of 2010 that fall into the andesitic range. Planchon consists mostly of basaltic andesites with a few basalts while Azufre samples reveal an andesite gap (57%-63% SiO₂) between basaltic andesites and dacites. The younger Peteroa tephra samples mark the first significant andesitic eruption at the complex and their compositional range is basaltic andesite to dacite without any samples containing less than 55% SiO₂. About half of the Azufre and Peteroa samples contain > 5 wt. % Na₂O + K₂O and plot in the TAS trachyandesite and trachydacite classification fields (Figure 4.1). Not surprisingly, these same samples also plot in the field of high K dacites and andesites (Figure 4.2). Planchon lavas and the other remaining lavas plot in the medium K field which is typical of arc lavas and calc-alkaline series magmas (Figure 4.2). The calc-alkaline magmatic series characterizes the majority of the samples in the APP complex; however, Azufre dacites are tholeiitic according to the calc-alkaline/tholeiitic distinction by Kuno (1968) and Irvine and Baragar (1971) (Figure 4.3). This switch is atypical of major centers of the SVZ, usually older volcanoes are andesitic and calc-alkaline while more recent centers are bimodal and tholeiitic. Tormey et al. (1991) suggested this change in magmatic series is likely due to changing magmatic supply rates which leads to distinctive compositional variation.

4.1.2 Major Element Variations

Planchon lavas show decreasing MgO, Fe₂O₃, and CaO with increasing SiO₂ (magma differentiation). The increase of Al₂O₃ between basalt and basaltic andesite (Figures 4.4-4.6), coupled with decreased FeO, MgO, and CaO could indicate fractionation of mafic phases like olivine, clinopyroxene, hornblende, and magnetite with suppression of plagioclase crystallization due to high water contents (Grove & Baker, 1984; Baker & Eggler, 1987; Kinzler & Grove, 1992;

Sisson & Grove, 1993; Grove et al., 2002). Planchon basalts are high-alumina basalts (HABS, $\geq 17\%$) as defined by Irvine and Baragar (1971) with an average of ~ 17.67 wt.% Al_2O_3 (Figure 4.4). With increased differentiation Planchon lavas also show an increase in Na_2O , K_2O , and P_2O_5 and no general trend (mostly scatter) for TiO_2 (Figures 4.4-4.7).

Azufre lavas follow similar major element differentiation trends to Planchon lavas, and continue to higher degrees of fractionation. Al_2O_3 enrichment is apparent in Azufre high alumina basaltic andesites and in some cases higher than Planchon HABS (Figure 4.4). Once you cross the “andesite gap” (increase SiO_2) in Azufre lavas there is a drastic decrease in Al_2O_3 and increase in P_2O_5 . Otherwise, much like Planchon trends, Fe_2O_3 , MgO , CaO , and TiO_2 decrease while Na_2O and K_2O increase across the andesite gap. A noticeable and important trend in the more differentiated Azufre samples is a decrease in P_2O_5 with increasing SiO_2 . This trend among Azufre dacites is a clear indication of possible apatite crystal fractionation and is confirmed by petrologic observation (see chapter 3).

The Peteroa lava and tephra samples show the most distinct major element compositions in the entire complex. These samples are the least in volume, are all higher than 55% wt. SiO_2 , and these lava and tephra samples record the first appearances of andesitic composition. The Peteroa andesite flows plot at the more evolved end of the Azufre trend and are lower in CaO and Al_2O_3 and higher in Na_2O than Azufre lavas (Figure 4.4-4.6). The most differentiated (highest silica) volcanic product from the entire complex is a Peteroa biotite rhyodacite pumice (69.2%). Peteroa samples PT-6b, 7, 8 and 9 plot along mixing trends between andesite and rhyodacite. All Peteroa lavas are calc-alkaline according to Kuno (1968) and Irvine and Baragar (1971) (Figure 4.3).

4.2 Comparison with Experimentally Determined Liquid Lines of Descent

The crystallization path of APP lavas is shown on the pseudo – ternary projection of APP samples (Plagioclase to Olivine-Clinopyroxene-Quartz) with 1atm saturation surfaces

(Grove et al., 1982; Grove et al., 1984) (Figure 4.8). The dominant phenocryst phases present in Planchon lavas are plagioclase, olivine, $\pm$ clinopyroxene and trace amounts of spinel and magnetite. The experimental phase equilibria suggest that Planchon lavas do not represent liquids that crystallized at atmospheric pressure because they do not plot along the 1atm olivine + clinopyroxene + plagioclase anhydrous pseudocotectic (Figure 4.8). Studies indicate that increasing pressures under anhydrous conditions will lead to a decrease in the olivine phase volume and shifts the olivine – augite cotectic towards the olivine apex (Kushiro, 1969; Stolper, 1980; Grove and Baker, 1984). All samples analyzed from Planchon plot in the olivine + plagioclase liquidus field which is consistent with dry experimental crystal evolution at pressures > 10 kb but < 20 kb and > 2 kb for H_2O saturated cotectics (Kushiro 1973; Bender et al. 1978; Villiger et al., 2004). From the Planchon basaltic andesite liquids, there is a nearly a complete continuous liquid line connecting the more SiO_2 rich Peteroa and Azufre liquids. The more silicic andesites and dacites from the APP complex more closely match the shallow 1-atm cotectics and follow the crystallization path consistent with advancement from the reaction point B (Figure 4.8). Reaction points B and A in Figure 4.8 are ternary eutectic reaction points where liquid compositions will evolve in those directions and once they reach either reaction points (invariant point) the liquid composition remains constant until solidification. The thermal divide (TD) from Figure 4.8 is the peak of liquidus surfaces and liquid compositions must move away from it from either end. This means that if Planchon basalts were fractionally crystallizing at low 1-atm pressures its assemblage would be olivine + plagioclase thus driving the liquid composition to the left and towards reaction point A and then toward the plagioclase-pigeonite-augite cotectic and avoiding reaction point B which is not the case. A continuous liquid line of descent that matches the observable data can be attained by continued fractionation involving oliv + plag thus driving the liquid past reaction point A and the thermal divide (TD) then this parental basaltic andesite liquid (Planchon) separates from its early forming olivine + augite + plagioclase assemblage at

pressures > 2 Kb H₂O saturated and ascends to a shallow magma reservoir to continue its 1 atm crystallization path toward andesitic composition (Figure 4.9). This observation suggests a higher pressure crystallization origin for the more mafic primary Planchon basalts. This process of polybaric fractional crystallization can be responsible for the production of calc-alkaline series lavas present at the Azufre-Planchon-Peteroa complex (Grove and Baker, 1984; Villiger et al., 2004).

It is paramount to consider the role of H₂O in subduction zone magmatism because arc lavas genesis is characterized by H₂O addition to mantle peridotite and lowering mantle solidus (Stolper and Newman, 1994; Gaetani and Grove, 1998). Experimental results of H₂O saturated high alumina basalts similar to the eruptive products at the APP yield multiple saturation of calcic plagioclase, olivine, high-Ca pyroxene, and spinel or magnetite along with high alumina basalt or basaltic andesitic liquid (Baker and Eggler, 1987; Helz, 1973, 1976; Sisson and Grove, 1993). The addition of H₂O to silicate melts lowers the temperature for first appearance of silicate minerals and shifts the cotectics towards the olivine apex and destabilizes plagioclase as a crystallizing phase. This induces more Mg and Fe rich phases to crystallize and fractionate relative to Ca in plagioclase which depletes the residual liquids in FeO and MgO and enriches it in silica, alumina, and alkalis, producing high alumina calc-alkaline magmas characteristic of subduction zone arc volcanics (Baker and Eggler, 1983; Gill, 1981; Grove and Baker 1984; Sisson and Grove, 1993; Yoder, 1965). The 2 kb H₂O saturated cotectic line proved a better fit for the more mafic magmas from the APP complex as compared to the 1 atm cotectics (Figure 4.8). It is also apparent that the residual liquids can follow the H₂O saturated cotectic line and bypass the reaction point A and the thermal divide (TD) and allow the shallow crystallization that is recorded by the silicic Peteroa and Azufre lavas. The Planchon lavas, however, do not perfectly fit along the 2Kb H₂O saturated cotectic line from Sisson and Grove (1993) and a more accurate higher pressure cotectic is traced along the appearance of augite as a crystallizing phase

in Figure 4.8. This is exemplified by the fact that some samples plotting in the olivine + plagioclase volume have augite as a crystallizing phase in their petrography (Figure 4.8), which suggests that crystallization occurred at a deeper/higher pressure than 2 Kb H₂O saturated cotectic. The petrologic appearance of augite in Planchon samples displays the shifting hypothetical cotectic lines towards the 2kb H₂O saturated cotectic line which seems to indicate the ascension of these magmas as they encounter shallower environments where augite becomes more stable.

The pseudo-ternary projection of the APP lavas from Diopside to Olivine-Plagioclase-Quartz shows that these liquids contain a higher proportion of plagioclase than similar 1-atm experimentally anhydrous saturated liquid basalt compositions (Grove and Baker, 1984; Figure 4.10). Similar to the plagioclase to OL-CPX-QTZ pseudo-ternary projection, the APP liquid line of descent follows slightly higher pressure phase proportions. The APP liquids plot closer to the higher pressure reaction points Takahashi and Kushiro of ~ 5kb (1983) in Figure 4.10, however, the difference in the 5kb and 1 atm anhydrous cotectics is very slight and may not be completely applicable and characteristic of wet arc magmas. This almost indistinguishable difference in crystallization paths can be better viewed in a pseudo-ternary diagram projecting the olivine component onto the Cpx-Plag-Qtz plane with H₂O varying cotectics from Sisson and Grove (1992; Figure 4.11). It is evident that Planchon lavas plot on and closer to the plagioclase apex from the 2kb H₂O saturated cotectic area (Figure 4.11). As the liquid differentiates, the liquid line of descent crosses the 0.7 p_{H₂O} cotectic line and approaches the 1 atm anhydrous field. The decrease in H₂O content and pressure of the magma suggests accelerated ascent and degassing of volatile species. The more silicic liquids from the APP complex plot closer to the 1 atm cotectic which agree with the pseudo-ternary diagram (PL to OL-CPX-QTZ) and suggest these highly differentiated liquids were emplaced in a shallow level magma chamber before eruption.

4.2.1 Liquid Compositions: Bulk Analysis versus Phenocryst Removal

In an attempt to exclude the possibility of crystal accumulation directly affecting the bulk composition of the rocks, the chemical compositions were recalculated by subtracting out the phenocrysts compositions from the whole rock analysis. This approach is necessary because some of these lavas have over 40% phenocrysts present which could alter the whole rock compositions via crystal accumulation and not be representative of the true liquids. In order to correct for crystal accumulation all analyzed phenocrysts oxide compositions from the Planchon center were averaged and then subtracted in their crystallizing proportions to calculate the new liquid (groundmass) compositions (Table 4.1). Over 34 samples from Planchon with microscopically determined modal analyses performed by Tormey et al. (1989) were recalculated and plotted to define a possibly more accurate liquid line of descent in the plagioclase onto OL-QTZ-CPX pseudo-ternary diagram (Figure 4.12). The Planchon samples with phenocryst subtraction exhibit a larger spread on the OL-QTZ-CPX pseudo-ternary diagram than the whole rock OL-QTZ-CPX pseudo-ternary diagram (Figure 4.8). The phenocryst subtraction treatment to the whole rock analysis was performed to tighten the data and have a more accurate depiction of the liquid line of descent; however, the opposite turned out to be true and the data now shows more variability and spread. This suggests that most of the Planchon lavas retained their minerals in crystallizing proportions and were part of the crystallizing liquid.

The use of bulk analysis on phyric samples as a representation of liquid compositions can possibly lead to inaccurate results, especially with samples containing up to 45% phenocrysts (Planchon). All samples collected at the APP complex are fresh flows and are unaltered which limits the chance of low temperature mobilization of elements. This leaves only crystal accumulation of phenocrysts or xenocrysts as possible sources of altered liquid compositions. Petrologic observations rule out any significant presence of wide spread xenocrystic populations, however, samples PL-16, PL-17, PL-24 and PL25 all contain high proportions of olivine and

olivine phenocryst core compositions that are too fayalitic for the lava compositions (Figure 3.7). Tormey (1989) determined when plotting MgO, Ni, Al_2O_3 , and Sr versus modal percentages in samples PL-16, 17, 24, and 25 that they all have high MgO and Ni and low Al_2O_3 and Sr contents as compared to the rest of the Planchon samples, which leads to the conclusion that these four samples are indeed olivine accumulates. From optical observation and mineralogical modal analysis it has been determined that the other 38 Planchon samples do not show correlations between mineral proportions and composition, which indicates the liquids retained their minerals in crystallizing proportions. This is in good agreement with the tight liquid line of descent of the pseudo-ternary diagrams and indicates that whole rock compositions do not need to be corrected via phenocryst subtraction and accurately represent liquid compositions for 38 out of 42 Planchon samples. A table of calculated liquid compositions used in Figure 4.12 can be seen in Appendix 3.

4.3 Thermo-Barometric Constraints on Melting Processes using Major Element Chemistry

The compositions of basalts can reflect the temperatures and pressures of magmatic generation in subduction zones. Using new thermobarometers developed by Lee et al. (2009) based on Si and Mg compositions in magmas; I estimated the temperature and pressure constraints on basaltic magma last equilibrium/separation from mantle sources at the APP complex. This model is a SiO_2 activity based barometer and is approximated by accounting for the chemical interactions between oxide components like ferromagnesian silicate and aluminosilicate species. Lee et al. (2009) found the SiO_2 activity calculations could reproduce experimental calculations for pressure. Lee et al. (2009) combined the Si based barometer with a robust thermometer based on Mg exchange between olivine and melt calibrated with experimental data. Thermobarometric equations and a more detailed explanation of the referenced model can be found in Lee et al. (2009). Primary magmas are calculated in this model by a reverse fractionation process (olivine addition) until the primary magmas are in equilibrium

with a mantle composition (residual mantle composition of $Mg\# = Mg/(Mg+Fe) = 0.9$). An obvious complication with this model is the possibility of co-crystallization of other mineral phases. Magmas from the APP may have fractionated other phases along with olivine like plagioclase and clinopyroxene. Both plagioclase and clinopyroxene are crystallizing phenocrysts in APP magmas. Ignoring the co-crystallization of plagioclase in primary melts results in a small over-estimate of SiO_2 and MgO giving higher T and P values. On the other hand, ignoring clinopyroxene results in an under estimate of SiO_2 and over estimate of MgO causing P outputs to be lower and T to be slightly higher. In order to minimize these systemic errors a sample selection filter was applied and only the most mafic magmas were chosen to run on the model. Samples were chosen to have SiO_2 wt. % < 55% (strictly basalts and basaltic andesites) and MgO wt % > 4%. With this most primitive magmatic sample selection ensures the most accurate and representative P and T values for primary magma separation from the mantle at the APP volcanic complex. As a consequence of selecting the most primitive magmas from the APP, most samples used in the model are from Planchon.

It is widely known that mantle melting at volcanic arcs is driven by the dehydration of the subducted slab as it plunges into depth and is heated up, which releases fluids into the overlying mantle wedge and depresses the solidus (Stolper and Newman, 1994; Kelly et al., 2006). What can't be easily determined are the pre-eruptive water contents of arc basalts. They have been recorded to vary from > 1 to < 7 wt. % H_2O (Lee et al. 2009). With this in consideration, I normalized the major element data from APP magmas to include 4 wt. % H_2O (low end) and 6 wt. % H_2O (high end). I used this H_2O range because it is a typical range exhibited by many arc magmas and Tormey (1989) analyzed an amphibole-bearing inclusion in an olivine phenocryst in a Planchon sample which contained 4.3 % volatiles. This direct measurement of H_2O species fall within the chosen range of primary magmatic water contents and would accurately depict possible primary magma compositions at Planchon. Additionally, this range of primary H_2O in

the magmas would serve to bracket the pressure and temperature values for the magmas and give a reasonable representation of possible P and T values. The oxygen fugacity (Fe^{3+}/Fe) is another parameter that is difficult to approximate and apply to subduction magmas so therefore I chose a range of appropriate Fe^{3+}/Fe values (0.10 and 0.15) to represent the possible range for APP magmas. This range in oxygen fugacity is suitable for subduction zone settings and provides a reasonable range for possible pressures and temperatures (Lee et al. 2009)

In addition to acquiring temperature and pressure constraints on basaltic magmas at the APP volcanic complex, I gathered density discontinuity data from Tassara et al. (2006) for the SVZ and overlaid this on the temperature vs. pressure diagram in Figures 4.14 and 4.15. This 3-D forward density modeling study predicts the approximate location of rheological and chemical boundaries associated with the SVZ subduction zone including the area around the APP complex. The predicted locations of the slab, lithosphere-asthenosphere boundary, and the Mohorovičić discontinuity are plotted on Figure 4.13 and allow a detailed understanding of the local geometry of the subduction zone and the ability to compare geochemical major element modeling constraints on temperature and pressure to chemical and rheological boundaries locations.

4.3.1 Primary Magmatic Conditions for the APP Complex

The primary magma compositions calculated by the Lee et al. (2009) model can be seen in Appendix 3 and on the T and P diagram Figure 4.14. The APP primary magmas with 4% H_2O and $\text{Fe}^{3+}/\text{Fe} = 0.1$ display a temperature range of 1266-1370°C and a pressure range of 1.24-1.89 GPa corresponding to a depth range of 46-70 km (37 km / 1 GPa). The average temperature and pressure conditions of APP magmas at 4% H_2O and $\text{Fe}^{3+}/\text{Fe} = 0.1$ of last equilibrium/magmatic separation from the mantle are ~1292°C and 1.42 GPa (52.5 km). Assuming primary H_2O is at 6 wt. % and $\text{Fe}^{3+}/\text{Fe} = 0.1$, the new temperature range is 1234-1306°C with an average temperature of ~1260°C and a pressure range of 1.26-1.84 GPa with an average pressure of 1.45 GPa (depth range: 47-68 km and average ~ 53.6 km). When the $\text{Fe}^{3+}/\text{Fe} = 0.15$ and primary magmatic H_2O

is 4 wt. % the temperature range is 1254-1347°C with an average of ~ 1275°C and the pressure range is 1.17-1.73 GPa (~ 42-64 km) with an average of ~ 1.32 GPa (~ 48 km) (Figure 4.16). With H₂O at 6 wt. % and Fe³⁺/Fe = 0.15, the temperature range is 1219-1310°C with an average of ~ 1242°C and a pressure range of 1.18 to 1.72 GPa (~ 44-64 km) with an average of 1.35 GPa (~50 km). With increasing primary magmatic water contents and keeping Fe³⁺/Fe constant, the magmas become cooler and separate (on average) at slightly greater depths than drier hotter magmas. When the Fe³⁺/Fe is increases from 0.1 to 0.15 with constant primary H₂O wt. %, the magmas are slightly cooler and separate at shallower depths than magmas with lower Fe³⁺/Fe values.

The APP primary magmatic compositions in all modeled parameters are consistent with the derived primary magmas with a high melt fraction of ~ 25% of averaged primitive upper mantle calculated by Plank and Langmuir (1988) with the exceptions of lower FeO and CaO wt. % and higher Na₂O wt. % which may be due to fractionation of plagioclase and clinopyroxene (Table 4.2). The chosen ranges in primary H₂O contents and Fe³⁺/Fe for all Planchon samples seem encompass reasonable values for typical subduction zone magmas and the results bracket all possible temperature and pressure conditions for primary generated basalts.

Regardless of the parameters chosen, the majority of Planchon magma separation estimates occur at depths that are confined to the lithosphere and many are located at the base of the crust (Moho). This would suggest that magmas at the APP complex have thermally abraded the lithosphere to lower crustal depths. With a thermally abraded lithosphere and possibly lower crust, partial mantle melts and mantle crystal mush itself must rise up to these depths in order for these magmas to remain in equilibrium with mantle olivine compositions. The range of possible temperatures of melt separation in Planchon primary basalts is 1219-1370 °C which is high enough to thermally alter the rigid lithospheric mantle and lower crust above the mantle melting zone.

4.3.2 Primary Magmatic Conditions for the CSVZ

In order to compare and contrast different volcanic zones settings within the SVZ along, I applied the same model with the same parameters (oxygen fugacity, H₂O content) to major centers of the CSVZ (Villarrica, Llaima, and small eruptive centers (SEC) near Villarrica). In the CSVZ the boundary locations and overall subduction geometry, as predicted by Tassara et al. (2006), differ from the TSVZ (where APP is located) shown in Figure 4.15. The Moho (0.95 GPa, ~ 35 km) and LAB (1.75 GPa, ~ 64.7 km) of the CSVZ are located at shallower depths than the Moho (1.21 GPa, ~ 44 km) and LAB (1.89 GPa, ~ 69 km) of the TSVZ. In the CSVZ it is apparent that most magmatic separation in these centers from the mantle occurs within the asthenospheric mantle on not the lithosphere (Figure 4.14). At Fe³⁺/Fe = 0.1 and H₂O contents at 4 wt. % the average temperature for magma separation in Villarrica is ~ 1324°C and average pressure of 1.55 GPa (~ 55 km) while at some of the SEC's near Villarrica the average temperature is ~ 1312°C and pressure of 1.57 GPa (~58 km). At Llaima with Fe³⁺/Fe = 0.1 and H₂O contents at 4 wt. % the average temperature of magma separation is ~ 1345°C and pressures of 1.70 GPa (~ 63 km).). At Fe³⁺/Fe = 0.1 and H₂O contents at 6 wt. % the average temperature for magma separation in Villarrica is ~ 1289°C and average pressure of 1.57 GPa (~ 58 km) while at some of the SEC's near Villarrica the average temperature is ~ 1277°C and pressure of 1.59 GPa (~58.8 km). At Llaima with Fe³⁺/Fe = 0.1 and H₂O contents at 6 wt. % the average temperature of magma separation is ~ 1307°C and pressures of 1.69 GPa (~ 62.5 km). When oxygen fugacity is varied among these volcanic centers all magmas are slightly cooler and separate at lower depths. At higher H₂O contents, the primary magmas across the centers are cooler but their origin is slightly deeper (larger pressure values).

The range of temperatures and pressures exhibited by the centers of the CSVZ mostly overlap the P and T values for Planchon magmas (TSVZ), however, the most pronounced difference is the subduction geometry across the arc. The Moho in the TSVZ is approximately

located at a depth of 45 km while the Moho in the CSVZ is at a depth of 30 to 35 km. Additionally the LAB in the TSVZ is at an approximate depth of 70 km and in the CSVZ it's at 60 km. These differences superimposed on the P-T results from the thermobarometer suggest that the lithosphere directly below the APP complex has undergone more lithospheric abrasion (up to crustal levels) than the lithosphere below the Villarrica and Llaima centers. This could indicate that at least locally, the APP sub arc crust is thinner and more thermally delaminated than the sub arc crust below Villarrica and Llaima. The centers of the CSVZ are mostly confined to depths of magma separation in the asthenosphere and plot along similar P-T paths (with same H_2O and Fe^{3+}/Fe) with Llaima extending to deeper and hotter P-T. This could indicate a thicker less abraded lithosphere below Llaima as compared to Villarrica and the SEC's. Additionally, assuming that magmas from Villarrica and the SEC's around Villarrica arise from similar depths and temperatures in the mantle wedge, the average temperature of the SEC magmas are lower for a given pressure than Villarrica magmas across varying parameters implying the SEC's have lower water contents. This is consistent with trace element features of the SEC, which are depleted in fluid mobile elements as compared to Villarrica and seem to have been generated at lower extents of melting.

4.4 Summary of Conclusions

New tephra samples collected from the Peteroa volcano exhibit a range in composition from basaltic trachyandesite to dacites and mark the first significant andesitic eruption since the onset of activity from Azufre. These new samples continue to show calc-alkaline affinities consistent with older Peteroa lavas. Azufre dacites have been petrologically determined to contain apatite in their glassy matrix which corresponds to the decreasing P_2O_5 decrease with increasing differentiation which suggests late stage fraction crystallization of apatite.

The pseudo-ternary projection of APP samples on the ternary diagram (Plagioclase to Olivine-Clinopyroxene-Quartz) is not consistent with 1 atm experimental surface saturations and

cotectic reaction lines (Grove et al., 1982; Grove et al., 1984; Figures 4.8 & 4.9). Mafic samples from Planchon and Azufre are more consistent with dry experimental crystal evolution at pressures 10 to < 20 kb and > 2 kb H₂O saturated cotectics (Figure 4.8). The 2Kb H₂O saturated cotectic lines proved a better fit and are more appropriate for the more mafic magmas from the APP complex as compared to the 1 atm dry cotectics, however, olivine+augite+plagioclase cotectic line should be shifted closer to the olivine apex suggesting a deeper/higher pressure origin for the crystallizing assemblage of Planchon lavas (Figure 4.8). The more silicic liquids from the APP complex plot closer to 1 atm cotectics which suggest these highly differentiated liquids were emplaced in a shallow level with continual crystallization (Figure 4.10 & 4.11). Even when recalculating liquid compositions via phenocryst subtraction, mafic samples continue to plot closer to the olivine apex of the OL-QTZ-CPX ternary diagram suggesting high pressure crystallization (Figure 4.12). The phenocrysts subtraction treatment to the whole rock data increases the variability of the liquid compositions which suggests that most samples have phenocrysts crystallizing in modal proportions.

By using thermobarometers developed by Lee et al. (2009) and appropriately varying estimates for initial water content and oxygen fugacity of parental magmas from the APP complex, it was revealed that the depth of primary magmatic separation from the mantle occurs at an average depth range of 48 to 53 km with an average temperature range of 1242 to 1292°C. In the CSVZ Llama had average calculated temperature range of 1295 to 1345°C and depths of 58 to 63 km. Villarrica and the SEC have calculated depth ranging from 51 to 58 km and temperatures of 1262 to 1324°C. The CSVZ as compared to the TSVZ show deeper melt segregation and hotter primary melt temperatures and most interestingly are confined to the asthenospheric mantle according to boundaries calculated from Tassara et al. (2006). The APP complex shows similar depth of magma separation than the CSVZ but the majority of these primary melts are confined to the lithosphere and at the base of the crust (Figure 4.14). This

major shift in sub-crustal geometry suggests that significant localized thermal abrasion of sub-continental lithospheric mantle and lower crust must occur below the APP complex. In the CSVZ based on these results it is implied that thermal abrasion of the localized lithospheric mantle is minimal as magma extraction depths are within the lithosphere/asthenosphere boundary, however with continued subduction magmatism and maturing/thickening of the continental crust at CSVZ, lithospheric abrasion may continue and accelerate in the future. Assuming that the magmas from Villarrica and the SEC's arose from similar depths and temperatures from the mantle source region, the lower average calculated temperature of the SEC magmas indicates that they actually have lower water contents than Villarrica which is consistent with depletions in fluid mobile elements in the SEC relative to Villarrica.

Figure 4.1: The total alkalis-silica diagram (TAS) showing the igneous rock classification for lavas from the Azufre-Planchon-Peteroa volcanic complex.

Figure 4.3: An AFM diagram showing the boundary between the calc-alkaline field and the tholeiitic field after Kuno (1968) and Irvine and Baragar (1971). App complex plots mostly in the calc-alkaline field with some Azufre dacites plotting in the tholeiitic field.

Figure 4.4: Bivariate plot of TiO_2 and Al_2O_3 versus SiO_2 of APP magmas.

Figure 4.5: Bivariate plot of Fe_2O_3 and MgO wt% versus SiO_2 wt%.

Figure 4.6: Bivariate plot of CaO and K_2O weight % versus SiO_2 wt. %.

Figure 4.7: Bivariate plot of Na_2O and P_2O_5 wt. % versus SiO_2 wt. %.

Figure 4.8: Pseudoternary projection using mineral components in oxygen and projecting from plagioclase onto olivine, high-Ca pyroxene (clinopyroxene), and quartz. Low pressure (1atm) plagioclase saturated cotectics (solid line) are plotted with reaction points A, B, and thermal divide (TD) from Grove and Baker (1984). The dashed line is the 2kb H₂O saturated cotectic from Sisson and Grove (1992). Azufre-Planchon-Peteroa samples are plotted showing a near continuous liquid line of descent. Black triangles within green circles are Planchon samples that contain Augite phenocrysts displaying the hypothetical high pressure cotectic lines.

Figure 4.9: Pseudoternary diagram of plagioclase projected onto olivine, quartz, and clinopyroxene. Plotted in the dark solid line is the proposed fractionation scheme/path that allows basaltic parent melts to bypass reaction point A and follow a calc-alkaline trend through early high pressure olivine + augite + plagioclase crystallization and fractionation (Grove and Baker, 1984). The liquid derived from high pressure fractional crystallization then ascends to a shallow magma chamber and the residual liquid follows the 1 atm cotectics to more silica rich liquids.

Figure 4.10: Pseudoternary diagram of diopside projected to olivine, quartz, and plagioclase with 1 atm anhydrous cotectics (solid line) and 5kb anhydrous cotectics (Takahashi and Kushiro, 1983; Grove and Baker, 1984).

Figure 4.11: Pseudoternary diagram of olivine projected onto clinopyroxene, quartz, and plagioclase with 1 atm pressure cotectics (solid line) and a bracketed area representative of 2kb H₂O saturated cotectics from Sisson and Grove (1992).

Figure 4.12: Pseudoternary diagram with plagioclase projected onto olivine, quartz, clinopyroxene with 1 atm cotectics (solid line) and 2kb H₂O saturated cotectic (dashed line) with phenocryst subtracted Planchon liquids plotted (Sisson and Grove, 1992; Grove and Baker, 1984). Here after phenocryst correction (average composition subtracted from whole rock analysis) an unreasonable spread resulted from Planchon liquids.

Table 4.1: Average composition of phenocrysts present in Planchon samples used in calculations

– Analysis from EPMA at FCAEM.

Oxides	Plagioclase	Olivine	Clinopyroxene
SiO ₂	52.34	38.85	52.37
Al ₂ O ₃	0.00	0.01	0.45
TiO ₂	28.95	0.00	2.39
FeO	0.83	23.84	17.37
MgO	0.00	0.20	7.29
CaO	0.13	38.62	15.79
MnO	12.88	0.00	3.57
Na ₂ O	3.71	0.00	0.41
K ₂ O	0.24	0.00	0.00

Figure 4.13: Density discontinuities underneath the South American continental margin. A) Subducted slab contoured at 25 km. B) Lithosphere-asthenosphere boundary (LAB) contoured at 20 km. C) The Mohorovičić discontinuity contoured at 10 km. (Tassara et al. 2006).

Figure 4.14: Temperature vs. pressure diagram of calculated primary magmas from the Azufre-Planchon-Peteroa complex using the model proposed by Lee et al. (2009). Primary magmatic H₂O contents are varied from 4 to 6 wt. % and $\text{Fe}^{3+}/\text{Fe} = 0.1$. Superimposed on the diagram are the boundary locations for the Mohorovičić discontinuity (MOHO), the lithosphere asthenosphere boundary (LAB), and the slab surface from Tassara (2006). Lherzolite solidi with varying H₂O contents are adopted from Katz et al. (2003). Error bars in temperature and pressure are shown on the right of the plot ($T \pm 40^\circ\text{C}$; $P \pm 0.2 \text{ GPa}$)

Figure 4.15: Temperature vs. pressure diagram of calculated primary magmas from Villarica, Llaima, and the small eruptive centers using the model proposed by Lee et al. (2009). Primary magmatic H₂O contents are varied from 4 to 6 wt. % and $\text{Fe}^{3+}/\text{Fe} = 0.1$. Superimposed on the diagram are the boundary locations for the Mohorovičić discontinuity (MOHO), the lithosphere asthenosphere boundary (LAB), and the slab surface from Tassara (2006). Lherzolite solidi with varying H₂O contents are adopted from Katz et al. (2003). Error bars in temperature and pressure are shown on the right of the plot ($T \pm 40^\circ\text{C}$; $P \pm 0.2 \text{ GPa}$).

Figure 4.16: Temperature vs. pressure diagram of calculated primary magmas from Villarica, Llaima, and the small eruptive centers using the model proposed by Lee et al. (2009). Primary magmatic H₂O contents are varied from 4 to 6 wt. % and $\text{Fe}^{3+}/\text{Fe} = 0.15$. Superimposed on the diagram are the boundary locations for the Mohorovičić discontinuity (MOHO), the lithosphere asthenosphere boundary (LAB), and the slab surface from Tassara (2006). Lherzolite solidi with varying H₂O contents are adopted from Katz et al. (2003). Error bars in temperature and pressure are shown on the right of the plot ($T \pm 40^\circ\text{C}$; $P \pm 0.2 \text{ GPa}$)

Table 4.2: Primary magmas derived from averaged primitive upper mantle (Plank and Langmuir, 1988) (wt%)

Elements	Mantle	25% Melt	10% Melt
SiO ₂	45.4	49.8	50.3
TiO ₂	0.18	0.65	1.15
Al ₂ O ₃	4.0	13.3	17.1
FeO	7.9	9.4	9.4
MgO	38.0	13.6	10.6
CaO	3.4	12.0	8.4
Na ₂ O	0.32	1.3	3.0

5. TRACE ELEMENT GEOCHEMISTRY

Trace element data on 53 samples from the APP complex and 25 basalts and basaltic andesite samples from CSVZ, TSVZ, and NSVZ centers presented here were determined by solution ICP-MS at the Trace Evidence Analysis Facility (TEAF) and are listed in Appendix 4. LA-ICP-MS analysis was also conducted on duplicate USGS rock powder standards in order to compare analytical accuracy of techniques using sample introduction of dissolved rock powder versus laser ablation of compressed powder pellets. Instrumental accuracy, uncertainties, bias and precision are presented in Appendix 4. Some data from the APP complex come from Tormey (1989) and were determined by Instrumental Neutron Activation (INAA) and X-Ray Fluorescence (XRF). One of the rationales for the present dissertation research is that the larger number of rare earth elements (REE), especially middle and heavy REE, determined by solution ICP-MS permits much more detailed examination of REE patterns as compared with INAA and XRF methods which were available during the initial examination of the APP volcanic center by Tormey (1989).

The following sections will discuss the different trace element behaviors during crystallization of appropriate mineral assemblages present in the Azufre-Planchon-Peteroa lavas. The dominant crystallizing assemblage determined petrologically by Tormey (1989) and confirmed by optical and hand sample observation is olivine + plagioclase $\pm$ clinopyroxene. Trace elements can be broadly separated into two types based on their behavior in magmatic systems; compatible elements (bulk solid/liquid partition coefficient $D \geq 1$) and incompatible elements (bulk partition coefficient $D < 1$). The goal is to be able to characterize the primary magma or magmas from which the different differentiated magmas formed and then to test different mantle partial melting models to produce that primary magma. Additionally, trace elements from basalts and basaltic andesites in other centers in the SVZ will be compared to APP basalts to establish localized variation and along-arc geochemical trends. Primary magmatic

compositions were also calculated for selected basalts from the TSVZ, CSVZ and NSVZ to compare and test mantle melting models.

5.1 Incompatible Elements

Incompatible elements are elements that are unsuitable in size and/or charge to the cation sites of crystallizing minerals defined by their mineral/melt bulk partition coefficients being less than 1. Incompatible elements can be divided into two main groups, large ion lithophile elements (LILE) and high field strength elements (HFSE). LILE are incompatible in mineral melt partitioning because of their large size and HFSE are incompatible because of their high charge.

5.1.1 Large Ion Lithophile Elements

Basalts and basaltic andesites at the APP complex have Rb concentrations from ~ 12 to 50ppm and Cs concentrations from ~ 0.3 to 2 ppm (Figure 5.1 and Figure 5.2). The andesites, trachyandesites and dacites have Rb concentrations from ~ 54 to 180 ppm, however most samples fall within the 54 to 120 ppm range. Cs compositions increase steadily in the andesitic to dacitic samples to ~ 1.7 to 4.6 ppm. PT-6 (rhyodacite pumice) has the most evolved SiO₂ compositions in the complex and correspondingly has extremely high Rb (~180 ppm) and Cs (~ 8.1 ppm). Ba abundances in basalts and basaltic andesites range from ~ 216 to 400 ppm and Pb varies 5.7 to 11.8 ppm (Figure 5.3 and 5.4). Within the small SiO₂ range of 51 to 55 wt. %, the basalts exhibit a large range in Ba and Pb which is different from the Cs and Rb ranges for the same samples. In more differentiated samples the Ba abundances increase from ~ 375 to 697 ppm and ~ 8.7 to 22 ppm Pb.

5.1.2 High Field Strength Elements

The basalts and basaltic andesites have Th, U, Nb, Zr and Hf abundance ranges of ~ 1.2-6.5 ppm, 0.4-1.6 ppm, 3.4-7.8 ppm, 94-163 ppm and 2.4-4.6 ppm (Figures 5.5-5.9). Within these ranges however, samples PL-26, PL-33, PL-34, PL-35, and PLII-5 are consistently higher in HFSE contents than all the rest of the Planchon suite. These samples are enriched in Zr (> 135

ppm), U (> 1 ppm), Nb (> 5.5 ppm), Th (> 3.4 ppm), and Hf (> 3.4 ppm) and stand apart from other basalt to basaltic andesite samples. These five samples are also distinguishable by their Pb concentrations (> 9.3 ppm). Higher SiO₂ samples (> 60 wt.%) show higher concentrations for Th, U, Nb and Hf ranges of ~ 5.5-19 ppm, 1.5-4.2 ppm, 5.7-10.7 ppm, and 3.8-6.8 ppm. Like the LILE, the HFSE show enrichments with increasing differentiation, which is expected with incompatible elements concentrations in melts that are undergoing fractional crystallization.

5.2 Compatible Elements

Compatibility of elements in mineral melt interaction is based on their valence, ionic radius and crystallizing assemblage. The crystallizing assemblage at APP is plagioclase-olivine-clinopyroxene and the corresponding compatible elements would be Sr, Ni, Cr, Sc, and Zn. Sc, Ni, and Cr data were obtained from Tormey et al. (1991). The abundances of Sr, Ni, Cr, Sc, and Zn in the basalts and basaltic andesites range from 422-580 ppm, 26-194 ppm, 33-328 ppm, 19-30 ppm, and 77-100 ppm (Figures 5.10-5.14). Samples PL-8, PL-16, PL-17, PL-18, PL-24, and PLII-4 show large enrichments in Ni and Cr which are both compatible in olivine. These enrichments may indicate olivine accumulation. Tormey (1989) determined samples PL-16, PL-17, PL-24, and PL-25 accumulated olivine based on petrographic observations which is in good agreement with the Cr and Ni versus SiO₂ plots. The andesite and dacites from Azufre and Peteroa have compatible element ranges 0.6-20 ppm Ni, 5.6-45.5 ppm Cr, 37-100 ppm Zn, 6.8-19 ppm Sc, and 175-478 ppm Sr. All compatible element concentrations decrease as the melt evolves to higher SiO₂ and lower MgO, which is expected due to their incorporation into fractionating phases. Ni and Cr initially decrease rapidly with small increases in SiO₂ and for more differentiated samples decrease more slowly indicating the decrease in the importance of olivine fractionation for more evolved melts and the early influence of olivine fractionation in more primary melts.

5.3 Rare Earth Elements (La to Lu)

The rare earth elements (REE) are useful trace elements and have important applications to igneous petrology. The REE in this study comprise of the series of elements with atomic numbers 57 to 71 (La to Lu). This group of elements can be further divided into light rare earth elements (LREE) La to Sm, middle rare earth elements (MREE) Eu to Ho, and heavy rare earth elements (HREE) Er to Lu. These distinctions are solely based on the small differences in ionic radius with increasing atomic number as all the REE form stable 3+ ions in magmatic systems. Only Eu commonly has another valence (+2), and the radius of this ion lies between that of Na⁺¹ and Ca⁺², which makes it compatible in feldspar. The small differences in size and chemical behavior are susceptible to petrologic processes causing REE fractionation.

Planchon La (LREE) concentrations vary from 12 ppm to 25 ppm; however, the majority of the samples (26 out 35 samples analyzed) fall within the 12 to 15 ppm range (Figure 5.15). Sm, another LREE, varies in from 3 to ~9 ppm in all samples but most fall within the 3 to 6 ppm range (Figure 5.16). Gd (MREE) in Planchon samples varies from 3.4 ppm to 5.5 ppm and Yb (HREE) varies from 1.5 ppm to 2.8 ppm (Figure 5.17 and Figure 5.18). Azufre and Peteroa exhibit higher and larger ranges in La 17 to 37 ppm (Azufre) and 17 to 45 ppm (Peteroa). Peteroa also has a larger range in Gd from 4 to 9.2 ppm while Azufe has a range of 4.7 to 8.7 ppm. The HREE (Yb) in Peteroa ranges from 1.7 to 2.7 ppm and Azufre ranges much higher from 2.5 ppm to 4.8 ppm.

5.3.1 Rare Earth Element Patterns of the APP Complex

The following rare earth element concentrations are normalized to primitive mantle (PM) values of McDonough and Sun(1995) and normalized values and ratios will be denoted with the subscript N. The purpose of this normalization is to eliminate the universal variation of abundances among even and odd atomic numbered elements and allows for identification of any

fractionation of the REE group relative to a hypothetical undifferentiated earth mantle (primitive mantle)

Basalts and basaltic andesites from Planchon show large enrichments in LREE. La, for example, has a range of 18 to 39 times relative to primitive mantle (Figure 5.19). Yb, a HREE, shows modest enrichments of 3.5 to 6.4 times relative to primitive mantle. Planchon basalts and basaltic andesites can be segregated into two groups based on their REE patterns. The majority (28 of 34 samples) of these Planchon samples fall into a tighter (less variability) LREE enriched (La, 18 to 24 times PM) smooth curve toward lower MREE (Dy, 4.7 to 5.5 times PM) and HREE (Yb, 3.6 to 4.2 times PM). These have small negative europium anomalies (Eu/Eu^* , where Eu^* is the abundance of Eu interpolated from adjacent REE assuming a smooth pattern) of ~ 0.88 to 0.91 (Figure 5.19), indicating that some Eu was in the +2 state. The other 6 Planchon samples (PL-25, PL-26, PL-33, PL-34, PL-35, and PLII-5) display a much larger LREE enrichment (La, 27 to 39 times PM), higher MREE (Dy, 6.1 to 8 times PM), higher HREE (Yb, 3.6 to 4.2 times PM) with large negative europium anomalies (Eu/Eu^*) of ~ 0.73 to 0.80 .

The Azufre dacites show much larger LREE (La, 48 to 58 times PM), MREE (Dy, 10 to 11 times PM), and HREE (Yb, 9 to 10 times PM) concentrations with extremely large negative europium anomalies of ~ 0.58 to 0.63 (Eu/Eu^*) (Figure 5.20). The one Azufre basaltic andesite plots well below the dacites and is compositionally similar to the Planchon basalts. Peteroa andesites compositionally fall in between Azufre dacites and Planchon basalts with La (LREE) ~ 23 to 45 times larger relative to primitive mantle values. Peteroa Dy and Yb (MREE and HREE representatives) also plot in between Planchon and Azufre samples.

5.3.2 REE Patterns along the SVZ Volcanic Arc

REE concentrations were analyzed for 34 basaltic and basaltic andesites ($<57\%$ SiO_2) from mafic along arc volcanic centers Casimiro (34.2°S , 69.8°W), Laguna del Maule (36.02°S , 70.5°W), Descabezado Grande (35.6°S , 70.7°W), Nevados de Longavi (36.2°S , 71.2°W),

Nevados de Chillan (36.8°S , 71.4°W), Antuco (37.4°S, 71.4°W) and Callaqui (37.9°S , 71.4°W). These volcanoes are located in NSVZ, TSVZ, and CSVZ which would provide an adequate along arc comparison of REE compositions and petrologic processes involved. The REE data is normalized to primitive mantle (PM) values of McDonough and Sun(1995).

The basalts from Antuco and Callaqui from the northern CSVZ mostly show moderate La_N enrichments ranging from 13 to 23 times primitive mantle which is typical for basalts in this volcanic zone (Figure 5.21). Three samples from Callaqui show higher LREE normalized enrichments of LREE of 26 to 33. The overall REE pattern for these basalts is flat from the LREE to the HREE. This is also exemplified by their low La_N/Yb_N values of 2.7 to 4.7. Callaqui and Antuco show high variability in Yb_N values giving their La_N/Yb_N ratios a larger range. Overall the patterns representing the CSVZ are comparatively flat with limited enrichment in LREE and should be considered baseline type values in comparison to the whole arc because these magmas have interacted minimally with the continental crust. Most samples from Callaqui and one sample from Antuco show negative europium anomalies indicating that plagioclase may have been a fractionating phase in these magmas.

The basalts from Nevados de Chillan, Nevados de Longavi, Descabezado, and Laguna del Maule display much steeper REE patterns with larger LREE enrichments and larger depletions in HREE (Figures 5.22 & 5.23). These centers are all located in the TSVZ where the sub arc crust thickens by ~ 10 km relative to the CSVZ. La_N enrichments are apparent and for all these centers their range is 15 to 35 times relative to primitive mantle. The extent of LREE/HREE fractionation increases in this portion of the arc represented by higher La_N/Yb_N values of 4.1 to 11.4. This LREE to HREE fractionation is apparent in the increases slope of the REE patterns. Laguna del Maule and Nevados de Longavi exhibit the largest depletions in Yb_N in the TSVZ centers and consequently have the highest La_N/Yb_N (6.5-11.4). Overall basalts from centers in the TSVZ show enrichments in the LREE (La to Sm), similar MREE (Eu to Dy), and

depletions in HREE (Ho to Lu) as compared to basalts from Antuco and Callaqui. Basalts from Nevados de Chillan also show small negative europium anomalies implying a small influence of plagioclase fractionation in the evolution of those samples.

Basalts have not been reported in the NSVZ; therefore in order to accurately compare the different volcanic zones the most mafic basaltic andesites from Casimiro were used. Casimiro basaltic andesite REE patterns are increasingly steep as a result of larger LREE enrichments and larger HREE depletions (Figure 5.23). The Yb_N values at Casimiro are the lowest and most severely depleted of all samples analyzed and have resulted in the largest range of La_N/Yb_N (7.5 to 11.7). Other HREE like Ho, Lu, and Er are consistently more depleted than other centers in the TSVZ and CSVZ. The MREE in all volcanic segments vary relative to one another and there no clear enrichment or depletion trend visible.

5.4 Modelling Trace and REE Processes

The rare earth element patterns in igneous rocks such as the ones at the APP complex and those along the SVZ arc are controlled by the crystal-melt interaction-equilibrium which has taken place during its ascent to the surface and the chemistry of the source region. The REE have low mobility during weathering, thus fresh unaltered volcanic rocks retain the relative abundances of their source magma. The roles of individual phases can be identified in a quantitative manner during partial melting of the source region or in later crystal fractionation and are entirely based upon the partition coefficients for REE in rock forming minerals. REE element partition coefficients for major minerals involved in crystal fractionation models and references therein can be found in appendix 4 and are plotted in figure 5.53.

In the following sections, Planchon basalts have been classified into three groups based on their REE compositions. Group 1 basalts are the most abundant group (20 samples) and define a high La_N/Yb_N range of ~ 5.3 and 6.1. Group 2 basalts make up 6 samples that are characterized by their low La_N/Yb_N range of 4.3 to 4.7. Group 3 basalts (6 samples) are highly

enriched in LREE, MREE, and HREE. The reasons for the compositional variability in Planchon basalts will be explored through mineral vector diagrams and partial melting models.

5.4.1 Determination of a Representative Primary Melt

In order to interpret and REE patterns and diagrams, understand mineral controls on REE compositions through fractional crystallization, and model partial melting of source components in arc magmatism, it is vitally important to estimate the composition of a parental or “primary” magma from which all other samples are derived. The method of olivine addition (from Cin-Ty Lee et al. 2009) was applied to a basalt sample believed to represent the initial mafic magmas from the APP complex. Olivine addition simply adds olivine of a composition in instantaneous equilibrium with magma, in small increments, after which the melt composition is recalculated until a magma composition is reached in equilibrium with olivine of composition Fo 90. This is assumed to be the average composition of the mantle residue after melt extraction (Lee et al. 2009). The assumption that olivine is the only crystallizing phase from melt extraction to basaltic compositions present in Planchon magmas is, strictly speaking, not true because at some extent they have undergone co-crystallization of either clinopyroxene or plagioclase. This could lead to inaccurate calculations of primary melt major element compositions. However, most Planchon basalts in the pseudo-ternary diagram Pl to Ol-Cpx-Qz (Figure 4.9) plot close to the olivine apex which suggests they have mostly begun to crystallize olivine and co-crystallization of clinopyroxene and plagioclase is minor. This effect on the major elemental compositions can also be limited by choosing a sample that plots further away from the olivine-clinopyroxene cotectic lines (Figure 4.9). Additionally, the olivine addition method does not affect the highly incompatible rare earth elements because the partition coefficients of these elements for olivine, clinopyroxene, and plagioclase are low (~ 0) which means any calculated primary melt REE composition would likely be representative regardless of how much each of these phases have fractionated.

Primary melt compositions were calculated for PL-7 and PL-19 (representative Planchon basalts) because of their low SiO₂ (51.7% and 52.5%), high MgO and Mg # (6.47%, 57 and 6.8%, 59), and low Rb/Y (~0.98 and 1.15). Two different primary magmas were calculated because Planchon basalts define two main groups based on their REE compositions; PL-7 represents the lower La_N/Yb_N group (~4.3 to 4.8) and PL-19 represents the higher La_N/Yb_N group (~5.3 to 6.1). La_N/Yb_N is largely used to measure the degree of REE fractionation and one primary melt may not completely explain the variation of La_N/Yb_N Planchon basalts. The calculated major element and rare earth element compositions for PL-7 and PL-19 can be seen in Table 5.1A. The relative amounts of olivine added to PL-7 was ~19% (~1.22 final mass relative to original mass), or in other words the calculated primary melt fractionated ~ 17% olivine en route to become PL-7 and ~ 15% for PL-19. The Lee et al. (2009) model uses a Fe-Mg olivine to magma partition coefficient value of 0.3 for the calculation of major element compositions. The highly incompatible REE compositions were modelled using 0 as a partition coefficient. The Rayleigh fractionation equation $\{(C_L/C_0) = F^{(D-1)}\}$ was used to approximate the initial compositions of elements that are compatible in olivine ($D > 1$) or slightly less incompatible ($D > 0.1$) like Cr, Sc, and Zn (Table 5.1B).

Table 5.1A: Calculated Primary Magmas Major Element Compositions (wt. %)

Sample	SiO₂	TiO₂	Al₂O₃	FeO	MnO	MgO	CaO	Na₂O	K₂O
PL-7	48.41	0.77	14.03	8.58	0.12	13.81	6.99	2.74	0.70
PL-19	49.24	0.74	14.13	8.12	0.12	13.11	7.10	2.71	0.79

Table 5.1B: Calculated Primary Magmas Rare Earth Element Compositions (ppm)

Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy
PL-7	14.898	13.496	12.127	10.455	7.740	5.699	5.485	4.626	3.998
PL-19	18.64	16.554	14.064	11.766	8.243	6.096	5.829	4.984	4.378
	Ho	Er	Yb	Lu	Zn	Ni	Cr	Sc	
PL-7	3.78	3.50	3.42	3.39	100.31	1690.06	145.32	22.68	
PL-19	3.902	3.820	3.386	3.300	101.49	1770.54	216.93	23.35	

*REE values are normalized to Primitive Mantle (McDonough and Sun1995)

5.4.2 REE and Trace Element Mineral Vector Diagrams (Basalt to Basaltic Andesite)

Rare earth and trace element compositions and ratios are plotted in bivariate diagrams in Figures 5.24 to 5.41. Two calculated primary magmas are plotted and represent possible parental magma compositions for Planchon Groups 1 and 2. Mineral vector diagrams originating from the primary magmatic composition of group 2 are also plotted showing fractional crystallization trends for olivine, garnet, clinopyroxene, amphibole, and/or plagioclase. The Rayleigh fractionation equation $\{(C_L/C_0) = F^{(D-1)}\}$ was used to approximate mineral controls on REE compositions and partition coefficients used can be found in Appendix 4. The percentages along the mineral vectors represent the amount of fractionation has occurred from the composition of the primary melt. To avoid clutter and confusion on the bivariate diagrams, mineral vectors were not applied to the Group 1 primary melt, however, the mineral vector trends do not change. Some

mineral vectors (like plagioclase) are not shown in many figures because they display similar vector trends to other phases or exert no control over REE or trace element trends ($K_d \sim 0$) especially for discriminant bivariate diagrams.

Although garnet has not been found as a phenocryst in any SVZ magma to date, garnet-bearing ultramafic and mafic cumulate rocks with calc-alkaline chemical trends are found in exposed crust-mantle sections at continental convergent margins like the south central Alaskan Tonsina complex and the Kohistan island arc in northern Pakistan as well as garnet-bearing volcanic ultramafic xenoliths from the Sierra Nevada region. These occurrences suggest that garnet has a potential role in calc-alkaline magmas via high pressure fractional crystallization (Miller et al. 1991; Miller and Christensen 1994; Debari and Coleman 1989; Debari 1997; Ducea and Saleeby, 1998). Crystallization and fractionation of garnet at high pressures in the generation of calc-alkaline melts has been proposed by Green and Ringwood (1968) with the observation of garnet phenocrysts in dacites and on experimental phase equilibria of calc-alkaline compositions (Day and Green 1992). New crystallization experiments on hydrous basalts at oxidizing conditions show that garnet becomes a primary igneous phase at high H_2O contents and at pressures between 800 and 1500 MPa (Muntener et al., 2001; Alonso-Perez, 2006). The crystal fractionation of garnet would have profound effects on the REE chemistry of magmas and could easily be distinguished, by a large fractionation of LREE/HREE (high La/Yb) and major depletions in HREE and Y. These geochemical signatures have been reported in mid-Holocene eruptive products from Nevado de Longavi volcano in the TSVZ of southern Chile and these signatures have been explained via the crystal fractionation of $\sim 1.5\%$ garnet (Rodriguez et al. 2007).

The increases of La_N/Yb_N from Group 2 basalts to Group 1 basalts can be explained by co-precipitation of ~ 3 percent garnet and up to ~ 20 percent olivine, assuming primary melt 2 is parental magma for both groups (Figure 5.24). Garnet exhibits large partition coefficients for Yb

(HREE) in basaltic melts of 6.6 to 8 and small (0.016) partition coefficients for La (LREE) (Hauri et al. 1994, Johnson 1998, Irving and Frey 1978). This large difference in partition coefficients in garnet would drastically increase the fractionation of La relative to Yb (high LREE/HREE). Similarly, ~ 3% fractionation of garnet could also account for the increase of D_{Y_N/Yb_N} , Gd_N/Yb_N , and Sm_N/Yb_N from group 2 to group 1 basalts (Figures 5.25, 5.26, 5.27). In the diagram of D_{Y_N/Yb_N} vs La_N/Yb_N , the garnet mineral vector encompasses the basaltic range with 3 to 4 percent fractionation (Figure 5.28). However, when looking at mineral vector diagrams with trace elements that are compatible in garnet ($K_d > 1$), a different trend emerges. Sc/Y vs Y and Sr/Sc vs Y both show an enrichment trend in Y from basalts to basaltic andesites (Figures 5.29 & 5.30). Y has partition coefficients of ~ 3.1 in garnet in basaltic liquids (Green et al., 2000). If garnet was a fractionating phase in Planchon basalts, the resulting trend would be depletion in Y not enrichment. The garnet mineral vectors in Figures 5.29 and 5.30 clearly do not represent the fractional crystallization trends of Planchon and is not responsible for the fractionation of LREE relative to HREE.

The importance of amphibole as a crystallizing igneous phase in calc-alkaline magmas has been established in numerous studies (Sisson and Grove, 1993; Carroll and Wyllie 1990; Allen and Boettcher, 2009). Additionally, experimental work has shown amphibole crystallization is probable when H₂O rich basaltic melts are trapped at in the deep crust (Barclay and Carmichael 2004). In the SVZ, amphibole is present in crystallizing assemblages in andesitic volcanic samples from Calbuco, a major volcanic complex in the SVZ, and plays a pivotal role in the geochemistry of this volcano (Lopez-Escobar et al. 1995). Amphibole could potentially enrich LREE relative to HREE, although not as strongly as garnet, and experimentally determined partition coefficients for amphibole in basaltic to basaltic andesitic melts is in the order of 0.2 to < 2 for LREE and HREE (Dalpe & Baker, 2000). In order to reach the degree of fractionation in La_N/Yb_N exhibited by group 1 basalts from primary melt 2, > 30% amphibole

fractionation would need to occur (Figures 5.24 & 5.31). This degree of amphibole fractionation can also explain the trends in $\text{La}_\text{N}/\text{Nd}_\text{N}$ vs Nd_N and $\text{La}_\text{N}/\text{Sm}_\text{N}$ vs Sm_N space along with the bivariate diagram of $\text{La}_\text{N}/\text{Nd}_\text{N}$ vs $\text{La}_\text{N}/\text{Yb}_\text{N}$ (Figures 5.32, 5.33 & 5.41). Contrastingly, amphibole partition coefficients for the MREE Gd, Dy, and Er are higher than that of Yb (HREE). If amphibole was a fractionating phase, the resulting Gd/Yb, Dy/Yb, and Er/Yb ratios would decrease, which is not the case (Figures 5.26, 5.25, & 5.34). Additionally, the assumption of 30% amphibole fraction is unreasonable because it would raise the SiO_2 compositions of derivative magmas and the range of SiO_2 in all Planchon basalts is small (Figure 5.35).

Olivine fractionation plays a vital role in the compositions of few trace elements in basalt to basaltic andesite differentiation. Olivine for all REE has partition coefficients that approach ~ 0 so it exerts little effect on REE, however, Ni is compatible in olivine with high partition coefficients from 4.36 to 15.5 in basalts (Seifert et al. 1998; Kloeck and Palme 1988). Zn is similar in its elemental behavior to Ni but it is not as compatible in olivine as Ni so if olivine is fractionated from basalts the Ni/Zn ratio would decrease as shown in Figure 5.36. Alternatively if olivine is an accumulative phase, which some Planchon samples have been shown to be, the Ni/Zn ratio would increase. Four accumulative samples have been identified as having Ni/Zn ratios > 1.2 . It is also worth noting that olivine is most likely the primary crystallizing phase and there was little or no co-precipitation of plagioclase for more mafic samples (Figure 5.37). Here Planchon groups 1 and 2 plot along changing Ni/Zn ratios with little change in Sr/Nd (Figure 5.37).

Sr and Nd have very similar chemical behaviors and are difficult to fractionate, however, Sr is compatible in plagioclase so if plagioclase was a significant fractionating phase then the Sr/Nd ratio would decrease. Planchon group 1 shows no significant change in Sr/Nd ratios suggesting little or no fractionation of plagioclase. Group 3 and some Group 2 basalts show major shifts in the Sr/Nd ratios from the main line of Planchon basalts due to major plagioclase

fractionation (Figure 5.37). The amount of plagioclase fractionation from estimated parental magmas in Group 2 basalts is ~ 10% and for Group 3 basalts is ~ 30% (Figure 5.38).

Europium exists in magmas in divalent and trivalent states and in its divalent state is compatible in plagioclase which contrasts from its incompatible trivalent state. As a result of this phenomenon magmas can show europium anomalies with either removal of feldspar via crystal fractionation or partial melting of rock containing abundant residual feldspar (negative anomaly) or accumulation of feldspar in a melt or crystal cumulate (positive anomaly). Most Planchon basalts show negative europium anomalies; however, the extent of the anomaly varies from sample to sample (Figure 5.39). Planchon basalts show Sr/Nd ratio and (Eu/Eu*) decreases as the magma differentiates (increasing SiO₂) which makes plagioclase a vital fractionating phase contributing to changing melt compositions especially in the more differentiated samples (Figures 5.39 and 5.40). Group 3 basalts (PL-25, 26, 33, 34, and 35) have unusually higher negative europium anomalies than the other 28 samples Planchon basalts and but show no significant changes to their SiO₂ composition with increasing negative Eu/Eu*. The average SiO₂ composition of these six samples is ~ 53 wt. % which is very close to the average SiO₂ (52.3 wt. %) compositions of Planchon plagioclase phenocrysts determined using the EPMA. These six samples underwent ~ 30% plagioclase crystal fractionation with little effect on SiO₂ compositions (due to compositional similarity) which explains their larger than normal enrichments in REE composition relative to the other Planchon basalts.

Clinopyroxene has been identified as a fractionating phase in Planchon basalts because of Sc compatibility in its crystal structure (Figures 5.29 & 5.30). Clinopyroxene also has a small effect towards the fractionation of La to Yb and La to Sm as shown from its mineral fractionation vectors in Figures 5.24 & 5.41. However, the differences in control that clinopyroxene has on La and Yb is minimal and it would take > 50% cpx fractionation to raise the La/Yb ratio of Group 2 basalts (~4.4) to Group 1 basalts (5.5). This amount of crystal fractionation is unreasonable and

would drastically change the major and trace elements compositions unseen in basalts and basaltic andesites.

Therefore, it is apparent that the degree of LREE to HREE enrichment from Group 2 to Group 1 basalts cannot be accounted for by crystal fractionation of major igneous phases. This leads to the possibility that multiple compositionally distinct parental magmas were generated with differing degrees of REE fractionation due to changes in the extents of melting of a mantle source and/or varying REE source compositions. Generation of basaltic magmas in subduction zones is known to be episodic and multiple distinct batches can be generated from the same source region.

5.4.3 Along-Arc REE Geochemical Trends

The La_N/Yb_N (LREE/HREE) ratio along the arc shows an increase from typical CSVZ basalts (Villarrica, Llaima, Osorno) with values of ~ 1.83 to 3.4 to larger TSVZ values for basalts ranging from 2.7 to 11.5 and the lone NSVZ mafic center Casimiro has normalized La/Yb ratios of 7.5 to 11.7 (Figure 5.42). Compared with "baseline" basalts from the CSVZ, the basalts and basaltic andesites from the TSVZ and NSVZ show between 3 and 4-fold increase in the fractionation of LREE to HREE. The increase in La/Yb along the arc could be attributed to both La enrichment and/or Yb depletion. La enrichment relative to Yb can be attained by smaller melt fractions for the mantle source regions which is possible in the TSVZ and NSVZ because of the thickening lithosphere which decreases the mantle melting column (Tormey et al. 1991). A smaller mantle melting column would lead to less mantle corner flow and smaller extents of melting. However, it is evident that most CSVZ centers have Yb_N compositions from 3.4 to 6 and the La_N/Yb_N increase in TSVZ and NSVZ basalts are mostly due to Yb depletion rather than La enrichment because of the negative sloping trend (Figure 5.43). The fractional crystallization or crustal assimilation with residual garnet or amphibole could be responsible for the LREE/HREE increases along the arc. When plotting normalized Gd/Yb and Dy/Yb against Yb_N

and normalized Dy/Yb against normalized Gd/Yb the patterns reveal involvement of garnet over amphibole (Figures 5.44, 5.45, & 5.46). Both Gd/Yb and Dy/Yb increase with decreasing Yb from CSVZ-like basalts starting from Antuco more northern centers Casimiro and Nevados de Longavi suggesting that the HREE like Yb are being systematically depleted causing MREE/HREE ratios to increase. The normalized Dy/Yb and Gd/Yb ratios of all basalts and basaltic andesites correlate positively from CSVZ baseline Antuco basalts on through to Laguna del Maule, Nevados de Longavi and Casimiro samples (Figure 5.46). If amphibole were involved the Dy/Yb and Gd/Yb ratios would decrease from CSVZ-like basalts which is an opposite behavior to garnet (Figure 5.46). Additionally, normalized La/Yb against normalized Dy/Yb also distinguishes the role of garnet (positive correlation) and amphibole where La/Yb would increase but Dy/Yb would decrease (Figure 5.47).

A role for garnet in the evolution of basaltic magmas along the volcanic front in the SVZ is suggested based upon the REE and trace element data presented. What is not clear is if garnet is present as a residual phase during partial melting of lower crustal granulite type lithology, equilibrating with arc derived mafic underplated basalt or basaltic gabbro with residual garnet, or garnet present as a residual phase in the partial melting of mantle peridotite.

5.5 Geochemical Modeling of Mantle Source Partial Melting

Once primary magmatic REE compositions were estimated for Planchon Group 1 and 2 basalts using the Lee et al. (2009) model, then these values could be used to constrain the source composition and the extent of melting of mantle sources that produced these primary basaltic magmas. Based on the assumption that the HREE remain unchanged during the subduction modification process (Pearce et al. 1993) the calculated primary magma compositions were used to “match” mantle partial melts with differing extents of melting and melting mineralogy. Mantle source compositions used in partial melting calculations were the Primitive Mantle estimate from McDonough and Sun (1995) and the Depleted Mantle estimate from Salters and Stracke (2004).

A dual approach using equilibrium modal and non-modal partial melting model was used (Shaw, 1970; Hofmann and Feigenson, 1983). The following three mantle mineral assemblages were used to encompass all possible melting scenarios and provide the best composition HREE match for primary Planchon magmas: 1) olivine 0.50, opx 0.25, cpx 0.20, spinel 0.05; 2) olivine 0.50, opx 0.20, cpx 0.15, garnet 0.05, spinel 0.05; and 3) olivine 0.50, opx 0.22, cpx 0.22, garnet 0.01, spinel 0.05. These three hypothetical mantle mineral assemblages were used to assess the influence of garnet on the initial REE compositions of primary basalts and to quantify the extent of garnets involvement as a residual phase in the mantle and to test the different extents of mantle melting needed to produce the HREE compositions of Planchon primary basalts.

Partially melting both hypothetical primitive and depleted mantle with a mineral assemblage of 50% olivine, 20% opx, 20% cpx, 5% garnet and 5% spinel produces liquids with compositions inconsistent with Planchon primary melts (Figure 5.48). The influence of garnet on the REE compositions is drastic causing major depletions in the HREE (Ho to Lu). The slope of the MREE to the HREE in these partial melts is much too steep to resemble Planchon primary melts. The depleted mantle partial melt compositions for melts fractions of ~ 2 to 4% approach similar LREE compositions of the Planchon primary magmas, however, the LREE compositions can be affected by subduction zone processes and are unreliable. Even when varying the extent of mantle melting (F values), the effect of garnet is too strong on the HREE. Regardless of the composition of the mantle and the extent to which it is melting, a mantle mineral assemblage of 50% olivine, 20% opx, 20% cpx, 5% garnet and 5% spinel could not produce primary Planchon magmas.

Adjusting the hypothetical mantle mineral assemblage of 50% olivine, 22% opx, 22% cpx, 1% garnet and 5% spinel and then applying varying amounts of melting extents produces liquids with HREE compositions that more closely resemble Planchon primary melts (Figure 5.49). In the case for a compositionally depleted mantle, a best fit for HREE would be a 4%

extent of melting. This low amount of partial melt is not consistent with predicted extents of partial melting for arc basalts of 10 to 20% (Plank and Langmuir, 1988) and 8-20% for MORBs (Klein and Langmuir 1987), because it would require unrealistically low viscosity in order to be separated from its source residue. Partial melting of the primitive mantle composition with this mineral assemblage yields a more reasonable extent of melting (~14%); however, this partial melt only matches one of the four HREE (Er) and the slope of this HREE pattern is too steep (depleted Yb and Lu). It is evident that even a mantle mineral assemblage that only consists of 1% garnet would not produce the calculated primary partial melts from Planchon.

With a mantle mineral assemblage of 50% olivine, 25% opx, 20% cpx, and 5% spinel, devoid of garnet, the predicted partial melts produced provide the most realistic matches to the calculated primary melts (Figure 5.50). Melting ~ 17% of primitive mantle yield melts with near identical HREE values as the primary melts and falls within predicted ranges extents of partial melting for arc basalts. Similarly, melting of ~15% of a depleted mantle source will produce melts very close in HREE composition to primary Planchon basalts, but not as close as the primitive mantle melts. Although both the primitive and depleted mantle sources yield reasonable extents of melting and match the HREE compositions of the primary Planchon basalt, the primitive mantle partial melt is more realistic because its LREE concentrations are closer to those of calculated primary magmas. Regardless of which mantle source is ultimately involved, it is clear that the mantle mineral assemblage does not require garnet as a residual phase of mantle melting.

Planchon Groups 1 and 2 have primary calculated magmas that are essentially identical in their HREE compositions and therefore the partial melting model that matches the HREE applies to both magmas. However, there are differences in the LREE from these calculated magmas which can be attributed to smaller extents of melting for group1 basalts relative to group 2 basalts (Figures 5.48, 5.49, & 5.50). For example, adjusting the partial melting percentage of the mantle

mineral assemblage of 50% olivine, 25% opx, 20% cpx, and 5% spinel of ~17%, which is the best match for the group 2 basalt, to a partial melt percentage of 13% would explain the LREE enrichment difference in both primary magmas. Another possible explanation for the difference in LREE composition in the Planchon Groups 1 and 2 could be slight compositional differences in mantle sources. This difference in mantle source compositions would have to exist on a small space and time scale given the fact that a pre Azufre mafic andesite flow gave K-Ar dates of 0.55 mya and the APP center spans approximately 6 km in length.

5.5.1 Primary Magmas of the SVZ

Primary magmatic REE compositions were calculated for selected basalts and basaltic andesites from the SVZ using the Lee et al. (2009) model and can be seen in appendix 4. Comparing primary basaltic compositions can provide a unique window into the factors controlling initial REE compositions of primary melts and the nature of mantle melting at different subduction zone environments. Calculated primary melt compositions for Villarrica, Antuco, Planchon, Descabezado, Laguna del Maule, and Casimiro are plotted on a REE diagram in Figure 5.51. Villarrica primary magmas show the flattest REE patterns with comparative depletion in LREE and enrichment in HREE relative to other primary magmas in the TSVZ and NSVZ. Antuco, another center from the CSVZ, has similar overall flat REE patterns with identical LREE compositions to Villarrica but more depleted HREE. Villarrica can be considered a representative primary basalt from the CSVZ where crustal contributions via assimilation have been ruled out on the basis of trace element and isotopic considerations (Hickey-Vargas et al., 1989; Sun et al., 2001). The centers of the TSVZ Planchon, Descabezado, and Nevados de Chillan show higher enrichments in LREE and larger depletions in HREE when compared to the CSVZ primary magmas. Casimiro and Laguna del Maule centers show the largest LREE enrichments and the largest HREE depletion compared to the CSVZ basalts. Shrinking of the mantle melting column from the CSVZ northwards through the TSVZ into the NSVZ can

decrease the extent of mantle melting and thus enriching primary melts in LREE; however, HREE elements would also be enriched assuming similar mantle compositions along the arc. The primary melts calculated here show combined LREE enrichment and HREE depletion hinging on either Sm or Gd (Figure 5.51). Garnet is a mineral phase that exerts major control in partitioning HREE in its crystal structure and excluding LREE. When plotting the primary magmas for each major complex along the arc in La/Yb vs Yb space it is also clear that TSVZ and NSVZ centers like Casimiro, Nevados de Longavi, Planchon, Antuco, and Descabezado all show increasing La/Yb coupled with decreasing Yb (Figure 5.52). These combined changes appear to be garnet related; however, it isn't clear whether garnet is systematically present in the mantle during melting or as a residual phase as primary mantle melts interact and partially melt lower crustal lithologies. Primary magmas may equilibrate with mafic lithologies (i.e., eclogite or pyroxenite) devoid of recycled crustal materials, underplated to the lower crust or within the mantle lithosphere.

5.6 Summary of Conclusions

Incompatible trace element abundances starting from the most mafic samples from Planchon are the lowest at the center and increase systematically to more differentiated Peteroa and Azufre andesites to rhyodacites (Figures 5.1 to 5.8). Within the Planchon basalts there are six samples that stand out by having enriched HFSE (Th, U, Nb, Hf, Zr) and these enrichments do not correlate with SiO₂ (Figures 5.5 to 5.10). Compatible elements in magmas from the APP complex show depletions in Sr, Ni, Cr, and Sc as liquids differentiate indicating crystal fractionation of plagioclase (Sr), olivine (Ni & Cr), and clinopyroxene (Sc) (Figures 5.10 to 5.14). Planchon basalts PL-8, 16, 17, 18, 24, and PLII-4 have extremely high Ni and Cr compositions which correlated with petrographically observed high modal olivine present in samples indicating that they are olivine accumulates. The REE patterns of Azufre and Peteroa magmas are elevated in LREE, MREE and HREE and have larger Eu negative anomalies of ~

0.58 to 0.63 (Eu/Eu*) as compared to Planchon magmas suggesting possibly less oxidizing conditions and plagioclase fractionation with increased differentiation (Figure 5.20). Most Planchon samples do exhibit small negative Eu anomalies $> \sim 0.90$, however, the six samples that are high in HFSE have smaller negative Eu anomalies of 0.73 to 0.80 (Figure 5.20). The steepness or LREE/HREE ratios in magmas are similar throughout the APP complex from normalized La/Yb range of 4 to 7. Planchon samples have tighter REE compositions (less variability) than Peteroa and Azufre samples.

When compared to other centers in different regions of the SVZ, Planchon basalts have REE patterns that fall in between the flat CSVZ center basalts (Villarrica, Antuco, Llaima, Osorno) and NSVZ and TSVZ center basaltic andesites (Casimiro and Nevados de Longavi) (Figures 5.19 to 5.23). The basalts of the CSVZ show low LREE/HREE patterns with elevated HREE and depleted LREE. The basalts and basaltic andesites of the TSVZ (Descabezado Grande, Nevados de Chillan, Nevados de Longavi, APP) all show increasing LREE/HREE ratios with enrichments in the LREE and depletions in the HREE relative to CSVZ samples. The lone NSVZ representative basaltic andesite samples continue this trend and display the highest LREE/HREE ratios. These patterns and the controls on REE compositions of these basalts could be attributed to the involvement of garnet in the partial melting of a garnet-lherzolite source, partial melting of mafic rocks at the base of the arc crust or within the upper mantle lithosphere leaving a garnet-bearing residue, or crystal fractionation of garnet at high pressures at the base of the crust.

Based on their trace element compositions Planchon basalts can be segregated into three groups; Group 3 basalts are characterized by their higher HFSE, LREE, and HREE and larger Eu negative anomalies, group 2 basalts have the lowest La/Yb which is due to low LREE and group 3 basalts, which make up the majority of samples generally have higher La/Yb than the other groups. Calculating the primary magmatic composition for both group 1 and group 2 basalts and

plotting modeled mineral vectors confirmed that the trace element variations, with exception to degree of LREE to HREE enrichment, among all Planchon samples can be explained through fractionation of plagioclase, olivine, and clinopyroxene. The crystal fractional modelling of Planchon basalts show that group 3 basalt compositions can be attained by continual fractionation of plagioclase and olivine. The increase in La/Yb from group 2 to group 3 basalts cannot be explained by the cryptic crystal fractionation of garnet or hornblende because of lack of correlation with other compatible elements in those phases. The increase in La/Yb from group 2 to group 3 basalts can be explained through changes in the extents of melting of a mantle source and/or varying REE source compositions. The genesis of basaltic magmas can be episodic and multiple distinct batches can be generated from the same source region.

A partial melting model of an enriched mantle source with a melting extent of $\sim 17\%$ revealed that a mantle source mineral assemblage of 50% olivine, 25% opx, 20% cpx, and 5% spinel and devoid of garnet provides the best match for HREE compositions of calculated primary Planchon basalts. Adjusting the extent of melting of this mantle source from $\sim 17\%$ to $\sim 13\%$ would account for the LREE enrichment exhibited by group 2 basalts. Two episodic batches of melt from the same source region with differing extents of melting could account for the LREE/HREE variability in Planchon basalts.

Calculated REE compositions of primary basalts from Planchon, as compared to calculated REE compositions of primary basalts from other centers in different regions of the SVZ, are part of an overall along arc HREE depletion and LREE enrichment trend (Figure 5.51). REE compositions of Villarrica and Antuco from the CSVZ show the flattest and lowest LREE/HREE ratios and the REE patterns of more northerly centers of the TSVZ and NSVZ have steeper more LREE enriched and HREE depleted signatures (Figure 5.51). This point is also shown in a La/Yb versus Yb plot where Villarrica and Calbuco calculated primary melts represent typical low CSVZ LREE/HREE ratios and higher Yb compositions compared to the

increase of La/Yb and depletion of Yb in centers of the TSVZ and NSVZ (Figure 5.52). These geochemical trends suggest the increased role of garnet in fractionating the HREE relative to the LREE from the baseline CSVZ primary magmas to the TSVZ and NSVZ primary melts. At the APP center it has been determined that it is not necessary to generate primary basaltic magmas from a mantle source containing garnet; furthermore, calculated pressures and corresponding depths for primary melt separation from the mantle source region at Planchon have an average range of 48 to 52 km, well above the depth of stability of garnet peridotite of ~ 70 to 90 km (Ulmer 1989; Green and Ringwood, 1970; Hirschmann and Stolper, 1996). The stability of garnet as a primary crystallizing phase in H₂O rich magmas have been experimentally shown at depth corresponding to 25 to 45 km and the stability of garnet-bearing lower crustal mafic rocks and/or sub-continental lithospheric mantle pyroxenite is stable from 30 to 60 km (Muntener and Ulmer 2006; Alonso-Perez, 2009; Atherton and Petford 1993; Wyllie 1977; Huang and Wyllie, 1986; Jagoutz and Schmidt 2013; Hirschmann and Stolper, 1996). At the APP volcanic center and at other volcanic centers in the TSVZ and NSVZ it is more likely that garnet is involved in the petrogenesis of these magmas occurs by either garnet fractionation at high pressures at lower crustal levels or by partial melting and/or equilibration of mafic derived rocks at the base of the arc crust given the depth of magma separation calculated in the Lee et al (2009) thermobarometric model. Based on the trace element crystal fractionation modeling, Planchon could not have crystallized garnet as a primary phase at higher pressures, therefore, partial melting and or equilibration with mafic lower arc crust explains the REE compositional variation best from CSVZ baseline basalts to Planchon basalts.

Figure 5.1 & 5.2: Bivariate plot of Rb and Cs versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex.

Figure 5.3 & 5.4: Bivariate plot of Pb and Ba versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex.

Figure 5.5 & 5.6: Bivariate plot of Th and U versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex.

Figures

5.7 & 5.8: Bivariate plot of Zr and Nb versus SiO_2 for samples from the Azufre-Planchon-Peteroa complex.

Figures 5.9 & 5.10: Bivariate plot of Sr and Hf versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex.

Figures 5.11 & 5.12: Bivariate plot of Cr and Ni versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex

Figures 5.13 & 5.14: Bivariate plot of Zn and Sc versus SiO_2 for samples from the Azufre-Planchon-Peteroa complex.

Figure 5.15 and 5.16: Bivariate plot of La (LREE) and Sm versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex.

Figure 5.17 and 5.18: Bivariate plot of Gd and Yb versus SiO₂ for samples from the Azufre-Planchon-Peteroa complex.

Figure 5.19: Rare earth element patterns for basalts and basaltic andesites at Planchon. Samples are normalized to primitive mantle values from McDonough and Sun(1995).

Figure 5.20: Rare earth element patterns for Azufre dacites and Peteroa andesites. Samples are normalized to primitive mantle values from McDonough and Sun(1995).

Figure 5.21: Rare earth element patterns for Antuco and Callaqui basalts and basaltic andesites. Samples that begin with 290 or 280 belong to the Callaqui volcano (5 samples). Any sample that begins with 511 or 310 belongs to the Antuco volcano (7 samples). These two volcanoes represent basalts from the CSVZ. Samples are normalized to primitive mantle values from McDonough and Sun(1995).

Figure 5.22: Rare earth element patterns for Nevados de Chillan, Nevados de Longavi, and Descabezado basalts and basaltic andesites. Samples that begin with 16 or 737 belong to Nevados de Chillan (4 samples). Any sample that begins with the prefix “MG” belong to Nevados de Longavi (3 samples) and samples that begin with 05 or 06 belong to Descabezado (4 samples). These volcanoes are representative basalts from the TSVZ. Samples are normalized to primitive mantle values from McDonough and Sun(1995).

Figure 5.23: Rare earth element patterns for Casimiro and Laguna del Maule basalts and basaltic andesites. Samples that begin with start with the prefix “LM” or “FM” are from Laguna del Maule (7 samples). Any sample that begins with the prefix “C6” belong to Casimiro (3 samples) . Casimiro is the lone representative basaltic andesite of the NSVZ and Laguna del Maule is from the TSVZ. Samples are normalized to primitive mantle values from McDonough and Sun(1995).

Figure 5.24: A bivariate plot of normalized La/Yb vs. Yb for the three groups of Planchon basalts. The filled black circle and square are the compositions of the calculated primary basalts for groups 1 and 2. The vectors radiate away from one of the primary basalts with calculated fractionation percentages. The Plagioclase vector is not shown because it plots along the olivine mineral vector. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.25: A bivariate plot of normalized Gd/Yb vs. Yb for the three groups of Planchon basalts. The filled black circle and square are the compositions of the calculated primary basalts for groups 1 and 2. The vectors radiate away from one of the primary basalts with calculated fractionation percentages. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.26: A bivariate plot of normalized Dy/Yb vs. Yb for the three groups of Planchon basalts. The filled black circle and square are the compositions of the calculated primary basalts for groups 1 and 2. Here plagioclase and clinopyroxene vectors are not plotted. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.27: A bivariate plot of normalized Sm/Yb vs. Yb for the three groups of Planchon basalts. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.28: Discriminatory bivariate plot of normalized Dy/Yb vs. La/Yb for the three groups of Planchon basalts. Olivine and plagioclase fractionation vectors are not plotted because that have to effect on REE ratio vs ratio diagrams. Values are normalized to primitive mantle from Mcdonough and Sun(1995).

Figure 5.29: Bivariate diagram of Sc/Y vs. Y for the three groups of Planchon basalts. Four mineral fractionation vectors plot in different directions from the calculated primary Planchon melt.

Figure 5.30: Bivariate diagram of Sr/Y vs. Y for the three groups of Planchon basalts. Five mineral fractionation vectors plot in different directions from the calculated primary Planchon melt.

Figure 5.31: Bivariate diagram of normalized La/Yb vs. La for the three groups of Planchon basalts. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.32: Bivariate diagram of normalized La/Nd vs. Nd for the three groups of Planchon basalts. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.33: Discriminatory bivariate diagram of normalized La/Nd vs. La/Yb for the three groups of Planchon basalts. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.34: A bivariate plot of normalized Er/Yb vs. Er for the three groups of Planchon basalts. The filled black circle and square are the compositions of the calculated primary basalts for groups 1 and 2. Here plagioclase and clinopyroxene vectors are not plotted. Values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.35: Plot of normalized La/Yb vs SiO₂ for basaltic samples from Planchon. It is apparent that all three REE distinct groups encompass the entire small range of SiO₂ values. REE values are normalized to primitive mantle from McDonough and Sun(1995).

Figure 5.36: Ni/Zn vs. Mg# showing all Planchon basalts and an olivine fractional crystallization vector trend. Some group 1 basalts are olivine accumulative and have very high Ni/Zn ratios.

Figure 5.37: Sr/Nd vs Ni/Zn showing all Planchon basalts with olivine, plagioclase, and co-saturation fractional crystallization vector trends. Most Planchon basalts have predominantly fractionated olivine; however, many have had influence from plagioclase with Sr/Nd being lowered from ~ 30 to 25. Group 3 basalts show clear plagioclase fractionation.

Figure 5.38: A bivariate diagram of Sr/Nd vs. Yb for the three groups of Planchon basalts. The filled black circle is the composition of the calculated primary basalt. Plagioclase and olivine fractionation vectors are plotted.

Figure 5.39: A bivariate diagram of Sr/Nd vs. normalized Eu/Eu* for the three groups of Planchon basalts. Any value of Eu/Eu* that is less than 1 would be considered a negative europium anomaly. A plagioclase fractionation trend has been added to its effect on basaltic compositions.

Figure 5.40: A bivariate diagram of Sr/Nd vs. SiO₂ for the three groups of Planchon basalts. The black filled circle represents a calculated primary Planchon melt. Group 3 basalts have low Sr/Nd but are among the least differentiated samples from Planchon.

Figure 5.41: A bivariate diagram of normalized La/Sm vs. Sm for the three groups of Planchon basalts. The black filled circle and square represent a calculated primary Planchon melts. Mineral fractionation vectors are shown for amphibole, olivine, and clinopyroxene.

Figure 5.42: A bivariate plot of normalized La/Yb vs. Ce_N in basalts and basaltic andesites from centers in the TSVZ. The yellow area represents the compositions of CSVZ basalts comprising of Villarrica, Llaima, and Osorno volcanic centers (Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001). Vector on diagram represents the similar effects of garnet and amphibole fractionation from common parent CSVZ magmas.

Figure 5.43: A bivariate plot of normalized La/Yb vs. Yb_N in basalts and basaltic andesites from centers in the TSVZ. The yellow area represents the compositions of CSVZ basalts comprising of Villarrica, Llaima, and Osorno volcanic centers (Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001). Vector on diagram represents the effects of garnet and amphibole fractionation from common parent CSVZ magmas.

Figure 5.44: A bivariate plot of normalized Gd/Yb vs. Yb_N in basalts and basaltic andesites from centers in the TSVZ. The yellow area represents the compositions of CSVZ basalts comprising of Villarrica, Llaima, and Osorno volcanic centers (Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001). Vector on diagram represents the effects of garnet and amphibole fractionation from common parent CSVZ magmas.

Figure 5.45: A bivariate plot of normalized Dy/Yb vs. Yb_N in basalts and basaltic andesites from centers in the TSVZ. The yellow area represents the compositions of CSVZ basalts comprising of Villarrica, Llaima, and Osorno volcanic centers (Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001). Vector on diagram represents the effects of garnet and amphibole fractionation from common parent CSVZ magmas.

Figure 5.46: A bivariate plot of normalized Dy/Yb vs. Gd/Yb in basalts and basaltic andesites from centers in the TSVZ. The yellow area represents the compositions of CSVZ basalts comprising of Villarrica, Llaima, and Osorno volcanic centers (Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001). Vector on diagram represents the effects of garnet and amphibole fractionation from common parent CSVZ magmas.

Figure 5.47: A bivariate plot of normalized La/Yb vs. Dy/Yb in basalts and basaltic andesites from centers in the TSVZ. The yellow area represents the compositions of CSVZ basalts comprising of Villarrica, Llaima, and Osorno volcanic centers (Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Rodriguez et al. 2007; Davidson and Dungan et al. 1987; Hickey-Vargas et al. unpublished; Sun thesis, 2001). Vector on diagram represents the effects of garnet and amphibole fractionation from common parent CSVZ magmas.

Figure 5.48: Primitive mantle-normalized REE patterns for modal batch partial melting of a primitive and depleted mantle source. Mantle mineralogy is 50% olivine, 20% orthopyroxene, 20% clinopyroxene, 5% garnet and 5% spinel. Curves are shown with varying F values and partition coefficients can be found in Appendix 4. Calculated primary Planchon melts are also shown.

Figure 5.49: Primitive mantle-normalized REE patterns for modal batch partial melting of a primitive and depleted mantle source. Mantle mineralogy is 50% olivine, 22% orthopyroxene, 22% clinopyroxene, 1% garnet and 5% spinel. Curves show varying partial melting extents.

Figure 5.50: Primitive mantle-normalized REE patterns for modal batch partial melting of a primitive and depleted mantle source. Mantle mineralogy is 50% olivine, 25% orthopyroxene, 20% clinopyroxene, and 5% spinel. Curves show varying partial melting extents (F) and Planchon primary magma compositions.

Figure 5.51: Rare earth element patterns for calculated primary magmas from Casimiro, Laguna del Maule, Calbuco, Antuco, Descabezado, Villarrica, Planchon, and Nevados de Chillan. Samples are normalized to primitive mantle values from McDonough and Sun(1995).

Figure 5.52: Bivariate plot of La/Yb and Yb of calculated primary magma compositions derived from the Lee et al. (2009) model for basalts and basaltic andesites along the SVZ arc. CSVZ primary basalts have a La/Yb of ~ 2 to 3 while TSVZ and NSVZ basalts and basaltic andesites increase towards ~ 18.

Figure 5.53: Partition coefficients used in major igneous phases associated used in crystal fractionation models. References of the partition coefficients used and tables of values can be found in appendix 4.

6. ISOTOPE GEOCHEMISTRY

Oxygen isotopic data from a country rock dolomitic limestone (CR-1) sample was collected at the Stable Isotope Laboratory at the University of Miami's Rosenstiel School of Marine and Atmospheric Science. Hafnium and Neodymium radiogenic isotopic data from 22 samples from volcanic centers along the SVZ were collected using the Thermo Finnigan NEPTUNE multi-collector inductively coupled plasma (MC-ICPMS) at the National High Magnetic Field Laboratory in Tallahassee Florida. Data collected, uncertainties, bias, and precision are all listed in Appendix 5. Some oxygen, strontium and neodymium isotopic data presented here are from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1989; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Isotopic ratios of high mass elements, such as Sr, Nd, Pb and Hf, in magmas are characteristic of the source region(s) from which they originated. These isotopic ratios will remain unchanged during subsequent petrologic processes like crystal fractionation and differentiation as well as melting. Fractionation, differentiation and melting do not affect heavy isotopes because the mass difference between any pair of radiogenic isotopes is minuscule compared to the total isotopic mass. This phenomenon has led to the identification and discovery of multiple isotopically distinct magmatic source regions and geochemical reservoirs in the Earth's mantle and crust, and to modeling of mixing relationships among these distinct components (Rollins, 1993; Faure and Mensing, 2005). The goal of this chapter is to distinguish and identify mixing and contamination processes in magmas generated at the convergent margin of the Southern Volcanic Zone (SVZ) where the thickness of the crust, mantle lithosphere and asthenosphere varies (See chapter 4). This variation has been hypothesized to be a major factor in the along-strike geochemical variation of SVZ magmas (Hickey et al., 1986; Hildreth and Moorbath, 1989; Tormey et al. 1991). The isotopic systems explored in this chapter will also be used to distinguish and quantify the role of different components within the continental crust,

lower and upper crustal reservoirs, and other distinct sources that have contributed to a particular magmatic suite.

6.1 Stable Isotope Systematics

Most naturally occurring elements in nature have more than one stable isotope, and the isotopes of elements with an atomic mass of less than 40 can undergo mass related fractionation through physical processes. This mass related fractionation has led to many diverse stable isotopic reservoirs which can be used to elucidate different geochemical processes in igneous rocks. For oxygen, these variations are largely controlled by processes of interaction with the meteoric water cycle and hydrothermal processes. In igneous petrology, a fresh un-altered subduction zone rock's stable isotopic values will largely be controlled by its magmatic source region, magma mixing, and/or crustal contamination of lithospheric rocks affected by water-rock interactions with the hydrosphere.

6.1.1 Oxygen Isotopes

Oxygen isotope compositions of unaltered igneous rocks can be sensitive indicators providing first order information about their origin and evolutionary history (Harmon and Hoefs, 1984). They also provide an effective way to distinguish rocks which formed in equilibrium with the mantle and those which formed from or assimilated continental crust. Source-liquid fractionation effects are small and negligible in high temperature environments in which magmas are typically generated and as a result a partial melt should have an oxygen isotopic composition representative of its source region. The oxygen isotopic compositions of fresh un-altered mid ocean ridge basalts (MORB) glasses are relatively homogenous with a range of 5.3 to 6.2‰ with an average of $5.7 \pm 0.2\text{‰}$ (Ito et al. 1987). Other mantle-derived rocks such as ocean island tholeiitic basalts have very similar δO^{18} compositions as to mid-ocean ridge basalts and oceanic island alkali basalts, are more enriched in δO^{18} with values of 5.7 to 6.7 per mil (Kyser et al.,

1981; Harmon and Hoefs, 1984). Therefore, pristine unaltered volcanic rocks with mantle origins should reflect those values.

Upper continental crustal reservoirs, which subduction zone magmas must transit on their way to the surface, are enriched in $\delta^{18}\text{O}$ as a consequence of long term interaction with the hydrosphere and partitioning of ^{18}O into crustal minerals during low-temperature sedimentary cycles involving weathering, chemical precipitation and diagenesis. As a result, rocks from the upper continental reservoir can reach enriched $\delta^{18}\text{O}$ values of 33‰, and sedimentary rock averages $\sim 25\text{‰}$ (Harmon and Hoefs, 1984; Taylor 1974). Therefore, oxygen isotopes are a valuable tracer in a continental arc environment where generated basaltic magmas must pass through thickened upper continental crustal reservoirs. The oxygen isotopic system can be used as a tracer for arc magmas that have come into contact/assimilated country rocks and this contributing component can be quantified and constrained if contaminant is known or estimated.

6.1.2 Oxygen Isotopes of Dacites from Azufre

Two dacite samples (AZ-8 and AZ-18) erupted from the Azufre volcanic center in southern Chile have anomalous δO^{18} values ranging from 7.1 to 7.3 per mil (Tormey 1989). These δO^{18} values are much higher than most magmas of the Southern Volcanic Zone, and the reported range of dacites and rhyolites in this region is 6.0 to 6.3 per mil (Harmon and Hoefs, 1984). The δO^{18} values of the more mafic basaltic andesites erupted at Azufre-Planchon-Peteroa complex (6.3 to 6.6 per mil) are within the normal range of δO^{18} values for the TSVZ. These basaltic and basaltic andesite values also encompass the full range of δO^{18} values of the lower mafic crust or sub-continental lithospheric mantle reservoirs. Thus, the mantle magma sources and the similar lower mafic crust do not account for the elevated δO^{18} composition of the Azufre dacites.

Dacites are an evolved differentiated volcanic rock that typically forms through fractional crystallization (see Chapter 5). Crystal fractionation could be expected to play a role in

determining the $^{18}\text{O}/^{16}\text{O}$ ratio in an igneous rock and large scale removal of phenocrysts phase may shift the $^{18}\text{O}/^{16}\text{O}$ ratio of the melt, however, the crystal-melt fractionations at temperatures greater than 1000°C would not cause a large shift in $^{18}\text{O}/^{16}\text{O}$ composition in the melt (Harmon and Hoefs, 1984). The change due to the fractionation would be a very slight variation of 0.5 to 0.8 per mil in δO^{18} values in the melt. Crystal fractionation alone could not account for the anomalous δO^{18} values from Azufre dacites.

Within the Azufre-Planchon-Peteroa volcanic field the oldest exposed rocks are Cretaceous marine sediments, mostly pure limestone and dolomitic limestone with thin silt layers (Davidson and Vicente, 1973; Tormey, 1989). These marine sediments are overlain by a tertiary lava section with compositions ranging from basalt to rhyolite (Llambias and Rapela, 1987). This whole section has been folded and cut by Tertiary granodiorite plutons (Tormey 1989). The tectonic history suggests that Paleozoic or older units could underlie the exposed marine sediment sections and Tertiary volcanics (Tormey, 1989). Tormey (1989) proposed that the exposed Cretaceous dolomitic limestone could be the contaminant or upper crustal source contributing the anomalously high δO^{18} values to the Azufre dacites, owing to the large fractionation between water and carbonate minerals at earth surface temperatures. Using measured Sr and Oxygen isotope values for the Cretaceous limestone, Tormey concluded, using assimilation-fractional crystallization equations, that approximately 12% of the limestone country rock would be required to partially melting in order to reconcile the higher δO^{18} values and $^{87}\text{Sr}/^{86}\text{Sr}$ values of the Azufre dacites.

A problem with this result is that limestone has an approximate anhydrous solidus at $> 800^{\circ}\text{C}$ and hydrous solidus at $\sim 700^{\circ}\text{C}$ which are excessively high temperatures for dacitic liquids in the uppermost 1 km of the crust, although bulk rock assimilation could occur through stopping and melting or decarbonation. In any case, incorporating a 12% of a limestone country rock would have significant impact on major and trace element contents of the rocks, and is therefore

difficult to reconcile chemically and thermodynamically. For these reasons, the outcropping dolomitic limestone was re-analyzed and its possible role as a contaminant in Azufre dacites was reassessed.

The results of the δO^{18} analysis on the dolomitic limestone country rock (CR-1) can be seen in table 6.1. Different layers (light and dark) of the dolomitic limestone were examined to test for within sample variability in addition to one replicate for each layer. Samples CR-A and CR-C are white layers and CR-B was an intermittent dark layer. The laboratory the results were reported in $\delta\text{O}^{18}_{\text{PDB}}$ and were therein converted and presented throughout this work as $\delta\text{O}^{18}_{\text{SMOW}}$ from the following equation: $\delta\text{O}^{18}_{\text{SMOW}} = 1.03091(\delta\text{O}^{18}_{\text{PDB}}) + 30.91$.

With newly acquired δO^{18} data I applied a binary component isotopic mixing equation between δO^{18} and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values of the dolomitic limestone and a representative basalt from the APP center. The simple two component mixing equation was adapted from Faure (2005). The compositions of the dolomitic limestone proposed contaminant and the representative un-contaminated basalt can be seen in table 6.2 and the binary mixing hyperbola results can be seen in figure 6.1. The compositions of AZ-8 and AZ-18 can be seen in table 6.3. I used the average δO^{18} values for all layers within sample CR-1 and calculated the oxygen mole percent. Sample PL-18 was chosen as the hypothetical starting composition because it is the most mafic Planchon samples with both oxygen and strontium isotopic data collected by Tormey 1989 (Table 6.2).

The mixing hyperbola provides estimates of contributing sources from each end member, one being a mafic primary basalt from the APP center representing a hypothetical un contaminated melt and the other the proposed contaminant CR-1 (Figure 6.1). It is apparent that in order to reach the enriched $^{87}\text{Sr}/^{86}\text{Sr}$ and δO^{18} values in AZ-8 and AZ-18 un-contaminated basalt would need to assimilate approximately between 3 to 5% of the dolomitic limestone

country rock (Figure 6.1). This is a more realistic percentage of partial melt or bulk rock needed to generate the elevated values in Azufre dacites. Given the new evidence that this occurred, the rocks may be explored further for the impact of carbonate assimilation.

It is still apparent that magmas generated in the APP complex with elevated isotopic values that approach upper crustal values have significantly interacted with the upper crustal reservoir.

Table 6.1 δO^{18} analysis on the dolomitic limestone country rock (CR-1), done at the Stable Isotope lab at RSMAS

Sample	$\delta\text{O}^{18}_{\text{PDB}}$	$\delta\text{O}^{18}_{\text{SMOW}}$
CR-A	-5.080	25.63
CR-B	-2.560	28.271
CR-C	-4.670	26.096
CR-A (duplicate)	-5.830	24.900
CR-B (duplicate)	-2.390	28.446
CR-C (duplicate)	-4.90	25.859

Table 6.2 Compositions of End Members in Mixing Model

Starting Composition Basalt PL-18	Contaminant CR-1
$^{87}\text{Sr}/^{86}\text{Sr} = 0.7041$	$^{87}\text{Sr}/^{86}\text{Sr} = 0.7068$
Sr ppm = 472.5	Sr ppm = 3500
$\delta\text{O}^{18} = 6.3$	$\delta\text{O}^{18} = 26.54$
Oxygen mol % = 0.456	Oxygen mol % = 0.52

Table 6.3 Compositions of Azufre Dacites

AZ-18	AZ-8
$^{87}\text{Sr}/^{86}\text{Sr} = 0.7048$	$^{87}\text{Sr}/^{86}\text{Sr} = 0.7046$
$\delta\text{O}^{18} = 7.3$	$\delta\text{O}^{18} = 7.1$

Figure 6.1: Bivariate diagram of $^{87}\text{Sr}/^{86}\text{Sr}$ vs δO^{18} showing a binary mixing relationship between an un-contaminated parent basalt (PL-18) and a dolomitic limestone contaminant CR-1. Mixing curves are plotted along with melt fractions. AZ-8 and AZ-18 are plotted along the proposed mixing curves between a melt fraction of 0.97 and 0.95.

6.2 Radiogenic Isotopes Systematics

Radiogenic isotopes are used in two principal ways in the geologic sciences. Through the process of radioactive decay, which occurs at known rates for various isotopes and has been determined to be constant and independent of chemical and physical conditions, radioactive parent and radiogenic daughter isotope ratios in minerals and rocks can be used for measurement of geologic time. Radiogenic isotopes can also be used to understand the different earth materials and reservoirs which are involved in the evolution of magma because different earth materials have different isotopic characteristics which depend on their parent-daughter element ratios and their ages. This approach helps to determine the origin and history of magmas and in a larger sense the origin and history of the crust and mantle and their subunits. Radiogenic isotope ratios of magmas are characteristic of their source regions because partial melts generated will have the same isotopic value as the source rock. Isotopic ratios of recent volcanic products are especially indicative of their source regions because the volcanic rocks will not develop distinct isotopic values through radioactive decay, and thus require age corrections. Additionally, isotopic ratios remain unchanged by subsequent crystal fractionation, thus providing first order information on source regions (reservoirs) like the upper mantle and crust since magmas form in both these regions, as well as crustal contaminants. The study of radiogenic isotopes has led to the discovery of multiple isotopically unique reservoirs in the mantle and in the crust (Rollins, 1993; Faure and Mensing, 2005). Source regions can develop unique isotopic characteristics because of past differentiation events (melting) and/or isolation for long periods of time where these regions develop distinct isotopic ratios through radioactive decay. Mixing and contamination processes can be recognized in magmas that have interacted with these distinct isotopic reservoirs because they impart their unique isotopic signatures on magmas via crustal assimilation and/or source contamination. For example, mantle derived melts with mantle

isotopic signatures may partially melt continental crustal wall rock en route to the surface, thus altering the isotopic value of the melt.

6.2.1 Behavior of Radiogenic Isotopic Systems

The long lived radiogenic isotopic systems interpreted in this study are (parent-daughter) Rb-Sr, Sm-Nd, Lu-Hf, and U-Pb and Th-Pb. These elements vary greatly in their chemical and behaviors and can be sensitive to different petrologic processes. Differing fractionation behaviors of parent and daughter elements in these isotopic systems lead to compositionally distinct isotopic reservoirs. The general order of incompatibility of these elements is $Rb > U \ \& \ Th > Pb, Nd \ \& \ Sr, > Hf \ \& \ Sm > Lu$, indicating the extent of which these elements are fractionated into the crust relative to the depleted mantle. Rb being the most incompatible is most concentrated in the crust and in the Rb-Sr system the parent daughter pair behave most disparately and are fractionated relatively easily. Rb is preferentially partitioned into the melts which transit upwards and enrich the upper crust relative to the mantle. As a result many upper crustal lithologies will have higher Rb/Sr ratios giving rise to higher and more radiogenic $^{87}Sr/^{86}Sr$ isotopic ratios. Consequently the depleted mantle sources will have lower Rb/Sr ratios because of repeated melting events, resulting in lower radiogenic Sr isotopic values. Lower continental crust reservoirs are characterized by mafic granulites that have low Rb/Sr ratios and low $^{87}Sr/^{86}Sr$ isotopic ratios that are slightly higher than modern mantle values (Rollins, 1993)

The isotopic behavior of Sm-Nd and Lu-Hf systems are markedly different from the Rb-Sr system in that the daughter elements Nd and Hf are slightly more incompatible than their parent elements. These isotopic systems are not significantly fractionated from one another within the continental crust by metamorphism or sedimentary processes and therefore preserve the parent/daughter ratio of their source region. Nd is preferentially partitioned into the melt phase therefore this has caused the continental crust to be enriched in Nd relative to Sm when compared to residual rocks in the mantle. Upper crustal rocks thus have lower Sm/Nd ratios and lower

$^{143}\text{Nd}/^{144}\text{Nd}$ ratios compared to the depleted mantle. As a result of the contrasting behavior of the Rb-Sr and the Sm-Nd systems, they can be used to assess the extent to which magmas have been affected by continental lithologies. Lower crustal lithologies will also have lower $^{143}\text{Nd}/^{144}\text{Nd}$ values as compared to depleted mantle sources; however, this ratio is higher as compared to upper crustal lithologies.

The Lu-Hf isotopic system behaves much the same as the Sm-Nd system, they fractionate in a similar fashion in all terrestrial reservoirs. Hf is preferentially partitioned into the melt phase therefore this has caused the continental crust to be enriched in Hf relative to Lu when compared to residual rocks in the mantle. As a result the upper crustal reservoir has progressively become lower in Lu/Hf and lower in their $^{176}\text{Hf}/^{177}\text{Hf}$ ratios as compared to mantle sources. The Lu-Hf system's behavior in the continental crust is important because the compatibility of Lu in garnet. Garnet is typical of both basaltic and pelitic lower crustal lithologies and may be a residue from melting or differentiation events, and it can impart elevated Lu/Hf ratios to residual bulk rock due to high partition coefficients of garnet for Lu compared to Hf (Vielzeuf & Holloway, 1988; Vervoort & Patchett, 2000). If high Lu/Hf lithologies are typical of older deep sub-arc crust, then it will evolve toward elevated radiogenic Hf isotopic compositions and would be recognizable in magmas that interact with the deep crust (Vervoort & Patchett, 2000). This sensitivity of the Lu-Hf system to residual garnet has been proposed as a potential fingerprint for deep-crustal involvement. Furthermore, if the lower crust contains widespread cumulative or residual garnet then Hf-Nd isotopic systems may decouple and their compositions will plot away from the terrestrial Hf-Nd array.

The radioactive decay of ^{238}U , ^{235}U and ^{232}Th produce three isotopes ^{206}Pb , ^{207}Pb , and ^{208}Pb and the isotopic compositions of lead are generally reported as the ratio of a radiogenic isotope to the non-radiogenic isotope; $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$. Natural chemical processes do not fractionate parent radioactive isotopes ^{238}U and ^{235}U to any measurable degree,

therefore daughter isotopes ^{206}Pb and ^{207}Pb can be used to distinguish systems with high U/Pb and low U/Pb. As a result Pb isotopes are a sensitive indicator of crustal assimilation because Pb concentrations are high in most crustal rocks, and it is a highly enriched LILE in subduction related rocks. A striking characteristic of Pb isotopic compositions of Cenozoic volcanic rocks of the SVZ is its limited range of composition. This absence of any large scale change in Pb isotopic composition rules out large amounts of crustal assimilation and any observed enrichment might be attributed to small components of recycled continental material in the form of subducted sediments (Barreiro 1984; Kay et al. 1978; Jacques et al. 2013). The Pb compositional range of the SVZ volcanic rocks are within the range of measured values of Chilean trench sediments on the Nazca plate (Barreiro 1984; Jacques et al. 2013).

6.2.2 Radiogenic Isotope Systematics of Azufre-Planchon-Peteroa and the SVZ

The $^{176}\text{Hf}/^{177}\text{Hf}$ isotopic data presented here from the Azufre-Planchon-Peteroa complex, CSVZ volcanic centers: Villarrica, Villarrica small eruptive centers, Calbuco, Osorno, Antuco, TSVZ centers Nevados de Chillan, Descabezado, Laguna del Maule, and NSVZ center, Casimiro were collected using a Thermo Finnigan NEPTUNE multi-collector inductively coupled plasma mass spectrometer at the National High Magnetic Field Laboratory (NHMFL) at Florida State University in Tallahassee, Florida. In addition, some suspect $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios from a previous analysis of APP samples were re-analyzed, while other $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic data and all $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic data was compiled from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001. All Pb isotope data discussed are also from published sources (Hildreth and Morrbath, 1988; Barreiro 1984; Davidson et al., 1987). All samples analyzed from the SVZ were specifically chosen with SiO_2 compositions < 57 wt. % in an attempt to avoid upper crustal influences on magmatic geochemical evolution.

Nd isotopic ratios in four basaltic lavas from the Planchon volcano range from 0.512775 to 0.512786 (Figure 6.2). One basaltic andesite samples from Peteroa has an Nd isotopic value of 0.512763 and a basaltic andesite from Azufre 0.512747. Villarrica basalts exhibit larger more mantle-like values of 0.51287 to 0.51290 and represent the highest Nd isotopic values of samples analyzed along the arc. Casimiro, the northernmost center, samples plot at the lower end of with less radiogenic Nd values of 0.512688 to 0.512699. A plot of $^{143}\text{Nd}/^{144}\text{Nd}$ vs. Sm/Nd for all samples defines a positive correlation from Sm/Nd values of 0.188 to 0.270 with increasing $^{143}\text{Nd}/^{144}\text{Nd}$ from 0.51268 to 0.51290 (Figure 6.3). Higher Sm/Nd (parent to daughter ratio) correlates with higher radiogenic $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic values.

Planchon basalts show limited Sr isotopic variability with a small range of 0.7040 to 0.7041 and the Peteroa and Azufre basaltic andesites are more radiogenic from 0.7041 to 0.7043 (Figure 6.4). In other centers along the volcanic front of the SVZ, Casimiro displays the most radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios ranging from 0.70441 to 0.70455. Antuco and an SEC volcano display the least radiogenic Sr isotope values of 0.70374 to 0.70391 (Figure 6.3). Surprisingly Villarrica show moderate $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values of 0.7039 to 0.7041 which is equivalent to many TSVZ volcanoes like APP, Descabezado, and Nevados de Longavi. Nevados de Chillan has anomalously low $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70386 despite being in the TSVZ.

Hf isotopic values from the Planchon basalts are very similar from 0.282950 to 0.282954 (Figure 6.5). Peteroa and Azufre $^{176}\text{Hf}/^{177}\text{Hf}$ values show small differences of 0.282937 and 0.282920. The Villarrica basalt displays the most radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ values at 0.283127 and Casimiro basaltic andesites in the NSVZ are the least radiogenic with $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282860 to 0.282822 (Figure 6.5). The Lu/Hf ratios of centers along the volcanic correlate well with the $^{176}\text{Hf}/^{177}\text{Hf}$ values with the lowest Lu/Hf values of 0.05 associated with the least radiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ values of 0.282822 all at Casimiro (Figure 6.6). The highest Lu/Hf ratios

(0.1423 and 0.1625) at Villarrica and Osorno in the CSVZ there is a maximum in the $^{176}\text{Hf}/^{177}\text{Hf}$ values becoming more radiogenic at 0.283127 and 0.283091 respectively.

6.3 Sources and Origin of Along-Strike changes in SVZ Arc Magmas

The volcanic centers from the CSVZ, where the crust is relatively thin < 35 km, predominantly yield magmas of basaltic composition and show little to no assimilation of continental crust based on Sr, Nd, Pb, and O isotopic data (Stern et al. 1990; Hickey-Vargas et al. 1984, 1986, 1989). These studies have concluded that CSVZ basalts form by melting of the sub-arc mantle invaded by fluids from the subducted ocean lithosphere (basaltic crust plus subducted sediments; Morris et al. 1990; Hickey-Vargas 1984, 1986, 1989, 2002). As a result, since these Andean magmas have not interacted extensively with the continental crust, they provide a “baseline” composition and character for evaluating the extent of crustal interaction of other magmas from different segments of the SVZ.

Sr and Nd isotopic results from the basaltic and basaltic andesite rocks from centers along the arc from Osorno in the CSVZ (41.06°S) to Casimiro in the NSVZ (34.16°S) define a regional trend that is complementary to each other (Figure 6.7). Nd and Hf isotopic data from the same centers also yields a complementary regional trend from radiogenic enriched CSVZ basalts toward more depleted un-radiogenic TSVZ and NSVZ basalts and basaltic andesites (Figure 6.8). In contrast, a well-recognized feature of SVZ volcanic rocks is that Pb-isotopes plot in a limited field coincident with both subducted sediment and upper continental crust, with no along strike variation (Hickey et al., 1986; Hildreth and Moorbath, 1989). The regional trends of Sr, Nd and Hf isotope ratios are echoed in the Sr vs Nd and ϵNd and ϵHf plots showing how these basalts and basaltic andesites deviate from the hypothetical chondritic uniform reservoir (CHUR) values (Figures 6.9 & 6.8). It can be hypothesized that the “baseline” basalts from the CSVZ (Villarrica, Osorno, Antuco) are most free of continental crust assimilation and that any other magmas deviating from baseline values of Sr, Nd, and Hf isotopes should require a varying proportion of

contaminating sources. Assuming that the magmas generated along the volcanic arc in the SVZ principally arise from similar mantle sources, the subsequent contaminating sources that could explain the Sr, Nd, and Hf isotopic trends could be: 1) slab derived fluids including subducted sediment 2) upper sialic crust, 3) arc-derived underplated mafic rocks or mafic granulites in the lower crust or lithospheric mantle.

6.3.1 Sediment and Slab Fluid Sources

Source contaminants like sediments and slab fluids from the subducted slab have been unequivocally shown to contribute to basalts generated in sub-arc mantle settings through Be isotopic studies (Sigmarsson et al. 1990; Hickey-Vargas et al. 2002). Additionally, other authors have shown that Pb isotopic signatures of SVZ arc magmas are derived from a mixture of mantle and subducted Nazca plate sediments (Hickey et al. 1986; Leeman et al., 1995; Morris and Leeman et al., 1990). Arc magmas can be differentiated from ocean island basalts (OIB) via higher ratios of large ion lithophile elements (LIL) vs light rare earth elements (LREE) like Ba/La which reflects the higher solubility of LIL's relative to LREE's and thus enriched in subduction fluids (Gill 1981; Pearce et al., 2005). Ocean island basalt magmatism is plume-related and therefore contains minimal subduction related sediments or slab fluids. Therefore subducted sediments and slab fluid sources should be explored as a possible contaminant in SVZ magmatism potentially creating regional isotopic trends.

Ba enrichment in basalts northward along arc SVZ magmas is evident with Casimiro basaltic andesites capping the most northern enrichment of approximately 447 ppm and correlates positively with $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 6.9 & 6.12). Ba enrichment may indicate a northward increase in a subduction component or perhaps a proportional increase in the subduction component with a northward decrease in the mantle melting column, however, this would only be true if the LIL/LREE ratio also correlated with an increase of $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values which is not the case (Figure 6.9). Ba/La ratios (LIL/LREE) along the entire arc show no correlation with Sr isotopic

data and remain relatively uniform with maximum values from Descabezado and Villarrica (Figure 6.10). Casimiro basaltic andesites from the NSVZ have the highest radiogenic Sr isotopic values also have the lowest Ba/La ratios of approximately 20. If slab-derived contributions were dominant there would be correlations existing in relative enrichment of alkaline earth elements (Ba) over LREE vs $^{87}\text{Sr}/^{86}\text{Sr}$ (Arculus and Johnson 1981).

Although it is clear that Nazca Plate sediments are subducted and contribute to basaltic magmas generated, their limited along-trench variability and low isotopic contrast to erupted basalts make it an unlikely source that controls the along-arc isotopic regional trends. Quaternary Chilean trench sediments from (36-40°S) have $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values ranging from 0.7044 to 0.7061 and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic values that range from 0.512673 to 0.51287 (Lucassen et al. 2009). The Nd and Sr isotopic values do not contrast the SVZ along arc basaltic ranges of 0.70382 to 0.70455 and 0.512688 to 0.51290 which would not provide enough differential isotopic leverage sufficient to create the along-arc isotopic trends. Chilean trench sediment Hf isotopes have not been determined; however, Vervoort et al. (2011) provided Hf isotopic data for Peruvian trench sediments which values ranging from 0.282471 to 0.282901 which is again not isotopically different enough from the basaltic along arc range of 0.282823 to 0.283127 to systematically control isotopic trends.

Recent authors have attribute the slab component, which is made up of fluids and/or melts produced by dehydration and/melting of the slab during subduction, as the reason for Pb, Sr, and Nd isotopic variability along the arc front in the SVZ (Jacques et al. 2013). The nature of the slab component consists of subducted sediment and altered ocean crust (AOC) and these two sources are the principal components that control isotopic and incompatible element variability of the SVZ frontal arc (Jaques et al. 2013). Geochemical evidence worldwide, especially from intra-oceanic island arcs (e.g. Elliot et al. 1997) confirms that subarc mantle melts are contaminated by fluids derived from dehydration of the subducting oceanic lithosphere including trench sediments;

however, in the SVZ there is no strong evidence for systematic and consistent along-arc changes to this slab component (Hickey et al. 1984, 1986; Hickey-Vargas 1989, 2003; Sigmarsson et al. 1990; Leeman et al., 1995). The subducting ocean lithospheric Nazca plate in the CSVZ has an age range of 18 to 25 Ma and the Nazca plate in the TSVZ ranges from 35 to 45 Ma while the rate of subduction in both regions remains the same of $\sim 7\text{-}9$ cm/yr (Jarrard 1986; Dewey & Lamb 1992; DeMets *et al.* 1990). Given those parameters the thermal structure of the subducting slab in the CSVZ would be predicted to be the same or hotter than the thermal structure of the subducting plate beneath the TSVZ (Peacock, 2003). As a result the magmas generated in the CSVZ should have equal if not a greater AOC and sediment signatures than the magmas from the TSVZ, which is not observed.

6.3.2 Continental Sources: Upper and Lower Crust

Anywhere mantle derived basaltic magmas are generated at continental convergent margins where a thick overlaying crust intercepts, stalls and stores these melts, assimilation of crustal components is to be expected. Elevated LREE, Ba, K, and Rb values in more northerly centers like Casimiro and Nevado de Longavi as compared to CSVZ centers like Antuco, Villarrica, and Osorno are consistent with an increase in crustal components in these basaltic magmas, which is well-correlated with increasing thickness of the crust and lithospheric mantle (see Chapter 4). The extent of continental contributions via assimilation and the distinct kind of crustal reservoirs involved are questions that remain.

The Sr isotopic ratios of the basalt and basaltic andesites along arc samples analyzed in this study show limited increases in radiogenic Sr from the CSVZ to the NSVZ from 0.70388 (Villarrica) to 0.70455 (Casimiro) (Figure 6.12). The span of basaltic magmas Sr isotopic composition of < 0.7046 contrasts sharply with estimated upper crustal Paleozoic sedimentary and igneous rocks of 0.725 to 0.77 (Hildreth and Moorbath 1988) (Figures 6.7 & 6.12). Sr isotopic values remain relatively unchanged from the CSVZ centers to the TSVZ and NSVZ

centers accompanied with large increases in La/Yb values suggesting crustal contributions in the TSVZ and NSVZ centers originates at greater depths where garnet is stable (Figure 6.11) (Wyllie 1977; Huang and Wyllie, 1986; Jagoutz and Schmidt 2013). The combination of large elemental overprints on primary signatures with Sr radiogenic isotope variability that does not greatly exceed mantle derived values suggests either assimilation of plutonic lithologies close in age to incoming magmas or similar Sr isotopic values and little involvement of a more variable and isotopically distinct upper crustal lithologies. In accord, whole rock $\delta^{18}\text{O}$ analysis on Planchon and Antuco basalts yield values of + 6.2 to + 6.6 falling within the range of Harmon and Hoefs (1985) defined for basalts and basaltic andesites with no upper crustal contamination of (5.2 to 6.8‰) in the Meridional Andes.

Increased Sr and Ba concentrations of basalts and basaltic andesites of NSVZ and TSVZ regions as compared to the CSVZ can also be explained through deep lower crustal/mantle lithosphere contributions (Figures 6.13 & 6.14). Mantle derived basaltic melts are high in Sr (400 to > 500 ppm) and it may be difficult or impossible to enrich these magmas in Sr via crustal assimilation based on average upper crustal Sr values of 340 to 350 ppm (Rudnick and Fountain 1995; Taylor and McLennan, 1995). However, many lower crustal mafic granulites are enriched in Sr and Ba with Sr values of 700 to 1800 ppm (Tarney and Windley, 1977; Rogers and Hawkesworth 1982; McCulloch et al. 1987). This is especially true if lower crustal rocks are composed of arc derived underplated H_2O rich basalts where plagioclase crystallization is suppressed due to the presence of H_2O (Muntener et al. 2001). With a plagioclase poor lithology, Sr rich lower crustal rocks can therefore yield Sr rich melt contributions (600 to 1000 ppm) to primary magmas as estimated by Hildreth and Moorbath (1988). The positive correlation of Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ values in basalts and basaltic andesites along the volcanic arc increasing from the CSVZ to the NSVZ reflects deep crustal contributions rather than negative correlations expected between Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ through assimilation and fractional crystallization processes (AFC)

involving more radiogenic upper crustal rocks (Figure 6.12). Sr is a compatible element in plagioclase and if these basaltic magmas had stagnated at upper crustal levels assimilating local wall rock, their mantle-like $^{87}\text{Sr}/^{86}\text{Sr}$ values would drastically increase to more radiogenic values and plagioclase becomes increasingly stable and would fractionate from the remaining melt thus depleting the residual liquid in Sr. This process is not reflective of the combined Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ values exhibited by the along arc basalts (Figure 6.16).

The major element composition of different reservoirs of the continental crust has been estimated by several studies and can be seen in Table 6.4 (Rudnick & Fountain, 1995; Taylor & McLennan, 1995; Wedephol, 1995). The calculated primary magmatic compositions of multiple centers using the Lee et al. (2009) model in Appendix 4 are compositionally similar to lower crustal major element estimates from Taylor and McLennan (1995) (Table 6.4). Assimilation of an upper crustal estimate from Table 6.4 would alter the major element chemistry of the primary melts too drastically thus resulting in residual melts too silicic than ones erupted at each respective volcanic center. The Taylor and McLennan (1995) estimation of the major element composition of the lower crust provides a potentially realistic assimilant that is compositionally similar to incoming mafic primary melts which may not alter their major element chemistry while systematically altering the trace element and isotopic values through equilibration.

Upper crustal rocks are distinguished from lower crustal rocks by their high Rb/Sr and high $^{87}\text{Sr}/^{86}\text{Sr}$ values along with low Sm/Nd and $^{143}\text{Nd}/^{144}\text{Nd}$ (Rollins, 1993). Upper crustal Paleozoic sedimentary and igneous rocks outcropped in the Chilean Andes have Sr isotopic values of 0.725 to 0.77 (Hildreth and Moorbath 1988). There are few estimates for the Sr isotopic values of lower crust rocks as they are most likely variable on a global scale and because of the difficulty in sampling, but this reservoir is estimated to have Rb depletion and lower Rb/Sr as compared to the upper crust with Sr isotopic values of 0.702 to 0.705 (Rollinson, 1993). These two isotopic reservoirs are shown in Figures 6.7 and 6.9 and the SVZ basaltic array shows a

directional mixing arrays towards less radiogenic Sr values and more un-radiogenic Nd which suggests that the lower crust is a more likely source component for changing isotopic compositions of SVZ along arc basalts and basaltic andesites.

6.3.3 Underplated Mafic Arc Rocks – 400 Ma of Convergent Margin Magmatism.

There is a strong regional trend toward crustal values of Hf and Nd isotopic compositions of basalts and basaltic andesites along the SVZ arc where both isotopic systems trend from “baseline” more mantle-like and more radiogenic CSVZ basalts from Villarrica, Osorno, and the SEC’s to less radiogenic/crust-like more northerly centers like Laguna del Maule, and Casimiro. Ancient underplated basaltic lithologies, as a result of 400 Ma of convergent magmatism, will have lower Nd and Hf isotopic compositions owing to their age. Long term retarded growth as the result of lower crustal storage of these underplated basalts provides an un-radiogenic component in which the current "baseline" subduction magmas equilibrate/assimilate thus altering their isotopic signature. Since upper crustal lithologies can be ruled out as a significant component contributing to the studied basalts and basaltic magmas, the less radiogenic Nd and Hf isotopic character of the TSVZ and NSVZ rocks can be explained through the interaction with ancient lower crustal lithologies.

I applied a two component isotopic mixing equation on the Nd-Sr and Hf-Nd isotopic systems using Villarrica basalts as one end member (representing a primitive basalt uncontaminated by crustal lithologies) and mafic metamorphic basement rocks of the coastal cordillera of Chile (36.5-39°S) from Lucassen et al. (2004) in order to simulate the along arc variations in Sr, Nd, and Hf of SVZ basaltic rocks. The mafic metamorphic basement rocks analyzed from Lucassen et al. (2004) were chosen as a best-available representative of lower crustal arc derived lithologies. The end member Sr, Nd, and Hf isotopic values and concentrations used in this mixing model be seen in Table 6.5 and associated mixing hyperbolas can be seen in figures 6.8 and 6.13. Although Hf concentrations and isotopic data were not

collected on mafic basement rocks from Lucassen et al. (2004), Hf concentration was inferred from the Nd/Hf ratio (~ 4.6) of typical lower crustal lithologies from Rudnick et al. (1995) and the Hf isotopic value was inferred from the Hf-Nd “terrestrial array” line given by Vervoort et al. (2011). The Nd and Sr isotopic values and concentrations were calculated as an average of the available data on mafic metamorphic basement rock samples from Lucassen et al. (2004).

The results of the two component Sr-Nd and Nd-Hf mixing hyperbolas show that approximately 14 to 16% of a mafic lower crustal component needs to be incorporated into Villarrica-like primary basalts in order to change the isotopic values to equal the isotopic compositions of the most northerly center (Casimiro) (Figure 6.8 & 6.13). Other centers in the TSVZ and CSVZ require less assimilated lower crustal contaminants like APP ($\sim 8\%$) and Antuco (4 to 6%). Given the large amount of assimilation, in some cases like Casimiro, this is only possible if the assimilant has major element compositions close to the incoming primary basalt, otherwise the major element compositions of the resultant magmas would show drastic changes which are not the case. Therefore a lower crustal assimilant with major element compositions from Table 6.4 are most likely.

6.4 Summary of Conclusions

Based on the δO^{18} analysis on a dolomitic limestone outcropping country rock near the APP volcanic center, new constraints on the role and level of involvement of this contaminant has been established with simple isotopic mixing models. Previous work on this CR-1 dolomitic limestone from Tormey thesis (1989) which analyzed Sr concentration and oxygen isotopic composition suggested approximately 12% incorporation assimilation of the country rock in order to raise the anomalous δO^{18} isotopic values of Azufre dacites AZ-8 and AZ-18 of 7.1 and 7.3 per mil. The new analysis and applied mixing model predicts only a 3 to 5% range for assimilation of the Cretaceous dolomitic limestone country rock in order to raise the δO^{18} isotopic values from the more primitive and parental type Planchon basalt of 6.3 per mil to the anomalous dacitic

values of 7.1 and 7.3. In accord with previous work, the Azufre center shows clear evidence of upper crustal involvement in the evolution of its silicic volcanic products. The level of involvement or extent to which possible upper crustal rocks altered the geochemistry of the dacites has been further constrained and mixing results can be seen in Tables 6.2 and in the Appendix 5.

6.4.1 Isotopic Evidence for Assimilation/Equilibration with of Mafic Rocks in the Lower Crustal/lithospheric Mantle APP and the TSVZ and NSVZ

Sr and Nd isotopic values of basalts and basaltic andesites used in this study show a complimentary regional trend from southerly centers in the CSVZ (Villarrica and Osorno) with isotopic values that does not greatly exceed the initial mantle-derived range with low $^{87}\text{Sr}/^{86}\text{Sr}$ with high $^{143}\text{Nd}/^{144}\text{Nd}$ to more northerly centers of the CSVZ, TSVZ and NSVZ with higher more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ with lower $^{143}\text{Nd}/^{144}\text{Nd}$. Assuming that all centers from the SVZ have arisen from similar mantle sources and the centers from the CSVZ are considered to have “baseline” isotopic values for magmas that have not incorporated continental lithologies via assimilation, then either a varying slab component consisting of subducted sediment and slab melts/fluids, and/or lower crustal/mantle lithospheric mafic rocks are responsible for the coherent regional trends presented by the SVZ mafic magmas.

6.4.2 Evidence against Control by Variations in Slab Component

The slab component does not appear to be a likely reason for the consistent change in Sr-Nd-Hf isotopic values in the SVZ magmas because: 1) LILE/HFSE ratios do not correlate with increases in $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values from centers of the CSVZ towards northerly centers of the TSVZ and NSVZ suggesting that a slab dominant signature, which would increase the Ba/LREE ratio and enrich the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic values, is not controlling the Sr isotopic regional trend. 2) There is no evidence for along arc variability in the isotopic composition of subducted trench sediments to account for the regional trends in Sr-Nd-Hf isotopes; furthermore, there is little Sr-

Nd-Hf isotopic contrast in the magmas from the TSVZ and NSVZ in comparison to subducted sediments which would not provide enough isotopic differential leverage to systematically change isotopic values. 3) There is also no evidence for along arc changes to the slab source component via increased subducted sediment and fluids and melts from the altered ocean crust in the TSVZ over the CSVZ. Slab surface temperatures, convergence rate, subduction angle, and age of subducting crust are all similar along the arc.

6.4.3 Evidence for Equilibration with Deep Mafic Rocks

The Sr-Hf-Nd-O isotopic regional trends in basaltic magmas along the SVZ suggest contamination or equilibration of primary arc melts with ancient mafic arc rocks in the lower crust or mantle lithosphere (Figure 6.14). In addition to along-strike isotopic trends, the HREE depletion and LREE enrichment is an indication of deep level processes where garnet becomes increasingly stable. Studies have shown that garnet-bearing lower crustal mafic rocks and/or sub-continental lithospheric mantle pyroxenite are stable at depths of 30 to 60 km (Wyllie 1977; Huang and Wyllie, 1986; Jagoutz and Schmidt 2013; Hirschmann and Stolper, 1996). A deep garnet-bearing lithospheric contaminant or equilibrant with similar major element chemistry provides the best explanation for the systematic regional variability in isotopic and trace element compositions. This contaminant could be older mantle derived mafic underplated basalts that have stabilized residual garnet and emplaced in the sub-arc crust from prior subduction related magmatism or an enriched garnet-bearing pyroxenite in the lithospheric mantle that has formed through ancient arc volcanism. Since convergent margin magmatism has occurred along this section of the Andes for as much as 400 Ma, it is likely that some material solidified in the lithospheric mantle and underplated beneath the sialic crust. Basaltic magmas from the volcanic centers of the CSVZ where the crust is < 35 km, and the lithosphere/asthenosphere boundary coincides with the depth of magma extraction probably do not undergo extended interaction with underplated arc rock, although this is also possible. The primitive basaltic magmas from the

volcanic centers of the TSVZ and NSVZ further north must transit through thicker continental crust of 35 to 40 km in the TSVZ and 55-60 km in the NSVZ, and the depth of magma separation is within the lithosphere, close to the Moho. In these regions primary subduction magma probably mixes with a thermally abrading mantle lithosphere and lower crust. The basalts and basaltic andesites therefore provide a unique insight into lower crustal and deep level processes that alter primary magma compositions. The thickening of the lithosphere in the TSVZ and NSVZ provides an environment where garnet is stabilized in a mafic lithology, and subduction magmas rising from the asthenosphere are subject to more extended equilibration with underplated rocks. An idealized schematic cross section of this process can be seen in Figure 6.14.

Table 6.4 Major Element Estimates of Continental Reservoirs (wt. %)

Reservoir	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
^A Upper Crust	66.0	15.2	4.5	2.2	4.2	3.9	3.4	0.4
^B Upper Crust	64.9	14.6	4.4	2.2	4.1	3.5	3.1	.15
^A Lower Crust	52.3	16.6	8.4	7.9	9.4	2.6	0.6	0.1
^B Lower Crust	58.7	15.4	8.9	4.9	6.3	3.9	1.2	.21

^A Upper and lower crustal estimates from Taylor & McLennan, 1995

^B Upper and felsic lower crustal estimates from Wedephol, 1995

Figure 6.2: Bivariate diagram of SiO_2 vs. $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic values. Along arc samples were chosen to have < 57 wt. % SiO_2 in order to minimize upper crustal influences. Planchon, Peteroa and Azufre samples we analyzed in this study and all other data plotted are from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001

Figure 6.3: Bivariate plot of Sm/Nd vs $^{143}\text{Nd}/^{144}\text{Nd}$ displaying a correlation with radiogenic isotopic values and higher Sm/Nd (parent-daughter) ratios. All Sm and Nd data were collected in this study, however, $^{143}\text{Nd}/^{144}\text{Nd}$ data are from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.4: SiO_2 oxide vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagram showing tight SiO_2 ranges with large variations in $^{87}\text{Sr}/^{86}\text{Sr}$ isotope values. All data in this plot come from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.5: SiO₂ oxide vs ¹⁷⁶Hf/¹⁷⁷Hf diagram showing tight SiO₂ ranges with large variations in ¹⁷⁶Hf/¹⁷⁷Hf isotope values. All ¹⁷⁶Hf/¹⁷⁷Hf data were analyzed in this study and SiO₂ values are from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.6: Bivariate plot of Lu/Hf vs $^{176}\text{Hf}/^{177}\text{Hf}$ displaying a correlation with radiogenic isotopic values and higher Lu/Hf (parent-daughter) ratios. All Lu and Hf data and $^{176}\text{Hf}/^{177}\text{Hf}$ were analyzed in this study.

Figure 6.7: Nd v. Sr isotopic diagram of basalts and basaltic andesites from the SVZ with hypothetical hyperbolic mixing curves plotted into differing reservoirs. Depleted mantle estimates are from Rollinson (1993). Lower and upper crustal fields are adapted from Depaolo and Wasserburg (1979). Sr and Nd data were compiled from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.8: ϵ_{Hf} vs ϵ_{Nd} isotopic diagram of basalts and basaltic andesites from the SVZ. The crustal or terrestrial array line (dashed) is plotted and adopted from Vervoort et al (2011). The Hf-Nd terrestrial area highlighted in yellow was collected from Vervoort et al. (2000). Nd isotopic data come from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001. The Hf-Nd mixing hyperbola (solid line) displays mixing quantities between a Villarrica basalt and a lower crustal assimilant.

Figure 6.9 Sr isotopic versus Ba plot of basalts and basaltic andesites from numerous centers along the SVZ arc. Sr isotopic data are from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.10: Ba/La versus Sr isotopic values of basalts and basaltic andesites from numerous centers along the SVZ arc. Sr isotopic data are from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.11: Plot of La/Yb versus Sr isotopic values for basalts and basaltic andesites in the SVZ. The CSVZ centers are comprised of Villarrica, Antuco, and Osorno. Sr isotopic data come from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Figure 6.12: Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ versus Sr in selected samples along the SVZ arc. Data were compiled from Hickey-Vargas et al. 1984, 1986, 1989; Lopez-Escobar et al. 1995; Tormey et al. 1991; Hickey-Vargas et al. unpublished; Sun thesis, 2001.

Table 6.5 Composition of End Members in Sr, Nd, and Hf Mixing

Villarrica Basalt	Mafic Metamorphic Basement Rocks (Averaged)
$^{87}\text{Sr}/^{86}\text{Sr} = 0.70406$	$^{87}\text{Sr}/^{86}\text{Sr} = 0.712$
Sr ppm = 429	Sr ppm = 112
$^{143}\text{Nd}/^{144}\text{Nd} = 0.512893$	$^{143}\text{Nd}/^{144}\text{Nd} = 0.51214$
Nd ppm = 14.1	Nd ppm = 31.43
$^{176}\text{Hf}/^{177}\text{Hf} = 0.283127$	$^{176}\text{Hf}/^{177}\text{Hf} = 0.28228$
Hf ppm = 2.6	Hf ppm = 6.8

*Values from “Villarrica Basalt” are from sample 151282-1 analyzed in this study. Sr and Nd concentrations and isotopic values for Mafic Metamorphic Basement Rocks (MMBR) are averaged values from multiple samples from Lucassen et al. (2004). Hf concentrations for MMBR are inferred using Nd/Hf ratio (~4.6) from Rudnick et al. (1995). Hf isotopic composition of MMBR was determined using the terrestrial array line of Vervoort et al. (2011).

Figure 6.13: Nd v. Sr isotopic diagram of basalts and basaltic andesites from the SVZ with proposed mixing hyperbola superimposed over SVZ array. Depleted mantle estimates are from Rollinson (1993). Lower and upper crustal fields are adapted from Depaolo and Wasserburg (1979). The lower crustal end member is an average of mafic metamorphic basement rocks from the coastal cordillera in southern Chile (Lucassen et al. 2004).

Figure 6.14: Idealized schematic cross section through the transitional southern volcanic zone (TSVZ). The development of a crustal hot zone is emphasized in the figure along with mafic underplating magmas interacting with lithospheric garnet pyroxenite. This process is proposed to account for the along arc geochemical variations in isotopic and rare earth element chemistry.

7. CONCLUSIONS: PETROGENESIS OF THE SVZ

The vision that emerges of the petrogenesis and subsequent evolution of magmas generated along the SVZ derived from my results of this study is one where deep beneath large magmatic centers, especially centers in the TSVZ and NSVZ; there are localized regions of thermally abraded mantle lithosphere caused by continual and episodic interaction of hydrous basaltic primary melts with local lithospheric mantle and possibly lower crustal lithologies at the mantle-crust transition (Moho; Figure 6.14). Subduction zone basalts generated in the mantle wedge asthenosphere ascend until they are intercepted and become neutrally buoyant at lithospheric levels where can they equilibrate, induce local melting and assimilation, emplace as dikes or sills, and/or re-establish buoyancy because of H₂O induced decreased viscosity or lowered density from differentiation. This process is similar to the lower crustal MASH (melting, assimilation, storage and homogenization) zone proposed by Hildreth and Moorbath (1988), and it is also similar to the production of intra-crustal hot zones at subduction zones, a model created by Annen & Sparks (2002; 2005) using experimental data and numerical modelling. They reason that during long terms of subduction magmatism, mantle derived hydrous melts are emplaced as a succession of sills into lower crustal depths thus raising the local geothermal gradient and generating a deep crustal hot zone. Convergent margin magmatism has occurred along sections of the NSVZ and TSVZ for as much as 400 Ma, the development of crustal hot zones and significant basaltic underplating is likely. Basaltic underplating at convergent margins has been proposed in many studies and is thought to be a recurring process and be an important means by which the continental crust grows (Rudnick, 1992; Bohlen and Mezger 1989). These mechanisms provide an additional and alternative manner of continental crustal growth and a supplementary reason for increasing crustal thickness from the CSVZ of $\sim < 35\text{km}$ to 55 to 60 km of the NSVZ. The distinction between the model proposed here and these earlier models of Hildreth and Moorbath (1989) and Annen and Sparks (2002; 2005) is that the location of

magmatic pooling and interaction is within the lithospheric mantle and lowermost mafic crust, much of which is formed by underplating of ancient, subduction related basaltic rocks.

Many studies have shown that garnet becomes increasingly stable in lower crustal mafic and granulitic rocks and lithospheric mantle pyroxenite at depth of 30 to 60 km (Wyllie 1977; Huang and Wyllie, 1986; Jagoutz and Schmidt 2013; Hirschmann and Stolper, 1996). The development of crustal hot zones provides an environment where either garnet becomes stable as a residual phase or as hydrous subduction melts arrive at these areas experimental constraints predict crystallization of garnet (Muntener et al., 2001; Alonso-Perez, 2006). Although modal garnet has yet to be reported in magmas from the SVZ, mid-Holocene products from Nevados de Longavi in the TSVZ have geochemical signatures consistent with cryptic fractionation of approximately 1.5 % garnet (Rodriguez et al. 2007). Cryptic crystallization of garnet is rare in SVZ magmas yet the REE geochemical signatures of primary melts from the TSVZ and NSVZ indicate a garnet influence. The thermobarometric model by Lee et al. (2008) predicts similar depths of melt separation from mantle sources across the SVZ and these depths are shallower than the predicted stability of garnet in the mantle source regions of 70 to 90 km (Ulmer 1989; Green and Ringwood, 1970; Hirschmann and Stolper, 1996). Therefore, the garnet influence on the geochemistry of magmas from the TSVZ and NSVZ as compared to CSVZ magmas, are the results of interaction with garnet stabilized in mafic rocks within the lithosphere. Through millions of years of subduction magmatism, we envision the crust-mantle boundary in the mature portions of the arc to be blurred and difficult to distinguish. Differentiated primary melts will intrude the sub-continental lithosphere and/or lower crust and crystallize within peridotitic and lower crustal lithologic wall rock and mafic cumulates will form in these hot crystal mushes (hot zone development) creating a complex interlayering of veined, dike-ridden and heterogeneous lower crustal hot zone. The development of this zone underneath maturing subduction zones acts as a density filter and intercepts incoming primary melts which then equilibrate or homogenize

from “baseline” geochemical signatures to more variable trace element characteristics and more crustal isotopic signatures. It is important to note that although Nd and Hf isotopic signatures approach crustal-like values, the lower crustal reservoir influencing primary subduction melts is most probably mafic arc derived mantle-like melts because of the invariability of Sr isotopic compositions of along arc magmas, and the invariable appearance of arc trace element signatures, such as Nb and Ta depletion relative to REE.

The existence of shallow level magma chambers is indisputable upon examination of geologic, petrologic and geophysical evidence along the arc in the SVZ; however, it is less clear whether most diversification and chemical differentiation occur at these shallow depths. Magmas of the CSVZ have not interacted extensively with the continental crust and thus provide a baseline compositional character for evaluating crustal interactions of magmas in regions of increased crustal thickness. The changes associated with the geochemistry of TSVZ and NSVZ magmas in comparison to CSVZ magmas is suggested by this study to be a complex multi-stage poly-baric fractional crystallization, where primary melts generated interact with developing hot zones at lower crustal depth imparting variable trace and isotopic signatures on magmas depending on the extent of interaction, mantle source heterogeneities, and extents of melting. Although a definitive and absolute model of magma generation and subsequent evolution in the Andean volcanic arc is a developing story, the data compiled and collected in this study provides a plausible model that explains the petrogenesis of volcanic rocks present in the SVZ

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APPENDICES

APPENDIX 1

ANALYTICAL METHODS

A1.1 Electron Microprobe

In preparation for analysis on the Electron Microprobe, 12 samples were cut into 2 by 1” inch billets with an approximate thickness of 0.5 inches using a trim saw provided by Florida International University. The billets were then labeled and sent to Van Petro Vancouver Petrographics for final polishing and mounting on thin sections with a final sample thickness of 30 microns which is suitable for EPMA analysis. In order to ensure electric conductivity with the beam the top layer of each thin section was coated with an approximate 250 angstrom thick layer of carbon using the PAC-1 PELCO advanced coater 9500 in the Florida Center for Analytical Electron Microscopy (FCAEM) at Florida International University (FIU). The remaining thick sections used in this study were provided by Rosemary Hickey-Vargas and Daniel Tormey’s sample collection.

Detailed work on mineral chemistry of samples from Azufre-Planchon-Peteroa was performed in the FCEAM at FIU. The electron probe micro-analyzer (EPMA) JEOL 8900R was used to obtain backscattered electron and cathodoluminescence images, quantitative point analysis, and compositional zoning profiles along mineral phases. The mineral phases analyzed included olivine, augite-clinopyroxene, plagioclase, orthopyroxene, and magnetite. The major element point and profile analysis was performed using 15kV with 20 to 30-nA beam with a 30 second count time and 10 second background count time. The trace element analysis used the same beam current parameters with 200 second count time and 80 second background count time per point analyzed. Plagioclase phenocrysts major element analysis included the following elements: Si, Al, Fe, Mg, Ca, Na, K, and Mn. Olivine major element analysis included Mg, Fe, and Si. Clinopyroxene major element analysis comprised of Si, Fe, Mg, Ca, Al, Na, and Mn.

Trace element analysis of Cr, Ni, and Ti were performed on varying mineral assemblages mentioned above. Na in all analysis was the first element analyzed in the first beam pass using the high count crystal (PETH) because of its high volatility of in mineral phases (Nielson & Sigurdsson, 1981). Compositional transects of olivine and phenocrysts phases used the same beam settings as before with points spacing of 5 to 20 microns on a transect line. The locations of core and rim point analysis on olivine, plagioclase, and pyroxenes phases were approximated depending on the shape and growth patterns of the phenocrysts. Standard analysis was regularly preformed using appropriate phases from the SPI-1 and SPI-2 standard block.

A1.2 Major, Trace, and Rare Earth Element Analysis

A1.2.1 Sample Preparation

Trace and rare earth element (REE) sample preparation was performed in the clean laboratory in the Department of Earth and Environment at FIU. A more detailed view of the analytical procedure, errors, and uncertainties used in this study is outlined in Doherty 1989; Jarvis 1988; Jenner et al. 1990; Licthe et al. 1987; Longerich et al. 1990. Powdered samples were weighed out to ~0.100 grams and digested in 23ml Savilex Teflon beakers with a mix of 6ml 8N HNO₃ and 3ml HF on a hot plate at temperatures of 150-200°C overnight. After the solution has dried-down 1ml 6N HCl is added to the beaker for 6 to 8 hours. Once the 6N HCl has come to dryness 1ml of 8N HNO₃ is added for 6 to 8 hours. When the sample is completely digested it is picked up (transferred) by adding 6ml 8N HNO₃ per 0.1mg of sample and placed on the hot plate at 150-200°C for 20 minutes then placed in a 250ml Nalgene bottle. A Ge internal standard was created with a concentration of 50 ppb and introduced to each sample, blank, and standard at a constant volume of 50 ml for the analysis preformed on 3/5/2012. The purpose of the internal standard was to improve the calibration of the known standards and correct for matrix effects, however, this is only true is the internal standard is added to each sample at high concentrations such that the samples “natural” concentration doesn’t affect the introduced concentration of the

internal standard. Soon after the analysis on 3/5/2012 it was discovered that the samples were contributing a small percent of Ge to the internal standard concentrations thus introducing error. As a result, the Ge standard was not used for calibration purposes for the analysis of 3/5/2012. For all subsequent analysis the Ge internal standard was introduced at a concentration of 500 ppb limiting the effect of “natural” Ge contributions from the samples. After the addition of the Ge internal standard the samples, blanks, and standards were diluted to a ratio of 1:1500 with the addition of the appropriate amount of double distilled water. Once the desired dilution factor was reached for every sample then they were sonicated for 20 minutes and stored until the analysis. Prior to the analysis (day of) the samples were shaken for 10 minutes to ensure homogeneity and transferred to 50ml test tubes suitable for an auto sampler. The standards used in the analysis on 3/5/2012 were BHVO-2, W-2, DNC-1, and AGV-2. For all subsequent analysis BCR-2 was added to the previous standard list. BCR-2 provided a better constraint on some of the REE’s with improved calibration curves and therefore more accurate results for the unknown samples.

A1.2.2 Trace and Rare Earth Element Analysis

The diluted sample solutions were analyzed by the inductively coupled mass spectrometer equipped with a dynamic reaction cell (ELAN DRC ICP-MS) at the Trace Evidence Analysis Facility (TEAF) in the Department of Chemistry at Florida International University. The ICP-MS ionizes incoming samples by generating an inductively coupled plasma reaching temperature of 5000-10000K. The ions are then accelerated into a mass selective detector and intensities of differing ions were acquired. The trace and rare earth element suite analyzed at TEAF on all occasions (3/5/2012, 8/3/2012, and 9/29/12) were Ge, Rb, Sr, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Hf, Pb, Th, and U. Each element was analyzed three times with an acquisition and dead time between each sample of 55 seconds. The raw data reported measured intensities for each analysis and all replicates were averaged together for a measured mean intensity. Three blanks were used to establish a background signal which was

used to then to subtract the measured intensities recorded for each sample and standard. An external calibration was used with AGV-2, BCR-2, W-2, DNC-1, and BHVO-2 as standards. Recommended values from the United States Geological Survey (USGS) geochemical referenced powdered materials were used to construct the calibration curves. The standards were analyzed at the beginning, middle and ending of the sample runs in order to constrain the accuracy and reproducibility of the measurements by applying a drift correction.

A1.3 Stable Isotope Analysis

A1.3.1 Sample preparation for O isotopic analysis

The limestone country rock sample CR-1 was trimmed and cut using the diamond coated trim saw in order to obtain a fresh and unaltered sample. This limestone has alternating darker and lighter layers so three samples were obtained from the trimming: one from the dark layer, one from the lighter layer, and a combination sample including both layers. These rock chips were then polished and transported to a clean ball mill/grinder to be crushed into a fine powder. A total of three samples were obtained CR-A, CR-B, and CR-C corresponding to the two different colored layers and the combination of both layers in the limestone country rock sample.

A1.3.2 Analysis of O isotopes

All powdered dolomitic samples were analyzed for oxygen isotopes using the Finnigan-MAT 251 at the Stable Isotope Laboratory in the University of Miami Rosenstiel School of Marine and Atmospheric Science. Each sample was converted to CO₂ with 100% phosphoric acid the data have been corrected for the usual isobaric interferences at masses of 45 and 46 using the equations of Craig (1957) modified for a triple collector mass spectrometer. All measurements were made with respect to a lab reference material with oxygen isotope ratios known relative to the VPDB standard. Isotope exchange between phosphoric acid and carbonate powder was assumed to be identical in both standards and samples.

A1.4 Radiogenic Isotope Analysis

A1.4.1 Sample preparation for Sr and Nd separation

Approximately 100 mg of sample powder was weighed and placed in a clear 10 ml savillex Teflon beaker along with ~ 1 ml of HNO_3 to prevent and static loss of powder and to ensure sample remains intact inside of beaker. Then a 5-7 ml concentrated mix of $\text{HF}:\text{HNO}_3$ (3:1) was added to each sample, capped, and place on a hot plate with temperatures of $\sim 110^\circ\text{C}$ for 6-12 hours to ensure complete dissolution do sample powders. Afterwards the beakers were uncapped and placed in the flow box to complete evaporation which usually takes 6-8 hours. When samples are completely dry then 1 ml of 6N HCl was added and then placed on the hot plate for ~ 1 hour. The samples were then uncapped and placed in the flow box to dryness. This step was repeated one more time to ensure complete dissolution of fluorides in samples. Samples were then picked up with 2 ml of 1.25N HCl and placed into double distilled water cleaned test tubes and centrifuged for 5 minutes.

A1.4.2 Column Preparation Sr and Nd separation 1st column

There are six Teflon columns in use at the clean lab in Florida International University and they consist of a 0.5 cm diameter by 19 cm height filled with Dowex AG50W-X8 200-400 mesh cation exchange resin that remain wet with 2.5N HCl acid. Prior to any sample introduction the columns are cleaned with 4 rinses of ~ 30 ml of 6 N HCl and then backwashed with 2.5 N HCl. For Sr and Nd separation, the columns are primed with 0.5 ml double distilled water. Then 2 ml of sample in 1.25N HCl is loaded in 0.25 ml aliquots into the columns. Afterwards 24-28 ml (depending on column) of 2.5N HCl is added to the columns as wash and discarded. Then 16 ml of 2.5N HCl is placed in each column and the Sr fraction is collected from that elution and dried down until the HCl has evaporated away. Then a 12 ml wash of 4N HCl is passed through the column and discarded. The final elution of REE including Nd is collected through the addition of 16 ml of 4N HCl. The sample beakers are then dried down in the flow box until the

HCl has evaporated. A more detailed evaluation of the Sr and Nd 1st column chemistry procedures can be found in Hart and Brooks (1977). Nd separation (from Sm and other REE) done at NHMFL.

A1.4.3 Analysis of Nd Isotopes

The Nd isotopic compositions were determined using a Thermo Finnigan NEPTUNE multi-collector inductively coupled plasma mass spectrometer. The dry samples are introduced to the MC-ICPMS by adding 1 ml of 2 % HNO₃ and extracting 300 µl of that solution in beakers suitable for analysis. This aliquot of the sample is then diluted between ~600 and 1100 µl in 2% HNO₃ in order to ensure a beam intensity of 10 – 15Kv for ¹⁴⁴Nd. The diluted samples are taken up by an APEX introduction system at 63 µl/min. This creates the fine sample aerosol from its nebulizer which is carried to the plasma and ionized.

A1.4.4 Sample preparation for Hf separation

The sample preparation for Hf separation is based on the work by Munker et al (2001) and included is a more detailed explanation on the procedures. Approximately 100 mg of sample powder was weighed and placed in a clear 10 ml savillex Teflon beaker along with ~ 1 ml of HNO₃ to prevent static loss of powder and to ensure sample remains intact inside of beaker. . Then a 5-7 ml concentrated mix of HF:HNO₃ (3:1) was added to each sample, capped, and place on a hot plate with temperatures of ~110°C for 6-12 hours. The sample are then re-dissolved in 3-4 ml 6N HCl and placed on the hot plat at gentle temperatures (~60 to 110°C) to dryness. This step is repeated two more times. Once the samples have been adequately dissolved and are ready for separation they put into a solution of 2 to 5 ml 3N HCl/0.1M ascorbic acid. The samples are then placed into clean test tubes and centrifuged for 5 minutes prior to placement on columns.

A1.4.5 Column Preparation Hf separation

The Teflon Columns are ¼ inch in diameter and approximately 10 cm in length and underneath and attached to a 30 ml Savillex reservoir. The columns are filled with ~ 1.2 ml of Ln

resin which fills the $\frac{1}{4}$ inch column to an approximate 4cm resin bed. The columns are closed at the bottom with polyethylene frits and the resin is capped with an anion resin with a $\frac{1}{2}$ cm length to ensure the Ln resin is not stirred with the introduction of elution acids and samples. The samples are loaded in ~ 5 ml solution of 3N HCl/0.1M ascorbic acid. Then a wash of 5 ml 3N HCl is added to the column and the total of 10 ml passed through the columns is collected for potential Sr and Nd analysis. Afterwards 5 ml of 3N HCl is added and discarded. 20 ml of 6N HCl is added and the wash is collected for Lu and Yb. 5 ml of double distilled water is loaded and then discarded. In order to remove the Ti in the samples 60 ml of Citric/HNO₃/H₂O₂ acid (0.09M Citric/0.4N HNO₃/1%H₂O₂) is passed through the column and thrown out. The next step is to add 5 ml 6N HCl/0.2N HF to the column and discarded. Finally 15 ml 6N HCl/0.2N HF is added to the column and collected for the samples Hf. The sample solutions are then placed into a flow box and evaporated to dryness. The columns are cleaned after this process by adding multiple steps of 2N HF (total volume 45 ml) and 6N HCl (total volume of 45 ml). Once ready for analysis the samples are then mixed with a solution of 2% HNO₃.

A1.4.6 Analysis of Hf isotope

The Hf isotopic compositions were determined using a Thermo Finnigan NEPTUNE multi-collector inductively coupled plasma mass spectrometer. The dry samples are introduced to the MC-ICPMS by adding 1 ml of 2 % HNO₃ and extracting 300 μ l of that solution in beakers suitable for analysis. This aliquot of the sample is then diluted between ~ 600 and 1100 μ l in 2% HNO₃ in order to ensure a beam intensity of 10 – 15Kv . The diluted samples are taken up by an APEX introduction system at 63 μ l/min. This creates the fine sample aerosol from its nebulizer which is carried to the plasma and ionized.

Appendix 2

ELECTRON PROBE MICRO-ANALYZER MEASUREMENT DATA

A2.1 Measured Major Element Data (Wt. %) Analyzed on Plagioclase Phenocrysts from Planchon

Sample/Phase	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Total	Anorthite	Ca/Na
PL-27-1CORE	55.13	27.22	0.79	0.25	11.51	4.50	0.28	0.06	99.76	57.62	1.19
PL-27-1RIM	53.07	29.24	0.87	0.12	13.06	3.69	0.19	0.03	100.29	65.43	1.64
PL-27-2CORE	54.51	28.02	0.90	0.13	11.67	4.54	0.26	0.08	100.10	57.82	1.20
PL-27-2RIM	53.86	27.63	1.02	0.08	11.45	4.27	0.26	0.09	98.67	58.76	1.25
PL-27-3CORE	50.59	30.75	0.79	0.12	15.00	2.73	0.10	0.00	100.09	74.79	2.56
PL-27-3RIM	53.71	28.13	1.03	0.13	12.36	4.01	0.20	0.04	99.60	62.28	1.43
PL-27-4CORE	55.36	27.54	0.76	0.16	11.27	4.52	0.26	0.04	99.92	57.04	1.16
PL-27-4RIM	51.90	29.84	0.90	0.08	13.81	3.34	0.17	0.04	100.09	68.83	1.92
PL-27-5CORE	55.51	28.20	0.73	0.14	11.61	4.41	0.23	0.10	100.94	58.44	1.22
PL-27-5RIM	54.66	27.83	0.81	0.11	11.80	4.36	0.24	0.04	99.85	59.10	1.26
PL-27-6CORE	47.54	33.14	0.80	0.07	17.23	1.52	0.05	0.02	100.37	86.00	5.27
PL-27-6RIM	54.47	27.90	0.80	0.15	11.32	4.64	0.24	0.08	99.61	56.57	1.13
PL-27-7CORE	48.79	30.63	0.67	0.08	14.66	2.85	0.11	0.06	97.85	73.47	2.39
PL-27-7RIM	53.14	29.14	0.98	0.11	13.03	3.50	0.19	0.08	100.18	66.53	1.73
PL-27-8CORE	55.21	27.32	0.79	0.10	11.33	4.52	0.23	0.09	99.60	57.26	1.16
PL-27-8RIM	54.42	27.69	1.06	0.14	11.72	4.29	0.25	0.07	99.66	59.29	1.27
PL-27-9CORE	54.38	27.72	0.90	0.11	11.82	4.42	0.25	0.08	99.67	58.78	1.24
PL-27-9RIM	57.05	25.96	1.22	0.09	9.34	5.46	0.44	0.15	99.70	47.29	0.79
PL-27-10CORE	54.46	27.90	0.77	0.11	11.90	4.34	0.26	0.05	99.80	59.32	1.28
PL-27-10RIM	50.55	31.13	0.54	0.08	14.89	2.72	0.13	0.03	100.09	74.62	2.55
PL-27-11CORE	46.33	32.36	0.78	0.07	16.38	1.80	0.05	0.06	97.82	83.17	4.24

Sample/Phase	SiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	Total	Anorthite	Ca/Na
PL-27-11RIM	57.28	24.52	1.13	0.07	8.13	6.18	0.68	0.20	98.21	40.41	0.61
PL-27-12CORE	47.71	32.13	0.76	0.07	15.77	2.26	0.08	0.03	98.86	79.03	3.25
PL-27-12RIM	50.62	28.47	0.69	0.11	13.42	3.32	0.12	0.01	96.74	68.61	1.88
PL-27-13CORE	47.57	30.26	0.85	0.04	14.52	2.98	0.13	0.01	96.39	72.34	2.26
PL-27-13RIM	53.26	28.13	0.94	0.12	11.67	4.34	0.23	0.12	98.83	58.92	1.25
PL-27-14CORE	51.60	28.98	0.75	0.07	12.97	3.77	0.16	0.06	98.35	64.93	1.60
PL-27-14RIM	50.90	29.52	0.86	0.13	13.11	3.48	0.17	0.04	98.24	66.83	1.75
PL-27-15CORE	48.92	29.88	0.80	0.08	14.94	2.69	0.09	0.02	97.43	75.05	2.59
PL-27-15RIM	52.43	27.63	0.92	0.11	12.13	4.07	0.21	0.07	97.56	61.44	1.39
PL-27-16CORE	53.17	27.71	0.86	0.11	11.30	4.62	0.23	0.06	98.07	56.67	1.14
PL-27-16RIM	50.05	30.07	0.84	0.12	13.73	3.16	0.13	0.03	98.12	70.00	2.02
PL-8-1CORE	52.05	29.52	0.72	0.12	13.18	3.56	0.17	0.10	99.41	66.51	1.40
PL-8-2CORE	48.49	31.75	0.55	0.13	15.55	2.24	0.06	0.05	98.83	79.02	2.62
PL-8-2RIM	50.83	29.74	0.63	0.16	13.65	3.33	0.12	0.04	98.49	68.83	1.54
PL-8-3CORE	55.59	22.16	5.28	1.05	9.46	3.96	1.18	1.26	100.01	52.45	0.90
PL-8-3RIM	49.01	31.77	0.54	0.11	15.68	2.25	0.08	0.05	99.49	78.97	2.62
PL-8-4CORE	49.90	31.68	0.55	0.13	15.15	2.54	0.09	0.02	100.06	76.31	2.25
PL-8-4RIM	48.86	29.90	0.65	0.10	13.98	3.06	0.10	0.04	96.70	71.16	1.72
PL-8-5CORE	51.94	28.90	0.52	0.12	12.75	3.87	0.18	0.04	98.34	63.83	1.24
PL-8-7CORE	50.56	29.77	0.72	0.18	14.06	2.97	0.15	0.01	98.41	71.66	1.78
PL-8-7RIM	55.34	26.02	1.11	0.14	10.18	5.16	0.41	0.11	98.47	50.89	0.74
PL-8-8CORE	54.70	27.90	0.61	0.16	11.99	4.21	0.21	0.06	99.87	60.38	1.07
PL-8-8RIM	50.43	31.26	0.74	0.11	15.26	2.49	0.08	0.01	100.38	76.81	2.31
PL-8-9CORE	48.88	31.45	0.53	0.08	16.23	1.77	0.07	0.00	99.01	83.16	3.46
PL-8-9RIM	55.04	27.30	1.06	0.18	11.74	4.28	0.30	0.06	99.97	59.17	1.04

Sample/Phase	SiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	Total	Anorthite	Ca/Na
PL-8-10RIM	54.53	28.20	0.72	0.17	12.24	4.14	0.19	0.08	100.27	61.31	1.12
PL-8-11CORE	50.97	31.20	0.58	0.11	15.04	2.67	0.10	0.04	100.72	75.23	2.12
PL-8-11RIM	52.86	29.10	0.77	0.13	13.26	3.54	0.12	0.03	99.87	66.93	1.41
PL-8-12CORE	54.85	27.18	1.25	0.35	11.62	4.28	0.35	0.12	100.02	58.77	1.03
PL-8-12RIM	53.80	28.03	0.82	0.17	12.31	4.13	0.27	0.07	99.62	61.27	1.13
PL-34-1 Core	49.02	29.36	0.70	0.07	14.03	3.35	0.21	0.04	96.77	68.99	1.62
PL-34-1 CoreA	50.31	28.66	0.70	0.05	14.59	3.30	0.19	0.00	97.80	70.20	1.71
PL-34-1 Rim	51.82	28.48	1.06	0.09	12.94	4.05	0.28	0.09	98.80	62.78	1.23
PL-34-2 Core	55.94	27.20	0.77	0.11	10.38	5.15	0.43	0.04	100.02	51.36	0.78
PL-34-2 Rim	54.04	28.53	0.82	0.09	11.95	4.26	0.31	0.08	100.08	59.67	1.08
PL-34-3 CORE	52.39	28.73	0.50	0.08	13.11	3.06	0.18	0.01	98.08	69.46	1.65
PL-34-3 RIM	52.76	29.07	0.73	0.08	12.89	3.14	0.19	0.02	98.89	68.61	1.59
PL-34-4 CORE	55.22	27.70	0.73	0.06	11.26	4.38	0.34	0.01	99.71	57.45	0.99
PL-34-4 RIM1	54.89	28.35	0.60	0.05	11.31	4.36	0.34	0.04	99.95	57.69	1.00
PL-34-4 RIM2	54.77	27.59	1.01	0.25	11.19	4.06	0.72	0.06	99.65	57.69	1.07
PL-34-5 CORE	54.46	28.21	0.98	0.14	11.73	4.17	0.35	0.06	100.09	59.54	1.09
PL-34-5 RIM	55.83	27.70	0.89	0.11	10.65	4.60	0.40	0.01	100.19	54.76	0.90
PL-34-6 CORE	54.98	27.68	0.85	0.11	11.07	4.52	0.36	0.06	99.62	56.26	0.95
PL-34-6 RIM	46.34	24.91	0.80	0.09	10.79	3.15	0.27	0.04	86.40	64.23	1.33
PL-34-7 CORE	56.62	27.50	0.69	0.11	10.50	4.95	0.42	0.08	100.86	52.65	0.82
PL-34-8 CORE	57.58	26.65	0.70	0.08	9.74	5.28	0.67	0.08	100.79	48.49	0.71
PL-34-8 RIM	52.49	29.53	0.95	0.07	13.20	3.44	0.35	0.06	100.09	66.52	1.48
PL-34-9CORE-A	52.54	27.79	0.66	0.11	12.24	3.98	0.28	0.08	97.68	61.91	1.19
PL-34-9CORE-B	53.95	28.01	0.64	0.07	11.88	4.21	0.30	0.06	99.12	59.83	1.09
PL-34-9RIM-A	53.90	28.34	0.87	0.11	12.06	4.23	0.29	0.06	99.87	60.09	1.10

Sample/Phase	SiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	Total	Anorthite	Ca/Na
PL-34-10CORE	54.63	28.12	0.58	0.12	11.92	4.18	0.27	0.04	99.87	60.19	1.10
PL-34-10RIM	53.85	27.83	0.80	0.09	11.61	4.39	0.31	0.05	98.93	58.30	1.02
PL-34-11CORE	53.18	28.43	0.84	0.10	12.50	3.92	0.19	0.07	99.22	63.06	1.23
PL-34-11RIM	51.70	29.84	0.64	0.08	13.67	3.18	0.19	0.02	99.33	69.58	1.66

A2.2 Measured Major Element Data Analyzed on Olivine Phenocrysts from Planchon (Wt. %)

Sample/Phase	SiO₂	TiO₂	FeO	MnO	MgO	NiO	Total	Fo	Apparent Fe/Mg
PL-16-OL1-1	40.65	0.00	19.46	0.06	43.43	0.08	103.68	79.86	0.45
PL-16-OL1-2	40.41	0.00	18.40	0.07	43.82	0.07	102.77	80.88	0.42
PL-16-OL1-3	40.12	0.00	19.41	0.12	43.30	0.05	102.99	79.81	0.45
PL-16-OL1-4	40.14	0.00	19.17	0.10	43.73	0.04	103.18	80.18	0.44
PL-16-OL1-5	40.33	0.02	18.80	0.16	42.00	0.05	101.37	79.79	0.45
PL-16-OL2-1	40.56	0.00	18.07	0.05	44.05	0.05	102.78	81.25	0.41
PL-16-OL2-2	39.78	0.00	21.84	0.26	40.78	0.06	102.72	76.68	0.54
PL-16-OL2-3	40.58	0.01	19.17	0.07	42.52	0.07	102.41	79.75	0.45
PL-16-OL2-4	39.90	0.00	18.75	0.08	44.39	0.09	103.20	80.78	0.42
PL-16-OL3-1	39.43	0.01	26.32	0.10	38.41	0.02	104.28	72.16	0.69
PL-16-OL3-2	39.60	0.01	23.24	0.17	38.29	0.00	101.30	74.46	0.61
PL-16-OL3-3	39.19	0.00	28.25	0.17	37.17	0.01	104.78	69.98	0.76
PL-16-OL4-1	39.24	0.00	23.50	0.25	40.42	0.01	103.42	75.21	0.58
PL-16-OL4-2	38.45	0.01	29.43	0.09	35.34	0.02	103.34	68.09	0.83
PL-16-OL5-1	40.46	0.00	18.72	0.09	43.43	0.04	102.74	80.45	0.43
PL-16-OL5-2	40.61	0.00	18.39	0.08	43.83	0.06	102.96	80.88	0.42
PL-16-OL5-3	41.16	0.01	19.04	0.07	44.47	0.06	104.81	80.57	0.43
PL-16-OL5-4	40.69	0.01	18.36	0.13	44.41	0.06	103.65	81.06	0.41
PL-16-OL-6-1	40.59	0.02	18.32	0.09	43.51	0.06	102.59	80.81	0.42
PL-16-OL-6-2	39.65	0.02	18.32	0.05	43.71	0.05	101.80	80.91	0.42
PL-16-OL-6-3	39.10	0.00	24.82	0.15	38.37	0.04	102.47	73.26	0.65
PL-16-OL-6-4	39.70	0.00	20.59	0.13	42.37	0.03	102.83	78.46	0.49
PL-16-OL7-1	40.14	0.00	18.57	0.13	43.51	0.06	102.40	80.57	0.43
PL-16-OL7-2	38.33	0.01	26.69	0.08	36.84	0.00	101.96	71.03	0.73
PL-16-OL7-3	40.17	0.02	18.04	0.05	43.49	0.03	101.79	81.08	0.42

Sample/Phase	SiO2	TiO2	FeO	MnO	MgO	NiO	Total	Fo	Apparent Fe/Mg
PL-16-OL7-4	39.06	0.01	24.78	0.15	38.19	0.01	102.21	73.19	0.65
PL-16-OL8-1	39.96	0.00	17.80	0.07	42.57	0.02	100.41	80.94	0.42
PL-16-OL8-2	39.47	0.02	16.82	0.12	42.12	0.06	98.60	81.59	0.40
PL-16-OL8-3	39.71	0.00	17.22	0.08	42.71	0.02	99.73	81.48	0.40
PL-16-OL8-4	39.43	0.01	16.36	0.08	42.84	0.06	98.78	82.28	0.38
PL-16-OL8-5	39.09	0.00	18.29	0.10	40.39	0.02	97.88	79.65	0.45
PL-16-OL8-6	38.96	0.01	20.52	0.11	40.99	0.04	100.62	77.99	0.50
PL-16-OL8-7	39.52	0.00	16.76	0.09	42.24	0.03	98.63	81.71	0.40
PL-16-OL9-1	39.40	0.00	17.63	0.10	43.32	0.04	100.49	81.33	0.41
PL-16-OL9-2	39.91	0.01	17.41	0.08	43.11	0.06	100.58	81.46	0.40
PL-16-OL9-3	38.93	0.00	22.18	0.20	40.55	0.02	101.89	76.35	0.55
PL-16-OL9-4	38.31	0.00	23.41	0.16	37.62	0.04	99.53	73.99	0.62
PL-25-OL-1-CORE	38.78	0.00	25.30	0.18	38.38	0.07	102.71	72.86	0.66
PL-25-OL-1-RIM	36.55	0.00	34.15	0.20	31.44	0.06	102.40	62.00	1.09
PL-25-OL-2-RIM	38.10	0.00	28.87	0.19	34.52	0.05	101.73	67.91	0.84
PL-25-OL-2-2	39.15	0.02	26.65	0.13	37.22	0.07	103.23	71.24	0.72
PL-25-OL-2-3	38.66	0.02	27.02	0.15	36.51	0.06	102.43	70.55	0.74
PL-25-OL-2-CORE	37.66	0.00	27.17	0.15	36.11	0.05	101.14	70.20	0.76
PL-25-OL-2-5	38.83	0.00	26.58	0.15	36.03	0.05	101.64	70.61	0.74
PL-25-OL-2-RIM2	38.75	0.01	27.92	0.15	34.40	0.04	101.26	68.59	0.82
PL-25-OL-3-RIM	37.19	0.00	34.39	0.20	31.04	0.05	102.87	61.53	1.11
PL-25-OL-3-2	38.99	0.01	24.54	0.14	38.76	0.03	102.47	73.68	0.64
PL-25-OL-3-CORE	37.94	0.00	25.38	0.14	39.44	0.06	102.96	73.36	0.65
PL-25-OL-3-4	38.52	0.01	27.77	0.13	36.53	0.08	103.04	70.00	0.76
PL-25-OL-4-CORE	40.18	0.00	18.55	0.10	43.59	0.22	102.64	80.64	0.43

Sample/Phase	SiO2	TiO2	FeO	MnO	MgO	NiO	Total	Fo	Apparent Fe/Mg
PL-25-OL-4-RIM	37.99	0.01	27.12	0.13	35.92	0.07	101.25	70.14	0.76
PL-25-OL-5-CORE	40.33	0.01	17.39	0.09	43.61	0.21	101.64	81.64	0.40
PL-25-OL-5-RIM	35.45	0.02	36.00	0.18	29.50	0.02	101.17	59.24	1.23
PL-25-OL-6-CORE	38.23	0.00	27.29	0.14	37.08	0.07	102.81	70.67	0.74
PL-25-OL-6-RIM	35.46	0.21	46.39	0.30	19.92	0.02	102.31	43.19	2.34
PL-25-OL-7-CORE	35.81	0.02	28.98	0.16	30.35	0.10	95.42	64.99	0.96
PL-25-OL-7-2	37.23	0.00	28.99	0.14	35.65	0.09	102.10	68.56	0.82
PL-25-OL-7-3	38.21	0.00	24.92	0.11	38.65	0.13	102.01	73.35	0.65
PL-25-OL-7-RIM	37.61	0.03	33.14	0.21	32.44	0.07	103.49	63.42	1.03
PL-25-OL-8-CORE	37.46	0.01	28.83	0.17	35.71	0.11	102.28	68.70	0.81
PL-25-OL-8-2	37.57	0.00	29.26	0.18	33.85	0.10	100.97	67.21	0.87
PL-25-OL-8-4	37.34	0.00	28.82	0.18	35.37	0.08	101.79	68.49	0.82
PL-25-OL-8-RIM	37.65	0.03	34.33	0.21	29.79	0.03	102.04	60.59	1.16
PL-25-OL-10-CORE	37.44	0.00	29.32	0.21	34.52	0.05	101.54	67.58	0.85
PL-25-OL-10-2	37.57	0.00	28.10	0.22	34.14	0.06	100.10	68.24	0.83
PL-25-OL-10-3	38.96	0.01	28.18	0.17	35.58	0.03	102.93	69.11	0.80
PL-25-OL-10-RIM	35.49	0.05	41.54	0.34	23.79	0.03	101.24	50.31	1.76
PL-25-OL-9-CORE	37.30	0.00	26.21	0.18	36.92	0.06	100.67	71.38	0.71
PL-25-OL-9-2	37.76	0.01	23.67	0.15	39.23	0.05	100.86	74.59	0.61
PL-25-OL-9-RIM	37.31	0.00	23.93	0.12	38.79	0.08	100.24	74.19	0.62
PL-25-OL-11-CORE	38.52	0.00	27.66	0.21	36.93	0.03	103.34	70.25	0.75
PL-25-OL-11-RIM	36.74	0.01	36.18	0.22	27.71	0.04	100.90	57.57	1.31
PL-25-OL-12-CORE	38.92	0.00	24.45	0.12	38.33	0.07	101.89	73.55	0.64
PL-25-OL-13-CORE	39.96	0.01	16.61	0.07	44.95	0.29	101.88	82.76	0.37

Sample/Phase	SiO2	TiO2	FeO	MnO	MgO	NiO	Total	Fo	Apparent Fe/Mg
PL-25-OL-13-2	39.78	0.00	15.90	0.01	44.46	0.24	100.39	83.28	0.36
PL-25-OL-13-3	39.68	0.00	16.63	0.07	44.18	0.21	100.77	82.50	0.38
PL-27-OL-1CORE1	39.21	0.01	19.35	0.40	41.03	0.19	100.18	78.73	0.32
PL-27-OL-1CORE2	39.78	0.00	19.64	0.29	40.63	0.19	100.54	78.41	0.31
PL-27-OL-1CORE3	38.34	0.00	19.01	0.29	39.38	0.15	97.17	78.43	0.41
PL-27-OL-1RIM	37.63	0.01	24.00	0.32	37.70	0.11	99.77	73.43	0.35
PL-27-OL-1RIM1	38.73	0.05	21.41	0.37	39.39	0.12	100.06	76.32	0.48
PL-27-OL-2CORE	38.31	0.02	26.59	0.45	35.84	0.04	101.25	70.25	0.49
PL-27-OL-2CORE1	37.83	0.01	26.35	0.41	34.86	0.09	99.54	69.90	0.48
PL-27-OL-2RIM1	38.02	0.03	25.87	0.44	34.93	0.10	99.39	70.30	0.55
PL-27-OL-3CORE	36.84	0.00	28.83	0.47	34.17	0.06	100.36	67.51	0.47
PL-27-OL-3RIM	38.30	0.04	26.25	0.38	36.35	0.10	101.42	70.86	0.46
PL-27-OL-4CORE	38.77	0.00	25.91	0.38	36.78	0.09	101.92	71.37	0.47
PL-27-OL-4RIM	38.10	0.04	25.87	0.40	35.64	0.11	100.17	70.74	0.24
PL-27-OL-5CORE	40.12	0.01	15.72	0.24	42.91	0.25	99.24	82.74	0.46
PL-27-OL-5RIM	39.16	0.01	25.39	0.45	36.30	0.11	101.43	71.45	0.35
PL-27-OL-6CORE	39.55	0.00	21.08	0.30	39.65	0.13	100.71	76.77	0.49
PL-27-OL-6RIM	38.70	0.05	26.64	0.42	35.50	0.07	101.38	70.03	0.30
PL-27-OL-7CORE	39.81	0.03	18.89	0.21	41.15	0.14	100.23	79.33	0.31
PL-27-OL-7CORE1	38.61	0.01	19.60	0.32	40.82	0.15	99.50	78.50	0.38
PL-27-OL-7RIM	39.25	0.07	22.69	0.30	39.10	0.17	101.58	75.19	0.55
PL-27-OL-8CORE	38.11	0.03	28.74	0.51	34.11	0.07	101.56	67.52	0.52
PL-27-OL-8RIM	38.12	0.06	26.52	0.42	33.47	0.03	98.61	68.89	0.50
PL-27-OL-9CORE	38.66	0.01	27.60	0.43	35.98	0.09	102.77	69.58	0.40
PL-28-OL1-1	38.96	0.00	27.01	0.09	37.26	0.01	103.32	71.02	0.50
PL-28-OL1-2	38.98	0.00	27.49	0.16	37.34	0.02	103.99	70.65	0.48
PL-28-OL1-3	39.38	0.00	27.01	0.11	37.99	0.02	104.51	71.40	0.42

Sample/Phase	SiO2	TiO2	FeO	MnO	MgO	NiO	Total	Fo	Apparent Fe/Mg
PL-28-OL1-4	39.58	0.00	24.57	0.17	39.50	0.00	103.81	74.00	0.31
PL-28-OL2-1	40.85	0.00	19.67	0.14	42.88	0.06	103.60	79.41	0.30
PL-28-OL2-2	40.60	0.02	19.42	0.04	42.90	0.06	103.02	79.72	0.29
PL-28-OL2-3	38.17	0.00	17.59	0.08	40.97	0.05	96.86	80.51	0.42
PL-28-OL2-4	39.78	0.01	24.45	0.20	39.23	0.02	103.69	73.93	0.29
PL-28-OL3-1	40.66	0.00	18.80	0.04	43.85	0.04	103.38	80.58	0.29
PL-28-OL3-2	40.32	0.00	18.80	0.08	43.71	0.05	102.97	80.49	0.28
PL-28-OL3-3	41.08	0.00	18.46	0.07	44.39	0.07	104.07	81.03	0.63
PL-28-OL3-4	38.59	0.00	31.61	0.19	33.69	0.03	104.11	65.38	0.64
PL-28-OL4-2	38.21	0.01	32.28	0.14	34.02	0.02	104.67	65.16	0.53
PL-28-OL5-1	38.69	0.00	28.38	0.21	36.08	0.02	103.38	69.23	0.54
PL-28-OL5-2	39.51	0.02	29.17	0.17	36.60	0.00	105.47	68.98	0.51
PL-28-OL5-3	39.44	0.04	27.82	0.10	36.53	0.00	103.92	69.99	0.51
PL-28-OL5-4	39.06	0.02	27.47	0.05	36.05	0.00	102.66	70.01	0.50
PL-28-OL6-1	38.85	0.00	27.64	0.11	37.15	0.02	103.76	70.47	0.51
PL-28-OL6-2	38.77	0.00	27.68	0.10	36.91	0.03	103.49	70.31	0.51
PL-28-OL6-3	39.23	0.00	27.51	0.14	36.58	0.02	103.48	70.22	0.55
PL-28-OL6-4	38.09	0.02	28.80	0.24	35.17	0.01	102.32	68.35	0.54
PL-28-OL7-1	38.29	0.01	28.71	0.23	35.59	0.00	102.83	68.67	0.54
PL-28-OL7-2	38.66	0.01	28.97	0.23	35.99	0.00	103.87	68.72	0.55
PL-28-OL7-3	38.47	0.03	29.33	0.13	35.82	0.05	103.83	68.43	0.35
PL-28-OL8-2	39.81	0.00	21.48	0.12	41.20	0.01	102.62	77.27	0.36
PL-28-OL8-3	40.25	0.02	21.81	0.01	40.79	0.02	102.90	76.92	0.42
PL-28-OL8-4	39.60	0.00	24.49	0.13	39.29	0.02	103.54	73.99	0.28
PL-28-OL9-1	40.46	0.02	18.07	0.03	43.48	0.06	102.11	81.07	0.29

Sample/Phase	SiO2	TiO2	FeO	MnO	MgO	NiO	Total	Fo	Apparent Fe/Mg
PL-28-OL9-2	40.79	0.00	18.84	0.11	43.27	0.05	103.06	80.27	0.29
PL-28-OL9-3	40.49	0.02	18.56	0.13	43.22	0.03	102.45	80.47	0.32
PL-28-OL9-4	40.18	0.00	20.14	0.11	42.81	0.07	103.31	79.03	0.38
PL-28-OL10-1	34.91	0.06	18.83	0.12	33.16	0.07	87.16	75.72	0.38
PL-28-OL10-2	39.94	0.00	22.77	0.12	40.72	0.05	103.61	76.02	0.37
PL-28-OL10-3	39.93	0.00	22.13	0.07	40.46	0.01	102.59	76.46	0.53

A2.3 Results of Modal Olivine Phenocryst Subtraction from Bulk Analysis

Average Major Element Composition of Olivines in Samples PL-16 & PL-25 in wt. %

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO
PL-16	39.75	0.01	0.00	20.35	0.11	41.68
PL-25	37.88	0.01	0.00	27.59	0.16	35.99

Major Element Bulk Composition of Samples PL-16 & PL-25 in wt. %

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
PL-16	52.75	0.88	16.41	8.72	0.15	8.74	7.88	3.40	1.07
PL-25	53.28	0.90	16.88	8.46	0.15	7.66	8.25	3.30	1.11

Major Element Composition of Samples PL-16 & PL-25 after Modal Phenocryst Subtraction (wt. %)

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	MG#
PL-16	54.19	0.98	18.23	7.43	0.16	5.08	8.76	3.78	1.19	54.93
PL-25	54.80	0.99	18.55	6.56	0.15	4.86	9.07	3.63	1.23	56.90

A2.4 Results of Olivine Phenocryst Transects in Planchon Samples (Wt. %)

Sample	Distance (Microns)	SiO ₂	TiO ₂	MnO	MgO	FeO	NiO	Total	Fo
Line 1 PL-8OL1	0	40.45	0.02	0.47	41.71	17.74	0.19	100.57	80.32
Line 2 PL-8OL1	20	40.33	0.00	0.41	42.42	15.69	0.17	99.02	82.44
Line 3 PL-8OL1	40	39.69	0.00	0.42	41.82	16.43	0.24	98.60	81.56
Line 4 PL-8OL1	60	40.12	0.00	0.39	42.39	15.75	0.18	98.82	82.40
Line 5 PL-8OL1	80	40.31	0.00	0.40	42.33	16.82	0.17	100.03	81.42
Line 6 PL-8OL1	100	40.17	0.00	0.43	42.09	17.10	0.19	99.98	81.05
Line 7 PL-8OL1	120	40.13	0.01	0.42	42.67	17.05	0.21	100.49	81.32
Line 8 PL-8OL1	140	39.52	0.00	0.44	42.51	16.80	0.09	99.37	81.46
Line 9 PL-8OL1	160	39.70	0.00	0.45	42.36	17.15	0.20	99.87	81.09
Line 10 PL-8OL1	180	40.17	0.01	0.45	42.28	16.80	0.19	99.90	81.37
Line 11 PL-8OL1	200	40.42	0.02	0.44	42.38	17.07	0.23	100.55	81.17
Line 12 PL-8OL1	220	40.31	0.00	0.43	42.32	17.01	0.17	100.24	81.23
Line 13 PL-8OL1	240	40.05	0.00	0.40	42.72	17.20	0.14	100.51	81.22
Line 14 PL-8OL1	260	40.23	0.00	0.41	42.34	16.89	0.19	100.05	81.35
Line 15 PL-8OL1	280	39.91	0.00	0.46	42.24	16.78	0.15	99.55	81.36
Line 16 PL-8OL1	300	40.14	0.01	0.48	42.55	17.43	0.22	100.82	80.89
Line 17 PL-8OL1	320	39.83	0.00	0.40	42.43	17.25	0.16	100.07	81.07
Line 18 PL-8OL1	340	40.29	0.00	0.43	42.12	15.97	0.21	99.02	82.07
Line 19 PL-8OL1	360	40.49	0.00	0.35	42.43	17.46	0.17	100.89	80.94
Line 20 PL-8OL1	380	39.79	0.00	0.41	42.20	16.72	0.18	99.29	81.45
Line 21 PL-8OL1	400	40.24	0.00	0.36	42.67	16.72	0.15	100.14	81.65
Line 22 PL-8OL1	420	40.29	0.00	0.37	42.88	16.70	0.22	100.46	81.74
Line 23 PL-8OL1	440	39.83	0.00	0.44	42.71	16.57	0.20	99.75	81.73
Line 24 PL-8OL1	460	27.82	0.00	0.28	29.07	12.42	0.18	69.76	NOT USED
Line 25 PL-8OL1	480	40.34	0.00	0.46	42.69	16.27	0.21	99.96	81.97

Sample	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 26 PL-8OL1	500	40.30	0.00	0.41	42.46	16.36	0.22	99.74	81.86
Line 27 PL-8OL1	520	40.30	0.00	0.45	42.89	16.72	0.23	100.58	81.66
Line 28 PL-8OL1	540	39.07	0.01	0.44	38.60	16.17	0.17	94.46	80.54
Line 29 PL-8OL1	560	60.23	1.63	0.06	0.48	2.89	0.00	65.29	
Line 1 PL-8OL2	0	38.67	0.01	0.80	34.42	27.02	0.10	101.01	68.79
Line 2 PL-8OL2	15	39.52	0.02	0.57	40.85	19.58	0.16	100.69	78.32
Line 3 PL-8OL2	30	40.16	0.00	0.40	41.48	16.82	0.16	99.02	81.10
Line 4 PL-8OL2	45	40.10	0.01	0.39	42.61	17.26	0.24	100.63	81.13
Line 5 PL-8OL2	60	40.21	0.00	0.40	42.72	16.65	0.12	100.10	81.70
Line 6 PL-8OL2	75	40.31	0.01	0.42	42.61	16.54	0.18	100.07	81.75
Line 7 PL-8OL2	90	40.13	0.00	0.32	42.45	16.50	0.23	99.63	81.81
Line 8 PL-8OL2	105	40.49	0.00	0.35	43.24	16.76	0.20	101.04	81.84
Line 9 PL-8OL2	120	40.49	0.00	0.34	42.57	16.21	0.19	99.80	82.09
Line 10 PL-8OL2	135	40.24	0.00	0.40	42.76	16.41	0.17	99.98	81.92
Line 11 PL-8OL2	150	40.19	0.02	0.37	42.81	16.82	0.20	100.41	81.61
Line 12 PL-8OL2	165	39.06	0.00	0.50	42.69	15.96	0.23	98.44	82.21
Line 13 PL-8OL2	180	40.65	0.02	0.43	42.59	16.67	0.22	100.57	81.61
Line 14 PL-8OL2	195	40.12	0.00	0.46	42.64	16.79	0.19	100.22	81.49
Line 15 PL-8OL2	210	39.95	0.00	0.48	41.96	16.93	0.16	99.47	81.12
Line 16 PL-8OL2	225	40.09	0.00	0.54	40.55	18.54	0.18	99.90	79.11
Line 17 PL-8OL2	240	51.41	0.73	0.01	0.25	2.08	0.00	54.48	
Line 1 PL-8OL3	0	39.72	0.01	0.64	37.83	23.25	0.14	101.58	73.83
Line 2 PL-8OL3	20	40.20	0.02	0.41	42.67	16.59	0.22	100.10	81.73
Line 3 PL-8OL3	40	40.45	0.01	0.42	42.13	14.95	0.20	98.18	83.00
Line 4 PL-8OL3	60	40.58	0.00	0.41	42.59	16.89	0.20	100.66	81.44
Line 5 PL-8OL3	80	40.10	0.00	0.41	42.55	16.34	0.13	99.52	81.91

Sample	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 6 PL-8OL3	100	39.24	0.00	0.37	41.93	15.89	0.19	97.62	82.12
Line 7 PL-8OL3	120	40.30	0.00	0.41	42.87	16.96	0.20	100.73	81.48
Line 8 PL-8OL3	140	39.93	0.00	0.40	41.88	15.45	0.23	97.90	82.48
Line 9 PL-8OL3	160	40.55	0.00	0.38	42.22	16.72	0.18	100.04	81.48
Line 10 PL-8OL3	180	39.80	0.00	0.40	41.88	16.41	0.19	98.67	81.62
Line 11 PL-8OL3	200	39.91	0.02	0.40	42.38	16.22	0.24	99.17	81.97
Line 12 PL-8OL3	220	40.48	0.00	0.44	42.64	16.97	0.15	100.68	81.36
Line 13 PL-8OL3	240	39.83	0.00	0.46	42.58	16.66	0.22	99.73	81.59
Line 14 PL-8OL3	260	39.80	0.00	0.44	42.14	16.46	0.18	99.03	81.63
Line 15 PL-8OL3	280	39.92	0.02	0.44	42.03	16.93	0.19	99.53	81.18
Line 16 PL-8OL3	300	40.19	0.00	0.39	42.59	16.92	0.16	100.26	81.42
Line 17 PL-8OL3	320	39.85	0.00	0.42	42.64	16.68	0.22	99.81	81.63
Line 18 PL-8OL3	340	40.09	0.00	0.42	41.97	16.72	0.23	99.43	81.35
Line 19 PL-8OL3	360	40.23	0.00	0.39	42.12	16.43	0.15	99.32	81.69
Line 20 PL-8OL3	380	40.08	0.01	0.45	42.57	17.62	0.18	100.90	80.76
Line 21 PL-8OL3	400	40.03	0.02	0.36	42.35	17.27	0.14	100.16	81.06
Line 22 PL-8OL3	420	39.54	0.00	0.42	42.16	15.82	0.17	98.11	82.23
Line 23 PL-8OL3	440	40.11	0.00	0.44	42.44	16.95	0.17	100.11	81.30
Line 24 PL-8OL3	460	40.29	0.00	0.43	42.87	16.94	0.19	100.72	81.48
Line 25 PL-8OL3	480	39.46	0.00	0.40	42.48	16.66	0.12	99.13	81.61
Line 26 PL-8OL3	500	40.34	0.01	0.40	42.53	16.33	0.19	99.79	81.92
Line 27 PL-8OL3	520	40.16	0.00	0.46	42.29	16.46	0.25	99.62	81.66
Line 28 PL-8OL3	540	40.19	0.00	0.42	42.50	16.54	0.14	99.79	81.70
Line 29 PL-8OL3	560	39.11	0.00	0.38	42.57	17.28	0.24	99.57	81.11

Sample	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 32 PL-8OL3	620	40.49	0.00	0.43	42.96	16.75	0.19	100.80	81.68
Line 33 PL-8OL3	640	40.02	0.01	0.44	42.80	16.48	0.13	99.87	81.85
Line 1 PL-27-OL4	0	38.12	0.02	27.30	35.54	0.00	0.52	101.50	69.48
Line 2 PL-27-OL4	15	37.98	0.00	26.79	36.15	0.07	0.44	101.42	70.29
Line 3 PL-27-OL4	30	37.72	0.00	25.23	36.82	0.10	0.47	100.33	71.86
Line 4 PL-27-OL4	45	38.36	0.00	25.28	37.32	0.11	0.39	101.45	72.16
Line 5 PL-27-OL4	60	38.72	0.00	25.11	37.50	0.10	0.47	101.90	72.32
Line 6 PL-27-OL4	75	38.75	0.01	24.92	37.14	0.17	0.44	101.44	72.30
Line 7 PL-27-OL4	90	38.63	0.02	24.62	37.04	0.02	0.41	100.73	72.50
Line 8 PL-27-OL4	105	38.64	0.00	24.65	36.15	0.07	0.37	99.88	72.03
Line 9 PL-27-OL4	120	39.39	0.00	25.44	37.43	0.11	0.45	102.81	72.04
Line 10 PL-27-OL4	135	38.51	0.05	25.25	37.02	0.11	0.38	101.31	72.02
Line 11 PL-27-OL4	150	38.70	0.01	25.17	37.13	0.13	0.44	101.58	72.10
Line 12 PL-27-OL4	165	38.96	0.00	25.56	36.82	0.12	0.35	101.81	71.69
Line 13 PL-27-OL4	180	38.62	0.03	25.69	36.37	0.07	0.41	101.18	71.29
Line 14 PL-27-OL4	195	38.79	0.00	25.29	36.82	0.03	0.45	101.38	71.82
Line 15 PL-27-OL4	210	38.79	0.02	24.51	36.70	0.11	0.43	100.57	72.39
Line 16 PL-27-OL4	225	38.59	0.00	25.21	37.04	0.07	0.47	101.38	71.99
Line 17 PL-27-OL4	240	38.84	0.00	25.37	36.73	0.08	0.45	101.46	71.72
Line 18 PL-27-OL4	255	38.51	0.01	25.27	37.14	0.05	0.44	101.41	72.02
Line 19 PL-27-OL4	270	38.93	0.00	25.02	37.17	0.12	0.30	101.55	72.34
Line 20 PL-27-OL4	285	38.19	0.01	23.80	37.39	0.05	0.37	99.80	73.38
Line 21 PL-27-OL4	300	38.39	0.00	23.59	38.06	0.09	0.38	100.51	73.88
Line 22 PL-27-OL4	315	38.73	0.04	25.54	35.81	0.11	0.38	100.60	71.11

Sample	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 23 PL-27-OL4	330	44.26	0.15	2.13	0.53	0.00	0.05	47.13	
Line 1 PL-27-OL8	0	38.89	0.03	26.65	35.73	0.10	0.37	101.77	70.21
Line 2 PL-27-OL8	20	37.51	0.00	25.33	32.79	0.04	0.45	96.12	69.39
Line 3 PL-27-OL8	40	38.36	0.05	28.35	34.80	0.05	0.48	102.08	68.26
Line 4 PL-27-OL8	60	37.96	0.03	28.81	34.33	0.00	0.51	101.64	67.60
Line 5 PL-27-OL8	80	37.99	0.00	28.98	34.17	0.07	0.42	101.63	67.44
Line 6 PL-27-OL8	100	37.67	0.02	28.97	34.12	0.06	0.46	101.30	67.39
Line 7 PL-27-OL8	120	37.78	0.00	28.30	34.19	0.00	0.49	100.76	67.91
Line 8 PL-27-OL8	140	37.83	0.02	27.62	34.11	0.02	0.44	100.04	68.42
Line 9 PL-27-OL8	160	38.26	0.00	28.53	33.74	0.05	0.42	100.99	67.51
Line 10 PL-27-OL8	180	37.92	0.00	28.71	33.56	0.14	0.42	100.76	67.25
Line 11 PL-27-OL8	200	38.14	0.02	29.16	33.80	0.05	0.49	101.66	67.01
Line 12 PL-27-OL8	220	38.19	0.02	29.37	34.08	0.07	0.48	102.21	67.04
Line 13 PL-27-OL8	240	38.13	0.00	29.39	34.02	0.04	0.46	102.05	67.00
Line 14 PL-27-OL8	260	37.39	0.00	28.74	33.88	0.04	0.38	100.44	67.46
Line 15 PL-27-OL8	280	37.96	0.00	29.19	33.85	0.04	0.43	101.46	67.07
Line 16 PL-27-OL8	300	37.90	0.01	28.09	33.84	0.03	0.50	100.38	67.84
Line 17 PL-27-OL8	320	37.98	0.02	28.51	33.76	0.03	0.51	100.79	67.46
Line 18 PL-27-OL8	340	38.38	0.03	28.55	33.95	0.08	0.45	101.44	67.60
Line 19 PL-27-OL8	360	37.86	0.00	29.31	33.92	0.09	0.39	101.58	67.05
Line 20 PL-27-OL8	380	37.78	0.01	28.76	33.79	0.04	0.44	100.82	67.34
Line 21 PL-27-OL8	400	38.41	0.00	29.19	33.49	0.02	0.39	101.50	66.86
Line 22 PL-27-OL8	420	37.85	0.02	26.28	32.70	0.10	0.43	97.37	68.57
Line 23 PL-27-OL8	440	38.22	0.00	28.87	33.89	0.03	0.48	101.49	67.29

Sample	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 24 PL-27-OL8	460	37.52	0.01	28.99	33.82	0.06	0.51	100.91	67.14
Line 25 PL-27-OL8	480	38.03	0.01	29.39	33.92	0.09	0.45	101.90	66.95
Line 26 PL-27-OL8	500	38.05	0.04	28.40	34.31	0.10	0.46	101.36	67.93
Line 27 PL-27-OL8	520	38.44	0.03	27.55	34.32	0.06	0.41	100.81	68.63
Line 28 PL-27-OL8	540	37.69	0.03	25.33	35.71	0.01	0.36	99.13	71.24
Line 29 PL-27-OL8	560	37.77	0.00	24.95	36.00	0.10	0.41	99.22	71.67
Line 1 PL-27-OL9	0		0.36	22.51	28.08	0.02	0.47	97.26	
Line 2 PL-27-OL9	15	38.43	0.01	25.13	36.15	0.10	0.38	100.21	71.63
Line 3 PL-27-OL9	30	38.93	0.00	22.77	38.53	0.10	0.35	100.68	74.81
Line 4 PL-27-OL9	45	38.69	0.00	21.22	38.72	0.12	0.37	99.11	76.17
Line 5 PL-27-OL9	60	38.24	0.00	22.66	38.63	0.11	0.36	100.00	74.94
Line 6 PL-27-OL9	75	39.02	0.01	23.42	37.82	0.07	0.35	100.69	73.93
Line 7 PL-27-OL9	90	38.74	0.00	24.58	37.22	0.10	0.45	101.08	72.60
Line 8 PL-27-OL9	105	38.40	0.06	24.88	36.56	0.11	0.35	100.36	72.08
Line 9 PL-27-OL9	120	38.09	0.00	25.58	36.62	0.06	0.41	100.76	71.51
Line 10 PL-27-OL9	135	38.54	0.01	26.29	35.98	0.06	0.39	101.28	70.63
Line 11 PL-27-OL9	150	38.46	0.04	26.24	35.95	0.09	0.36	101.15	70.66
Line 12 PL-27-OL9	165	38.23	0.00	26.12	35.86	0.06	0.41	100.68	70.66
Line 13 PL-27-OL9	180	38.12	0.00	26.37	35.82	0.07	0.45	100.83	70.42
Line 14 PL-27-OL9	195	38.03	0.00	25.89	35.88	0.04	0.39	100.23	70.87
Line 15 PL-27-OL9	210	38.33	0.05	25.73	35.81	0.08	0.40	100.41	70.95
Line 16 PL-27-OL9	225	38.50	0.05	25.83	35.69	0.05	0.39	100.50	70.81
Line 17 PL-27-OL9	240	36.40	0.00	25.79	35.82	0.13	0.41	98.55	70.90
Line 18 PL-27-OL9	255	38.41	0.02	27.16	35.63	0.05	0.40	101.66	69.74

Sample	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 19 PL-27-OL9	270	38.43	0.01	26.39	35.65	0.14	0.43	101.05	70.32
Line 20 PL-27-OL9	285	38.28	0.00	26.49	34.95	0.10	0.44	100.24	69.82
Line 21 PL-27-OL9	300	38.40	0.00	26.60	35.77	0.02	0.45	101.24	70.21
Line 22 PL-27-OL9	315	38.19	0.03	26.46	35.48	0.08	0.40	100.64	70.18
Line 23 PL-27-OL9	330	38.60	0.00	26.08	35.39	0.10	0.42	100.58	70.42
Line 24 PL-27-OL9	345	37.86	0.00	27.12	35.89	0.04	0.43	101.35	69.90
Line 25 PL-27-OL9	360	38.76	0.01	25.82	35.64	0.08	0.42	100.72	70.77
Line 26 PL-27-OL9	375	31.89	0.05	22.38	32.77	0.05	0.36	87.50	71.97
Line 27 PL-27-OL9	390	38.22	0.00	25.56	36.07	0.08	0.42	100.35	71.21
Line 28 PL-27-OL9	405	38.88	0.01	25.27	36.50	0.08	0.37	101.11	71.73
Line 29 PL-27-OL9	420	36.51	0.00	22.05	37.72	0.11	0.31	96.70	75.05
Line 30 PL-27-OL9	435	39.30	0.00	22.11	39.16	0.12	0.30	101.00	75.69
Line 31 PL-27-OL9	450	38.98	0.01	25.67	34.87	0.07	0.44	100.04	70.41

A2.5 Results of Clinopyroxene Phenocryst Analysis in Planchon Samples (Wt. %)

Sample	SiO ₂	CaO	Na ₂ O	Al ₂ O ₃	FeO	MgO	Total	WO	EN	FS	Apparent Kd
PL-8-CPX-1 1	53.43	17.21	0.28	2.10	9.83	15.55	99.08	37.01	46.50	16.49	0.48
PL-8-CPX-1 2	53.68	18.36	0.29	2.14	10.49	15.83	101.60	37.81	45.34	16.86	0.51
PL-8-CPX-1 3	53.27	17.46	0.32	1.80	11.12	15.63	99.88	36.46	45.42	18.12	0.54
PL-8-CPX-2 1	53.81	19.50	0.40	1.31	10.66	14.47	100.47	40.66	41.98	17.36	0.56
PL-8-CPX-2 2	53.78	19.45	0.36	1.36	10.86	14.34	100.46	40.63	41.67	17.70	0.58
PL-8-CPX-2 3	53.44	19.65	0.31	1.37	10.44	14.03	99.49	41.52	41.25	17.23	0.57
PL-8-CPX-2 4	53.91	19.65	0.30	1.06	11.19	14.13	100.77	40.90	40.92	18.18	0.61
PL-8-CPX-2 5	53.34	19.21	0.34	1.16	11.37	14.01	99.72	40.37	40.98	18.65	0.62
PL-8-CPX-2 6	53.84	18.85	0.33	1.59	10.97	14.75	100.81	39.32	42.81	17.87	0.57
PL-8-CPX-3 1	53.58	19.69	0.36	1.14	11.03	14.29	100.63	40.86	41.28	17.86	0.59
PL-8-CPX-3 2	53.56	19.71	0.31	1.42	10.55	14.53	100.43	40.93	41.97	17.10	0.56
PL-8-CPX-4 1	53.72	19.13	0.30	1.26	11.08	14.24	100.12	40.20	41.63	18.18	0.60
PL-8-CPX-5 1	53.36	18.49	0.35	1.35	11.35	14.67	100.03	38.73	42.73	18.54	0.59
PL-8-CPX-5 2	53.87	19.37	0.31	1.26	11.31	14.57	101.04	39.96	41.83	18.21	0.59
PL-8-CPX-6 1	53.41	18.97	0.32	1.62	9.14	15.51	99.47	39.79	45.24	14.97	0.45
PL-8-CPX-6 2	53.58	19.39	0.33	1.61	9.26	15.77	100.43	39.93	45.18	14.89	0.45
PL-8-CPX-6 3	53.56	18.92	0.27	1.85	9.94	15.28	100.21	39.46	44.35	16.19	0.50
PL-27-CPX-1 1	53.52	19.23	0.65	1.88	8.72	15.54	100.14	40.35	45.37	14.28	0.43
PL-27-CPX-1 2	52.90	19.24	0.33	2.40	8.94	15.61	100.17	40.15	45.29	14.56	0.44
PL-27-CPX-1 3	52.97	19.54	0.49	1.96	8.82	15.78	100.18	40.39	45.37	14.23	0.43
PL-27-CPX-2 1	53.28	19.26	0.35	2.61	8.95	15.28	100.57	40.55	44.75	14.70	0.45
PL-27-CPX-2 2	53.20	19.53	0.40	2.41	8.99	15.11	100.31	41.05	44.20	14.75	0.46
PL-27-CPX-3 1	52.53	19.59	0.33	2.45	7.11	15.47	98.13	41.97	46.13	11.90	0.35
PL-27-CPX-3 2	53.27	19.45	0.38	2.16	9.51	15.33	100.77	40.36	44.24	15.40	0.47
PL-27-CPX-3 3	52.91	18.59	0.31	2.16	9.09	15.55	99.33	39.28	45.72	14.99	0.45
PL-27-CPX-3 4	53.24	18.95	0.35	2.09	9.17	15.56	99.93	39.68	45.33	14.99	0.45
PL-27-CPX-3 5	52.25	17.21	0.32	1.83	10.26	16.26	98.83	35.98	47.28	16.75	0.48
PL-27-CPX-4 1	53.54	18.99	0.34	2.04	9.65	15.01	100.26	40.05	44.05	15.90	0.49
PL-27-CPX-4 2	53.16	18.89	0.39	2.10	9.34	15.05	99.52	40.09	44.43	15.48	0.48
PL-27-CPX-4 3	53.25	19.38	0.40	2.40	9.15	15.14	100.76	40.72	44.26	15.01	0.46

Sample	SiO2	CaO	Na2O	Al2O3	FeO	MgO	Total	WO	EN	FS	Apparent Kd
PL-27-CPX-5_1	53.01	18.79	0.37	1.96	8.93	15.62	99.43	39.57	45.76	14.67	0.44
PL-27-CPX-6_1	53.59	18.77	0.36	2.09	8.72	15.66	100.04	39.63	46.00	14.37	0.43
PL-27-CPX-7_1	52.61	19.90	0.67	2.40	7.16	15.88	99.46	41.82	46.43	11.75	0.35
PL-27-CPX-8_1	52.54	19.57	0.38	1.83	8.77	15.17	98.77	41.17	44.42	14.40	0.44
PL-27-CPX-9_1	52.34	18.62	0.31	2.25	9.64	14.93	98.67	39.69	44.28	16.03	0.49
PL-27-CPX-9_2	52.74	19.31	0.36	2.31	9.01	14.87	99.00	41.06	43.98	14.96	0.46
PL-27-CPX-9_3	52.80	19.50	0.34	2.10	8.58	15.16	99.08	41.24	44.60	14.16	0.43
PL-27-CPX-10_1	52.74	19.56	0.31	2.37	8.14	15.47	99.53	41.23	45.37	13.40	0.40
PL-27-CPX-10_2	52.97	19.72	0.35	2.24	8.34	15.50	100.01	41.26	45.12	13.62	0.41
PL-27-CPX-10_3	51.47	18.84	0.50	2.57	7.86	15.40	97.33	40.60	46.18	13.22	0.39
PL-27-CPX-10_4	52.19	18.27	0.34	2.30	9.74	15.52	99.05	38.50	45.49	16.02	0.48
PL-27-CPX-10_5	52.77	18.21	0.33	1.91	9.11	15.76	98.75	38.54	46.41	15.05	0.44
PL-27-CPX-10_6	51.97	18.77	0.35	2.46	9.32	14.86	98.24	40.18	44.24	15.58	0.48
PL-27-CPX-11_1	50.89	18.49	0.40	2.09	10.16	14.57	97.30	39.59	43.42	16.99	0.53
PL-27-CPX-11_2	52.32	18.98	0.40	2.07	8.68	14.69	97.82	41.08	44.25	14.67	0.45
PL-27-CPX-12_1	52.00	19.28	0.39	3.12	8.98	14.97	99.88	40.93	44.20	14.87	0.46
PL-27-CPX-12_2	51.68	19.59	0.36	3.04	8.38	14.71	98.70	42.04	43.93	14.03	0.44
PL-27-CPX-12_3	51.67	19.37	0.34	2.94	8.79	14.81	98.72	41.36	43.99	14.65	0.45
PL-27-CPX-12_4	51.93	19.41	0.33	2.30	8.34	15.46	98.55	40.93	45.35	13.72	0.41
PL-27-CPX-12_5	53.00	19.30	0.32	2.19	8.78	15.16	99.31	40.86	44.64	14.50	0.44
PL-27-CPX-12_6	51.65	19.07	0.35	2.25	9.61	15.21	98.91	39.95	44.33	15.72	0.48
PL-27-CPX-12_7	52.56	18.60	0.35	2.09	10.24	14.97	99.35	39.23	43.92	16.85	0.52
PL-27-CPX-13_1	49.17	18.33	0.34	2.88	8.61	14.57	94.65	40.44	44.72	14.83	0.45
PL-27-CPX-14_1	53.60	17.86	0.34	1.85	10.06	16.22	100.48	37.00	46.74	16.26	0.47
PL-27-CPX-15_1	52.37	18.94	0.40	2.33	7.61	15.33	97.80	40.99	46.15	12.86	0.38
PL-27-CPX-16_1	53.15	18.96	0.42	2.37	9.06	15.69	100.36	39.61	45.61	14.78	0.44
PL-27-CPX-16_2	53.26	19.28	0.37	2.07	9.06	16.14	100.63	39.50	46.01	14.49	0.43
PL-27-CPX-17_1	54.10	17.51	0.37	2.08	9.37	16.52	100.81	36.62	48.08	15.30	0.43
PL-27-CPX-18_1	52.39	19.19	0.37	2.34	8.03	15.46	98.90	40.86	45.81	13.34	0.40
PL-27-CPX-18_2	52.97	19.77	0.42	2.36	8.40	15.51	100.27	41.27	45.04	13.69	0.41
PL-16-CPX1-1	52.71	18.99	0.30	2.12	9.13	16.93	100.73	38.23	47.41	14.35	0.54
PL-16-CPX1-2	52.87	18.87	0.27	2.18	9.13	16.82	100.73	38.20	47.37	14.42	0.54

Sample	SiO2	CaO	Na2O	Al2O3	FeO	MgO	Total	WO	EN	FS	Apparent Kd
PL-16-CPX1-3	52.15	20.26	0.28	3.01	8.76	15.99	101.45	41.06	45.09	13.85	0.55
PL-16-CPX1-4	53.04	17.50	0.26	1.78	9.87	17.77	100.75	35.05	49.52	15.43	0.56
PL-25-CPX-1-1	50.19	21.39	0.38	2.96	7.94	15.81	99.60	43.14	44.37	12.50	0.46
PL-25-CPX-1-2	51.10	21.31	0.39	2.74	7.70	15.76	99.95	43.27	44.53	12.20	0.44
PL-25-CPX-1-3	50.58	21.27	0.37	2.97	5.64	15.21	97.26	45.43	45.17	9.40	0.34
PL-25-CPX-1-4	50.92	21.35	0.39	2.86	7.82	15.49	99.91	43.57	43.98	12.45	0.46
PL-25-CPX-2-1	51.31	21.61	0.40	2.74	7.85	15.75	100.65	43.53	44.14	12.34	0.45
PL-25-CPX-2-2	51.80	20.28	0.37	2.61	7.99	16.29	100.42	41.24	46.08	12.68	0.44
PL-25-CPX-2-3	51.32	21.56	0.40	2.76	7.63	15.50	100.24	43.93	43.93	12.14	0.45
PL-25-CPX-3-1	50.06	18.62	0.45	2.88	10.55	15.33	99.28	38.64	44.26	17.09	0.62
PL-25-CPX-3-2	51.09	19.15	0.39	3.12	8.02	16.21	99.58	39.93	47.02	13.05	0.45
PL-25-CPX-4-1	50.42	19.96	0.44	3.37	8.39	16.05	100.18	40.87	45.72	13.40	0.47
PL-25-CPX-4-2	52.40	18.02	0.32	1.70	8.34	18.04	99.78	36.31	50.57	13.12	0.42
PL-25-CPX-5-1	51.98	19.01	0.35	1.88	7.72	17.24	99.35	38.78	48.92	12.30	0.41
PL-25-CPX-5-2	50.02	19.19	0.37	3.93	7.88	15.76	98.69	40.60	46.39	13.01	0.45
PL-25-CPX-6-1	50.95	17.27	0.38	1.39	12.72	15.37	99.35	35.56	44.01	20.43	0.75
PL-25-CPX-6-2	52.18	17.02	0.30	1.52	8.57	18.60	99.29	34.32	52.20	13.48	0.42
PL-25-CPX-6-3	50.74	19.94	0.37	3.07	7.60	16.22	99.40	41.16	46.58	12.25	0.43
PL-25-CPX-7-1	51.90	20.26	0.46	2.04	6.08	17.48	99.03	41.07	49.31	9.62	0.32
PL-25-CPX-7-2	49.99	20.11	0.41	3.19	8.01	15.75	99.05	41.66	45.39	12.95	0.46
PL-25-CPX-7-3	51.92	17.94	0.34	1.60	8.73	17.37	98.83	36.67	49.40	13.93	0.46
PL-25-CPX-8-1	50.76	19.54	0.31	3.30	8.68	16.14	100.12	40.08	46.03	13.90	0.49
PL-25-CPX-8-2	51.20	19.65	0.35	2.09	8.35	16.88	99.56	39.58	47.30	13.12	0.45
PL-25-CPX-8-3	51.28	19.76	0.34	2.33	8.13	16.55	99.66	40.21	46.87	12.92	0.45
PL-25-CPX-8-4	51.16	19.80	0.33	2.16	7.95	16.37	98.94	40.59	46.69	12.72	0.44
PL-25-CPX-8-5	51.81	20.22	0.36	2.64	8.22	16.04	100.58	41.30	45.59	13.11	0.46
PL-25-CPX-9-1	51.60	19.85	0.43	1.71	7.30	16.91	98.87	40.45	47.95	11.60	0.39
PL-25-CPX-9-2	52.35	19.46	0.31	1.64	7.76	17.53	100.10	38.99	48.87	12.15	0.40
PL-25-CPX-9-3	51.03	20.84	0.40	2.68	7.18	16.34	99.81	42.37	46.23	11.40	0.40
PL-28-CPX1-1	52.78	20.36	0.32	2.36	8.54	16.26	101.53	41.02	45.56	13.43	0.35
PL-28-CPX1-2	52.52	20.06	0.35	2.36	8.29	16.68	101.32	40.34	46.65	13.01	0.33
PL-28-CPX1-3	52.88	20.34	0.45	1.89	7.11	15.25	98.63	43.18	45.04	11.78	0.31

Sample	SiO2	CaO	Na2O	Al2O3	FeO	MgO	Total	WO	EN	FS	Apparent Kd
PL-28-CPX1-4	53.28	20.48	0.44	1.81	6.94	17.29	100.92	41.01	48.15	10.84	0.27
PL-28-CPX1-5	52.41	20.44	0.34	2.84	8.52	15.78	101.26	41.68	44.76	13.56	0.36
PL-28-CPX1-6	51.21	16.94	0.39	3.04	12.65	15.66	100.88	34.86	44.82	20.32	0.54
PL-28-CPX2-2	53.32	18.81	0.32	1.76	9.98	15.50	100.53	39.06	44.78	16.17	0.43
PL-28-CPX2-3	51.67	19.84	0.36	2.90	8.93	16.10	101.07	40.32	45.52	14.16	0.37
PL-28-CPX3-1	52.31	19.12	0.29	2.72	9.67	16.37	101.77	38.67	46.06	15.27	0.40
PL-28-CPX3-2	52.02	19.95	0.30	2.47	9.30	16.34	101.53	39.94	45.52	14.54	0.38
PL-28-CPX3-3	52.64	19.05	0.34	2.19	9.35	16.41	101.01	38.74	46.43	14.83	0.38
PL-28-CPX3-4	51.22	19.66	0.30	3.13	9.27	15.43	100.30	40.66	44.38	14.96	0.40
PL-28-CPX3-5	51.42	19.72	0.35	3.03	9.23	15.92	100.85	40.19	45.13	14.68	0.39
PL-28-CPX3-6	52.65	18.28	0.30	2.14	11.23	15.34	100.72	37.78	44.11	18.11	0.49
PL-28-CPX4-2	52.94	17.61	0.28	2.01	11.50	16.69	101.80	35.35	46.62	18.03	0.46
PL-28-CPX4-3	52.51	19.73	0.31	2.65	9.49	16.04	101.93	39.89	45.13	14.98	0.40
PL-28-CPX5-1	52.77	18.62	0.32	2.33	10.32	16.56	101.89	37.46	46.33	16.21	0.42
PL-28-CPX5-2	52.39	19.24	0.32	2.43	9.73	16.30	101.31	38.85	45.81	15.34	0.40
PL-28-CPX5-3	52.12	18.84	0.33	2.57	9.54	16.40	100.91	38.37	46.46	15.17	0.39
PL-28-CPX5-4	52.59	17.38	1.37	5.13	10.54	13.67	101.45	38.95	42.61	18.44	0.52
PL-28-CPX6-2	52.76	18.20	0.30	1.95	10.08	16.73	100.93	36.89	47.17	15.94	0.41

A2.6 Results of Core to Rim Transect Analysis of Plagioclase Phenocrysts in Peteroa Samples in Wt. %

Sample/Phase	SiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	Total	An
PT-15A-1	55.43	27.61	0.76	0.08	11.85	4.64	0.58	0.05	100.99	56.64
PT-15A-2	56.57	26.54	0.75	0.11	10.78	5.00	0.68	0.00	100.42	52.26
PT-15A-3	56.81	26.66	0.74	0.11	10.80	4.95	0.68	0.05	100.81	52.53
PT-15A-4	56.42	26.69	0.65	0.09	11.29	4.87	0.65	0.15	100.81	54.04
PT-15A-5	54.47	28.20	0.79	0.11	12.94	4.07	0.45	0.07	101.09	62.09
PT-15A-6	56.37	26.87	0.72	0.11	11.03	4.74	0.65	0.12	100.61	54.09
PT-15A-7	55.90	26.61	0.74	0.13	11.88	4.65	0.56	0.05	100.51	56.70
PT-15A-8	55.97	27.38	0.67	0.06	12.02	4.62	0.56	0.16	101.44	57.10
PT-15A-9	55.51	27.02	0.85	0.28	12.13	4.46	0.52	0.07	100.84	58.23
PT-15A-10	55.35	27.60	0.78	0.18	12.29	4.31	0.50	0.00	101.01	59.41
PT-15A-11	54.84	27.26	0.73	0.14	12.52	4.31	0.53	0.00	100.33	59.74
PT-15A-12	55.12	26.90	0.67	0.12	11.64	4.64	0.56	0.11	99.75	56.24
PT-15A-13	55.38	27.59	0.73	0.11	12.51	4.32	0.51	0.07	101.22	59.79
PT-15A-14	55.61	27.28	0.71	0.10	11.90	4.54	0.60	0.10	100.85	57.12
PT-15A-15	54.99	27.88	0.79	0.13	12.21	4.35	0.55	0.00	100.90	58.88
PT-15A-16	55.34	27.21	0.82	0.15	12.13	4.50	0.54	0.15	100.84	57.98
PT-15A-17	56.96	26.60	0.79	0.27	11.16	4.88	0.73	0.14	101.51	53.50
PT-15A-18	56.20	26.27	0.99	0.15	11.13	4.65	0.69	0.22	100.31	54.67
PT-15A-19	54.56	26.55	1.00	0.17	11.76	4.46	0.61	0.12	99.22	57.22
PT-15A-20	55.96	26.52	0.85	0.04	11.46	4.74	0.65	0.03	100.24	55.08
PT-15A-21	55.95	27.06	1.09	0.18	11.54	4.87	0.62	0.09	101.40	54.71
PT-15A-1A-1	57.15	26.99	0.80	0.12	11.44	4.99	0.41	0.03	101.93	54.58
PT-15A-1A-2	56.91	26.81	0.75	0.12	11.11	5.11	0.39	0.03	101.22	53.38
PT-15A-1A-3	56.77	26.68	0.78	0.09	11.42	5.04	0.37	0.11	101.24	54.46
PT-15A-1A-4	56.49	27.08	0.77	0.08	11.60	5.05	0.39	0.03	101.49	54.69
PT-15A-1A-5	54.92	27.91	0.77	0.11	12.74	4.26	0.29	0.10	101.08	61.27
PT-15A-1A-6	55.31	27.89	0.75	0.08	12.20	4.58	0.32	0.02	101.15	58.47
PT-15A-1A-7	56.81	26.81	0.72	0.12	10.75	5.24	0.40	0.08	100.94	51.91
PT-15A-1A-8	54.74	27.72	0.79	0.16	12.48	4.51	0.29	0.03	100.73	59.47
PT-15A-1A-9	55.86	27.55	0.72	0.09	12.18	4.82	0.33	0.10	101.66	57.20
PT-15A-1A-10	55.40	27.41	0.81	0.13	12.45	4.55	0.33	0.07	101.16	59.06

Sample/Phase	SiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	Total	An
PT-15A-1A-12	56.12	27.15	0.69	0.08	11.88	4.79	0.35	0.05	101.10	56.68
PT-15A-1A-13	56.38	26.95	0.77	0.09	11.84	4.88	0.32	0.00	101.23	56.23
PT-15A-1A-14	55.88	27.55	0.78	0.15	11.87	4.77	0.35	0.00	101.35	56.74
PT-15A-1A-15	55.86	27.61	0.75	0.16	12.35	4.77	0.35	0.14	102.00	57.71
PT-15A-1A-16	55.65	27.39	0.76	0.15	12.01	4.66	0.32	0.03	100.97	57.66
PT-15A-1A-17	55.02	27.91	0.85	0.10	12.37	4.64	0.33	0.00	101.21	58.46
PT-15A-1A-18	56.72	26.62	0.72	0.14	10.86	5.35	0.41	0.00	100.82	51.63
PT-15A-1A-19	56.92	25.87	0.77	0.13	10.77	5.32	0.41	0.03	100.21	51.57
PT-15A-1A-20	56.79	27.25	0.85	0.10	11.37	4.98	0.41	0.19	101.94	54.48
PT-15A-1A-21	55.68	27.58	0.93	0.08	11.93	4.78	0.36	0.09	101.43	56.77
PT-15A-1A-22	59.06	22.55	2.87	0.59	9.07	5.03	1.26	0.40	100.82	46.11
PT-15A-3-1	55.67	27.98	0.68	0.13	12.74	4.41	0.34	0.06	101.99	60.34
PT-15A-3-2	55.85	27.54	0.64	0.07	12.30	4.24	0.29	0.00	100.93	60.53
PT-15A-3-3	55.63	27.50	0.67	0.10	12.19	4.37	0.31	0.10	100.86	59.53
PT-15A-3-4	57.53	26.17	0.70	0.12	10.77	5.21	0.47	0.11	101.09	51.87
PT-15A-3-5	57.84	26.50	0.69	0.08	10.63	5.16	0.42	0.07	101.39	51.93
PT-15A-3-6	57.80	26.40	0.67	0.11	10.91	5.06	0.41	0.00	101.36	53.08
PT-15A-3-7	57.50	26.00	0.65	0.13	11.06	4.97	0.41	0.05	100.76	53.83
PT-15A-3-8	56.98	26.50	0.69	0.12	11.36	4.77	0.40	0.08	100.90	55.48
PT-15A-3-9	57.11	27.01	0.72	0.09	11.60	4.72	0.39	0.13	101.77	56.30
PT-15A-3-10	56.85	26.64	0.68	0.11	11.55	4.82	0.42	0.03	101.08	55.62
PT-15A-3-11	48.18	21.41	0.47	0.07	8.77	4.56	0.38	0.13	83.97	50.20
PT-15A-3-12	58.00	26.08	0.71	0.11	10.56	4.95	0.42	0.12	100.96	52.78
PT-15A-3-13	58.08	26.14	0.70	0.10	10.88	5.22	0.44	0.06	101.62	52.19
PT-15A-3-14	58.28	25.97	0.73	0.08	10.96	5.12	0.43	0.08	101.63	52.88
PT-15A-3-15	56.72	26.37	0.63	0.13	11.04	5.08	0.41	0.00	100.36	53.30
PT-15A-3-16	57.86	26.90	0.67	0.09	11.27	4.97	0.38	0.15	102.28	54.40
PT-15A-3-17	56.66	25.85	0.71	0.11	11.27	4.92	0.39	0.07	99.97	54.63
PT-15A-3-18	57.12	26.47	0.72	0.13	10.94	4.91	0.42	0.05	100.75	53.85
PT-15A-3-19	56.14	26.16	1.05	0.21	11.97	4.04	0.49	0.12	100.17	60.24
PT-15A-3-20	53.63	27.86	0.75	0.06	14.86	3.34	0.22	0.00	100.71	70.24
PT-15A-3-21	56.76	26.88	0.81	0.05	10.79	4.83	0.41	0.13	100.66	53.89
PT-15A-3-22	53.20	29.46	0.81	0.07	14.03	3.57	0.20	0.13	101.47	67.66

Sample/Phase	SiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	TiO2	Total	An
PT-15A-3-24	52.84	29.42	0.78	0.08	14.72	3.31	0.21	0.02	101.37	70.22
PT-15A-3-25	50.98	30.37	0.72	0.05	15.74	2.81	0.18	0.00	100.84	74.84
PT-15A-3-27	51.28	29.86	0.97	0.12	15.78	2.78	0.20	0.03	101.01	74.96
PT-15A-3-28	50.92	29.77	0.76	0.08	14.50	2.95	0.19	0.04	99.21	72.27
PT-15A-3-29	49.75	30.49	0.74	0.03	15.95	2.68	0.14	0.10	99.88	76.10
PT-15A-3-30	54.35	28.63	0.78	0.09	13.76	3.96	0.24	0.11	101.91	64.88
PT-15A-3-31	55.00	26.90	0.72	0.13	12.14	4.32	0.31	0.08	99.61	59.74
PT-15A-3-32	56.37	26.56	0.88	0.08	11.37	4.73	0.38	0.12	100.47	55.81
PT-15A-3-33	58.22	25.51	1.16	0.08	10.27	4.81	0.67	0.08	100.81	51.92
PT-15A-2-1	56.45	27.84	0.72	0.11	11.32	4.52	0.38	0.01	101.34	56.72
PT-15A-2-2	55.36	27.42	0.74	0.10	11.32	4.47	0.32	0.00	99.72	57.23
PT-15A-2-4	51.37	30.31	0.71	0.05	14.47	2.81	0.29	0.17	100.18	72.71
PT-15A-2-5	53.49	27.94	0.81	0.10	11.77	3.95	0.54	0.08	98.68	60.18
PT-15A-2-6	54.19	28.61	0.77	0.05	12.21	4.05	0.45	0.05	100.38	60.83
PT-15A-2-7	53.60	27.93	0.74	0.06	12.70	3.77	0.42	0.01	99.22	63.41
PT-15A-2-8	53.84	27.66	1.38	0.21	12.36	4.03	0.53	0.17	100.18	60.92
PT-15A-2-9	51.77	30.32	0.74	0.07	13.55	2.79	0.32	0.07	99.63	71.36
PT-15A-2-10	53.16	29.35	0.86	0.04	13.37	3.30	0.37	0.07	100.52	67.58
PT-15A-2-11	50.99	30.18	0.83	0.12	14.39	2.95	0.35	0.04	99.85	71.43
PT-15A-2-13	50.37	31.34	0.75	0.00	15.68	2.50	0.21	0.00	100.85	76.68
PT-15A-2-15	51.33	30.37	0.83	0.10	14.82	2.80	0.24	0.00	100.49	73.48
PT-15A-2-16	57.31	27.74	0.86	0.11	11.43	4.57	0.58	0.08	102.67	56.04
PT-15A-2-17	58.71	26.53	0.97	0.10	9.91	5.36	0.79	0.00	102.36	48.25

A2.7 Results of Rim to Rim Transect Analysis of Olivine Phenocrysts in Peteroa Samples in wt. %

Sample/Phase	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 1 PT-3AOL1	0	37.52	0.00	0.88	34.10	27.11	0.05	99.66	68.46
Line 2 PT-3AOL1	20	37.31	0.00	0.82	34.98	26.93	0.04	100.07	69.20
Line 3 PT-3AOL1	40	38.04	0.00	0.79	35.27	26.01	0.02	100.13	70.10
Line 4 PT-3AOL1	60	38.12	0.01	0.75	34.62	26.25	0.01	99.76	69.55
Line 5 PT-3AOL1	80	38.21	0.00	0.80	35.23	25.75	0.01	100.01	70.28
Line 6 PT-3AOL1	100	38.14	0.02	0.80	35.37	26.10	0.02	100.45	70.09
Line 7 PT-3AOL1	120	38.11	0.00	0.79	35.09	25.84	0.06	99.89	70.13
Line 8 PT-3AOL1	140	38.11	0.00	0.77	35.49	26.36	0.01	100.74	69.98
Line 9 PT-3AOL1	160	38.06	0.01	0.78	35.21	25.74	0.05	99.84	70.29
Line 10 PT-3AOL1	180	38.42	0.00	0.78	35.41	25.82	0.04	100.46	70.35
Line 11 PT-3AOL1	200	38.47	0.00	0.73	35.35	26.33	0.03	100.90	69.95
Line 12 PT-3AOL1	220	38.36	0.02	0.72	35.10	26.31	0.04	100.54	69.82
Line 13 PT-3AOL1	240	38.32	0.03	0.77	35.29	25.79	0.04	100.24	70.31
Line 14 PT-3AOL1	260	37.84	0.01	0.77	35.59	26.13	0.01	100.34	70.21
Line 15 PT-3AOL1	280	38.37	0.01	0.75	35.43	26.11	0.04	100.70	70.15
Line 16 PT-3AOL1	300	38.20	0.00	0.79	35.47	26.84	0.01	101.31	69.59
Line 17 PT-3AOL1	320	38.27	0.00	0.75	35.33	26.31	0.09	100.76	69.94
Line 18 PT-3AOL1	340	38.25	0.00	0.79	35.28	26.59	0.03	100.93	69.66
Line 19 PT-3AOL1	360	37.36	0.00	0.83	35.41	26.08	0.06	99.74	70.10
Line 20 PT-3AOL1	380	38.46	0.00	0.75	35.22	26.48	0.04	100.95	69.75
Line 21 PT-3AOL1	400	37.36	0.01	0.80	34.79	26.44	0.05	99.44	69.47
Line 2 PT-3AOL2	20	38.80	0.01	0.62	38.30	21.42	0.04	99.18	75.59
Line 3 PT-3AOL2	40	38.75	0.00	0.57	38.28	21.38	0.00	98.99	75.65
Line 4 PT-3AOL2	60	39.40	0.01	0.59	38.27	22.74	0.02	101.02	74.51
Line 5 PT-3AOL2	80	39.08	0.00	0.62	38.11	22.72	0.06	100.58	74.42
Line 6 PT-3AOL2	100	39.44	0.00	0.71	37.60	23.65	0.00	101.40	73.33
Line 7 PT-3AOL2	120	38.90	0.01	0.69	37.22	23.80	0.02	100.63	73.04
Line 8 PT-3AOL2	140	38.56	0.02	0.71	37.01	24.70	0.03	101.03	72.19

Sample/Phase	Distance (Microns)	SiO2	TiO2	MnO	MgO	FeO	NiO	Total	Fo
Line 11 PT-3AOL2	200	38.95	0.01	0.69	36.86	23.12	0.00	99.64	73.39
Line 12 PT-3AOL2	220	38.32	0.01	0.58	37.25	22.95	0.01	99.13	73.83
Line 13 PT-3AOL2	240	39.21	0.01	0.67	38.50	21.69	0.04	100.11	75.41
Line 14 PT-3AOL2	260	39.45	0.00	0.58	39.15	21.36	0.02	100.55	76.08
Line 15 PT-3AOL2	280	39.37	0.00	0.58	39.54	21.21	0.07	100.76	76.38
Line 16 PT-3AOL2	300	38.99	0.00	0.59	39.54	20.55	0.00	99.68	76.92
Line 17 PT-3AOL2	320	38.89	0.00	0.57	36.70	20.08	0.08	96.32	76.00
Line 18 PT-3AOL2	340	39.55	0.01	0.56	39.59	20.42	0.05	100.18	77.07
Line 19 PT-3AOL2	360	38.91	0.01	0.68	38.70	22.27	0.04	100.60	75.03
Line 20 PT-3AOL2	380	37.56	0.04	0.78	32.05	30.12	0.08	100.64	64.89
Line 1 PT-3AOL3	0	38.23	0.01	0.74	34.06	27.70	0.01	100.75	68.10
Line 2 PT-3AOL3	20	38.27	0.00	0.80	34.83	26.95	0.05	100.89	69.10
Line 3 PT-3AOL3	40	38.69	0.02	0.73	34.71	26.25	0.00	100.39	69.63
Line 4 PT-3AOL3	60	37.92	0.00	0.73	34.84	26.68	0.02	100.19	69.36
Line 5 PT-3AOL3	80	38.43	0.01	0.74	35.01	26.07	0.02	100.28	69.94
Line 6 PT-3AOL3	100	38.33	0.00	0.77	35.04	25.96	0.04	100.13	70.03
Line 7 PT-3AOL3	120	37.29	0.04	0.73	34.97	26.73	0.05	99.80	69.41
Line 8 PT-3AOL3	140	38.19	0.02	0.80	35.30	27.01	0.01	101.32	69.34
Line 9 PT-3AOL3	160	37.94	0.00	0.77	35.15	26.43	0.00	100.28	69.72
Line 10 PT-3AOL3	180	37.95	0.01	0.81	35.15	26.55	0.07	100.53	69.60
Line 11 PT-3AOL3	200	38.09	0.01	0.84	34.78	26.72	0.02	100.46	69.21
Line 12 PT-3AOL3	220	36.99	0.02	0.81	35.19	26.88	0.00	99.88	69.37
Line 13 PT-3AOL3	240	38.02	0.01	0.77	35.35	26.28	0.04	100.47	69.96
Line 14 PT-3AOL3	260	38.04	0.02	0.70	35.44	26.89	0.03	101.12	69.60
Line 15 PT-3AOL3	280	37.62	0.01	0.80	34.94	26.61	0.08	100.05	69.43
Line 16 PT-3AOL3	300	37.89	0.00	0.86	34.89	26.45	0.00	100.09	69.47
Line 17 PT-3AOL3	320	37.69	0.00	0.79	33.98	26.70	0.08	99.24	68.78
Line 18 PT-3AOL3	340	37.50	0.01	0.77	34.35	27.84	0.03	100.49	68.15
Line 19 PT-3AOL3	360	37.66	0.02	0.84	32.97	29.04	0.00	100.53	66.29
Line 20 PT-3AOL3	380	35.99	0.00	1.06	25.86	38.13	0.00	101.03	54.04
Line 2 PT-3AOL4	20	36.99	0.01	0.78	31.28	31.43	0.08	100.56	63.37

Sample/Phase	Distance (Microns)	SiO ₂	TiO ₂	MnO	MgO	FeO	NiO	Total	Fo
Line 3 PT-3AOL4	40	37.15	0.00	0.84	32.26	29.65	0.00	99.90	65.34
Line 4 PT-3AOL4	60	37.19	0.00	0.86	32.27	29.26	0.04	99.61	65.63
Line 5 PT-3AOL4	80	37.30	0.01	0.82	31.39	29.32	0.01	98.87	64.98
Line 6 PT-3AOL4	100	37.61	0.00	0.78	32.77	28.19	0.00	99.35	66.84
Line 7 PT-3AOL4	120	37.61	0.01	0.73	34.04	26.40	0.01	98.80	69.10
Line 8 PT-3AOL4	140	37.66	0.02	0.76	34.87	27.27	0.06	100.64	68.91
Line 9 PT-3AOL4	160	38.19	0.00	0.77	34.08	23.82	0.05	96.92	71.18
Line 10 PT-3AOL4	180	38.19	0.01	0.72	34.81	26.01	0.08	99.82	69.88
Line 11 PT-3AOL4	200	38.22	0.01	0.74	34.31	26.74	0.05	100.06	68.99
Line 12 PT-3AOL4	220	37.96	0.00	0.76	34.97	27.31	0.08	101.07	68.94
Line 13 PT-3AOL4	240	37.78	0.01	0.65	34.78	26.69	0.04	99.96	69.38
Line 14 PT-3AOL4	260	38.11	0.01	0.74	34.81	26.36	0.05	100.09	69.59
Line 15 PT-3AOL4	280	38.11	0.00	0.76	34.70	26.98	0.08	100.63	69.03
Line 16 PT-3AOL4	300	38.27	0.00	0.78	34.42	25.17	0.05	98.69	70.27
Line 17 PT-3AOL4	320	38.12	0.00	0.72	34.70	26.24	0.02	99.79	69.64
Line 18 PT-3AOL4	340	38.12	0.00	0.78	34.90	26.75	0.02	100.57	69.32
Line 19 PT-3AOL4	360	37.69	0.01	0.77	34.41	26.02	0.11	99.00	69.59
Line 20 PT-3AOL4	380	38.28	0.00	0.80	34.75	26.71	0.03	100.57	69.24
Line 21 PT-3AOL4	400	37.78	0.00	0.74	33.85	27.02	0.06	99.46	68.48
Line 22 PT-3AOL4	420	34.88	0.04	0.95	26.45	33.13	0.09	95.54	58.03

A2.8 Results of Core & Rim Analysis of Plagioclase Phenocrysts in Peteroa Sample PT-3 in wt. %

Sample/Phase	SiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Total	An
PT-3A-1CORE	53.97	27.70	0.69	0.10	11.90	4.23	0.25	0.09	98.94	59.93
PT-3A-1RIM	52.30	28.43	0.77	0.13	13.16	3.50	0.23	0.09	98.60	66.61
PT-3A-2CORE	50.88	29.82	0.65	0.08	14.31	2.99	0.19	0.04	98.98	71.76
PT-3A-2RIM	55.66	26.57	0.81	0.12	10.42	4.99	0.44	0.07	99.07	52.18
PT-3A-3CORE	53.47	28.50	0.72	0.13	12.33	4.16	0.23	0.03	99.57	61.24
PT-3A-3RIM	51.40	29.92	0.86	0.11	13.93	3.06	0.17	0.04	99.51	70.79
PT-3A-4CORE	54.69	27.56	0.76	0.13	11.69	4.33	0.27	0.04	99.47	58.90
PT-3A-4RIM	54.29	27.57	0.77	0.12	11.70	4.40	0.30	0.04	99.18	58.44
PT-3A-5CORE	55.91	26.12	0.63	0.06	10.14	5.07	0.44	0.07	98.47	51.12
PT-3A-5RIM	56.70	25.96	0.86	0.13	9.68	5.53	0.49	0.10	99.45	47.77
PT-3A-6CORE	50.51	29.92	0.81	0.10	14.14	3.06	0.19	0.02	98.76	71.06
PT-3A-6RIM	55.45	25.90	0.87	0.13	10.01	5.12	0.46	0.06	98.00	50.49
PT-3A-7CORE	54.50	27.81	0.59	0.10	11.72	4.28	0.31	0.07	99.39	59.12
PT-3A-7RIM	52.66	29.19	0.80	0.14	13.16	3.51	0.25	0.05	99.79	66.47
PT-3A-7ACORE	54.34	27.49	0.63	0.12	11.45	4.46	0.30	0.07	98.84	57.62
PT-3A-7ARIM	54.50	27.37	0.68	0.10	11.71	4.43	0.30	0.05	99.17	58.29
PT-3A-8CORE	53.96	28.02	0.78	0.11	12.00	4.16	0.27	0.07	99.37	60.47
PT-3A-8RIM	54.43	27.36	0.80	0.13	11.47	4.38	0.29	0.13	98.99	58.11
PT-3A-9CORE	56.17	26.42	0.75	0.12	10.35	4.95	0.37	0.08	99.20	52.42
PT-3A-9RIM	53.93	27.66	0.75	0.09	11.85	4.29	0.29	0.08	98.95	59.36

Appendix 3

MAJOR ELEMENT ANALYSIS AND THERMOBAROMETRIC MODELING DATA

A3.1 Major Element Analysis on Planchon and Peteroa Samples using Quadrupole ICP-MS

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
PL-8	54.37	0.85	14.35	8.64	0.15	8.12	7.81	3.43	1.11	0.21
PL-16	51.95	0.85	15.31	8.97	0.15	9.41	7.71	3.37	1.07	0.21
PL-17	54.75	0.91	17.13	7.96	0.14	4.12	8.75	3.88	1.26	0.22
PL-18	54.67	0.92	17.16	7.96	0.14	4.39	8.58	3.79	1.28	0.23
PL-19	52.93	0.90	18.23	7.93	0.14	4.88	8.77	3.83	1.28	0.22
PL-19 Dup	56.29	0.87	16.70	7.57	0.13	4.11	8.37	3.68	1.23	0.21
PL-22	54.46	0.89	15.16	8.34	0.15	6.48	8.85	3.48	1.06	0.21
PL-24	51.79	1.00	17.88	8.57	0.15	5.70	8.98	3.67	1.08	0.24
PL-27	57.59	0.92	13.43	8.77	0.15	5.41	8.45	3.26	0.82	0.22
PL-29	52.14	0.97	17.09	8.72	0.15	6.09	9.04	3.66	0.94	0.23
PL-9	51.23	0.86	16.03	9.02	0.15	9.14	7.86	3.42	1.07	0.21
PT-100	59.79	1.03	14.07	7.73	0.14	2.63	7.68	4.12	1.71	0.23
PT-101A	63.65	0.88	18.17	4.32	0.07	1.87	4.16	3.67	2.58	0.15
PT-102A	61.44	0.81	15.42	6.19	0.11	2.79	5.52	4.24	2.60	0.18
PT-102B	62.36	0.86	14.01	6.41	0.11	2.83	5.80	4.24	2.48	0.19
PT-6	64.03	0.44	19.78	2.67	0.05	0.72	2.18	4.90	4.85	0.09
PT-7	58.77	0.85	19.37	5.41	0.10	2.02	4.58	4.89	3.17	0.23
PT-8	59.51	1.01	14.62	7.56	0.14	2.79	7.29	4.14	1.88	0.22
PT-9	54.56	1.01	17.67	8.10	0.15	4.05	7.88	3.99	1.45	0.24
PT-91A-2	60.59	0.86	19.29	5.35	0.08	2.25	4.71	3.54	2.56	0.18
PT-91B-3	59.96	1.02	14.48	7.53	0.14	2.77	7.23	3.98	1.82	0.23

A3.2 Calculated Liquid Compositions via Phenocryst Removal

A3.2.1 Table of Averaged Phenocryst Compositions used in Calculating Liquid Compositions (wt.%)

Planchon	SiO₂	TiO₂	Al₂O₃	FeO	MnO	MgO	CaO	Na₂O	K₂O
Olivine	38.85	0.01	0.00	23.84	0.20	38.62	0.00	0.00	0.00
Plagioclase	52.34	0.00	28.95	0.83	0.00	0.13	12.88	3.71	0.24
Clinopyroxene	52.37	0.45	2.39	17.37	7.29	15.79	3.57	0.41	0.00

A3.2.2 Table of Modal Phenocryst Proportions of Olivine, Plagioclase and Clinopyroxene: Major Element Compositions of Planchon samples used in Calculating Liquid Compositions from Tormey et al. 1991 (wt. %)

Sample	Md OL	Md PL	Md CPX	Md Sum	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O
1PL-2	0.09	0.325	0.008	0.423	52.26	1.07	17.99	8.343	0.15	6.06	8.48	3.58	1.07
1PL-3	0.06	0.16	0	0.22	52.36	1.01	17.78	8.325	0.15	5.97	8.79	3.5	1.03
3PL-4	0.105	0.333	0.001	0.439	52.27	0.96	17.59	8.325	0.15	6.41	8.86	3.57	0.96
3PL-5	0.04	0.16	0	0.2	52.51	0.97	17.59	8.424	0.16	6.5	8.85	3.37	0.95
3PL-8	0.076	0.292	0.004	0.372	51.73	0.97	17.86	8.604	0.16	6.58	8.88	3.35	0.83
3PL-9	0.073	0.284	0.011	0.368	51.95	0.97	17.77	8.613	0.15	6.57	8.9	3.48	0.85
2PL-10	0.043	0.161	0	0.204	54.31	1.15	17.35	8.001	0.15	4.38	7.19	4.1	1.75
1PL-11	0.067	0.156	0	0.223	53.39	0.99	17.5	8.181	0.14	6.12	7.94	3.67	1.23
1PL-12	0.054	0.182	0	0.236	53.38	0.96	17.82	7.92	0.14	5.56	8.31	3.57	1.12
1PL-13	0.06	0.21	0	0.27	53.32	0.96	17.8	7.893	0.14	5.47	8.32	3.73	1.12
1PL-15	0.05	0.2	0.001	0.251	54.03	0.92	18.14	7.56	0.14	4.95	8.48	3.67	1.21
1PL-16	0.1	0.09	0.001	0.191	52.21	0.87	16.24	8.631	0.15	8.65	7.8	3.37	1.06
1PL-17	0.08	0.09	0.001	0.171	52.21	0.87	16.24	8.613	0.15	8.55	7.8	3.39	1.07
1PL-18	0.07	0.21	0	0.28	52.47	0.91	17.17	8.262	0.15	7.03	8.72	3.26	0.99
1PL-19	0.07	0.21	0	0.28	52.55	0.91	17.36	8.208	0.15	6.8	8.72	3.33	0.97
1PL-20	0.04	0.06	0	0.1	52.47	1	17.46	8.271	0.15	6.23	8.89	3.34	1.02
1PL-21	0.05	0.24	0	0.29	54.06	0.9	18.31	7.461	0.14	5.08	8.47	3.55	1.22
1PL-22	0.05	0.15	0	0.2	53.98	0.92	18.23	7.587	0.14	5.08	8.46	3.55	1.21
1PL-23	0.05	0.17	0	0.22	54.22	0.93	18.22	7.623	0.14	5.01	8.52	3.6	1.21
1PL-24	0.1	0.06	0	0.16	52.16	0.86	16.22	8.649	0.15	8.7	7.75	3.34	1.07
1PL-25	0.09	0.09	0	0.18	52.57	0.89	16.66	8.343	0.15	7.56	8.14	3.26	1.1
1PL-26	0.074	0.275	0	0.349	52.34	0.96	17.55	8.352	0.15	6.44	8.82	3.71	0.98
2PL-27	0.05	0.19	0	0.24	53.89	1.02	17.53	7.947	0.14	5.18	7.83	3.64	1.41
2PL-28	0.04	0.15	0	0.19	53.91	1.06	17.48	8.001	0.15	5.39	7.78	3.7	1.45
2PL-29	0.05	0.15	0.001	0.201	53.73	1.06	17.42	8.01	0.15	5.35	7.87	3.84	1.45
1PL-30	0.038	0.172	0.001	0.211	53.09	0.98	18.87	7.659	0.14	4.56	8.86	3.66	1.04

*Ol=olivine, PL=plagioclase, CPX=clinopyroxene, and Md=modal analysis

A3.2.2 Table of Calculated Liquid Compositions after Modal Phenocryst Subtraction in wt. %. Data here used in Figure 4.12.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
1PL-2	55.22	1.86	15.15	10.18	0.13	4.29	7.54	4.17	1.74
1PL-3	53.10	1.31	17.11	8.79	0.18	4.74	8.75	3.77	1.29
3PL-4	53.14	1.72	14.45	9.99	0.22	4.20	8.29	4.22	1.59
3PL-5	52.99	1.22	16.35	9.24	0.19	6.22	8.56	3.50	1.15
3PL-8	52.55	1.56	15.26	10.46	0.19	5.75	8.28	3.66	1.23
3PL-9	53.24	1.54	15.28	10.30	0.09	5.68	8.34	3.87	1.25
2PL-10	55.93	1.47	16.30	8.76	0.18	3.48	6.58	4.48	2.19
1PL-11	54.27	1.28	16.90	8.40	0.16	4.59	7.72	4.02	1.55
1PL-12	54.56	1.27	16.72	8.61	0.17	4.61	7.94	3.85	1.43
1PL-13	54.60	1.33	16.36	8.75	0.18	4.38	7.84	4.11	1.49
1PL-15	55.31	1.24	16.70	8.35	0.17	4.04	7.98	3.95	1.57
1PL-16	52.91	1.08	17.06	7.72	0.15	6.00	8.30	3.79	1.30
1PL-17	52.95	1.06	16.66	8.09	0.16	6.67	8.11	3.73	1.28
1PL-18	53.28	1.28	15.65	9.03	0.19	6.07	8.48	3.49	1.32
1PL-19	53.36	1.28	15.91	8.95	0.19	5.75	8.48	3.59	1.29
1PL-20	53.17	1.12	17.70	8.18	0.16	5.28	9.14	3.51	1.13
1PL-21	55.37	1.28	16.21	8.63	0.18	4.45	7.67	3.79	1.65
1PL-22	54.96	1.16	17.55	7.92	0.16	3.97	8.25	3.78	1.48
1PL-23	55.11	1.20	17.17	8.12	0.17	3.95	8.17	3.83	1.51
1PL-24	52.82	1.03	17.46	7.51	0.16	5.87	8.41	3.76	1.27
1PL-25	53.48	1.10	17.41	7.60	0.16	5.09	8.65	3.62	1.33
1PL-26	52.89	1.48	14.92	9.86	0.21	5.52	8.20	4.17	1.42
2PL-27	55.39	1.36	16.16	8.83	0.17	4.34	7.23	3.93	1.82
2PL-28	55.00	1.32	16.45	8.65	0.18	4.80	7.32	3.93	1.77
2PL-29	54.90	1.34	16.61	8.47	0.17	4.31	7.54	4.16	1.79
1PL-30	54.13	1.26	17.88	8.47	0.16	3.94	8.55	3.88	1.28

A3.3 Calculated Primary Melt Compositions in wt. %

A3.3.1 Primary Melt Compositions and melting conditions of Azufre-Planchon-Peteroa melts with SiO₂ < 57 wt. % with initial magmatic H₂O set at 6% and oxygen fugacity = 0.1.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass relative to melt mass	T	Gpa
PL-1	48.03	0.78	13.88	8.09	13.12	6.87	2.69	0.79	4.91	1.22	1261.30	1.48
PL-2	47.90	0.83	13.98	8.14	13.20	6.59	2.78	0.83	4.91	1.22	1263.42	1.52
PL-3	48.01	0.79	13.83	8.15	13.12	6.84	2.72	0.80	4.91	1.22	1261.55	1.49
PL-4	47.99	0.76	13.86	8.01	12.99	6.98	2.81	0.76	4.98	1.20	1258.36	1.49
PL-5	48.09	0.76	13.83	8.07	13.05	6.96	2.65	0.75	4.98	1.20	1258.07	1.46
PL-6	47.78	0.76	13.94	8.25	13.35	6.70	2.79	0.73	4.86	1.23	1268.13	1.54
PL-7	47.63	0.76	13.87	8.25	13.39	6.91	2.71	0.69	4.93	1.21	1268.05	1.55
PL-8	47.58	0.76	14.02	8.25	13.30	6.97	2.63	0.65	4.96	1.21	1265.70	1.53
PL-9	47.64	0.76	13.91	8.24	13.27	6.97	2.72	0.67	4.96	1.21	1265.48	1.54
PL-10	49.16	0.85	12.78	8.47	13.74	5.30	3.02	1.29	4.63	1.30	1272.87	1.49
PL-13	48.82	0.75	13.87	7.88	12.72	6.48	2.91	0.87	4.91	1.22	1249.77	1.38
PL-14	49.28	0.71	14.29	7.49	12.05	6.64	2.86	0.96	4.96	1.21	1234.23	1.27
PL-15	49.18	0.71	14.01	7.70	12.44	6.55	2.84	0.93	4.89	1.23	1243.05	1.31
PL-16	48.53	0.73	13.67	7.82	12.70	6.57	2.84	0.89	5.32	1.13	1243.30	1.39
PL-17	48.56	0.73	13.68	7.82	12.62	6.57	2.86	0.90	5.32	1.13	1241.76	1.38
PL-18	48.45	0.74	13.96	7.79	12.51	7.09	2.65	0.80	5.14	1.17	1243.44	1.36
PL-20	48.22	0.79	13.73	8.03	13.02	6.99	2.63	0.80	4.96	1.21	1257.40	1.44
PL-21	49.26	0.70	14.27	7.53	12.22	6.60	2.77	0.95	4.94	1.21	1237.39	1.27
PL-22	49.16	0.71	14.14	7.67	12.38	6.56	2.75	0.94	4.91	1.22	1241.20	1.30
PL-23	49.17	0.72	14.02	7.72	12.47	6.56	2.77	0.93	4.89	1.23	1243.45	1.31
PL-26	47.96	0.75	13.80	8.02	13.01	6.94	2.92	0.77	4.98	1.20	1259.32	1.51
PL-27	49.19	0.78	13.48	8.05	12.97	6.02	2.80	1.08	4.84	1.24	1253.30	1.36
PL-28	49.12	0.82	13.46	8.01	12.97	5.99	2.85	1.12	4.86	1.23	1253.57	1.38
PL-29	49.00	0.82	13.42	8.04	12.93	6.06	2.96	1.12	4.86	1.23	1254.21	1.41
PL-30	48.33	0.74	14.25	7.99	12.93	6.69	2.76	0.79	4.77	1.26	1258.58	1.44
PL-31	48.44	0.74	14.32	7.95	12.79	6.74	2.71	0.77	4.79	1.25	1254.57	1.40
PL-32	48.00	0.78	13.93	8.08	12.99	6.88	2.77	0.80	4.94	1.21	1258.98	1.48
PL-33	48.07	0.78	13.93	8.11	13.03	6.87	2.63	0.81	4.94	1.21	1258.71	1.46

A3.3.1 Continued Table from above

Sample	SiO₂	TiO₂	Al₂O₃	FeO	MgO	CaO	Na₂O	K₂O	H₂O	final mass relative to original melt mass	T	Gpa
PL-34	48.19	0.78	13.84	8.14	13.16	6.84	2.51	0.79	4.91	1.22	1260.11	1.44
PL-35	47.87	0.78	14.04	8.12	13.04	6.92	2.68	0.78	4.94	1.21	1260.20	1.49
PLII-1 (PT-4)	48.06	0.93	12.37	8.94	14.47	5.81	2.65	1.09	4.77	1.26	1289.57	1.64
PLII-2 (PT-5)	48.07	0.81	13.84	8.08	13.06	6.60	2.92	0.74	5.01	1.20	1258.41	1.49
PLII-3 (PT-6)	48.11	0.81	13.89	8.06	13.06	6.61	2.85	0.74	5.01	1.20	1257.60	1.47
PLII-4 (PT-7)	48.60	0.85	13.26	8.21	13.29	6.28	2.80	0.91	4.93	1.21	1260.64	1.45
PLII-5 (PT-8)	48.44	0.83	13.59	8.27	13.36	6.41	2.77	0.91	4.67	1.28	1268.21	1.48
PLII-7 (PT-12)	48.67	0.81	13.64	7.83	12.70	6.73	2.80	0.86	5.09	1.18	1246.96	1.38
AZ-3	47.17	0.65	12.53	9.78	15.72	6.05	2.36	0.58	4.31	1.39	1328.98	1.84
AZ-13	49.57	0.74	13.83	7.95	12.82	5.73	2.96	0.93	4.74	1.26	1250.08	1.31
AZ-16	47.95	0.71	12.85	9.31	15.01	5.95	2.23	0.79	4.40	1.36	1306.37	1.63
AZ-17	48.41	0.71	13.32	8.81	14.19	5.43	2.79	0.99	4.56	1.32	1285.60	1.57
PT-9 (PT-15)	49.75	0.77	13.19	8.03	12.95	5.85	2.88	1.09	4.74	1.26	1252.20	1.31

A3.3.2 Primary Melt Compositions and melting conditions of Azufre-Planchon-Peteroa melts with SiO₂ < 57 wt. % with initial magmatic H₂O set at 4% and oxygen fugacity = 0.1.

Sample	SiO₂	TiO₂	Al₂O₃	FeO	MgO	CaO	Na₂O	K₂O	H₂O	final mass relative to original melt mass	T	Gpa
PL-3	48.84	0.80	14.05	8.29	13.39	6.95	2.77	0.81	3.26	1.23	1296.65	1.48
PL-4	48.87	0.77	14.16	8.15	13.09	7.13	2.87	0.77	3.32	1.20	1289.49	1.45
PL-5	48.92	0.77	14.05	8.21	13.33	7.07	2.69	0.76	3.31	1.21	1293.71	1.44
PL-6	48.59	0.77	14.17	8.39	13.62	6.81	2.83	0.74	3.22	1.24	1303.51	1.54
PL-7	48.49	0.78	14.16	8.39	13.49	7.06	2.77	0.70	3.29	1.21	1300.08	1.52
PL-8	48.41	0.77	14.25	8.40	13.58	7.08	2.67	0.66	3.29	1.21	1301.98	1.52
PL-9	48.46	0.77	14.14	8.39	13.55	7.08	2.77	0.68	3.29	1.21	1301.61	1.53
PL-10	49.97	0.86	12.99	8.61	13.97	5.38	3.07	1.31	3.07	1.30	1306.52	1.48
PL-11	49.69	0.79	14.00	8.08	13.01	6.35	2.94	0.98	3.31	1.21	1282.70	1.36
PL-12	49.74	0.76	14.17	8.01	12.88	6.61	2.84	0.89	3.27	1.22	1280.22	1.32

Table A3.3.2 Continued

Sample	SiO2	TiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	H2O	final mass	T	Gpa
PL-14	50.13	0.73	14.52	7.62	12.31	6.74	2.90	0.98	3.29	1.21	1266.21	1.24
PL-15	50.02	0.72	14.24	7.83	12.69	6.66	2.88	0.95	3.24	1.23	1275.65	1.29
PL-16	49.46	0.75	13.96	7.97	12.85	6.71	2.90	0.91	3.55	1.13	1276.09	1.36
PL-17	49.45	0.74	13.90	7.98	12.95	6.68	2.90	0.92	3.53	1.13	1278.40	1.37
PL-18	49.32	0.75	14.19	7.93	12.81	7.20	2.69	0.82	3.41	1.17	1278.60	1.34
PL-19	49.32	0.75	14.27	7.93	12.77	7.17	2.74	0.80	3.39	1.18	1278.23	1.34
PL-20	49.09	0.80	14.02	8.16	13.12	7.14	2.68	0.82	3.31	1.21	1288.50	1.40
PL-22	50.01	0.73	14.37	7.80	12.63	6.67	2.80	0.95	3.26	1.23	1273.85	1.27
PL-23	50.01	0.73	14.25	7.85	12.73	6.66	2.82	0.95	3.24	1.23	1276.19	1.28
PL-24	49.45	0.74	13.96	7.98	12.90	6.67	2.87	0.92	3.55	1.13	1277.03	1.36
PL-25	49.67	0.75	14.01	7.91	12.78	6.85	2.74	0.93	3.46	1.16	1274.85	1.31
PL-26	48.84	0.77	14.09	8.15	13.11	7.08	2.98	0.79	3.32	1.20	1290.40	1.48
PL-27	50.03	0.80	13.69	8.19	13.22	6.12	2.84	1.10	3.21	1.25	1286.93	1.34
PL-28	49.95	0.83	13.68	8.15	13.23	6.09	2.90	1.13	3.23	1.24	1287.34	1.36
PL-29	49.83	0.83	13.64	8.17	13.19	6.16	3.01	1.14	3.23	1.24	1287.81	1.39
PL-30	49.14	0.75	14.48	8.12	13.17	6.80	2.81	0.80	3.16	1.26	1291.83	1.42
PL-31	49.25	0.76	14.55	8.08	13.03	6.85	2.75	0.79	3.18	1.26	1287.65	1.38
PL-32	48.82	0.79	14.15	8.23	13.26	6.99	2.81	0.82	3.27	1.22	1293.87	1.47
PL-33	48.89	0.79	14.16	8.25	13.31	6.98	2.67	0.82	3.27	1.22	1293.82	1.45
PL-34	49.02	0.79	14.07	8.29	13.43	6.95	2.55	0.81	3.26	1.23	1295.47	1.42
PL-35	48.70	0.79	14.27	8.26	13.31	7.03	2.72	0.79	3.27	1.22	1295.33	1.48
PLII-1 (PT-4)	48.86	0.95	12.57	9.09	14.74	5.90	2.70	1.11	3.16	1.26	1327.18	1.65
PLII-2 (PT-5)	48.91	0.83	14.06	8.22	13.35	6.71	2.96	0.76	3.32	1.20	1294.06	1.48
PLII-4 (PT-7)	49.44	0.87	13.48	8.36	13.56	6.38	2.84	0.93	3.27	1.22	1296.25	1.43
PLII-5 (PT-8)	49.24	0.85	13.81	8.40	13.59	6.51	2.82	0.92	3.10	1.29	1301.79	1.47
PLII-6 (PT-9)	49.18	0.85	13.98	8.31	13.36	6.56	2.96	0.93	3.11	1.28	1297.41	1.47
PLII-7 (PT-12)	49.57	0.83	13.93	7.97	12.81	6.88	2.86	0.88	3.39	1.18	1277.92	1.34
PLII-8 (PT-13)	49.94	0.80	13.90	8.11	13.03	6.50	2.86	0.99	3.13	1.28	1285.57	1.33
PLII-9 (PT-14)	49.39	0.75	14.08	8.10	13.10	6.96	2.70	0.86	3.24	1.23	1287.41	1.37

Table A3.3.2 Continued

Sample	SiO₂	TiO₂	Al₂O₃	FeO	MgO	CaO	Na₂O	K₂O	H₂O	final mass relative to original melt mass	T	Gpa
AZ-3	47.86	0.66	12.67	9.93	16.09	6.11	2.39	0.59	2.85	1.40	1370.86	1.89
AZ-13	50.39	0.75	14.05	8.08	13.06	5.83	3.01	0.94	3.15	1.27	1282.47	1.28
AZ-16	48.70	0.72	13.06	9.46	15.22	6.05	2.27	0.80	2.92	1.37	1342.67	1.64
AZ-17	49.19	0.72	13.53	8.95	14.41	5.52	2.83	1.01	3.02	1.32	1320.35	1.57
PT-9 (PT-15)	50.58	0.78	13.41	8.17	13.19	5.94	2.93	1.11	3.15	1.27	1284.92	1.28

A3.3.3 Primary Melt Compositions and melting conditions of Azufre-Planchon-Peteroa melts with SiO₂ < 57 wt. % with initial magmatic H₂O set at 6% and oxygen fugacity = 0.15.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass	T	Gpa
PL-1	48.22	0.80	14.23	7.61	12.30	7.04	2.75	0.81	5.03	1.19	1242.63	1.38
PL-2	48.08	0.85	14.33	7.65	12.37	6.75	2.85	0.85	5.03	1.19	1244.73	1.42
PL-4	48.17	0.78	14.21	7.53	12.15	7.16	2.88	0.78	5.11	1.17	1239.60	1.38
PL-5	48.27	0.78	14.17	7.58	12.21	7.13	2.72	0.77	5.11	1.17	1239.34	1.35
PL-6	47.96	0.77	14.29	7.76	12.54	6.87	2.86	0.75	4.98	1.20	1249.44	1.44
PL-7	47.80	0.78	14.21	7.76	12.56	7.08	2.78	0.71	5.06	1.18	1249.24	1.45
PL-8	47.75	0.78	14.37	7.76	12.47	7.14	2.70	0.67	5.08	1.18	1246.87	1.43
PL-10	49.39	0.87	13.10	7.99	12.96	5.43	3.09	1.32	4.74	1.26	1254.82	1.39
PL-11	49.00	0.80	14.05	7.47	12.08	6.38	2.95	0.99	5.08	1.18	1233.80	1.30
PL-12	49.07	0.77	14.22	7.40	11.97	6.63	2.85	0.89	5.03	1.19	1231.99	1.27
PL-14	49.46	0.73	14.58	7.04	11.38	6.77	2.91	0.98	5.06	1.18	1219.70	1.20
PL-16	48.71	0.75	14.01	7.34	11.82	6.73	2.91	0.91	5.45	1.10	1224.47	1.30
PL-17	48.71	0.75	13.95	7.35	11.92	6.70	2.91	0.92	5.42	1.10	1226.70	1.31
PL-18	48.60	0.75	14.24	7.32	11.83	7.23	2.70	0.82	5.24	1.14	1228.52	1.28
PL-19	48.61	0.75	14.32	7.32	11.80	7.19	2.75	0.80	5.21	1.15	1228.50	1.28
PL-20	48.40	0.81	14.07	7.54	12.19	7.16	2.69	0.82	5.08	1.18	1238.71	1.34
PL-21	49.47	0.72	14.63	7.07	11.37	6.77	2.84	0.97	5.06	1.18	1219.04	1.18
PL-24	48.70	0.74	14.00	7.36	11.87	6.69	2.88	0.92	5.45	1.10	1225.25	1.30

Table A3.3.3 Continued

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass	T	Gpa
PL-25	48.94	0.75	14.06	7.30	11.78	6.87	2.75	0.93	5.32	1.13	1224.47	1.25
PL-26	48.14	0.77	14.14	7.53	12.17	7.11	2.99	0.79	5.11	1.17	1240.54	1.41
PL-28	49.33	0.84	13.79	7.53	12.15	6.14	2.92	1.14	4.98	1.20	1235.24	1.29
PL-30	48.53	0.76	14.61	7.51	12.12	6.86	2.83	0.81	4.88	1.23	1240.19	1.34
PL-31	48.60	0.76	14.60	7.48	12.15	6.87	2.76	0.79	4.88	1.23	1240.07	1.32
PL-32	48.14	0.79	14.20	7.61	12.34	7.02	2.82	0.82	5.03	1.19	1244.16	1.40
PL-33	48.21	0.80	14.21	7.63	12.39	7.00	2.68	0.82	5.03	1.19	1243.90	1.38
PL-34	48.38	0.80	14.18	7.66	12.33	7.01	2.57	0.81	5.03	1.19	1241.49	1.34
PL-35	48.02	0.80	14.32	7.64	12.40	7.05	2.73	0.80	5.03	1.19	1245.36	1.41
PLII-1 (PT-4)	48.24	0.95	12.68	8.44	13.69	5.95	2.72	1.12	4.88	1.23	1270.98	1.54
PLII-2 (PT-5)	48.25	0.83	14.18	7.59	12.22	6.77	2.99	0.76	5.13	1.17	1239.66	1.39
PLII-3 (PT-6)	48.29	0.83	14.24	7.57	12.21	6.78	2.92	0.76	5.13	1.17	1238.87	1.37
PLII-4 (PT-7)	48.80	0.87	13.59	7.72	12.46	6.43	2.87	0.94	5.06	1.18	1242.07	1.35
PLII-5 (PT-8)	48.65	0.86	13.93	7.78	12.57	6.56	2.84	0.93	4.79	1.25	1249.94	1.38
PLII-6 (PT-9)	48.55	0.86	14.02	7.71	12.51	6.58	2.97	0.93	4.79	1.25	1250.00	1.41
PLII-7 (PT-12)	48.87	0.83	13.98	7.36	11.84	6.90	2.87	0.88	5.21	1.15	1228.29	1.28
PLII-8 (PT-13)	49.30	0.81	13.95	7.51	12.18	6.52	2.87	0.99	4.81	1.25	1239.02	1.28
AZ-3	47.35	0.67	12.84	9.26	15.03	6.20	2.42	0.60	4.42	1.36	1310.81	1.73
AZ-13	49.79	0.76	14.17	7.47	12.01	5.88	3.03	0.95	4.86	1.23	1232.02	1.22
AZ-16	48.15	0.73	13.17	8.80	14.29	6.10	2.29	0.81	4.51	1.33	1288.33	1.53
AZ-17	48.62	0.73	13.65	8.31	13.43	5.57	2.86	1.02	4.67	1.28	1267.49	1.47
PT-9 (PT-15)	49.98	0.78	13.52	7.56	12.14	5.99	2.95	1.12	4.86	1.23	1234.14	1.22
PLII-8 (PT-13)	49.35	0.81	13.97	7.52	12.18	6.53	2.87	0.99	4.72	1.25	1240.55	1.28

A3.3.4 Primary Melt Compositions and melting conditions of Azufre-Planchon-Peteroa melts with SiO₂ < 57 wt. % with initial magmatic H₂O set at 4% and oxygen fugacity = 0.15.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass	T	Gpa
PL-3	49.04	0.82	14.40	7.80	12.57	7.12	2.83	0.83	3.34	1.20	1276.50	1.37
PL-4	49.03	0.79	14.44	7.67	12.44	7.27	2.93	0.79	3.39	1.18	1273.37	1.37
PL-5	49.12	0.79	14.40	7.72	12.50	7.25	2.76	0.78	3.39	1.18	1273.43	1.33
PL-6	48.79	0.79	14.52	7.90	12.81	6.98	2.91	0.76	3.30	1.21	1283.38	1.43
PL-8	48.60	0.79	14.60	7.90	12.75	7.26	2.74	0.68	3.37	1.18	1281.64	1.41
PL-9	48.65	0.79	14.49	7.89	12.73	7.26	2.84	0.69	3.37	1.18	1281.27	1.42
PL-12	49.92	0.78	14.45	7.54	12.24	6.74	2.90	0.91	3.34	1.20	1264.43	1.24
PL-13	49.89	0.78	14.44	7.54	12.15	6.75	3.03	0.91	3.34	1.20	1263.44	1.26
PL-15	50.25	0.74	14.59	7.36	11.86	6.82	2.95	0.97	3.32	1.20	1255.77	1.19
PL-16	49.62	0.76	14.24	7.49	12.16	6.84	2.95	0.93	3.62	1.10	1259.62	1.27
PL-17	49.66	0.76	14.25	7.49	12.07	6.84	2.97	0.94	3.62	1.10	1257.81	1.26
PL-19	49.49	0.76	14.55	7.46	12.11	7.31	2.79	0.81	3.46	1.16	1262.04	1.26
PL-20	49.26	0.82	14.30	7.68	12.47	7.28	2.73	0.84	3.37	1.18	1272.48	1.32
PL-22	50.24	0.74	14.73	7.33	11.80	6.84	2.87	0.98	3.34	1.20	1253.94	1.17
PL-23	50.24	0.75	14.60	7.38	11.89	6.83	2.89	0.97	3.32	1.20	1256.31	1.18
PL-26	49.00	0.79	14.37	7.67	12.46	7.22	3.04	0.80	3.39	1.18	1274.28	1.39
PL-27	50.26	0.82	14.03	7.71	12.41	6.27	2.91	1.13	3.29	1.21	1267.19	1.24
PL-28	50.19	0.85	14.02	7.67	12.41	6.24	2.97	1.16	3.31	1.21	1267.54	1.26
PL-29	50.06	0.85	13.97	7.69	12.37	6.31	3.08	1.16	3.31	1.21	1267.99	1.29
PL-30	49.36	0.77	14.84	7.64	12.37	6.97	2.88	0.82	3.24	1.23	1272.01	1.31
PL-31	49.47	0.77	14.91	7.60	12.22	7.02	2.82	0.81	3.26	1.23	1267.83	1.27
PL-32	49.03	0.81	14.50	7.74	12.44	7.17	2.88	0.84	3.35	1.19	1273.67	1.36
PL-33	49.10	0.81	14.51	7.76	12.48	7.15	2.74	0.84	3.35	1.19	1273.64	1.34
PL-34	49.23	0.81	14.41	7.80	12.61	7.12	2.61	0.83	3.34	1.20	1275.35	1.31
PL-35	48.90	0.81	14.62	7.77	12.49	7.20	2.79	0.81	3.35	1.19	1275.11	1.37
PLII-1 (PT-4)	49.11	0.97	12.95	8.58	13.79	6.08	2.78	1.14	3.26	1.23	1303.13	1.51
PLII-2 (PT-5)	49.11	0.85	14.41	7.73	12.52	6.87	3.04	0.77	3.41	1.17	1273.76	1.37
PLII-4 (PT-7)	49.66	0.89	13.81	7.86	12.74	6.54	2.92	0.95	3.35	1.19	1276.19	1.33

Table A3.3.4 Continued

Sample	SiO₂	TiO₂	Al₂O₃	FeO	MgO	CaO	Na₂O	K₂O	H₂O	final mass relative to original melt mass	T	Gpa
PLII-5 (PT-8)	49.46	0.87	14.16	7.92	12.81	6.67	2.89	0.95	3.18	1.26	1282.20	1.36
PLII-7 (PT-12)	49.75	0.85	14.20	7.50	12.14	7.01	2.92	0.90	3.46	1.16	1261.79	1.26
PLII-9 (PT-14)	49.61	0.77	14.43	7.62	12.27	7.14	2.76	0.88	3.32	1.20	1267.40	1.26
AZ-3	48.09	0.68	13.05	9.40	15.24	6.30	2.46	0.61	2.93	1.36	1347.56	1.74
AZ-13	50.64	0.77	14.40	7.60	12.26	5.97	3.08	0.97	3.22	1.24	1263.00	1.18
AZ-16	48.92	0.74	13.39	8.94	14.51	6.20	2.33	0.82	2.99	1.34	1323.62	1.52
AZ-17	49.41	0.74	13.87	8.45	13.66	5.66	2.90	1.04	3.10	1.29	1301.07	1.46
PT-9 (PT-15)	50.83	0.80	13.74	7.69	12.39	6.09	3.00	1.13	3.22	1.24	1265.46	1.19

A3.3.5 Primary Melt Compositions and melting conditions of Llaima, Villarrica and Small Eruptive Centers melts with SiO₂ < 57 wt. % with initial magmatic H₂O set at 4% and oxygen fugacity = 0.1. Data is from Hickey-Vargas et al. (unpublished)

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass relative to original melt mass	T	Gpa
Villarrica												
111275-9	48.62	0.88	13.01	8.90	14.31	7.43	2.46	0.49	3.18	1.26	1319.78	1.54
270976-3	48.98	0.84	13.08	8.88	14.40	7.42	2.17	0.48	3.08	1.30	1320.50	1.46
280976-1	48.23	0.88	13.09	9.01	14.56	7.57	2.25	0.47	3.19	1.25	1326.83	1.59
290976-2	48.36	0.86	13.20	8.94	14.37	7.62	2.32	0.51	3.11	1.28	1324.09	1.57
300976-5	48.63	0.92	13.61	8.65	14.04	7.39	2.52	0.51	3.07	1.30	1315.99	1.52
210281-1	48.76	0.88	12.88	8.93	14.39	7.38	2.39	0.50	3.16	1.26	1320.85	1.52
151282-1	48.61	0.88	12.93	8.92	14.45	7.35	2.46	0.50	3.16	1.26	1323.27	1.56
151282-3	49.53	0.94	11.10	9.99	16.12	5.58	2.64	0.59	2.83	1.41	1361.59	1.66
101283-1	48.58	0.78	13.70	8.67	14.04	7.70	2.32	0.44	3.11	1.28	1314.99	1.49
191284-1	48.45	0.88	12.72	9.23	14.85	7.16	2.40	0.49	3.10	1.29	1334.28	1.62
250884-1	48.19	0.86	13.29	9.00	14.58	7.36	2.42	0.48	3.11	1.28	1329.42	1.63
250884-4	48.69	0.80	13.78	8.31	13.43	8.00	2.38	0.47	3.37	1.18	1296.09	1.41
240884-1	48.45	0.78	13.87	8.75	14.17	7.58	2.26	0.45	3.05	1.31	1319.47	1.52
270884-3	48.62	0.93	12.58	9.27	14.99	6.84	2.34	0.54	3.13	1.28	1334.56	1.60

Table A3.3.5 Continued

Sample	SiO2	TiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	H2O	final mass	T	Gpa
270884-5	48.00	0.95	11.93	9.85	15.91	6.88	2.25	0.56	2.95	1.36	1364.59	1.83
270884-11	48.36	0.83	13.44	8.88	14.30	7.71	2.24	0.49	3.08	1.30	1322.93	1.55
260884-8	48.71	0.80	13.85	8.62	13.87	7.60	2.37	0.49	3.07	1.30	1311.53	1.47
290884-4	48.26	0.87	13.41	8.98	14.52	7.36	2.39	0.50	3.05	1.31	1328.91	1.61
280884-9	48.33	0.71	14.41	8.04	12.97	8.89	2.19	0.35	3.39	1.18	1288.12	1.37
SEC												
150194-02	47.67	0.81	13.98	9.21	14.83	7.22	2.06	0.51	3.02	1.32	1338.48	1.68
150194-03	48.17	0.86	14.06	8.77	14.20	7.34	2.11	0.56	3.21	1.25	1316.94	1.54
150194-04	48.26	0.86	13.89	8.95	14.42	7.16	2.03	0.57	3.15	1.27	1322.22	1.54
L81	47.88	0.90	14.42	8.30	13.38	7.84	2.66	0.54	3.36	1.19	1300.69	1.57
L82	48.05	0.91	14.51	8.32	13.39	7.33	2.87	0.59	3.32	1.20	1300.44	1.58
120194-04A	47.98	0.88	14.24	8.54	13.85	7.15	2.79	0.65	3.23	1.24	1312.65	1.64
120194-05	48.10	0.88	14.43	8.38	13.54	7.33	2.73	0.61	3.29	1.21	1303.56	1.57
120194-04B	48.02	0.88	14.20	8.62	13.87	7.12	2.75	0.62	3.21	1.25	1313.07	1.63
120194-04C	48.01	0.87	14.15	8.52	13.79	7.23	2.80	0.63	3.27	1.22	1310.30	1.63
150194-01	47.91	0.88	14.48	8.42	13.66	7.32	2.78	0.57	3.27	1.22	1307.77	1.61
110194-02	47.99	0.82	12.79	9.83	15.94	6.57	1.96	0.58	2.86	1.40	1365.01	1.78
110194-01	48.13	0.94	13.24	9.28	15.04	6.45	2.47	0.81	2.98	1.34	1342.31	1.74
L84	47.78	0.91	13.39	9.40	15.12	6.49	2.63	0.62	2.98	1.34	1347.08	1.81
120194-01	47.31	0.82	14.17	8.92	14.43	7.32	2.58	0.63	3.13	1.28	1331.77	1.79
120194-02	47.26	0.84	14.24	8.95	14.51	7.21	2.49	0.64	3.15	1.27	1332.81	1.79
110194-03	47.97	0.92	13.78	8.80	14.20	6.95	2.69	0.83	3.16	1.26	1321.81	1.70
120194-03	48.33	0.69	14.30	7.80	12.58	9.12	2.24	0.38	3.73	1.07	1273.76	1.33
150194-07	47.99	0.84	13.70	9.04	14.62	6.75	2.67	0.70	3.02	1.32	1333.87	1.73
140194-5A	48.37	0.67	14.03	8.17	13.19	9.14	1.69	0.37	3.56	1.12	1287.76	1.31
140194-03	48.33	0.70	14.21	7.86	12.72	9.07	2.27	0.36	3.67	1.09	1277.89	1.35
140194-02	48.24	0.69	14.30	7.84	12.69	9.05	2.28	0.37	3.71	1.08	1276.97	1.36
140194-04	48.18	0.70	14.22	7.96	12.90	8.95	2.31	0.37	3.60	1.11	1283.86	1.40
140194-5B	48.40	0.67	14.05	8.18	13.17	9.13	1.66	0.36	3.56	1.12	1286.91	1.30
140194-7B	48.47	0.67	13.90	8.15	13.24	9.13	1.67	0.39	3.56	1.12	1288.24	1.30

Table A3.3.5 Continued

Sample	SiO2	TiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	H2O	final mass	T	Gpa
140194-07	48.28	0.69	14.36	7.86	12.65	9.07	2.24	0.36	3.67	1.09	1276.41	1.34
140194-11	47.32	0.80	13.96	9.47	15.32	6.90	1.99	0.61	2.95	1.36	1353.11	1.81
140194-10	48.55	0.78	14.07	8.79	14.19	7.16	1.95	0.60	3.19	1.25	1313.98	1.46
140194-09	48.39	0.81	14.32	8.46	13.68	7.04	2.65	0.67	3.27	1.22	1304.59	1.54
L16	48.37	0.81	14.26	8.40	13.59	7.21	2.67	0.73	3.26	1.23	1303.70	1.55
L17	47.25	0.86	14.47	9.04	14.59	6.79	2.58	0.70	3.05	1.31	1336.47	1.82
240394-6B	48.38	0.88	14.22	8.26	13.31	7.32	2.68	0.90	3.32	1.20	1296.75	1.53
240394-6A	48.54	0.86	13.97	8.40	13.59	7.20	2.63	0.88	3.24	1.23	1303.27	1.54
Llaima												
111276-1	48.06	0.78	13.46	8.98	14.54	7.18	2.68	0.49	3.11	1.28	1330.13	1.69
121276-1	48.10	0.86	12.74	9.56	15.52	6.62	2.39	0.52	2.98	1.34	1353.30	1.77
121276-2	48.15	0.92	12.77	9.53	15.47	6.61	2.36	0.52	2.98	1.34	1351.64	1.74
121276-3	48.14	0.85	12.77	9.54	15.41	6.65	2.44	0.52	2.99	1.34	1350.51	1.75
121276-4	48.07	0.86	12.74	9.64	15.50	6.62	2.36	0.52	2.98	1.34	1353.22	1.76
LL 281079-1	49.04	0.59	14.52	8.18	13.28	7.60	2.36	0.53	3.23	1.24	1292.88	1.36
281079-1	48.00	0.78	12.72	9.73	15.78	6.72	2.33	0.42	2.88	1.39	1362.60	1.80
281079-2	48.60	0.86	11.54	10.28	16.62	5.73	2.38	0.53	2.78	1.44	1379.85	1.84
3381-1	48.07	0.84	12.72	9.64	15.55	6.64	2.35	0.52	2.96	1.35	1354.59	1.77
3381-2	48.10	0.78	13.49	9.06	14.62	7.37	2.31	0.43	3.13	1.28	1329.90	1.62
3381-3	48.10	0.77	13.55	9.02	14.60	7.36	2.31	0.44	3.13	1.28	1329.45	1.62
3381-4	48.25	0.83	13.31	9.10	14.73	7.14	2.37	0.48	3.08	1.30	1332.42	1.63
4381-1	48.96	0.73	11.53	10.25	16.56	5.44	2.40	0.65	2.80	1.42	1374.84	1.78
5381-1	47.78	0.76	14.05	8.80	14.28	7.69	2.37	0.41	3.15	1.27	1324.41	1.64
5381-2	48.53	0.82	12.85	9.29	15.06	6.76	2.41	0.54	3.04	1.32	1338.96	1.64
5381-3	48.24	0.78	13.70	8.87	14.25	7.40	2.39	0.47	3.18	1.26	1320.03	1.57
260483-1	48.19	0.77	13.38	9.10	14.65	7.23	2.38	0.45	3.13	1.28	1330.15	1.62
260483-2	48.10	0.81	13.38	9.13	14.74	7.19	2.37	0.45	3.10	1.29	1333.44	1.65
260483-4	48.11	0.72	13.56	9.09	14.74	7.15	2.43	0.42	3.08	1.30	1333.51	1.65
270483-1	47.79	0.85	11.84	10.32	16.65	6.04	2.54	0.45	2.82	1.42	1386.37	2.01
270483-2	48.34	0.77	13.49	9.18	14.84	6.96	2.41	0.38	2.99	1.34	1335.93	1.62

Table A3.3.5 Continued

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass relative to original melt mass	T	Gpa
270483-4	48.79	0.82	12.31	9.74	15.76	5.86	2.55	0.59	2.90	1.38	1355.71	1.71
270483-7	48.19	0.89	11.53	10.35	16.73	5.76	2.51	0.51	2.80	1.42	1385.03	1.94

A3.3.6 Primary Melt Compositions and melting conditions of Llaima, Villarrica and Small Eruptive Centers melts with SiO₂ < 57 wt. % with initial magmatic H₂O set at 6% and oxygen fugacity = 0.1. Data is from Hickey-Vargas et al. (unpublished)

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	H ₂ O	final mass relative to original melt mass	T	Gpa
Villarrica												
111275-9	47.78	0.86	12.74	8.76	14.22	7.28	2.41	0.48	4.77	1.26	1286.17	1.57
270976-3	48.19	0.82	12.87	8.73	14.16	7.30	2.13	0.47	4.65	1.30	1283.73	1.47
280976-1	47.43	0.87	12.88	8.85	14.29	7.45	2.22	0.47	4.81	1.25	1288.14	1.59
300976-5	47.85	0.90	13.39	8.51	13.81	7.27	2.48	0.51	4.63	1.28	1280.80	1.53
210281-1	47.96	0.87	12.67	8.78	14.13	7.26	2.36	0.49	4.77	1.30	1283.24	1.53
151282-1	47.81	0.87	12.73	8.77	14.19	7.24	2.42	0.49	4.77	1.26	1285.54	1.56
151282-3	48.79	0.93	10.92	9.85	15.91	5.49	2.60	0.58	4.27	1.26	1324.02	1.66
101283-1	47.79	0.76	13.49	8.53	13.80	7.57	2.28	0.43	4.70	1.41	1278.94	1.50
191284-1	47.66	0.86	12.52	9.08	14.60	7.05	2.36	0.48	4.67	1.28	1296.13	1.62
250884-1	47.41	0.85	13.08	8.85	14.33	7.24	2.38	0.48	4.70	1.29	1291.91	1.63
250884-4	47.84	0.79	13.56	8.16	13.13	7.87	2.34	0.47	5.09	1.28	1258.71	1.43
240884-1	47.67	0.76	13.65	8.61	13.94	7.46	2.23	0.44	4.60	1.18	1283.85	1.53
270884-3	47.83	0.92	12.38	9.12	14.73	6.73	2.30	0.53	4.72	1.31	1295.64	1.60
270884-5	47.26	0.93	11.74	9.70	15.68	6.78	2.21	0.55	4.44	1.28	1325.45	1.81
270884-11	47.58	0.82	13.22	8.73	14.06	7.59	2.21	0.49	4.65	1.36	1286.49	1.56
260884-8	47.92	0.79	13.63	8.48	13.64	7.48	2.33	0.48	4.63	1.30	1276.68	1.48
290884-4	47.49	0.85	13.20	8.83	14.28	7.24	2.35	0.50	4.60	1.30	1292.41	1.61

Table A3.3.6 Continued

Sample SEC	SiO2	TiO2	Al2O3	FeO	MgO	CaO	Na2O	K2O	H2O	final mass relative to original melt mass	T	Gpa
150194-02	46.92	0.80	13.76	9.06	14.60	7.11	2.02	0.50	4.56	1.32	1301.29	1.68
150194-03	47.37	0.85	13.83	8.62	13.93	7.23	2.08	0.55	4.84	1.24	1279.25	1.54
150194-04	47.47	0.85	13.67	8.81	14.16	7.04	1.99	0.56	4.74	1.26	1284.65	1.54
L82	47.19	0.90	14.20	8.18	13.28	7.17	2.81	0.58	4.99	1.20	1268.29	1.60
120194-04A	47.17	0.87	14.01	8.40	13.58	7.03	2.74	0.64	4.86	1.23	1276.44	1.64
120194-05	47.28	0.86	14.20	8.23	13.26	7.21	2.68	0.60	4.96	1.21	1267.39	1.57
120194-04C	47.20	0.85	13.93	8.37	13.51	7.11	2.76	0.62	4.94	1.21	1273.64	1.63
150194-01	47.10	0.86	14.25	8.27	13.38	7.21	2.73	0.56	4.94	1.21	1271.43	1.61
110194-02	47.29	0.81	12.65	9.68	15.56	6.50	1.94	0.57	4.34	1.38	1322.99	1.74
110194-01	47.38	0.92	13.03	9.13	14.81	6.35	2.43	0.80	4.49	1.34	1305.84	1.73
L84	47.03	0.89	13.18	9.25	14.90	6.38	2.59	0.61	4.49	1.34	1310.27	1.80
120194-01	46.54	0.80	13.94	8.78	14.17	7.20	2.54	0.62	4.72	1.27	1294.86	1.78
120194-02	46.49	0.83	14.01	8.81	14.25	7.09	2.45	0.63	4.74	1.26	1295.43	1.78
110194-03	47.18	0.90	13.56	8.65	13.94	6.84	2.64	0.82	4.77	1.26	1285.46	1.69
120194-03	47.38	0.68	14.01	7.65	12.39	8.93	2.19	0.37	5.59	1.07	1238.64	1.37
150194-07	47.23	0.83	13.48	8.90	14.40	6.64	2.63	0.69	4.56	1.32	1297.98	1.73
140194-01	47.42	0.67	13.98	7.65	12.31	8.90	2.26	0.37	5.62	1.07	1245.36	1.41
140194-04	47.30	0.69	13.99	7.81	12.55	8.81	2.27	0.36	5.43	1.10	1251.21	1.34
140194-5B	47.48	0.66	13.76	8.03	13.01	8.94	1.62	0.35	5.35	1.12	1248.52	1.33
140194-7B	47.58	0.66	13.68	8.00	12.90	8.99	1.64	0.38	5.37	1.12	1241.67	1.39
140194-07	47.35	0.68	14.06	7.71	12.47	8.88	2.20	0.35	5.51	1.09	1315.67	1.79
140194-11	46.58	0.79	13.74	9.33	15.10	6.79	1.96	0.60	4.44	1.35	1276.48	1.47
140194-10	47.74	0.77	13.84	8.64	13.92	7.05	1.91	0.59	4.81	1.25	1268.21	1.54
140194-09	47.57	0.79	14.09	8.32	13.40	6.93	2.60	0.66	4.94	1.21	1267.86	1.55
L16	47.55	0.80	14.03	8.25	13.32	7.10	2.63	0.72	4.91	1.22	1300.26	1.81
L17	46.49	0.85	14.24	8.89	14.36	6.68	2.54	0.69	4.60	1.30	1300.26	1.81
240394-6A	47.73	0.85	13.75	8.25	13.32	7.08	2.59	0.86	4.89	1.23	1267.73	1.54
L20	47.60	0.92	14.01	8.06	13.05	7.25	2.58	0.89	4.96	1.21	1262.07	1.53

Table A3.3.6 Continued

Sample	SiO₂	TiO₂	Al₂O₃	FeO	MgO	CaO	Na₂O	K₂O	H₂O	final mass relative to original melt mass	T	Gpa
111276-1	47.28	0.77	13.24	8.83	14.29	7.07	2.64	0.48	4.70	1.28	1292.97	1.68
121276-1	47.35	0.84	12.54	9.41	15.29	6.52	2.36	0.51	4.49	1.34	1315.03	1.75
121276-2	47.43	0.91	12.63	9.38	15.07	6.54	2.33	0.51	4.51	1.33	1309.51	1.71
121276-3	47.38	0.84	12.56	9.39	15.17	6.55	2.40	0.51	4.51	1.33	1312.35	1.74
121276-4	47.32	0.85	12.54	9.49	15.27	6.51	2.32	0.51	4.49	1.34	1314.95	1.75
LL 281079-1	48.22	0.58	14.29	8.05	13.02	7.48	2.33	0.52	4.86	1.23	1257.92	1.38
281079-1	47.30	0.77	12.58	9.58	15.40	6.64	2.30	0.41	4.36	1.38	1320.90	1.76
281079-2	47.88	0.85	11.36	10.13	16.42	5.64	2.34	0.52	4.19	1.43	1341.50	1.82
281079-6	45.95	0.93	8.84	12.25	19.76	5.06	2.02	0.46	3.68	1.63	1316.40	1.75
3381-2	47.31	0.77	13.27	8.91	14.36	7.25	2.28	0.43	4.72	1.27	1291.95	1.62
3381-3	47.31	0.76	13.34	8.87	14.35	7.24	2.27	0.43	4.72	1.27	1291.56	1.62
3381-4	47.47	0.81	13.10	8.95	14.48	7.03	2.33	0.47	4.65	1.29	1294.88	1.63
4381-1	48.23	0.72	11.35	10.10	16.36	5.35	2.37	0.64	4.23	1.42	1336.43	1.76
5381-1	47.00	0.75	13.83	8.65	14.02	7.57	2.34	0.41	4.74	1.26	1287.30	1.64
5381-2	47.76	0.81	12.64	9.14	14.82	6.65	2.37	0.53	4.58	1.31	1301.19	1.64
5381-3	47.41	0.77	13.42	8.73	14.17	7.24	2.34	0.46	4.77	1.26	1286.59	1.60
260483-1	47.40	0.76	13.17	8.95	14.39	7.12	2.34	0.44	4.72	1.27	1292.17	1.62
260483-2	47.32	0.79	13.17	8.98	14.49	7.08	2.33	0.44	4.67	1.28	1295.61	1.65
260483-4	47.33	0.71	13.34	8.94	14.49	7.03	2.39	0.41	4.65	1.29	1295.95	1.65
270483-1	47.07	0.84	11.65	10.17	16.45	5.94	2.49	0.45	4.25	1.41	1347.28	1.97
270483-2	47.58	0.76	13.28	9.03	14.61	6.85	2.37	0.38	4.51	1.33	1299.29	1.62
270483-4	48.04	0.80	12.11	9.59	15.55	5.77	2.51	0.58	4.38	1.37	1318.06	1.70
270483-7	47.48	0.88	11.35	10.20	16.52	5.67	2.47	0.50	4.23	1.42	1346.01	1.91

Appendix 4

TRACE ELEMENT RESULTS AND EXPERIMENTAL PARTITION COEFFICIENTS

A4.1.1 Trace Element Analysis of Planchon, Peteroa, and Azufre Samples at the Trace Evidence Analysis Facility (TEAF) in September of 2013. Data is reported in parts per million (ppm)

Sample	Rb	Sr	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Tb
PL3	22.21	580.75	122.28	4.67	0.91	268.04	13.74	32.08	4.28	17.93	4.07	1.16	0.57
PL4	21.21	545.65	115.10	4.47	0.91	327.04	14.63	33.91	4.53	19.24	4.36	1.25	0.61
PL6	20.09	566.90	116.83	4.53	0.89	267.25	13.74	31.58	4.24	17.85	4.06	1.16	0.56
PL7	19.73	499.30	108.31	3.91	0.99	284.05	11.87	27.81	3.79	16.19	3.87	1.08	0.56
PL8	26.58	475.11	116.30	4.32	1.16	266.97	12.91	29.66	3.88	16.19	3.68	1.03	0.52
PL12	24.99	560.79	118.95	4.60	1.06	296.47	14.00	32.13	4.24	17.89	4.05	1.14	0.55
PL14	28.29	500.46	127.98	4.79	1.39	365.78	15.65	35.62	4.74	19.91	4.42	1.19	0.62
PL23	21.92	545.19	115.55	4.47	0.94	315.50	14.35	33.00	4.41	18.78	4.20	1.21	0.59
PL27	17.90	536.04	103.51	3.78	0.39	239.77	11.85	27.84	3.79	16.29	3.87	1.12	0.57
PL28	16.45	527.56	105.65	3.74	0.61	244.08	12.14	28.28	3.89	16.66	3.95	1.12	0.58
PL30	20.39	553.61	107.23	3.92	1.04	312.30	13.38	30.87	4.14	17.86	4.13	1.18	0.59
PL33	39.41	481.88	167.41	6.40	1.97	397.80	19.32	44.11	5.85	24.08	5.41	1.33	0.74
PT9	42.52	442.95	178.73	6.63	2.05	325.20	21.36	48.30	6.46	26.83	6.09	1.43	0.83
PT13	40.59	527.98	146.25	5.85	2.22	305.31	17.95	40.40	5.32	21.86	4.90	1.28	0.67
PT16B	107.49	340.83	161.36	7.92	4.99	503.56	23.21	49.93	6.11	23.10	4.79	1.04	0.66
AZ1	111.88	282.37	363.75	10.58	4.22	513.06	34.63	75.74	9.87	39.30	8.85	1.68	1.24
AZ3	37.82	476.37	143.82	5.10	1.37	295.81	16.93	38.43	5.12	21.27	5.00	1.29	0.72
AZ9	104.45	244.08	366.29	10.39	2.87	550.25	34.72	75.14	9.92	39.74	8.86	1.79	1.22
AZ10	105.19	253.93	300.73	10.53	3.22	697.68	31.61	70.90	9.52	38.27	8.61	1.75	1.17
AZ11	108.09	257.64	383.11	10.65	3.18	557.49	37.23	79.20	10.36	41.58	9.25	1.83	1.32

*PL = Planchon, PT = Peteroa, AZ = Azufre

Table A.4.1.1 Continued

Sample	Gd	Dy	Ho	Er	Yb	Lu	Hf	Ta	Pb	Th	U
PL3	3.82	3.23	0.67	1.80	1.70	0.26	2.95	0.22	6.83	2.24	0.54
PL4	4.10	3.54	0.73	1.98	1.91	0.28	3.19	0.25	7.77	2.65	0.63
PL6	3.75	3.22	0.67	1.80	1.71	0.26	2.85	0.21	6.56	2.18	0.52
PL7	3.67	3.31	0.69	1.89	1.85	0.28	2.80	0.19	6.86	2.08	0.53
PL8	3.50	3.00	0.61	1.70	1.63	0.25	2.81	0.20	7.66	2.48	0.61
PL12	3.69	3.15	0.64	1.74	1.66	0.25	2.90	0.20	7.83	2.28	0.55
PL14	4.10	3.52	0.72	1.99	1.92	0.29	3.49	0.27	9.56	3.41	0.85
PL23	3.99	3.36	0.70	1.91	1.82	0.28	3.04	0.23	7.37	2.50	0.59
PL27	3.66	3.31	0.68	1.87	1.79	0.28	2.56	0.16	6.43	1.84	0.44
PL28	3.76	3.34	0.70	1.90	1.81	0.28	2.61	0.16	6.42	1.86	0.46
PL30	3.91	3.42	0.72	1.96	1.89	0.29	2.88	0.20	7.85	2.59	0.61
PL33	5.02	4.27	0.88	2.41	2.39	0.36	4.42	0.40	11.27	5.12	1.29
PT9	5.65	4.78	1.01	2.71	2.66	0.40	4.40	0.38	11.82	5.19	1.18
PT13	4.52	3.84	0.80	2.17	2.12	0.32	3.58	0.33	9.68	4.82	1.15
PT16B	4.46	3.91	0.82	2.29	2.40	0.36	4.55	0.59	22.38	13.99	3.35
AZ1	8.24	7.17	1.57	4.18	4.37	0.66	7.45	0.79	20.06	11.96	2.85
AZ3	4.73	4.36	0.92	2.52	2.54	0.38	3.57	0.28	9.01	3.79	0.83
AZ9	8.16	7.17	1.55	4.17	4.33	0.65	7.56	0.73	20.71	11.47	2.65
AZ10	7.86	6.86	1.48	4.00	4.22	0.63	7.44	0.69	20.25	11.74	2.67
AZ11	8.80	7.76	1.71	4.64	4.81	0.73	7.84	0.75	18.43	11.71	2.73

*PL = Planchon, PT = Peteroa, AZ = Azufre

A4.1.2 Trace Element Analysis of Planchon and Peteroa Samples at the Trace Evidence Analysis Facility (TEAF) in August of 2012.

Data is reported in parts per million (ppm)

Sample	Rb	Sr	Zr	Nb	Ba	La	Ce	Pr	Nd	Sm	Eu	Tb
PL 8	25.53	456.96	100.89	4.59	307.92	13.10	30.35	3.96	16.48	3.67	1.03	0.54
PL 9	25.21	453.36	100.10	4.55	302.00	12.73	29.78	3.86	16.21	3.57	1.01	0.52
PL 16	25.64	459.24	100.72	4.56	306.30	12.99	30.16	3.91	16.46	3.68	1.04	0.53
PL 17	27.32	456.04	88.17	4.26	308.03	12.27	28.72	3.74	15.78	3.59	1.02	0.54
PL 18	30.14	483.31	94.58	4.57	330.60	13.39	30.99	4.05	16.82	3.81	1.08	0.56
PL 19	32.72	530.09	100.37	4.86	349.30	14.24	32.69	4.21	17.46	3.95	1.11	0.58
PL 22	22.14	489.91	109.25	4.57	289.33	12.74	29.95	3.87	16.24	3.66	1.06	0.55
PL 24	19.84	529.19	91.95	4.74	285.02	12.94	30.36	4.00	16.93	3.82	1.11	0.56
PL 27	17.30	522.27	90.46	4.10	271.58	12.07	28.88	3.85	16.56	3.85	1.12	0.57
PL 29	18.46	510.88	89.24	4.17	272.29	12.23	29.31	3.89	16.69	3.87	1.15	0.59
PLII 5	39.84	431.35	132.46	6.65	358.85	20.40	46.21	6.02	25.45	5.60	1.36	0.79
PT 6	274.44	186.20	165.08	10.72	595.85	29.19	61.00	6.98	25.12	4.91	0.87	0.67
PT 7	118.14	338.56	325.42	9.61	546.92	27.59	59.70	7.22	28.19	5.84	1.25	0.80
PT 8	63.26	446.45	145.21	6.46	408.29	18.79	41.90	5.30	21.61	4.77	1.24	0.67
PT 9	43.47	439.66	111.06	5.15	342.81	15.02	34.39	4.43	18.43	4.12	1.15	0.60
PT 100	54.73	478.11	120.05	6.09	390.32	18.10	40.72	5.17	21.23	4.62	1.25	0.68
PT 101A	88.29	331.10	237.00	7.68	450.17	17.32	35.62	4.14	15.68	3.20	0.90	0.47
PT 102 A	97.52	368.10	226.41	7.85	452.51	21.78	47.75	5.82	22.95	4.80	1.12	0.67
PT 102B	85.97	346.08	205.21	7.09	415.21	19.58	43.34	5.34	21.18	4.47	1.05	0.62
PT 91A-2	84.22	336.19	185.95	7.39	429.53	19.32	41.78	5.03	19.32	4.00	0.94	0.56
PT 91B 3	58.33	422.72	119.89	6.04	375.53	17.48	39.58	4.99	20.43	4.44	1.18	0.66

*PL = Planchon, PT = Peteroa

Table A4.1.2 Continued

Sample	Gd	Dy	Ho	Er	Yb	Lu	Hf	Pb	Th	U
PL 8	3.49	3.28	0.64	1.87	1.63	0.25	2.87	7.60	2.46	0.62
PL 9	3.43	3.19	0.62	1.84	1.60	0.24	2.82	7.65	2.41	0.60
PL 16	3.49	3.24	0.63	1.87	1.64	0.25	2.89	7.52	2.45	0.62
PL 17	3.41	3.25	0.63	1.87	1.63	0.24	2.78	8.10	2.74	0.69
PL 18	3.63	3.37	0.66	1.93	1.73	0.26	2.96	8.49	3.09	0.77
PL 19	3.74	3.48	0.69	1.97	1.76	0.26	3.05	8.66	3.24	0.82
PL 22	3.50	3.28	0.64	1.89	1.65	0.25	2.76	6.77	2.06	0.52
PL 24	3.63	3.33	0.65	1.90	1.62	0.24	2.82	6.31	2.08	0.51
PL 27	3.79	3.53	0.71	2.01	1.82	0.27	2.62	6.35	1.81	0.45
PL 29	3.87	3.59	0.71	2.03	1.86	0.28	2.73	6.47	1.98	0.51
PLII 5	5.23	4.57	0.96	2.55	2.50	0.38	4.22	10.87	4.94	1.13
PT 6	4.17	4.11	0.87	2.49	2.73	0.41	5.48	22.60	21.27	5.21
PT 7	5.25	4.73	1.01	2.71	2.89	0.43	6.52	9.84	13.68	3.38
PT 8	4.45	4.05	0.85	2.33	2.31	0.34	4.16	11.64	7.45	1.85
PT 9	3.97	3.69	0.74	2.13	1.97	0.29	3.26	8.00	5.10	1.32
PT 100	4.43	4.02	0.84	2.29	2.20	0.33	3.87	10.43	6.47	1.64
PT 101A	2.86	3.00	0.58	1.82	1.73	0.26	4.28	16.63	10.14	2.50
PT 102 A	4.40	4.06	0.83	2.31	2.34	0.34	4.06	14.50	10.71	2.56
PT 102B	4.08	3.83	0.78	2.18	2.14	0.32	3.81	13.29	9.46	2.31
PT 91A-2	3.59	3.39	0.66	1.98	1.84	0.28	3.90	16.58	9.81	2.37
PT 91B 3	4.20	3.91	0.81	2.25	2.18	0.32	3.94	11.37	6.97	1.74

*PL = Planchon, PT = Peteroa

A4.1.3 Trace Element Analysis of Planchon Samples at the Trace Evidence Analysis Facility (TEAF) in March of 2012. Data is reported in parts per million (ppm)

Sample	Rb	Sr	Zr	Nb	Ba	La	Ce	Pr	Nd	Sm	Eu	Tb
PL-2	22.37	621.39	113.27	5.33	270.32	14.08	33.29	4.38	18.81	4.22	1.26	0.61
PL-13	25.34	579.29	123.98	5.75	295.18	15.13	35.26	4.57	19.21	4.23	1.22	0.61
PL-10	32.07	553.64	125.00	5.60	302.92	15.09	35.09	4.50	19.01	4.19	1.18	0.62
PL-11	34.74	569.20	129.83	5.88	313.52	15.70	36.38	4.65	19.39	4.27	1.21	0.64
PL-15	26.14	513.53	123.21	5.62	280.55	14.10	33.32	4.29	17.77	3.94	1.11	0.59
PL-20	22.28	553.99	124.56	5.93	268.79	14.89	35.38	4.62	19.76	4.40	1.28	0.65
PL-25	23.84	655.67	132.60	6.49	302.81	17.65	41.13	5.33	22.75	4.96	1.41	0.70
PL-26	60.81	555.82	192.35	9.25	368.45	25.89	58.92	7.45	31.35	6.62	1.58	0.92
PL-18	33.87	593.51	133.63	6.09	327.90	16.22	37.64	4.85	20.38	4.49	1.29	0.67
PL-34	44.47	548.02	174.83	8.39	342.84	21.86	50.42	6.43	27.27	5.82	1.48	0.82
PL-32	21.03	555.43	124.92	5.56	269.55	14.06	33.92	4.48	19.17	4.41	1.26	0.68
PL-35	38.33	538.61	165.92	7.67	334.93	20.25	46.37	5.92	25.13	5.42	1.40	0.79

Sample	Gd	Dy	Ho	Er	Yb	Lu	Hf	Pb	Th	U
PL-2	4.02	3.65	0.70	2.01	1.82	0.26	2.98	8.08	2.29	0.60
PL-13	3.96	3.56	0.66	1.92	1.73	0.24	3.25	8.91	2.44	0.63
PL-10	3.99	3.64	0.70	2.01	1.86	0.27	3.31	9.95	3.27	0.86
PL-11	4.05	3.71	0.70	2.04	1.88	0.27	3.41	10.22	3.59	0.94
PL-15	3.73	3.47	0.63	1.88	1.71	0.24	3.14	8.98	2.61	0.69
PL-20	4.24	3.87	0.75	2.18	1.93	0.29	3.31	8.05	2.38	0.63
PL-25	4.67	4.12	0.79	2.24	1.99	0.29	3.52	9.19	2.98	0.77
PL-26	6.25	5.41	1.13	3.09	2.84	0.46	5.46	13.86	7.67	1.98
PL-18	4.30	3.94	0.76	2.17	2.00	0.29	3.55	10.39	3.61	0.93
PL-34	5.55	4.90	1.00	2.79	2.58	0.40	4.86	11.70	5.22	1.34
PL-32	4.27	4.06	0.78	2.28	2.08	0.30	3.28	8.48	2.15	0.60
PL-35	5.27	4.72	0.97	2.70	2.49	0.39	4.55	11.40	4.73	1.27

A4.1.4 Trace Element Analysis of Basalts from Major Volcanic Centers of the SVZ at the Trace Evidence Analysis Facility (TEAF).

Data is reported in parts per million (ppm)

Sample	Rb	Sr	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Tb
Maipo													
C662-L72	38.34	576.70	120.24	7.23	1.38	215.74	19.03	56.64	5.02	19.71	3.97	1.14	0.48
C663-L73	37.10	558.58	104.44	7.00	1.35	212.30	18.18	35.33	4.76	18.62	3.73	1.08	0.47
C644-L74	25.32	549.39	93.09	5.53	1.62	189.71	13.70	29.30	4.00	16.32	3.53	1.06	0.47
Laguna Del Maule													
LM-4	22.87	558.13	97.87	6.49	0.67	206.32	16.49	33.53	4.53	18.19	3.80	1.12	0.52
LM-5	32.35	629.54	105.13	7.07	0.98	222.44	19.72	38.46	5.54	22.69	4.79	1.40	0.62
LM-6	25.69	621.81	98.92	6.59	0.68	209.26	16.85	34.65	4.90	19.85	4.20	1.26	0.55
LM-7	25.02	571.13	88.41	5.76	0.81	188.73	14.56	30.35	4.05	16.30	3.34	1.00	0.45
LM-8	26.57	681.25	101.78	6.77	0.86	216.05	18.30	36.53	5.20	21.29	4.43	1.33	0.58
FM-94	19.46	549.36	86.74	4.84	0.54	185.17	13.88	28.65	4.00	16.52	3.57	1.11	0.51
FM-49	31.66	520.19	92.40	5.26	1.03	197.22	15.45	31.90	4.48	18.53	4.14	1.24	0.56
Descabezado													
050283-6	24.10	559.88	77.44	3.49	1.10	189.80	10.61	24.85	3.34	14.52	3.48	1.14	0.55
060283-9	18.51	624.59	77.36	3.76	0.93	188.21	9.84	25.23	3.38	14.86	3.61	1.11	0.53
060283-1	33.11	600.13	92.71	4.87	1.51	196.86	13.81	30.04	4.10	17.05	3.81	1.15	0.55
060283-2	25.81	626.51	84.67	4.51	1.13	185.95	12.97	28.56	3.92	16.38	3.71	1.17	0.54
Nevados De Longavi													
MG159	20.09	625.94	169.09	8.70	0.61	216.48	22.88	44.05	6.39	25.76	4.98	1.43	0.60
MG161	20.16	671.33	150.04	8.37	0.63	208.23	21.78	41.28	5.91	23.85	4.77	1.37	0.57
MG179	18.78	722.60	100.85	4.20	1.48	220.27	12.03	27.51	3.76	15.87	3.47	1.09	0.44
Nevados De Chillan													
73765-L3	32.24	468.34	126.04	4.91	0.98	195.88	14.27	31.55	4.44	18.87	4.30	1.16	0.64
16C	32.63	416.70	101.11	4.65	1.98	185.67	11.56	26.12	3.44	14.15	3.21	0.90	0.49
16D	32.01	488.22	115.79	4.45	0.91	183.55	12.50	27.77	4.09	17.49	4.08	1.12	0.63
16F	36.58	519.63	123.00	4.98	2.41	195.55	14.07	30.73	4.30	18.28	4.31	1.18	0.66

Table A4.1.4 Continued

Sample	Gd	Dy	Ho	Er	Yb	Lu	Hf	Ta	Pb	Th	U
Maipo											
C662-L72	3.27	2.84	0.49	1.54	1.14	0.16	3.17	0.33	8.36	4.82	1.46
C663-L73	3.16	2.74	0.48	1.48	1.05	0.16	2.97	0.30	7.91	4.67	1.42
C644-L74	3.13	2.81	0.51	1.59	1.23	0.19	2.70	0.26	8.13	2.47	1.13
Laguna Del Maule											
LM-4	3.35	3.06	0.57	1.68	1.33	0.20	2.96	0.32	6.37	4.27	1.28
LM-5	4.16	3.58	0.67	1.91	1.59	0.24	3.41	0.39	8.90	4.83	1.45
LM-6	3.57	3.20	0.60	1.73	1.43	0.21	3.25	0.35	6.90	3.84	1.26
LM-7	2.89	2.70	0.48	1.51	1.11	0.17	2.46	0.24	6.15	3.22	1.01
LM-8	3.78	3.36	0.63	1.82	1.49	0.22	3.24	0.36	6.93	4.15	1.25
FM-94	3.24	3.10	0.58	1.75	1.46	0.22	2.55	7.07	6.40	3.02	0.91
FM-49	3.62	3.32	0.66	1.85	1.62	0.24	2.86	3.70	7.74	3.88	1.22
Descabezado											
050283-6	3.48	3.37	0.68	1.95	1.75	0.27	2.56	0.11	8.48	2.52	0.86
060283-9	3.30	3.22	0.60	1.83	1.45	0.21	2.32	0.09	6.93	1.76	0.65
060283-1	3.48	3.28	0.63	1.86	1.61	0.24	3.00	0.21	9.82	4.03	1.38
060283-2	3.44	3.26	0.62	1.80	1.53	0.23	2.68	0.18	8.11	3.13	1.07
Nevados De Longavi											
MG159	4.15	3.27	0.59	1.72	1.36	0.20	3.52	0.41	9.91	2.70	0.86
MG161	3.94	3.23	0.61	1.76	1.40	0.21	3.48	0.40	8.30	2.89	0.89
MG179	2.86	2.57	0.44	1.44	1.02	0.15	2.86	0.14	13.10	1.54	0.61
Nevados De Chillan											
73765-L3	4.11	3.82	0.77	2.15	1.97	0.29	3.77	0.22	8.21	3.64	1.24
16C	3.05	2.99	0.58	1.72	1.49	0.22	3.15	15.75	10.21	3.54	1.18
16D	3.97	3.78	0.76	2.13	1.88	0.28	3.58	10.18	7.06	3.40	1.17
16F	4.25	3.96	0.79	2.18	1.98	0.29	3.61	13.60	10.82	3.36	1.13

Table A4.1.4 Continued

Sample	Rb	Sr	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Tb
Antuco													
511771-L41	17.97	463.39	80.21	3.62	0.59	173.36	10.43	25.68	3.61	15.97	3.99	1.34	0.67
511773-L42	14.91	492.53	65.20	3.15	0.88	146.74	8.34	21.90	2.92	12.68	3.06	1.00	0.49
511775-L43	20.44	482.77	74.67	3.61	1.09	163.71	9.74	24.07	3.13	13.10	2.98	0.92	0.46
511776-L44	18.89	532.47	70.52	3.31	0.98	158.31	9.02	22.56	2.95	12.65	3.01	0.97	0.48
310183-2	27.91	507.19	98.52	3.98	0.71	179.60	11.93	27.69	3.88	16.74	3.96	1.19	0.62
310183-3	28.57	368.34	95.48	3.90	1.16	172.55	10.03	24.97	3.32	14.32	3.48	0.95	0.58
310183-8	47.20	430.88	130.96	4.76	1.78	198.86	15.16	32.82	4.86	21.02	5.08	1.31	0.80
Callequen													
280483-2	54.45	604.25	193.64	6.04	3.66	228.20	21.49	42.97	6.57	28.37	6.44	1.60	0.91
280483-1	23.58	592.09	80.51	3.49	1.55	171.61	11.36	26.55	3.75	16.36	3.93	1.15	0.57
290483-3	43.78	603.74	163.57	5.24	2.93	206.58	17.10	35.95	5.30	22.50	5.29	1.37	0.75
290483-1	16.56	586.93	78.11	3.57	1.03	175.49	11.41	26.81	3.62	15.69	3.74	1.14	0.58
290483-2	37.12	515.40	159.63	5.41	2.42	202.51	16.94	35.57	5.23	22.24	5.19	1.33	0.76

Sample	Gd	Dy	Ho	Er	Yb	Lu	Hf	Ta	Pb	Th	U
Antuco											
511771-L41	4.19	4.26	0.92	2.51	2.55	0.39	2.69	0.12	6.06	1.85	0.68
511773-L42	2.99	3.03	0.61	1.78	1.55	0.24	2.00	0.09	5.37	1.41	0.51
511775-L43	2.85	2.87	0.54	1.69	1.40	0.21	2.18	0.10	5.92	1.98	0.65
511776-L44	2.92	2.95	0.55	1.70	1.37	0.21	2.03	0.10	6.12	1.83	0.55
310183-2	3.84	3.83	0.78	2.20	2.10	0.31	2.91	0.15	6.41	2.77	0.84
310183-3	3.51	3.61	0.76	2.17	2.08	0.31	3.04	0.12	22.73	2.14	1.07
310183-8	4.99	4.78	1.04	2.75	2.89	0.43	4.06	0.23	9.33	4.16	1.41
Callequen											
280483-2	6.07	5.20	1.12	2.88	2.96	0.44	4.95	0.31	15.87	8.04	2.71
280483-1	3.53	3.35	0.67	1.93	1.80	0.27	2.58	0.09	9.33	3.37	1.12
290483-3	4.91	4.34	0.88	2.40	2.33	0.35	4.00	0.24	14.08	6.48	2.18
290483-1	3.66	3.54	0.72	2.07	1.88	0.28	2.23	0.07	8.40	3.12	1.00
290483-2	4.94	4.51	0.95	2.52	2.44	0.36	3.78	0.21	12.52	5.22	1.73

A4.2 Partition Coefficients used in selected Trace Elements

Mineral Phase	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Basalt-CPX	0.0536	0.0858	0.112	0.1873	0.291	0.41	0.41	0.42
Basalt-Garnet	0.0016	0.01	0.054	0.06	0.5	0.8	1.2	2.1
Basalt-Plag	0.065	0.049	0.049	0.04	0.044	0.156	0.03	0.029
Basalt-Olivine	0.0001	0.0001	0.0002	0.0003	0.0011	0.001	0.0029	0.0015
Basalt OPX	0.0008	0.0016	0.0032	0.0056	0.015	0.03	0.034	0.054
Basalt -Spinel	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Basalt Amphibole	0.17	0.26	0.35	0.44	0.76	0.88	0.86	0.83

Mineral Phase	Dy	Ho	Er	Tm	Yb	Lu	Y	Sr	Sc
Basalt-CPX	0.442	0.44	0.458	0.255	0.432	0.433	0.647	0.1283	1.31
Basalt-Garnet	3	4	4.6	3	6.6	6.9	3.1	0.0011	2.62
Basalt-Plag	0.0293	0.02	0.024	0.049	0.03	0.0069	0.023	1.504	0.072
Basalt-Olivine	0.002	0.013	0.0025	0.003	0.01	0.051	0.0036	0.00019	0.22
Basalt OPX	0.077	0.1	0.12	0.24	0.22	0.22	0.095	0.0012	0.016
Basalt -Spinel	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.003	0.36
Basalt Amphibole	0.78	0.2	0.68	0.64	0.59	0.51	0.5	0.12	2.18

References for partition Coefficients

Basalt-Clinopyroxene: Hart and Dunn 1993. **Basalt-Garnet:** Green et al. 2000. **Basalt-Plagioclase:** Bindeman et al. 1998. **Basalt-Olivine:** Neilson et al. 1992. **Basalt-Orthopyroxene:** Green et al. 2000; Salter and Longhi 1999. **Basalt-Spinel:** Mckenzie & O'nions 1991. **Basalt-Amphibole:** Mckenzie & O'nions 1999.

A4.3 Calculated Primary Magmatic Major Element Compositions for Selected Centers of the SVZ (wt. %)

SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O
Casimiro								
50.78	0.88	13.93	7.72	0.11	12.49	6.03	3.04	1.20
50.49	0.89	14.06	7.76	0.10	12.54	6.04	3.10	1.20
50.26	0.80	14.32	7.64	0.11	12.36	6.70	2.93	0.94
Laguna Del Maule								
47.82	0.88	11.88	10.59	0.08	17.12	5.16	2.43	0.75
46.45	0.81	13.46	10.25	0.08	16.59	5.73	2.54	0.63
Descabezado								
49.30	0.79	14.08	8.33	0.12	13.45	6.72	2.79	0.65
Nevados De Chillan								
51.21	0.86	13.70	7.98	0.09	12.96	5.75	2.81	0.85
Antuco								
48.04	0.71	13.79	9.09	0.12	14.76	6.87	2.60	0.51
49.20	0.81	14.46	8.16	0.15	13.12	6.92	2.75	0.62
Osorno								
47.80	0.61	15.17	8.41	0.11	13.53	8.19	2.20	0.34
Calbuco								
50.55	0.66	13.75	8.52	0.12	13.78	5.97	2.62	0.45
Villarrica								
48.61	0.88	12.93	8.92	0.12	14.45	7.35	2.46	0.50
SEC's								
48.12	0.94	13.24	9.28	0.12	15.04	6.45	2.47	0.81
48.16	0.86	14.06	8.76	0.13	14.20	7.34	2.11	0.56

A4.3.1 Calculated Primary Magmatic REE compositions of Selected Centers of the SVZ (ppm)

Center	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Casimiro	15.67	29.09	4.13	16.23	0.00	3.27	0.94	2.70	0.40	2.34	0.41	1.27		0.94	0.14
	14.97	29.08	3.92	15.33	0.00	3.07	0.89	2.60	0.39	2.26	0.39	1.22		0.87	0.13
	11.56	24.73	3.37	13.77	0.00	2.98	0.89	2.64	0.40	2.37	0.43	1.34		1.04	0.16
Laguna Del Maule	11.23	22.84	3.09	12.39	0.00	2.59	0.76	2.28	0.36	2.08	0.39	1.15		0.91	0.14
	9.88	20.41	2.85	11.77	0.00	2.54	0.79	2.31	0.36	2.21	0.42	1.25		1.04	0.16
Descabezado Grande	7.86	20.16	2.70	11.87	0.00	2.88	0.89	2.64	0.42	2.57	0.48	1.46		1.16	0.17
Nevados De Chillan	9.89	21.96	3.23	13.84	0.00	3.23	0.89	3.14	0.50	2.99	0.61	1.68		1.49	0.22
Antuco	6.53	17.15	2.29	9.93	0.00	2.40	0.78	2.34	0.39	2.37	0.48	1.39		1.22	0.19
	7.94	19.62	2.55	10.68	0.00	2.43	0.75	2.32	0.38	2.34	0.44	1.37		1.14	0.17
Osorno	4.17	10.44		6.67	0.00	1.81	0.70		0.42					1.27	0.20
Calbuco	4.97	13.97		8.91	0.00	2.40	0.79		0.40					1.57	0.23
Villarrica	6.36	16.61		11.23		2.99	0.90		0.55					1.89	0.29
SEC's	10.95	0.00	3.23	14.44	0.00	3.20	1.01	3.12	0.46	2.67	0.54	1.42		1.37	0.21
	19.99	0.00	5.11	21.19	0.00	4.47	1.30	4.30	0.63	3.63	0.73	1.94		1.87	0.29

A4.4.1 Solution ICP-MS Standard Analysis at TEAF on 3/5/2012

Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd 147	Sm 149	Eu 151
W-2	20.29	195.29	84.28	8.23	161.53	10.42	23.99	3.05	12.84	3.23	1.06
W-2 Duplicate	19.26	187.17	87.10	7.79	155.52	9.87	22.95	2.91	12.18	3.05	1.00
W-2 (Reference Value)	21	190	100	7.9	170	10	23	2.919	13	3.3	1
MEAN	19.78	191.23	85.69	8.01	158.52	10.15	23.47	2.98	12.51	3.14	1.03
STDV	0.73	5.75	2.00	0.31	4.25	0.39	0.74	0.10	0.47	0.13	0.05
%RSD	3.67	3.00	2.33	3.85	2.68	3.88	3.15	3.46	3.73	4.08	4.58
% BIAS	-5.83	0.65	-14.31	1.40	-6.75	1.45	2.03	2.02	-3.74	-4.97	3.14
Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd 147	Sm 149	Eu 151
BHVO-2	9.62	376.37	150.50	18.24	135.20	14.86	37.38	5.15	24.00	5.97	1.98
BHVO-2 (Reference Value)	9.8	389	172	18	130	15	38	5.351	25	6.2	2.036
% BIAS	-1.81	-3.25	-12.50	1.36	4.00	-0.95	-1.62	-3.79	-3.98	-3.67	-2.85
Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd 147	Sm 149	Eu 151
AGV-2	68.55	663.75	249.74	14.57	1140.37	38.01	69.57	8.05	30.67	5.53	1.60
AGV-2 (Reference Value)	68.6	658	230	15	1140	38	68	8.3	30	5.7	1.54
% BIAS	-0.08	0.87	8.58	-2.88	0.03	0.03	2.31	-3.06	2.22	-3.03	4.04
Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd 147	Sm 149	Eu 151
DNC-1	4.44	245.11	28.89	2.61	21.16	6.76	13.42	3.11	2.78	1.36	1.59
DNC-1 (Reference Value)	4.5	144	38	3	118	3.6	10.6	1.3	5.2	1.38	0.59
% BIAS	-1.29	70.21	-23.97	-12.99	-82.07	87.91	26.57	138.91	-46.56	-1.15	170.00

A4.4.1 Continued

Element	Tb 159	Gd 160	Dy 163	Ho 165	Er 166	Yb 172	Lu 175	Hf 178	Pb 207	Th 232	U 238
W-2	0.61	3.63	3.91	0.81	2.27	2.05	0.31	2.23	8.41	2.12	0.51
W-2 Duplicate	0.58	3.46	3.69	0.76	2.10	1.92	0.29	2.09	8.08	2.04	0.49
W-2 (Reference Value)	0.63	3.692	3.6	0.76	2.5	2.1	0.33	2.6	9.3	2.4	0.53
MEAN	0.60	3.54	3.80	0.78	2.18	1.99	0.30	2.16	8.25	2.08	0.50
STDV	0.02	0.12	0.16	0.03	0.12	0.09	0.01	0.10	0.23	0.05	0.01
%RSD	3.77	3.33	4.12	4.25	5.36	4.46	4.42	4.52	2.83	2.60	2.69
% BIAS	-5.13	-4.05	5.52	2.85	-12.60	-5.44	-9.33	-16.82	-11.30	-13.32	-6.20
Element	Tb 159	Gd 160	Dy 163	Ho 165	Er 166	Yb 172	Lu 175	Hf 178	Pb 207	Th 232	U 238
BHVO-2	0.90	6.17	5.26	1.03	2.54	1.96	0.27	4.33	2.58	1.21	0.45
BHVO-2 (Reference Value)	0.9	6.3	5.3	1.04	2.5	2	0.28	4.1		1.2	0.404
% BIAS	0.10	-2.10	-0.83	-0.49	1.77	-2.18	-2.62	5.59		0.70	10.29
Element	Tb 159	Gd 160	Dy 163	Ho 165	Er 166	Yb 172	Lu 175	Hf 178	Pb 207	Th 232	U 238
AGV-2	0.65	4.67	3.55	0.66	1.86	1.62	0.23	5.05	13.40	6.13	1.88
AGV-2 (Reference Value)	0.64	4.531	3.6	0.71	1.79	1.6	0.25	5.08	13	6.1	1.88
% BIAS	2.13	3.15	-1.51	-6.37	3.78	0.98	-7.43	-0.52	3.07	0.43	-0.07
Element	Tb 159	Gd 160	Dy 163	Ho 165	Er 166	Yb 172	Lu 175	Hf 178	Pb 207	Th 232	U 238
DNC-1	1.89	2.01	2.72	2.59	2.70	2.16	1.81	1.79	7.37	1.49	1.02
DNC-1 (Reference Value)	0.41	2	3	0.62	2	2	0.32	1.01	6.3	0.2	0.1
% BIAS	361.31	0.36	-9.36	318.04	35.10	8.01	464.21	77.49	16.96	646.49	921.32

A4.4.2 Solution ICP-MS Standard Analysis at TEAF on 8/32012

Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147	Sm 149
BCR 2	55.73	831.61	251.96	16.07	265.95	43.42	83.68	13.93	9.91	2.39	2.21
BCR2	45.39	320.65	188.03	12.19	667.30	24.21	51.30	6.54	27.03	6.34	6.36
BCR 2	50.16	353.23	295.30	13.29	704.38	26.67	56.27	7.09	29.71	6.84	6.81
BCR 2	46.18	327.97	160.87	12.05	660.52	24.65	52.43	6.62	27.88	6.50	6.51
BCR 2 (Reference Value)	48	346	188	10.9	683	25	53	6.8	28	6.7	6.7
MEAN	49.37	458.36	224.04	13.40	574.54	29.74	60.92	8.54	23.63	5.52	5.47
STDV	4.73	249.22	60.95	1.87	206.63	9.19	15.32	3.60	9.22	2.10	2.18
%RSD	9.58	54.37	27.20	13.93	35.96	30.89	25.15	42.08	39.00	38.03	39.93
% BIAS	2.84	32.48	19.17	22.92	-15.88	18.95	14.95	25.66	-15.61	-17.66	-18.34
Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147	Sm 149
DNC1	4.17	144.27	41.29	2.47	109.24	3.21	9.06	1.22	4.88	1.43	1.44
DNC 1	4.28	150.48	42.10	2.52	114.87	3.46	9.54	1.29	5.16	1.50	1.48
DNC1	4.29	148.78	33.22	2.49	110.30	3.47	9.48	1.24	4.94	1.38	1.38
DNC1	4.11	140.16	38.29	2.38	104.95	3.26	9.04	1.20	4.77	1.37	1.35
DNC-1 (Reference Value)	4.5	145	38	3	118	3.6	10.6	1.3	4.9	1.38	1.38
MEAN	4.21	145.92	38.73	2.47	109.84	3.35	9.28	1.24	4.94	1.42	1.41
STDV	0.09	4.65	4.02	0.06	4.07	0.13	0.27	0.04	0.17	0.06	0.06
%RSD	2.09	3.19	10.37	2.54	3.71	3.96	2.86	3.05	3.34	4.15	4.00
% BIAS	-6.41	0.64	1.91	-17.78	-6.92	-6.88	-12.43	-4.80	0.74	2.81	2.38

A4.4.2 Continued

Element	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172	Yb 174
BCR 2	2.33	2.55	2.56	2.41	3.16	2.65	3.26	2.71	2.69	1.83	2.47
BCR2	1.87	1.90	6.53	1.00	6.54	5.88	5.83	1.29	3.26	3.39	3.39
BCR 2	2.04	2.06	6.97	1.04	6.96	6.21	6.23	1.37	3.41	3.59	3.59
BCR 2	1.93	1.96	6.61	0.99	6.63	6.00	5.97	1.32	3.29	3.41	3.41
BCR 2 (Reference Value)	2.0	2	6.8	1.07	6.8	6.0	6.0	1.33	3.3	3.5	3.5
MEAN	2.04	2.12	5.67	1.36	5.82	5.19	5.32	1.67	3.16	3.05	3.22
STDV	0.21	0.29	2.08	0.70	1.78	1.69	1.39	0.69	0.32	0.82	0.51
%RSD	10.07	13.92	36.72	51.75	30.59	32.67	26.06	41.33	10.13	26.97	15.81
% BIAS	2.16	5.89	-16.67	27.07	-14.37	-13.56	-11.28	25.69	-4.17	-12.77	-8.11
Element	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172	Yb 174
DNC1	0.57	0.57	1.98	0.41	2.02	2.93	2.96	0.63	1.97	1.90	1.90
DNC 1	0.61	0.59	2.02	0.42	2.09	3.03	3.10	0.66	2.03	2.01	2.01
DNC1	0.57	0.56	1.93	0.40	2.00	2.91	2.95	0.64	1.96	1.91	1.95
DNC1	0.55	0.54	1.88	0.39	1.94	2.86	2.91	0.62	1.93	1.88	1.85
DNC-1 (Reference Value)	0.59	0.59	2	0.41	2	3	3	0.62	2	2	2
MEAN	0.57	0.56	1.95	0.41	2.01	2.93	2.98	0.64	1.97	1.93	1.93
STDV	0.02	0.02	0.06	0.01	0.06	0.07	0.08	0.02	0.04	0.06	0.07
%RSD	4.24	3.74	3.25	2.81	3.10	2.41	2.68	3.06	2.07	3.16	3.52
% BIAS	-2.78	-4.72	-2.42	-0.93	0.57	-2.26	-0.69	2.76	-1.39	-3.71	-3.69

A4.4.2 Continued

Element	Lu175	Hf 178	Pb 206	Pb 207	Pb 208	Th 232	U 238
BCR 2	1.38	2.96	4.17	3.57	8.14	8.10	2.53
BCR2	0.50	4.54	9.88	9.86	9.91	5.62	1.55
BCR 2	0.53	4.92	10.92	10.93	10.83	6.21	1.74
BCR 2	0.50	4.73	10.35	10.43	10.26	5.92	1.65
BCR 2 (Reference Value)	0.51	4.8	11	11	11	6.2	1.69
MEAN	0.73	4.29	8.83	8.70	9.79	6.46	1.87
STDV	0.44	0.90	3.14	3.44	1.16	1.12	0.45
%RSD	60.06	20.93	35.54	39.61	11.85	17.27	24.13
% BIAS	42.57	-10.66	-19.73	-20.95	-11.04	4.21	10.48
Element	Lu175	Hf 178	Pb 206	Pb 207	Pb 208	Th 232	U 238
DNC1	0.29	1.10	6.17	6.16	6.13	0.22	0.08
DNC 1	0.30	1.15	6.55	6.55	6.50	0.23	0.08
DNC1	0.29	1.12	6.39	6.43	6.20	0.23	0.09
DNC1	0.29	1.09	6.19	6.22	5.98	0.22	0.09
DNC-1 (Reference Value)	0.32	1.01	6.3	6.3	6.3	0.2	0.1
MEAN	0.29	1.11	6.32	6.34	6.20	0.22	0.08
STDV	0.01	0.03	0.18	0.18	0.22	0.01	0.00
%RSD	2.65	2.45	2.88	2.85	3.53	2.77	1.60
% BIAS	-8.29	10.08	0.36	0.60	-1.55	12.26	-15.26

A4.4.2 Continued

Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147	Sm 149
AGV2	71.80	683.94	299.46	15.05	2077.82	38.92	70.12	8.12	30.12	5.50	5.44
AGV2	68.50	662.53	287.65	14.17	2027.97	37.22	67.57	7.78	29.31	5.29	5.33
AGV 2	70.63	679.59	365.93	14.65	2173.23	38.56	69.84	8.07	30.45	5.54	5.57
AGV2	66.13	639.36	341.69	13.55	2088.52	36.49	66.74	7.77	29.29	5.34	5.33
AGV-2 (Reference Value)	68.6	658	230	15	1140	37.92	69.61	7.957	30.42	5.46	5.46
MEAN	69.26	666.36	323.68	14.36	2091.89	37.80	68.57	7.93	29.79	5.42	5.42
STDV	2.50	20.23	36.49	0.65	60.31	1.14	1.67	0.18	0.58	0.12	0.11
%RSD	3.61	3.04	11.27	4.50	2.88	3.01	2.44	2.33	1.96	2.22	2.11
% BIAS	0.97	1.27	40.73	-4.30	83.50	-0.32	-1.50	-0.29	-2.07	-0.77	-0.72
Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147	Sm 149
W2	23.34	218.53	99.85	8.95	245.93	14.97	33.57	4.28	17.62	4.45	4.40
W2	20.59	199.29	105.00	7.95	174.29	10.37	23.90	3.05	12.79	3.24	3.23
W2	21.00	204.29	98.94	8.03	177.86	10.57	24.45	3.10	13.02	3.29	3.29
W2	19.79	191.31	109.52	7.48	170.21	10.08	23.29	2.98	12.49	3.16	3.18
W-2 (Reference Value)	20	194	100	7.9	170	10.23	22.8	2.919	12.71	3.234	3.234
MEAN	21.18	203.36	103.33	8.10	192.07	11.50	26.30	3.35	13.98	3.54	3.53
STDV	1.53	11.44	4.91	0.61	36.04	2.32	4.87	0.62	2.44	0.61	0.59
%RSD	7.20	5.63	4.76	7.56	18.76	20.21	18.52	18.50	17.43	17.20	16.65
% BIAS	5.90	4.82	3.33	2.58	12.98	12.39	15.36	14.88	9.99	9.34	9.05

A4.4.2 Continued

Element	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172	Yb 174
AGV2	1.59	1.65	4.88	0.66	4.66	3.66	3.63	0.69	1.96	1.65	1.64
AGV2	1.56	1.60	4.77	0.65	4.54	3.62	3.56	0.67	1.94	1.62	1.62
AGV 2	1.60	1.68	5.02	0.65	4.70	3.68	3.63	0.69	1.95	1.64	1.66
AGV2	1.58	1.65	4.84	0.64	4.58	3.63	3.50	0.67	1.91	1.60	1.60
AGV-2 (Reference Value)	1.51	1.51	4.531	0.64	4.531	3.496	3.496	0.71	1.829	1.612	1.612
MEAN	1.58	1.64	4.88	0.65	4.62	3.65	3.58	0.68	1.94	1.63	1.63
STDV	0.02	0.04	0.10	0.01	0.07	0.03	0.06	0.01	0.02	0.02	0.03
%RSD	1.10	2.20	2.11	0.93	1.57	0.74	1.74	1.63	1.17	1.40	1.68
% BIAS	4.88	8.93	7.68	1.35	1.94	4.34	2.44	-4.15	5.98	1.00	1.01
Element	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172	Yb 174
W2	1.45	1.43	4.95	0.80	4.94	4.88	4.87	1.04	2.69	2.64	2.65
W2	1.08	1.05	3.61	0.62	3.71	3.85	3.86	0.81	2.23	2.05	2.05
W2	1.09	1.07	3.61	0.61	3.73	3.89	3.93	0.82	2.25	2.08	2.07
W2	1.05	1.02	3.52	0.60	3.58	3.81	3.84	0.78	2.19	2.02	2.00
W-2 (Reference Value)	1.072	1.072	3.692	0.63	3.692	3.825	3.825	0.76	2.248	2.02	2.02
MEAN	1.17	1.14	3.92	0.66	3.99	4.11	4.13	0.86	2.34	2.20	2.19
STDV	0.19	0.19	0.69	0.10	0.64	0.52	0.50	0.12	0.24	0.29	0.30
%RSD	16.41	16.72	17.51	14.48	15.94	12.59	12.04	13.71	10.05	13.38	13.90
% BIAS	8.76	6.61	6.21	4.50	8.10	7.41	7.88	13.39	4.06	8.78	8.57

A4.4.2 Continued

Element	Lu175	Hf 178	Pb 206	Pb 207	Pb 208	Th 232	U 238
AGV2	0.25	4.99	13.83	13.71	13.72	6.18	1.88
AGV2	0.24	4.91	13.79	13.80	13.73	6.11	1.85
AGV 2	0.25	5.04	14.28	14.12	13.99	6.36	1.91
AGV2	0.24	4.92	13.70	13.75	13.44	6.15	1.85
AGV-2 (Reference Value)	0.2366	5.08	13	13	13	6.1	1.88
MEAN	0.24	4.96	13.90	13.85	13.72	6.20	1.87
STDV	0.00	0.06	0.26	0.18	0.23	0.11	0.03
%RSD	1.65	1.26	1.87	1.33	1.64	1.83	1.43
% BIAS	2.50	-2.27	6.92	6.50	5.53	1.65	-0.49
Element	Lu175	Hf 178	Pb 206	Pb 207	Pb 208	Th 232	U 238
W2	0.38	2.92	9.60	9.64	9.71	2.56	0.59
W2	0.30	2.38	8.19	8.16	8.17	2.15	0.51
W2	0.31	2.38	8.25	8.19	8.04	2.19	0.52
W2	0.29	2.34	7.91	7.96	7.77	2.11	0.50
W-2 (Reference Value)	0.2937	2.6	9.3	9.3	9.3	2.2	0.53
MEAN	0.32	2.51	8.49	8.49	8.42	2.25	0.53
STDV	0.04	0.28	0.76	0.78	0.88	0.21	0.04
%RSD	13.00	11.10	8.90	9.16	10.40	9.29	8.02
% BIAS	9.62	-3.65	-8.74	-8.75	-9.41	2.31	0.10

A4.4.2 Continued

Element	Rb 85	Sr 88	Zr 90	Nb 93	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147	Sm 149
BHV02	10.04	406.21	223.05	19.18	143.14	15.90	39.86	5.52	24.81	6.17	6.22
BHVO 2	9.93	405.65	193.74	18.63	141.61	15.65	39.36	5.44	24.70	6.15	6.20
BHVO 2	9.98	402.97	193.40	18.56	139.97	15.56	39.05	5.42	24.55	6.20	6.18
BHVO2	9.46	376.14	145.97	17.07	133.54	14.65	37.03	5.16	23.69	5.93	5.95
BHVO-2 (Reference Value)	9.8	389	172	18	130	15.25	37.84	5.351	24.39	6.03	6.03
MEAN	9.85	397.74	189.04	18.36	139.56	15.44	38.83	5.38	24.44	6.11	6.14
STDV	0.26	14.47	31.90	0.90	4.22	0.55	1.24	0.16	0.51	0.12	0.12
%RSD	2.69	3.64	16.88	4.92	3.02	3.53	3.19	2.92	2.08	1.97	2.00
% BIAS	0.53	2.25	9.91	1.99	7.36	1.25	2.60	0.58	0.20	1.37	1.76

Element	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172	Yb 174
BHV02	2.01	1.98	6.16	0.93	6.30	5.15	5.15	1.02	2.51	2.06	2.05
BHVO 2	2.01	1.96	6.12	0.93	6.24	5.15	5.17	1.01	2.49	2.07	2.05
BHVO 2	2.02	1.97	6.14	0.91	6.30	5.19	5.22	1.02	2.50	2.04	2.04
BHVO2	1.97	1.89	5.95	0.88	6.06	5.04	5.02	0.98	2.44	1.97	1.99
BHVO-2 (Reference Value)	2.036	2.036	6.229	0.9	6.229	5.3	5.3	1.04	2.547	1.955	1.955
MEAN	2.00	1.95	6.09	0.91	6.22	5.13	5.14	1.01	2.48	2.04	2.03
STDV	0.03	0.04	0.10	0.02	0.11	0.07	0.09	0.02	0.03	0.04	0.03
%RSD	1.25	1.96	1.64	2.43	1.84	1.30	1.67	1.80	1.27	2.18	1.50
% BIAS	-1.61	-4.20	-2.19	1.32	-0.07	-3.16	-3.02	-2.84	-2.49	4.13	4.01

A4.4.2 Continued

Element	Lu175	Hf 178	Pb 206	Pb 207	Pb 208	Th 232	U 238
BHV02	0.28	4.40	1.74	1.71	1.74	1.22	0.44
BHVO 2	0.29	4.36	1.77	1.74	1.75	1.23	0.44
BHVO 2	0.29	4.38	1.77	1.73	1.55	1.22	0.45
BHVO2	0.27	4.25	1.69	1.67	1.51	1.18	0.43
BHVO-2 (Reference Value)	0.2709	4.1	1.4	1.4	1.4	1.2	0.404
MEAN	0.28	4.34	1.74	1.71	1.64	1.21	0.44
STDV	0.01	0.07	0.03	0.03	0.13	0.02	0.01
%RSD	2.28	1.50	2.00	1.74	7.68	1.82	1.45
% BIAS	4.06	5.97	24.50	22.23	16.92	1.10	8.98

A4.4.3 Solution ICP-MS Standard Analysis at TEAF on 9/12/2012

Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
BHVO-2	9.79	395.03	175.66	18.32	0.13	132.98	15.36	34.84	5.34	24.03	6.09
BHVO-2	9.57	385.92	171.38	17.46	0.12	132.16	15.13	34.39	5.34	24.42	6.27
BHVO-2 (Reference Value)	9.8	389	172	18	0.08	130	15.25	37.84	5.351	24.39	6.03
MEAN	9.68	390.48	173.52	17.89	0.12	132.57	15.24	34.62	5.34	24.23	6.18
STDV	0.15	6.44	3.02	0.60	0.01	0.58	0.16	0.32	0.00	0.27	0.12
%RSD	1.59	1.65	1.74	3.38	4.47	0.44	1.06	0.93	0.07	1.13	1.97
% BIAS	-1.25	0.38	0.88	-0.61	53.46	1.98	-0.06	-8.52	-0.22	-0.66	2.50
Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
DNC-1	4.20	149.15	48.66	2.57	0.25	128.83	3.78	13.88	1.29	5.13	1.44
DNC-1	4.07	144.86	47.06	2.42	0.22	126.17	3.57	13.64	1.27	5.15	1.42
DNC-1 (Reference Value)	4.5	145	38	3		118	3.6	10.6	1.3	4.9	1.38
MEAN	4.14	147.01	47.86	2.49	0.24	127.50	3.68	13.76	1.28	5.14	1.43
STDV	0.09	3.03	1.14	0.10	0.02	1.88	0.15	0.17	0.01	0.02	0.02
%RSD	2.24	2.06	2.37	4.14	6.94	1.48	3.95	1.22	1.13	0.38	1.07
% BIAS	-8.11	1.39	25.95	-16.90	#DIV/0!	8.05	2.12	29.78	-1.84	4.88	3.91
Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
W-2	19.75	181.12	82.04	7.63	0.86	142.98	9.91	23.23	2.85	11.69	2.94
W-2	20.66	199.73	85.34	7.75	0.90	147.38	10.46	24.10	3.09	12.99	3.25
W-2 (Reference Value)	20	194	100	7.9	0.68	170	10.23	22.8	2.919	12.71	3.234
MEAN	20.21	190.43	83.69	7.69	0.88	145.18	10.19	23.67	2.97	12.34	3.09
STDV	0.64	13.15	2.33	0.08	0.03	3.11	0.39	0.61	0.17	0.92	0.21
%RSD	3.19	6.91	2.79	1.08	3.73	2.14	3.86	2.58	5.60	7.45	6.91
% BIAS	1.04	-1.84	-16.31	-2.68	29.64	-14.60	-0.43	3.80	1.71	-2.90	-4.32

A4.4.3 Continued

Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
BHVO-2	6.14	2.03	1.98	6.19	0.94	6.26	5.25	5.27	1.04	2.55	2.12
BHVO-2	6.23	2.05	1.99	6.22	0.96	6.41	5.32	5.30	1.05	2.53	2.10
BHVO-2 (Reference Value)	6.03	2.036	2.036	6.229	0.9	6.229	5.3	5.3	1.04	2.547	1.955
MEAN	6.19	2.04	1.99	6.21	0.95	6.34	5.28	5.28	1.05	2.54	2.11
STDV	0.06	0.01	0.01	0.02	0.02	0.11	0.05	0.02	0.01	0.01	0.02
%RSD	1.03	0.66	0.30	0.30	1.73	1.74	0.86	0.41	0.73	0.53	0.72
% BIAS	2.60	0.08	-2.32	-0.37	5.62	1.71	-0.31	-0.36	0.83	-0.25	7.79
Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
DNC-1	1.40	0.57	0.54	1.93	0.40	1.94	2.93	2.95	0.63	1.99	1.94
DNC-1	1.41	0.59	0.57	1.96	0.41	1.94	2.95	2.99	0.64	1.99	1.90
DNC-1 (Reference Value)	1.38	0.59	0.59	2	0.41	2	3	3	0.62	2	2
MEAN	1.41	0.58	0.56	1.95	0.40	1.94	2.94	2.97	0.64	1.99	1.92
STDV	0.00	0.01	0.02	0.02	0.00	0.00	0.02	0.03	0.00	0.00	0.03
%RSD	0.18	1.95	2.87	0.95	1.16	0.03	0.51	0.89	0.11	0.07	1.35
% BIAS	1.89	-2.18	-5.73	-2.63	-1.62	-2.92	-2.11	-0.93	2.43	-0.56	-3.87
Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
W-2	2.96	0.98	0.97	3.31	0.57	3.31	3.60	3.63	0.73	2.06	1.87
W-2	3.31	1.10	1.10	3.70	0.64	3.59	3.92	3.93	0.81	2.22	2.07
W-2 (Reference Value)	3.234	1.072	1.072	3.692	0.63	3.692	3.825	3.825	0.76	2.248	2.02
MEAN	3.13	1.04	1.03	3.50	0.60	3.45	3.76	3.78	0.77	2.14	1.97
STDV	0.25	0.08	0.09	0.27	0.05	0.20	0.23	0.21	0.05	0.11	0.14
%RSD	8.02	8.08	9.15	7.73	8.80	5.82	6.05	5.65	7.01	5.27	6.87
% BIAS	-3.07	-2.86	-3.55	-5.10	-3.98	-6.57	-1.70	-1.13	1.59	-4.66	-2.45

A4.4.3 Continued

Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
BHVO-2	2.07	0.28	4.39	1.33	1.42	1.41	1.41	1.16	0.57
BHVO-2	2.08	0.29	4.42	1.34	1.42	1.40	1.40	1.17	0.58
BHVO-2 (Reference Value)	1.955	0.2709	4.1	0.97	1.4	1.4	1.4	1.2	0.404
MEAN	2.07	0.28	4.40	1.34	1.42	1.41	1.40	1.17	0.57
STDV	0.00	0.00	0.02	0.01	0.00	0.01	0.01	0.01	0.01
%RSD	0.17	0.94	0.47	0.50	0.29	0.64	0.85	0.87	1.70
% BIAS	6.09	4.77	7.44	37.78	1.36	0.43	0.26	-2.90	42.03
Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
DNC-1	1.96	0.31	1.14	0.02	6.83	6.80	6.80	0.27	0.11
DNC-1	1.91	0.30	1.11	0.01	6.62	6.68	6.72	0.27	0.11
DNC-1 (Reference Value)	2	0.32	1.01	0.07	6.3	6.3	6.3	0.2	0.1
MEAN	1.94	0.30	1.13	0.02	6.72	6.74	6.76	0.27	0.11
STDV	0.04	0.01	0.02	0.01	0.15	0.09	0.06	0.00	0.00
%RSD	1.99	2.26	2.15	32.20	2.19	1.32	0.83	0.84	0.38
% BIAS	-3.23	-5.54	11.65	-77.78	6.70	7.00	7.26	33.82	6.49
Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
W-2	1.87	0.27	2.19	0.41	7.70	7.69	7.66	2.05	0.62
W-2	2.06	0.30	2.41	0.46	8.33	8.39	8.35	2.23	0.67
W-2 (Reference Value)	2.02	0.2937	2.6	0.34	9.3	9.3	9.3	2.2	0.53
MEAN	1.96	0.29	2.30	0.43	8.02	8.04	8.00	2.14	0.64
STDV	0.14	0.02	0.16	0.04	0.45	0.49	0.49	0.12	0.03
%RSD	7.07	6.52	6.96	8.72	5.59	6.13	6.13	5.83	5.37
% BIAS	-2.79	-2.22	-11.60	27.77	-13.80	-13.57	-13.93	-2.59	21.61

A4.4.3 Continued

Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
BCR-2	51.32	358.22	198.40	13.17	1.22	716.35	25.65	46.49	6.88	29.01	6.61
BCR-2	46.67	335.40	185.83	12.15	1.14	702.21	24.17	44.49	6.60	28.25	6.48
BCR 2 (Reference Value)	48	346	188	10.9	0.75	683	25	53	6.8	28	6.7
MEAN	48.99	346.81	192.12	12.66	1.18	709.28	24.91	45.49	6.74	28.63	6.54
STDV	3.29	16.13	8.88	0.73	0.05	10.00	1.05	1.42	0.20	0.54	0.09
%RSD	6.71	4.65	4.62	5.73	4.58	1.41	4.20	3.11	2.94	1.87	1.40
% BIAS	2.07	0.23	2.19	16.16	57.11	3.85	-0.37	-14.17	-0.86	2.25	-2.34
Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
AGV-2	73.22	710.45	244.50	15.10	1.27	1205.31	41.66	99.67	8.65	32.31	6.02
AGV-2	62.53	604.13	217.51	13.01	1.09	1047.73	34.32	53.31	7.35	27.87	5.08
AGV-2 (Reference Value)	68.6	658	230	15	0.79	1140	37.92	69.61	7.957	30.42	5.46
MEAN	67.88	657.29	231.00	14.05	1.18	1126.52	37.99	76.49	8.00	30.09	5.55
STDV	7.56	75.18	19.09	1.48	0.13	111.43	5.19	32.79	0.92	3.14	0.66
%RSD	11.14	11.44	8.26	10.50	10.87	9.89	13.65	42.87	11.50	10.45	11.86
% BIAS	-1.06	-0.11	0.44	-6.32	49.03	-1.18	0.18	9.88	0.55	-1.09	1.66

A4.4.3 Continued

Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
BCR-2	6.64	2.01	2.01	6.78	1.05	6.68	6.03	6.04	1.33	3.35	3.50
BCR-2	6.40	1.89	1.92	6.61	1.02	6.40	5.99	5.99	1.33	3.31	3.49
BCR 2 (Reference Value)	6.7	2.0	2	6.8	1.07	6.8	6.0	6.0	1.33	3.3	3.5
MEAN	6.52	1.95	1.96	6.70	1.03	6.54	6.01	6.01	1.33	3.33	3.49
STDV	0.17	0.08	0.06	0.12	0.02	0.20	0.03	0.03	0.00	0.03	0.01
%RSD	2.55	4.24	3.30	1.78	2.21	3.04	0.42	0.52	0.10	0.86	0.23
% BIAS	-2.65	-2.57	-1.94	-1.53	-3.46	-3.85	0.15	0.25	-0.28	1.05	-0.18
Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
AGV-2	5.95	1.71	1.78	5.19	0.69	4.81	3.79	3.71	0.71	1.98	1.67
AGV-2	5.16	1.50	1.56	4.61	0.63	4.39	3.47	3.43	0.64	1.85	1.51
AGV-2 (Reference Value)	5.46	1.51	1.51	4.531	0.64	4.531	3.496	3.496	0.71	1.829	1.612
MEAN	5.55	1.60	1.67	4.90	0.66	4.60	3.63	3.57	0.68	1.92	1.59
STDV	0.56	0.15	0.16	0.41	0.04	0.30	0.23	0.20	0.05	0.09	0.11
%RSD	10.02	9.54	9.35	8.43	6.14	6.45	6.25	5.68	7.32	4.78	6.97
% BIAS	1.70	6.20	10.53	8.17	2.70	1.49	3.89	2.16	-4.53	4.80	-1.45

A4.4.3 Continued

Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
BCR-2	3.49	0.51	4.76	0.84	11.77	11.78	11.91	6.28	2.28
BCR-2	3.50	0.52	4.83	0.84	11.93	11.87	11.78	6.07	2.18
BCR 2 (Reference Value)	3.5	0.51	4.8	0.43	11	11	11	6.2	1.69
MEAN	3.50	0.51	4.80	0.84	11.85	11.82	11.84	6.18	2.23
STDV	0.01	0.00	0.05	0.00	0.12	0.06	0.09	0.15	0.07
%RSD	0.21	0.96	1.01	0.48	0.97	0.50	0.77	2.48	3.32
% BIAS	-0.01	0.86	-0.09	95.80	7.74	7.49	7.66	-0.38	32.04
Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
AGV-2	1.70	0.26	5.22	0.93	21.75	21.72	21.73	6.44	2.53
AGV-2	1.52	0.23	4.70	0.85	19.93	19.62	19.22	5.86	2.24
AGV-2 (Reference Value)	1.612	0.2366	5.08	0.61	13	13	13	6.1	1.88
MEAN	1.61	0.24	4.96	0.89	20.84	20.67	20.48	6.15	2.38
STDV	0.13	0.02	0.37	0.06	1.29	1.48	1.77	0.41	0.21
%RSD	8.07	9.38	7.44	6.67	6.18	7.18	8.65	6.61	8.75
% BIAS	-0.07	2.70	-2.37	45.75	60.33	59.01	57.51	0.82	26.84

A4.4.4 Solution ICP-MS Standard Analysis at TEAF on 9/29/2013

Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
BHVO2	9.66	390.18	166.36	17.52	0.10	127.45	14.42	36.00	5.11	23.43	5.95
BHVO-2	9.90	401.28	172.75	18.36	0.12	139.15	15.74	38.84	5.56	25.05	6.40
BHVO-2	9.99	403.91	175.35	18.63	0.12	141.98	16.15	39.91	5.65	25.53	6.49
BHVO-2 (Reference Value)	9.8	389	172	18	0.08	130	15.25	37.84	5.351	24.39	6.03
MEAN	9.85	398.45	171.49	18.17	0.11	136.20	15.43	38.25	5.44	24.67	6.28
STDV	0.17	7.29	4.63	0.58	0.01	7.70	0.90	2.02	0.29	1.10	0.29
%RSD	1.76	1.83	2.70	3.20	6.58	5.66	5.85	5.28	5.26	4.45	4.62
% BIAS	0.51	2.43	-0.30	0.95	39.16	4.77	1.21	1.07	1.70	1.15	4.16
Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
DNC1	4.22	151.67	38.72	2.02	0.23	110.17	3.46	9.16	1.15	5.20	1.49
DNC-1	4.25	151.31	38.84	2.05	0.23	115.22	3.61	9.51	1.19	5.44	1.54
DNC-1	4.25	150.24	38.48	2.02	0.23	113.47	3.53	9.27	1.17	5.22	1.51
DNC-1 (Reference Value)	4.5	145	38	3		118	3.6	10.6	1.3	4.9	1.38
MEAN	4.24	151.08	38.68	2.03	0.23	112.95	3.54	9.31	1.17	5.29	1.52
STDV	0.02	0.75	0.19	0.01	0.00	2.56	0.07	0.18	0.02	0.13	0.02
%RSD	0.40	0.49	0.48	0.73	1.47	2.27	2.10	1.93	1.95	2.52	1.42
% BIAS	-5.74	4.19	1.79	-32.31	#DIV/0!	-4.28	-1.80	-12.17	-10.08	7.91	9.82

A4.4.4 Continued

Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
BHVO2	6.00	1.95	1.93	6.11	0.94	6.29	5.30	4.99	1.03	2.52	2.12
BHVO-2	6.37	2.04	2.02	6.33	0.97	6.50	5.36	5.06	1.05	2.56	2.14
BHVO-2	6.50	2.10	2.05	6.40	0.97	6.56	5.41	5.08	1.05	2.56	2.14
BHVO-2 (Reference Value)	6.03	2.036	2.036	6.229	0.9	6.229	5.3	5.3	1.04	2.547	1.955
MEAN	6.29	2.03	2.00	6.28	0.96	6.45	5.36	5.04	1.04	2.55	2.13
STDV	0.26	0.07	0.06	0.15	0.02	0.14	0.06	0.05	0.01	0.02	0.01
%RSD	4.08	3.54	2.93	2.37	1.57	2.17	1.07	1.01	1.04	0.89	0.40
% BIAS	4.29	-0.31	-1.73	0.78	6.73	3.55	1.06	-4.87	-0.02	0.01	9.18
Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
DNC1	1.49	0.58	0.59	2.01	0.41	2.15	2.89	2.76	0.70	2.00	2.16
DNC-1	1.53	0.60	0.60	2.04	0.41	2.16	2.90	2.80	0.69	2.01	2.12
DNC-1	1.51	0.59	0.58	1.96	0.40	2.08	2.84	2.68	0.66	1.90	2.04
DNC-1 (Reference Value)	1.38	0.59	0.59	2	0.41	2	3	3	0.62	2	2
MEAN	1.51	0.59	0.59	2.00	0.41	2.13	2.88	2.75	0.68	1.97	2.11
STDV	0.02	0.01	0.01	0.04	0.01	0.04	0.03	0.06	0.02	0.06	0.06
%RSD	1.45	1.60	1.86	1.98	1.62	2.06	1.21	2.21	2.57	3.17	3.00
% BIAS	9.63	-0.10	0.29	0.11	-0.46	6.52	-4.08	-8.45	10.41	-1.51	5.29

A4.4.4 Continued

Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
BHVO2	2.15	0.31	4.61	1.43	2.13	2.10	2.05	1.49	0.50
BHVO-2	2.18	0.31	4.65	1.42	2.12	2.09	2.11	1.49	0.50
BHVO-2	2.14	0.31	4.54	1.40	2.05	2.05	2.03	1.42	0.49
BHVO-2 (Reference Value)	1.955	0.2709	4.1	0.97	1.4	1.4	1.4	1.2	0.404
MEAN	2.16	0.31	4.60	1.42	2.10	2.08	2.06	1.46	0.50
STDV	0.02	0.00	0.05	0.02	0.04	0.03	0.04	0.04	0.01
%RSD	1.00	0.29	1.14	1.21	2.11	1.22	1.97	2.81	1.20
% BIAS	10.36	13.84	12.21	45.94	49.77	48.62	47.21	22.06	23.59
Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
DNC1	2.22	0.34	1.16	0.07	7.99	7.90	7.83	0.33	0.09
DNC-1	2.20	0.34	1.13	0.06	7.65	7.65	7.55	0.31	0.08
DNC-1	2.09	0.32	1.06	0.05	7.00	6.93	6.95	0.28	0.07
DNC-1 (Reference Value)	2	0.32	1.01	0.07	6.3	6.3	6.3	0.2	0.1
MEAN	2.17	0.33	1.12	0.06	7.55	7.49	7.44	0.30	0.08
STDV	0.07	0.01	0.05	0.01	0.50	0.50	0.45	0.03	0.01
%RSD	3.27	4.20	4.32	14.19	6.66	6.72	6.06	8.39	8.16
% BIAS	8.51	4.23	10.57	-12.91	19.76	18.94	18.13	52.04	-18.14

A4.4.4 Continued

Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
W-2	20.92	203.68	107.87	7.95	0.97	180.79	11.13	24.95	3.18	13.69	3.50
W-2	20.96	203.14	92.62	7.91	0.98	183.15	11.14	25.25	3.23	13.77	3.52
W-2	21.00	201.07	104.78	7.82	0.97	180.82	10.92	24.74	3.18	13.60	3.45
W-2 (Reference Value)	20	194	100	7.9	0.68	170	10.23	22.8	2.919	12.71	3.234
MEAN	20.96	202.63	101.76	7.89	0.97	181.59	11.06	24.98	3.20	13.69	3.49
STDV	0.04	1.37	8.07	0.07	0.01	1.36	0.12	0.26	0.03	0.08	0.04
%RSD	0.19	0.68	7.93	0.88	0.89	0.75	1.10	1.03	0.80	0.61	1.09
% BIAS	4.80	4.45	1.76	-0.08	43.22	6.82	8.11	9.56	9.52	7.68	7.90
Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
BCR-2	48.62	346.21	190.85	12.74	1.25	672.05	26.68	55.58	7.26	30.06	6.98
BCR-2	48.09	345.08	189.78	12.62	1.25	680.36	26.91	56.31	7.35	30.22	7.12
BCR-2	47.87	338.75	187.62	12.58	1.26	686.51	27.18	56.85	7.43	30.79	7.15
BCR 2 (Reference Value)	48	346	188	10.9	0.75	683	25	53	6.8	28	6.7
MEAN	48.19	343.35	189.42	12.65	1.25	679.64	26.92	56.25	7.34	30.36	7.08
STDV	0.39	4.02	1.64	0.08	0.00	7.26	0.25	0.64	0.08	0.38	0.09
%RSD	0.80	1.17	0.87	0.65	0.32	1.07	0.95	1.13	1.13	1.26	1.26
% BIAS	0.40	-0.77	0.76	16.01	67.19	-0.49	7.70	6.12	8.00	8.42	5.69

A4.4.4 Continued

Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
W-2	3.52	1.13	1.14	3.91	0.66	4.09	4.08	3.87	0.88	2.36	2.33
W-2	3.56	1.14	1.13	3.85	0.65	3.99	4.01	3.82	0.86	2.29	2.27
W-2	3.48	1.11	1.10	3.73	0.63	3.84	3.93	3.69	0.83	2.24	2.18
W-2 (Reference Value)	3.234	1.072	1.072	3.692	0.63	3.692	3.825	3.825	0.76	2.248	2.02
MEAN	3.52	1.13	1.12	3.83	0.65	3.98	4.01	3.79	0.86	2.30	2.26
STDV	0.04	0.01	0.02	0.09	0.02	0.13	0.08	0.09	0.03	0.06	0.07
%RSD	1.15	1.26	1.60	2.43	2.55	3.19	1.89	2.36	2.92	2.68	3.28
% BIAS	8.72	5.23	4.63	3.68	2.44	7.70	4.72	-0.83	12.85	2.12	11.88
Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
BCR-2	7.07	2.09	2.08	7.23	1.12	7.30	6.69	6.26	1.44	3.75	3.77
BCR-2	7.13	2.08	2.12	7.26	1.13	7.27	6.67	6.31	1.43	3.74	3.77
BCR-2	7.25	2.12	2.13	7.23	1.13	7.36	6.70	6.35	1.43	3.75	3.74
BCR 2 (Reference Value)	6.7	2.0	2	6.8	1.07	6.8	6.0	6.0	1.33	3.3	3.5
MEAN	7.15	2.10	2.11	7.24	1.13	7.31	6.69	6.31	1.43	3.75	3.76
STDV	0.09	0.02	0.03	0.02	0.01	0.05	0.01	0.04	0.01	0.00	0.02
%RSD	1.26	1.08	1.31	0.25	0.64	0.64	0.19	0.69	0.38	0.10	0.50
% BIAS	6.68	4.88	5.59	6.45	5.41	7.50	11.45	5.12	7.59	13.58	7.41

A4.4.4 Continued

Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
W-2	2.38	0.35	2.72	0.58	10.46	10.26	10.23	2.88	0.67
W-2	2.30	0.34	2.60	0.55	9.82	9.81	9.73	2.71	0.61
W-2	2.18	0.32	2.48	0.51	8.93	8.92	8.90	2.45	0.56
W-2 (Reference Value)	2.02	0.2937	2.6	0.34	9.3	9.3	9.3	2.2	0.53
MEAN	2.29	0.34	2.60	0.55	9.74	9.67	9.62	2.68	0.61
STDV	0.10	0.02	0.12	0.04	0.76	0.68	0.67	0.22	0.05
%RSD	4.30	4.61	4.54	6.55	7.85	7.06	6.99	8.15	8.96
% BIAS	13.21	15.55	0.01	61.66	4.68	3.95	3.42	21.88	15.47
Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
BCR-2	3.84	0.58	5.41	0.98	13.34	13.13	13.28	7.69	2.12
BCR-2	3.80	0.57	5.31	0.95	12.86	12.70	12.72	7.36	2.05
BCR-2	3.73	0.56	5.19	0.94	12.30	12.32	12.27	6.99	1.94
BCR 2 (Reference Value)	3.5	0.51	4.8	0.43	11	11	11	6.2	1.69
MEAN	3.79	0.57	5.30	0.96	12.83	12.71	12.76	7.35	2.04
STDV	0.05	0.01	0.11	0.02	0.52	0.41	0.51	0.35	0.09
%RSD	1.37	2.06	2.03	2.03	4.04	3.19	3.99	4.82	4.37
% BIAS	8.29	12.02	10.45	122.12	16.67	15.58	15.96	18.47	20.45

A4.4.4 Continued

Element	Rb 85	Sr 88	Zr 90	Nb 93	Cs 133	Ba 137	La 139	Ce 140	Pr 141	Nd147	Sm147
AGV-2	69.72	679.41	237.22	14.37	1.26	1856.63	40.46	71.75	8.69	31.70	5.91
AGV-2	69.51	672.78	235.68	14.30	1.27	1876.69	40.60	72.99	8.77	32.24	6.01
AGV-2	69.39	662.61	235.60	14.32	1.27	1378.36	41.06	73.94	8.87	32.78	6.02
AGV-2 (Reference Value)	68.6	658	230	15	0.79	1140	37.92	69.61	7.957	30.42	5.46
MEAN	69.54	671.60	236.16	14.33	1.27	1703.89	40.71	72.89	8.78	32.24	5.98
STDV	0.17	8.46	0.91	0.04	0.00	282.10	0.32	1.10	0.09	0.54	0.06
%RSD	0.24	1.26	0.39	0.25	0.35	16.56	0.78	1.50	1.01	1.67	1.07
% BIAS	1.37	2.07	2.68	-4.45	60.41	49.46	7.35	4.72	10.30	5.98	9.50

Element	Sm 149	Eu 151	Eu 153	Gd 157	Tb 159	Gd 160	Dy 161	Dy 163	Ho 165	Er 166	Yb 172
AGV-2	5.94	1.68	1.72	5.36	0.70	5.06	3.80	3.45	0.73	1.95	1.80
AGV-2	6.02	1.69	1.77	5.34	0.70	5.08	3.83	3.45	0.73	1.96	1.83
AGV-2	6.13	1.73	1.78	5.49	0.72	5.16	3.87	3.52	0.74	2.00	1.82
AGV-2 (Reference Value)	5.46	1.51	1.51	4.531	0.64	4.531	3.496	3.496	0.71	1.829	1.612
MEAN	6.03	1.70	1.76	5.40	0.71	5.10	3.83	3.47	0.73	1.97	1.82
STDV	0.10	0.03	0.03	0.08	0.01	0.05	0.04	0.04	0.01	0.02	0.01
%RSD	1.60	1.47	1.83	1.54	0.92	1.01	0.99	1.18	0.76	1.20	0.76
% BIAS	10.45	12.57	16.45	19.16	10.57	12.54	9.65	-0.63	3.09	7.82	12.78

A4.4.4 Continued

Element	Yb 174	Lu175	Hf 178	Ta 181	Pb 206	Pb 207	Pb 208	Th 232	U 238
AGV-2	1.82	0.28	5.51	1.03	16.68	16.62	16.53	7.68	2.31
AGV-2	1.82	0.28	5.47	1.01	16.37	16.07	16.08	7.40	2.22
AGV-2	1.86	0.28	5.46	1.00	15.68	15.58	15.54	7.08	2.13
AGV-2 (Reference Value)	1.612	0.2366	5.08	0.61	13	13	13	6.1	1.88
MEAN	1.83	0.28	5.48	1.01	16.25	16.09	16.05	7.39	2.22
STDV	0.02	0.00	0.03	0.01	0.51	0.52	0.50	0.30	0.09
%RSD	1.31	0.79	0.46	1.39	3.14	3.24	3.10	4.08	4.08
% BIAS	13.79	18.73	7.81	65.51	24.97	23.80	23.46	21.07	18.09

A4.5 Pellet LA-ICP-MS Analysis using In115 as internal standard (300ug/g) and AGV2 as calibrator at TEAF

Element	Rb85	Sr88	Zr90	Nb93	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm148	Sm149	Eu151
DLBHV021	8.62	385.93	146.21	22.26	0.10	131.19	14.14	34.38	5.27	22.66	4.65	5.96	2.12
DLBHV022	9.37	404.65	159.80	23.72	0.11	137.20	15.08	35.72	5.31	24.37	4.80	6.58	2.10
DLBHV023	9.15	413.61	164.20	23.74	0.10	141.88	15.41	36.34	5.50	23.51	5.02	6.73	2.16
DLBHV024	9.43	404.16	161.41	23.48	0.11	135.34	14.92	35.89	5.39	23.23	4.70	6.17	2.03
mean	9.14	402.09	157.91	23.30	0.11	136.40	14.89	35.58	5.37	23.44	4.79	6.36	2.10
stdev	0.37	11.61	8.01	0.70	0.00	4.43	0.54	0.84	0.10	0.71	0.16	0.36	0.05
%RSD	4.03	2.89	5.07	3.02	3.39	3.25	3.62	2.37	1.89	3.04	3.42	5.61	2.59
ref. value	9.80	389.00	172.00	18.00	0.11	130.00	15.00	38.00	5.35	25.00	6.20	6.20	2.04
% bias	-6.71	3.36	-8.19	29.44	-4.55	4.93	-0.75	-6.36	0.31	-6.23	-22.70	2.58	3.27
Element	Rb85	Sr88	Zr90	Nb93	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm148	Sm149	Eu151
DLBCR21	38.90	294.60	141.94	12.36	1.06	647.98	22.15	46.65	6.84	27.60	5.60	6.74	1.94
DLBCR22	47.10	338.59	172.05	15.16	1.07	681.75	24.32	51.36	6.84	28.09	5.42	6.59	1.95
DLBCR23	46.43	339.52	173.13	15.04	1.06	677.81	24.12	49.60	6.74	26.91	5.48	6.60	1.95
DLBCR24	46.34	345.25	182.88	15.14	1.07	676.44	25.08	49.10	6.77	28.01	5.57	7.21	1.99
mean	44.69	329.49	167.50	14.43	1.07	671.00	23.92	49.18	6.80	27.65	5.52	6.79	1.96
stdev	3.88	23.45	17.72	1.38	0.01	15.51	1.25	1.94	0.05	0.54	0.08	0.29	0.02
%RSD	8.67	7.12	10.58	9.55	0.61	2.31	5.22	3.95	0.74	1.95	1.50	4.30	1.13
ref. value	48.00	436.00	188.00	10.90	1.10	683.00	25.00	53.00	6.80	28.00	6.70	6.70	2.00
% bias	-6.89	-24.43	-10.90	32.34	-3.14	-1.76	-4.33	-7.21	-0.04	-1.24	-17.65	1.27	-2.13

A4.5 Continued

Element	Tb159	Gd160	Dy161	Dy163	Ho165	Er166	Yb172	Yb174
DLBHV021	0.88	6.01	4.84	5.10	0.94	2.22	1.93	1.81
DLBHV022	0.94	6.53	5.06	5.21	0.99	2.38	2.47	1.88
DLBHV023	0.94	6.20	4.93	5.45	1.12	2.37	1.86	1.87
DLBHV024	0.96	6.34	5.02	5.24	1.02	2.35	1.95	1.90
mean	0.93	6.27	4.96	5.25	1.02	2.33	2.05	1.87
stdev	0.03	0.22	0.10	0.15	0.08	0.07	0.28	0.04
%RSD	3.45	3.51	1.98	2.79	7.49	3.19	13.69	2.08
ref. value	0.90	6.30	5.30	5.30	1.04	2.55	2.00	2.00
% bias	3.25	-0.48	-6.37	-0.94	-2.28	-8.52	2.63	-6.75
Element	Tb159	Gd160	Dy161	Dy163	Ho165	Er166	Yb172	Yb174
DLBCR21	1.02	6.57	6.07	6.57	1.35	3.32	2.99	3.18
DLBCR22	0.96	6.54	6.08	6.18	1.31	3.32	3.55	3.20
DLBCR23	0.98	6.73	5.95	6.34	1.31	3.52	3.38	3.46
DLBCR24	1.06	6.60	5.94	6.43	1.29	3.37	3.24	3.50
mean	1.00	6.61	6.01	6.38	1.32	3.38	3.29	3.34
stdev	0.04	0.08	0.08	0.16	0.03	0.09	0.24	0.17
%RSD	4.33	1.27	1.25	2.56	1.91	2.80	7.20	5.05
ref. value	1.07	6.80	6.00	6.00	1.33	3.30	3.50	3.50
% bias	-6.10	-2.79	0.17	6.33	-1.13	2.50	-6.00	-4.71

A4.5 Continued

Element	Lu175	Hf178	Ta181	Pb206	Pb207	Pb208	Th232	U238
DLBHV021	0.26	4.10	2.67	2.04	2.20	1.92	1.18	0.47
DLBHV022	0.27	4.50	2.74	1.72	1.94	2.00	1.16	0.45
DLBHV023	0.30	3.87	2.62	1.93	1.91	1.99	1.18	0.46
DLBHV024	0.25	4.13	2.73	2.04	2.11	1.98	1.19	0.47
mean	0.27	4.15	2.69	1.93	2.04	1.97	1.18	0.46
stdev	0.02	0.26	0.06	0.15	0.14	0.04	0.01	0.01
%RSD	6.75	6.28	2.08	7.81	6.78	1.82	1.09	2.52
ref. value	0.28	4.10	1.40	1.40	1.40	1.40	1.20	0.40
% bias	-3.66	1.22	92.14	38.04	45.71	40.89	-1.92	14.23
Element	Lu175	Hf178	Ta181	Pb206	Pb207	Pb208	Th232	U238
DLBCR21	0.54	4.57	1.39	11.39	11.26	11.77	5.54	1.80
DLBCR22	0.49	4.49	1.41	10.18	10.55	10.40	5.56	1.51
DLBCR23	0.46	4.24	1.49	9.39	9.76	9.93	5.53	1.58
DLBCR24	0.55	4.84	1.58	10.12	10.09	10.40	5.97	1.55
mean	0.51	4.54	1.47	10.27	10.42	10.63	5.65	1.61
stdev	0.04	0.25	0.09	0.83	0.65	0.79	0.21	0.13
%RSD	8.81	5.45	5.90	8.07	6.24	7.48	3.78	8.07
ref. value	0.51	4.80	0.63	11.00	11.00	11.00	6.20	1.69
% bias	-0.15	-5.52	132.94	-6.64	-5.32	-3.41	-8.87	-4.73

A4.5 Continued

Element	Rb85	Sr88	Zr90	Nb93	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm148	Sm149	Eu151
DLAVG25	61.90	619.68	217.65	14.30	1.18	1111.66	36.97	64.86	8.29	29.48	6.01	6.04	1.58
DLAVG26	66.41	648.48	223.79	14.16	1.23	1134.92	37.65	67.13	8.50	30.79	5.70	5.87	1.72
DLAVG27	65.96	634.74	214.89	13.73	1.26	1122.03	37.75	66.34	8.21	29.75	5.59	5.52	1.49
DLAVG28	67.22	652.42	216.25	13.65	1.16	1122.04	37.11	66.92	8.30	29.16	5.64	5.94	1.55
mean	65.37	638.83	218.15	13.96	1.21	1122.66	37.37	66.31	8.33	29.80	5.74	5.84	1.59
stdev	2.37	14.85	3.93	0.32	0.04	9.52	0.39	1.02	0.12	0.71	0.19	0.23	0.10
%RSD	3.63	2.32	1.80	2.28	3.66	0.85	1.04	1.54	1.48	2.37	3.29	3.87	6.15
ref. value	68.60	658.00	230.00	15.00	1.16	1140.00	38.00	68.00	8.30	30.00	5.70	5.70	1.54
% bias	-4.70	-2.91	-5.15	-6.93	4.31	-1.52	-1.66	-2.48	0.30	-0.68	0.61	2.50	2.92
Element	Rb85	Sr88	Zr90	Nb93	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm148	Sm149	Eu151
DLPL81	25.28	467.29	97.87	17.00	1.15	317.00	12.32	28.15	3.98	15.53	3.13	3.64	1.02
DLPL82	25.27	495.50	112.23	18.16	1.17	332.17	13.82	29.32	4.14	16.12	3.28	3.99	1.12
DLPL83	26.55	504.43	116.70	17.33	1.16	335.41	14.21	29.86	4.27	16.58	3.31	4.08	1.15
DLPL84	26.22	507.10	114.74	18.41	1.03	338.76	14.10	30.18	4.28	16.94	3.29	3.91	1.12
mean	25.83	493.58	110.39	17.73	1.13	330.84	13.61	29.38	4.17	16.29	3.25	3.91	1.10
stdev	0.65	18.22	8.54	0.67	0.07	9.61	0.88	0.89	0.14	0.61	0.08	0.19	0.06
%RSD	2.54	3.69	7.74	3.77	5.84	2.90	6.44	3.04	3.37	3.74	2.54	4.86	5.32

A4.5 Continued

Element	Tb159	Gd160	Dy161	Dy163	Ho165	Er166	Yb172	Yb174
DLAVG25	0.67	4.50	3.76	3.60	0.72	1.80	1.68	1.82
DLAVG26	0.64	4.81	3.74	3.47	0.71	1.88	1.44	1.56
DLAVG27	0.52	4.45	3.40	3.36	0.68	1.58	1.62	1.60
DLAVG28	0.57	4.47	3.63	3.37	0.66	1.65	1.60	1.48
mean	0.60	4.56	3.63	3.45	0.69	1.73	1.59	1.62
stdev	0.07	0.17	0.17	0.11	0.03	0.14	0.10	0.15
%RSD	11.50	3.72	4.55	3.24	3.80	7.93	6.46	9.01
ref. value	0.64	4.69	3.60	3.60	0.71	1.79	1.60	1.60
% bias	-6.41	-2.83	0.90	-4.17	-2.36	-3.49	-0.94	0.94
Element	Tb159	Gd160	Dy161	Dy163	Ho165	Er166	Yb172	Yb174
DLPL81	0.48	3.16	2.79	2.75	0.58	1.61	1.41	1.44
DLPL82	0.54	3.48	3.02	3.12	0.66	1.73	1.71	1.67
DLPL83	0.54	3.91	3.05	3.25	0.73	1.80	1.88	1.76
DLPL84	0.60	3.75	3.41	3.25	0.63	1.62	1.44	1.78
mean	0.54	3.58	3.07	3.09	0.65	1.69	1.61	1.66
stdev	0.05	0.33	0.26	0.24	0.06	0.09	0.22	0.16
%RSD	8.66	9.19	8.35	7.64	9.63	5.40	13.97	9.37

A4.5 Continued

Element	Lu175	Hf178	Ta181	Pb206	Pb207	Pb208	Th232	U238
DLAVG25	0.26	5.48	1.02	13.86	14.68	13.86	6.44	2.02
DLAVG26	0.29	5.12	0.93	13.50	12.96	13.31	6.28	1.89
DLAVG27	0.26	4.85	0.89	13.47	13.64	12.61	5.89	1.73
DLAVG28	0.27	4.90	0.85	13.31	13.45	13.25	5.93	1.76
mean	0.27	5.09	0.92	13.54	13.68	13.26	6.14	1.85
stdev	0.01	0.29	0.07	0.23	0.72	0.51	0.27	0.13
%RSD	4.17	5.64	7.89	1.72	5.29	3.86	4.37	7.18
ref. value	0.25	5.08	0.89	13.00	13.00	13.00	6.10	1.88
% bias	8.40	0.15	3.65	4.12	5.25	1.98	0.57	-1.60
Element	Lu175	Hf178	Ta181	Pb206	Pb207	Pb208	Th232	U238
DLPL81	0.25	2.62	2.49	8.26	8.13	8.58	2.23	0.63
DLPL82	0.24	2.87	2.56	8.27	8.01	7.80	2.45	0.62
DLPL83	0.28	2.93	2.58	8.04	8.18	8.04	2.52	0.64
DLPL84	0.27	3.07	2.53	7.78	8.12	7.83	2.31	0.62
mean	0.26	2.87	2.54	8.09	8.11	8.06	2.38	0.63
stdev	0.02	0.19	0.04	0.23	0.07	0.36	0.13	0.01
%RSD	8.25	6.55	1.54	2.85	0.88	4.48	5.53	1.57

A4.5 Continued

Element	Rb85	Sr88	Zr90	Nb93	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm148	Sm149	Eu151
DLPL271	13.55	428.23	74.95	6.23	0.45	249.86	10.39	23.97	3.73	16.02	3.02	3.91	1.17
DLPL272	15.04	497.58	89.53	7.24	0.38	271.97	11.60	25.83	3.91	16.57	3.44	4.18	1.27
DLPL273	15.59	496.88	90.29	7.01	0.40	263.92	11.60	25.71	3.83	15.71	3.17	4.00	1.23
DLPL274	16.07	518.92	91.04	7.94	0.39	275.54	12.19	26.44	3.89	15.80	3.20	3.86	1.13
mean	15.06	485.40	86.45	7.11	0.40	265.32	11.45	25.49	3.84	16.03	3.21	3.99	1.20
stdev	1.09	39.46	7.69	0.70	0.03	11.40	0.76	1.06	0.08	0.39	0.17	0.14	0.06
%RSD	7.25	8.13	8.90	9.92	7.35	4.30	6.61	4.16	2.10	2.41	5.42	3.53	5.37
Element	Rb85	Sr88	Zr90	Nb93	Cs133	Ba137	La139	Ce140	Pr141	Nd146	Sm148	Sm149	Eu151
DLPL161	22.78	427.58	93.02	13.91	1.18	315.77	12.82	28.26	4.12	16.81	3.28	4.36	1.17
DLPL162	24.41	477.63	104.62	14.19	1.14	329.03	13.49	29.41	4.12	16.86	3.35	3.95	1.15
DLPL163	25.80	494.78	106.87	15.79	1.18	334.09	13.95	30.03	4.19	17.22	3.38	4.10	1.13
DLPL164	25.64	501.16	110.05	15.21	1.30	337.65	13.90	30.14	4.26	17.09	3.19	3.89	1.20
DLPL165	25.30	486.22	108.81	14.63	1.16	327.99	13.43	29.44	4.00	17.02	3.34	3.83	1.28
mean	25.29	489.95	107.59	14.96	1.19	332.19	13.69	29.76	4.14	17.05	3.32	3.94	1.19
stdev	0.62	10.24	2.37	0.70	0.07	4.51	0.27	0.38	0.11	0.15	0.09	0.12	0.07
%RSD	2.46	2.09	2.20	4.65	6.19	1.36	1.97	1.29	2.68	0.88	2.57	2.94	5.62

A4.5 Continued

Element	Tb159	Gd160	Dy161	Dy163	Ho165	Er166	Yb172	Yb174
DLPL271	0.55	3.77	3.20	3.45	0.69	1.89	1.56	1.78
DLPL272	0.59	3.77	3.36	3.17	0.69	1.76	1.82	1.83
DLPL273	0.56	3.83	3.67	3.41	0.74	1.94	1.51	1.93
DLPL274	0.54	4.07	3.40	3.01	0.68	1.96	1.65	1.75
mean	0.56	3.86	3.41	3.26	0.70	1.89	1.64	1.82
stdev	0.02	0.14	0.20	0.21	0.03	0.09	0.14	0.08
%RSD	4.29	3.70	5.73	6.37	3.76	4.77	8.33	4.33
Element	Tb159	Gd160	Dy161	Dy163	Ho165	Er166	Yb172	Yb174
DLPL161	0.49	3.60	3.18	2.97	0.68	1.52	1.60	1.73
DLPL162	0.48	3.33	3.16	2.81	0.61	1.65	1.49	1.63
DLPL163	0.52	3.33	3.23	2.97	0.57	1.65	1.64	1.75
DLPL164	0.55	3.64	3.49	3.07	0.66	1.86	1.36	1.80
DLPL165	0.52	3.64	3.21	3.20	0.71	1.66	1.44	1.78
mean	0.52	3.49	3.27	3.01	0.64	1.71	1.48	1.74
stdev	0.03	0.18	0.15	0.16	0.06	0.10	0.12	0.08
%RSD	5.06	5.14	4.52	5.46	9.47	6.07	7.95	4.38

A4.5 Continued

Element	Lu175	Hf178	Ta181	Pb206	Pb207	Pb208	Th232	U238
DLPL271	0.24	2.39	1.26	7.63	6.47	7.37	1.69	0.45
DLPL272	0.29	2.60	1.28	6.35	6.70	6.38	1.75	0.48
DLPL273	0.30	2.48	1.21	6.45	6.02	6.64	1.71	0.45
DLPL274	0.24	2.54	1.25	6.16	6.49	6.23	1.77	0.44
mean	0.27	2.50	1.25	6.65	6.42	6.66	1.73	0.45
stdev	0.03	0.09	0.03	0.67	0.29	0.51	0.04	0.02
%RSD	12.24	3.58	2.36	10.02	4.46	7.60	2.11	4.41
Element	Lu175	Hf178	Ta181	Pb206	Pb207	Pb208	Th232	U238
DLPL161	0.26	2.85	2.75	8.68	8.53	8.70	2.60	0.66
DLPL162	0.25	2.50	2.67	8.25	8.36	7.98	2.40	0.57
DLPL163	0.27	2.70	2.86	7.64	8.47	7.86	2.36	0.59
DLPL164	0.28	3.08	2.92	7.78	8.46	8.05	2.42	0.61
DLPL165	0.26	2.92	2.58	8.15	8.69	8.06	2.40	0.60
mean	0.26	2.80	2.76	7.96	8.50	7.99	2.40	0.59
stdev	0.01	0.25	0.16	0.29	0.14	0.09	0.03	0.02
%RSD	5.29	9.05	5.77	3.66	1.64	1.15	1.05	3.18

Appendix 5

RADIOGENIC ISOTOPE RESULTS

A5.1 Hf Isotopic Analysis of Casimiro, Laguna del Maule, Descabezado, Nevados de Chillan, Antuco, Osorno, Villarrica, Calbuco, SEC's, and Azufre-Planchon-Peteroa at the National High Magnetic Field Laboratory Geochemistry Program.

Sample	176Hf	177Hf	176/177Hf	6th 2 SD
JMC475_1	1.93659	6.89715	0.282129	±4
JMC475_2	1.92477	6.855166	0.282129	±4
JMC475_3	1.92202	6.845521	0.282131	±4
PL-2	2.94996	10.48228	0.282952	±3
PL-8	3.34923	11.90345	0.282954	±3
PL-27	2.16147	7.681988	0.282954	±3
PL-29	2.09532	7.446583	0.28295	±4
C662	2.89813	10.30424	0.282823	±3
JMC475_4	1.91698	6.830051	0.282134	±4
JMC475_5	1.92453	6.857179	0.282129	±4
C663	2.70141	9.604457	0.282822	±3
C664	1.61819	5.752177	0.28286	±4
LM4	2.33574	8.301744	0.282903	±4
FM94	1.75374	6.230977	0.283003	±4
060283-9	1.06083	3.769297	0.283015	±4
JMC475_6	1.93705	6.902054	0.28213	±4
JMC475_7	1.91329	6.81728	0.282132	±3
51177-3	1.41839	5.039874	0.282997	±3

Table A5.1 Continued

Sample	176Hf	177Hf	176/177Hf	6th 2 SD
51177-5	1.3837	4.916504	0.282995	±4
151282-1	1.75939	6.248767	0.283127	±4
150194-01	1.62077	5.758104	0.283041	±4
24281-1	0.87675	3.11466	0.283091	±5
JMC475_8	1.80385	6.427404	0.282132	±4
JMC475_9	1.80389	6.427543	0.282136	±4
32822B	1.40998	5.010488	0.282986	±4
110194-03	2.59753	9.228328	0.283024	±4
AZ-15	1.70564	6.062074	0.28292	±4
PT-15	1.79913	6.393723	0.282937	±4
16D	1.86293	6.617718	0.283058	±4
PL-27-D	1.89425	6.730035	0.283026	±4
JMC475_10	1.86898	6.659833	0.282136	±3
JMC475_11	1.84048	6.55806	0.282132	±3

A5.2 Nd Isotopic Analysis of Azufre-Planchon –Peteroa Samples at the National High Magnetic Field Laboratory Geochemistry Program.

Sample	¹⁴³Nd	¹⁴⁴Nd	¹⁴³Nd/¹⁴⁴Nd
LaJolla_8	2.032781	4.019300	0.511862
LaJolla_9	2.021727	3.997523	0.511849
AZ-15	5.474908	10.807166	0.512747
PL-2	4.703757	9.284082	0.512784
PL-8	5.133006	10.131383	0.512775
PL-27	6.811106	13.443513	0.512781
PL-29	5.129716	10.124481	0.512786
PT-15	7.402643	14.611086	0.512763
LaJolla_10	2.100463	4.153003	0.511847
LaJolla_11	2.052193	4.057506	0.511852
LaJolla_12	2.037090	4.027614	0.511864

A5.2 Results of Simple Mixing

Melt Fraction	$^{87}\text{Sr}/^{86}\text{Sr}$ Mixture	δO^{18} Mixture
0.1	0.7068	24.74
0.2	0.7067	22.90
0.3	0.7066	21.01
0.4	0.7066	19.07
0.5	0.7065	17.08
0.6	0.7063	15.04
0.7	0.7061	12.94
0.8	0.7058	10.79
0.9	0.7053	8.58
0.94	0.7049	7.67
0.95	0.7048	7.45
0.96	0.7047	7.22
0.97	0.7045	6.99

A5.3 Results of Simple Mixing Sr-Nd

Fa	1-Fa	⁸⁷ Sr/ ⁸⁶ Sr Mix	¹⁴³ Nd/ ¹⁴⁴ Nd Mix	ε Sr Mix	ε Nd Mix
0	1	0.7120	0.5121	106.4585	-9.5586
0.1	0.9	0.7096	0.5122	72.8120	-8.8612
0.2	0.8	0.7081	0.5122	51.3273	-8.0774
0.3	0.7	0.7071	0.5123	36.4198	-7.1900
0.4	0.6	0.7063	0.5123	25.4701	-6.1771
0.5	0.5	0.7057	0.5124	17.0869	-5.0099
0.6	0.4	0.7052	0.5124	10.4624	-3.6504
0.7	0.3	0.7049	0.5125	5.0957	-2.0466
0.8	0.2	0.7045	0.5126	0.6597	-0.1264
0.9	0.1	0.7043	0.5127	-3.0684	2.2143
0.92	0.08	0.7042	0.5128	-3.7438	2.7453
0.94	0.06	0.7042	0.5128	-4.3982	3.3006
0.96	0.04	0.7041	0.5128	-5.0328	3.8819
0.98	0.02	0.7041	0.5129	-5.6483	4.4912
0.99	0.01	0.7041	0.5129	-5.9491	4.8069
1	0	0.7041	0.5129	-6.2456	5.1304

*End member components from these mixing results are Villarrica basalt sample 151282-1 and averaged values of mafic metamorphic rocks from Lucassen et al. (2004). When Fa = 1 that is the composition of the Villarrica sample and 1-Fa = 1 is the composition of the proposed contaminant.

A5.4 Results of Simple Mixing Hf-Nd

Fa	1-Fa	$^{176}\text{Hf}/^{177}\text{Hf}$ Mix	$^{143}\text{Nd}/^{144}\text{Nd}$ Mix	ϵ Hf Mix	ϵ Nd Mix
0	1	0.2823	0.5121	-17.8581	-9.5586
0.1	0.9	0.2823	0.5122	-16.6368	-8.8611
0.2	0.8	0.2824	0.5122	-15.2435	-8.0773
0.3	0.7	0.2824	0.5123	-13.6388	-7.1898
0.4	0.6	0.2825	0.5123	-11.7709	-6.1768
0.5	0.5	0.2825	0.5124	-9.5692	-5.0096
0.6	0.4	0.2826	0.5124	-6.9353	-3.6500
0.7	0.3	0.2827	0.5125	-3.7283	-2.0462
0.8	0.2	0.2828	0.5126	0.2619	-0.1260
0.9	0.1	0.2829	0.5127	5.3619	2.2145
1	0	0.2831	0.5129	12.1096	5.1304

*End member components from these mixing results are Villarrica basalt sample 151282-1 and averaged values of mafic metamorphic rocks from Lucassen et al. (2004). When Fa = 1 that is the composition of the Villarrica sample and 1-Fa = 1 is the composition of the proposed contaminant. Hf isotopic values were inferred from the terrestrial array line given by Vervoort (2011) and Hf concentrations for the mafic component was inferred using Runick et al. (1995) Nd/Hf ratio of ~4.6 for lower crustal lithologies.

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PUBLICATIONS AND PRESENTATIONS

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