

**The Geochemistry of Cenozoic Volcanism in the Andean Southern Volcanic Zone,
34°S-38°S: Evaluating the Role of Subcontinental Lithospheric Mantle in Alkali
Magma Petrogenesis**

by

Benjamin H Chilson-Parks

B.A. Carleton College, 2011

M.Sc. Brown University, 2016

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The dissertation by Benjamin Chilson-Parks is accepted in its present form by the Department of Earth, Environmental and Planetary Sciences as satisfying the dissertation requirement for the degree of Doctor of Philosophy.

Date _____

Alberto Saal, Advisor

Recommended to the Graduate Council

Date _____

Katherine Kelley, External Reader

Date _____

Greg Hirth, Reader

Date _____

Stephen Parman, Reader

Date _____

Reid Cooper, Reader

Approved by the Graduate Council

Date _____

Andrew Campbell
Dean of the Graduate School

CURRICULUM VITAE

Benjamin H Chilson-Parks

Brown University • 324 Brook Street, Box 1846 • Providence, RI 02912
+1 (860) 861-2762 • benjamin_chilson-parks@brown.edu

Education

Ph.D., Earth, Environmental, and Planetary Sciences, **Brown University**, Providence, RI, **2019**

- Advisor: Dr. Alberto Saal
M.S., Earth, Environmental, and Planetary Sciences, **Brown University**, Providence, RI, **2016**
B.A., magna cum laude, Geology, **Carleton College**, Northfield, MN, **2011**
- Thesis: “Metamorphic petrology of Archean metapelites and ironstones in the Garnet Hill area, Yellowstone National Park, USA”
- Advisor: Dr. Cameron Davidson

Fields of Specialization

Igneous petrology, isotope geochemistry

Current Research Interests

Geochemical evolution of subcontinental mantle lithosphere, mantle metasomatism, Andean volcanism, tectonic evolution of the Wyoming Craton, subduction zone magmatism

Teaching Interests

Introductory geology; introductory field geology; natural hazards; mineralogy; igneous and metamorphic petrology; global plate tectonics; economic geology (e.g., ore deposits, mineral resources); seminars on isotope geochemistry, volatiles in magmas, evolution of cratons, kimberlites, and diamond formation

Publications

- Parks, B. H.**, Saal, A. E., Wang, Z., Calabozo, F., Mallick, S., and Frey, F. A.
Unraveling the signature of metasomatized subcontinental lithospheric mantle in the sources of basaltic magmatism in the Payenia volcanic province, Argentina. *In prep.*
- Parks, B. H.**, Saal, A. E., Calabozo, F., and Hauri, E.H. The major, trace, and volatile elements of olivine-hosted melt inclusions from the back-arc of the Andean Southern Volcanic Zone (34°-39°S). *In prep.*

Meeting Abstracts (Oral Presentations)

** = Presenting Author*

- Chilson-Parks, B. H.***, Saal, A. E., Wang, Z., Calabozo, F., Mallick, S., Frey, F. A. Deciphering the geochemistry of lithospheric mantle in the melt source of the Payenia volcanic province, Argentina. Goldschmidt Conference. 2018.
- Kiraly, A.*, Makishkina, A., Ghosh, T., Haynie, K. L., **Chilson-Parks, B. H.**, Portner, D. E., Metcalf, K., Manga, M., Jadamec, M. A., O'Farrell, K.A., Moresi, L. N., and Stern, R.J. Understanding the Effects of Slab Holes on Mantle Flow and Surface Dynamics. 2018 EGU General Assembly. EGU2018-12544-1.
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Meeting Abstracts (Posters)

- Chilson-Parks, B. H.**, Saal, A. E., Wang, Z., Calabozo, F., Mallick, S., Frey, F. A. The Payenia volcanic province, deciphering the role of the lithospheric mantle. 2018 AGU Fall Meeting.
- Boneh, Y., Chin, E.J., **Chilson-Parks, B.H.**, Hirth, G. New perspective on recovery processes in the upper mantle and their geophysical implications from natural and experimental peridotites. 2018 AGU Fall Meeting.
- Portner, D. E., Kiraly, A., Makishkina, A., **Chilson-Parks, B. H.**, Ghosh, T., Haynie, K. L., Metcalf, K., Manga, M., O'Farrell, K.A., Moresi, L. N., Jadamec, M. A., and Stern, R.J. The Effect of Slab Holes on the Surrounding Mantle Flow Field and the Surface from a Multi-Disciplinary Approach. 2017 AGU Fall Meeting. D111A-0277.
- Parks, B. H.**, Chin, E. J., Saal, A. E., and Hirth, G. Linking composition, deformation, and P-T conditions using peridotite xenoliths from the subcratonic mantle lithosphere, Wyoming craton, Montana, USA. 2015 AGU Fall Meeting. T11B-2889.
- Parks, B. H.**, Wang, Z., Saal, A. E., Frey, F. A., and Blusztajn, J. Oxygen Isotopes in Intra-Back Arc Basalts from the Andean Southern Volcanic Zone. 2013 AGU Fall Meeting. V51A-2640.
- Parks B. H.**, Davidson, C., Henry, D. J., and Mogk, D. Evolution of the Precambrian Rocks of Yellowstone National Park (YNP): High Grade Metamorphic Rocks at Garnet Hill. 2011 GSA Rocky Mountain/Cordilleran Section Meeting.
- Kelley, K., Cottrell, E., Brounce, M., and **Parks, B.** "The Influence of Magmatic Differentiation on the Oxidation State of Fe in Arc Magmas. 2010 Goldschmidt Conference.
- Parks B.H.**, Kelley K.A., Cottrell E., and Posner E.S. "The Influence of Cooling History on the Redox Conditions of Subduction Zone Magmas." 2009 AGU Fall Meeting. V11D-1982.

Teaching Experience

Teaching Assistant , GEOL 0010: Face of the Earth, Brown U.	<i>Spring 2017</i>
Teaching Assistant , GEOL 0010: Face of the Earth, Brown U.	<i>Spring 2016</i>
Teaching Assistant , GEOL 0220: Physical Processes in Geology, Brown U.	<i>Fall 2014</i>
Teaching Assistant , Introductory Geology, Carleton College	<i>Spring 2011</i>

Field Experience

Somuncura Plateau, Argentina: Sampling lava-hosted mantle xenoliths with colleagues from Universidad Nacional de Río Negro.	<i>7 days, Oct 2016</i>
Sierras Pampeanas, Argentina: Field trip surveying geologic features of the area with fellow students in Brown U. Global Tectonics seminar.	<i>17 days, Jan 2016</i>
Colorado, USA: Field trip surveying geologic features of the Front Range and San Juan Mountains with fellow Brown U. graduate students.	<i>7 days, Aug 2014</i>
Nova Scotia, Canada: Field trip surveying geologic features of the region with fellow Brown U. graduate students.	<i>7 days, Aug 2013</i>
Mecca Hills, CA, USA: Mapping geologic features related to the San Andreas fault in a Carleton structural geology class with Dr. Sarah Titus.	<i>4 days, Feb 2011</i>
Yellowstone National Park, USA: Sampling and mapping exposures of Archean rocks.	<i>1 month, Jun-Jul 2010</i>
New Zealand: Field-intensive program surveying and mapping geologic features of the region with fellow Carleton geology students and Dr. Clint Cowan.	<i>3 months, Jan-Mar 2010</i>

Technical Experience/Skills

Proficient, independent usage of CO₂ laser fluorination line and Thermo MAT-253 IR-MS for oxygen isotope analysis at City College of New York (formerly at Yale U.).

Working knowledge of Thermo Scientific Neptune Plus multi-collector ICP-MS and Thermo Scientific X-series-2 ICP-MS and Photon-Machines Analyte G2 laser ablation system at Brown U.

Proficient, independent usage of Cameca SX-100 electron microprobe at Brown U.

Proficient, independent usage of Cameca 6F secondary ion mass spectrometer, Department of Terrestrial Magnetism, Carnegie Institute, Washington, D.C.

Proficient, independent usage of metal-free Pico Trace Clean Lab at Brown U. for sample preparation for solution-based MC-ICP-MS analysis.

Proficient with Brunton Compass, Microsoft Windows, MacOS, Adobe Creative Suite, MATLAB, Mathematica.

Proficient in conversational Spanish.

Awards and Affiliations

Deans' Faculty Fellowship	<i>Spring 2019</i>
Tinker Foundation Field Research Grant	<i>Fall 2016</i>
Brown University Graduate Fellowship	<i>Fall 2013-Spring 2014</i>
First place award for undergraduate poster presentations at the GSA Rocky Mountain/Cordilleran Section meeting	<i>2011</i>
Grade of distinction for undergraduate senior thesis	<i>2011</i>
SMART Grant and Pick Foundation Geology Financial Award	<i>2010-2011</i>

Member of American Geophysical Union, National Association of Geoscience Teachers, Sigma Xi

Outreach Activities

Guest Lecturer , Environmental Geology, Wheaton College, MA	<i>Fall 2018</i>
Science Curriculum Developer and Instructor for Vartan Gregorian Elementary School (Providence, RI): Creating and teaching lesson plans tailored to Next Generation Science Standards for 4 th Grade classrooms	<i>Summer 2017- Spring 2018</i>
2nd-grade Volunteer Science Instructor , Vartan Gregorian Elementary School, Providence, RI	<i>Fall 2013-Spring 2017</i>
Guest Speaker , Reggio Magnet School, Avon, CT	<i>Spring 2016</i>

Professional Development and Experience

Participant , Course Design Seminar, Sheridan Center for Teaching and Learning, Brown U.	<i>Spring 2018</i>
Participant , Teaching and Teaching-Intensive Schools Conference, Westfield State U.	<i>Fall 2017</i>
Teaching Consultant , Sheridan Center for Teaching and Learning, Brown U.	<i>Fall 2015 - Spring 2017</i>
Participant , Certificate I, Sheridan Center for Teaching and Learning, Brown U.	<i>Fall 2014 - Spring 2015</i>
Research assistant , Brown U. Department of Earth Environmental and Planetary Sciences	<i>2013</i>

Program instructor and naturalist , YMCA Camp Jewell, CT	<i>2012</i>
Undergraduate Research Intern , Evolution of the Precambrian Rocks of Yellowstone National Park (An REU Site Project), Yellowstone National Park and Bozeman, MT, with advisors Dr. David Mogk of Montana State U. and Dr. Darrell Henry of Louisiana State U.	<i>2010-2011</i>
Undergraduate Research Intern , Summer Undergraduate Research Fellowship in Oceanography, U. of Rhode Island Grad School of Oceanography, Narragansett, RI, with advisor Dr. Katherine Kelley	<i>2009</i>

Service and Leadership Activities

Departmental Liaison , Sheridan Center for Teaching and Learning, Brown U.	<i>Fall 2016- Spring 2018</i>
Departmental Graduate Student-Faculty Representative , Brown U.	<i>Spring 2016-Spring 2018</i>
President , Grad Student Geo-Club, Brown U.	<i>Summer 2014- Spring 2015</i>
Trip Organizer and Leader , Graduate Student Geology Field Trip to Colorado, Brown U.	<i>Summer 2014</i>
Captain , Men's Varsity Cross Country Team, Carleton College	<i>Fall 2010</i>

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Figures 4 through 11 are from the 11th International Kimberlite Conference oral presentation.

Figures 12 through 26 are mineral phase maps and crystallographic-preferred orientations of Homestead, Williams, and Bearpaw peridotite xenoliths.

INTRODUCTION

The investigation of continental basaltic rocks has been essential in the understanding of the chemical, thermal, and structural identity of the subcontinental mantle and its evolution over geologic time. At subduction zones, the compositions of continental basaltic rocks are influenced by geologic processes that have important implications for volatiles (H_2O , CO_2 , F, Cl, and S) and other geological materials exchanged between Earth's surface and interior, the origins of and modifications experienced by continental lithosphere, and the variety and age of chemical heterogeneities that exist in the convecting mantle. The large compositional diversity of basaltic rocks from continental arcs demonstrate that numerous processes play important roles in continental arc magmatism. These include 1) the transfer of fluids, melts, sediments, or other subducted material from the subducting slab to the mantle wedge, 2) the extent of melting experienced by the mantle source, 3) the type of melting mechanism controlling the extent of melting (e.g. adiabatic decompression versus fluid flux), 4) petrogenetic contributions from a heterogeneous mantle wedge, and 5) contribution from the lithospheric mantle and continental crust through which basaltic magmas travel en route to the surface.

A distinction that has elicited long-lasting debate is the relative contributions of asthenospheric versus lithospheric mantle to the generation of mafic continental arc volcanism. Subcontinental lithospheric mantle (SCLM) can be formed and reworked by the tectonic and magmatic processes that occur at subduction zones (e.g., Hawkesworth et al., 1999; Rudnick, 1995). Subduction processes have the potential to extensively metasomatize SCLM and to wear away the base of the SCLM via subduction erosion and/or eclogitization and delamination (e.g., Kay and Kay, 1993; Kay et al., 2005). In turn, the shape, viscosity, and temperature of SCLM can have an influence on the flow structure,

temperature, composition and extent of melting of the underlying mantle wedge. Details of the influence that asthenospheric mantle wedge has on SCLM and vice versa remain poorly understood. For this reason, basaltic rocks from continental arcs, which have the primitive (high MgO) compositions expected from mantle-derived melts, serve as a powerful probe of the compositional variability of the mantle source and its asthenospheric and/or lithospheric character. If one were to choose a continental arc setting in which to study basaltic rocks that reflect this mantle signal, one would look for an abundance of monogenetic eruptive centers, given their tendency to be formed by less evolved magmas that rapidly ascend to the surface without significant residence time in the crust, which can lead to differentiation and crustal contamination (Valentine and Gregg, 2008).

One such locality that matches this description is the Andean Transitional Southern Volcanic Zone (TSVZ, 34°-38°S), which represents an area of some of the most productive mafic volcanism in South America during the last two million years, although basaltic volcanism can be found in this region dating back at least to the Early Miocene (Kay et al., 2006). Over this period formed the Payenia volcanic province, which consists of 8400 km³ of volcanic rock covering an area of 40,000 km² in western Argentina (Ramos and Folguera, 2011). Over 800 eruptive centers occur in Payenia, most of which are monogenetic eruptive centers of basaltic lavas and tephra. Basaltic rocks from Payenia display a large chemical and isotopic variability, ranging from lavas with compositions that resemble ocean island basalts in the central and southeastern regions to lavas with compositions that resemble volcanic front lavas in the northern and southwestern regions (e.g., Jacques et al., 2013, Söager et al., 2013). A debate has persisted over the origin of this compositional variability, with some workers attributing the intraplate signature to EM-1 type asthenosphere that is flowing into the mantle wedge as the subducting Nazca

slab steepens (Søager and Holm, 2013; Søager et al., 2013; Søager et al., 2015a; Søager et al., 2015b), and others proposing that enriched SCLM is responsible (Jacques et al., 2013; Kay et al., 2013; Søager et al., 2018).

The objective of this thesis is to evaluate the role of SCLM versus asthenospheric mantle in the source of mafic TSVZ volcanism that has occurred since the Early Miocene. The measurements presented in this thesis considerably expands the geochemical dataset for basaltic rocks from the TSVZ, improving our resolution of geochemical character of TSVZ volcanism and the mantle sources it represents. The motivation for this thesis can be summarized by these guiding questions:

- 1.) What is the origin of the intraplate signature in TSVZ back-arc lavas?
- 2.) What is the role of lithospheric versus asthenospheric melting in the generation of mafic TSVZ volcanism? Can we deconvolve their geochemical signatures?
- 3.) If melt is coming from the metasomatized SCLM, does it only produce volcanism with an intraplate signature, or can it also pass on an arc signature inherited from parent melt/metasomatic agent?
- 4.) What is the volatile budget of mafic TSVZ volcanism? Do magmatic volatile contents give any indication of the melting mechanisms that occur in the TSVZ mantle source? What are the distinctive volatile budgets of the asthenospheric and lithospheric melt sources?
- 5.) Do compositional variations in TSVZ lavas correspond to spatial and/or temporal variations in the lavas?

Chapter 1 (referred to as Chilson-Parks et al., *in prep* in subsequent chapters) reports whole-rock major and trace element concentrations and Sr-, Nd-, Hf-, and Pb-isotope ratios and olivine phenocryst high-precision oxygen-isotope ratios in a suite of 34

alkaline basalts and 1 basaltic trachyandesite from the Payenia volcanic province. Because oxygen isotope contents of subduction-related basalts have the potential to be significantly modified by both high- and low- ^{18}O slab derived components (Eiler, 2001), and because olivine is an early-liquidus phase, $\delta^{18}\text{O}_{\text{olivine}}$ values have the potential to add a new compositional dimension to the identification of mantle source components. Results from this chapter show that $\delta^{18}\text{O}_{\text{olivine}}$ values for Payenia basalts vary with arc signature, but not necessarily toward compositions of volcanic front lavas. Instead, Payenia basalts that both have and lack arc signature have more negative $\Delta\epsilon_{\text{Hf}}$ values than the volcanic front. Because correlations between Nd, Hf, and O isotopes and trace element contents are not clearly explained by an asthenospheric melt source, this chapter presents forward model calculations that predict the chemical and isotopic signature of metasomatic cumulates in the SCLM and of the melt products it would produce. Model results demonstrate that Payenia lava compositional variations can be explained by the mixing of three melts: one from mantle wedge asthenosphere, one from a SCLM cumulate that lacks arc signature, and one from SCLM cumulate that has arc signature. Nd and Hf isotope ingrowth patterns indicate that the timescale necessary to attain the $\Delta\epsilon_{\text{Hf}}$ values exhibited by Payenia lavas is $\sim 150\text{-}200$ million years, which coincides with the breakup of the Gondwanan supercontinent and the development of the proto-Pacific convergent margin. Model results demonstrate that in addition to the variability that slab inputs can cause in continental arc basalts, the mineral-melt fractionations that would take place during the fractional crystallization of SCLM cumulates also has the potential to lower $\delta^{18}\text{O}_{\text{olivine}}$ values in their melt products.

Chapter 2 presents the first dataset to include volatile, major, and trace element concentrations for olivine-hosted melt inclusions and embayments from the SVZ back-arc.

The melt inclusions analyzed in this study were taken from three TSVZ back-arc tephras, two of which (from the Diamante and Loncopué areas) erupted significantly closer to the trench than the third (from the Auca Mahuida volcanic field). Due to this spatial relationship, slab-derived materials released from the subducting slab are expected to enrich the Diamante and Loncopué source in volatiles, which is consistent with the enrichments in H₂O, S, Cl, and F and the arc-like trace element patterns displayed by melt inclusions from these localities. However, the calculated primary melt compositions of Diamante and Loncopué reflect different source compositions, such that their relationship cannot be explained by different degrees of melting as controlled by the contribution of slab-derived material to the mantle wedge. The modeled arc-type cumulate presented in chapter 1 produces a melt that closely resembles the Diamante MIs, whereas Loncopué MIs have primary melt compositions that more closely resemble those of melt inclusions from the volcanic front. Auca Mahuida melt inclusions have intraplate-like trace element patterns, and lower H₂O, S, F, and Cl contents, which clearly shows the lack of slab-derived inputs in the Auca Mahuida source. Nonetheless, Auca Mahuida have distinctively high F/Cl ratios, which are not predicted from a MORB-like source but rather an amphibole- and/or phlogopite-bearing SCLM source. The discussion of this chapter is used to consider the resemblance between melt inclusion compositions and the modeled cumulate-derived melt compositions presented in Chapter 1, and their significance in demonstrating the role of metasomatized SCLM in TSVZ back-arc melt generation.

Lastly, chapter 3 presents a broader data set of whole-rock major and trace element concentrations, Sr, Nd, Pb, and Hf isotope contents, and Ar-Ar ages for volcanic front and back-arc TSVZ lavas and tephras. These new data, compiled with previously published compositions of basaltic rocks from the TSVZ, are used to unravel the mantle source

components that control compositional variability in the mafic TSVZ volcanism that has persisted since the Early Miocene. This approach allows for the assessment of the spatio-temporal variations in the TSVZ mantle source—consideration is given to volcanism that occurred contemporaneously at various locations in the TSVZ and to volcanism that occurred at different times but in close proximity. Toward this goal, two principal component analyses (PCAs) were performed, one using trace element concentrations and the other using Sr, Nd, and Pb isotopes. PCA results reveal a strong control on composition from slab-derived inputs, but also a secondary component that is correlates with LILE, Th, and U contents of TSVZ lavas. This secondary component is consistent with compositions reflecting the melting of amphibole and/or phlogopite which would be stable in the SCLM. Moreover, compositions of melt pockets from Patagonian xenoliths show a clear resemblance to Payenia and Early Miocene intraplate basalts from the TSVZ, which reinforces the interpretation that the TSVZ intraplate signature is associated with the melting of SCLM cumulates. The discussion that follows considers the spatio-temporal variations in lavas with the SCLM cumulate affinity in the context of the tectono-magmatic history of the TSVZ.

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CHAPTER 1

Unraveling the signature of metasomatized subcontinental lithospheric mantle in the sources of basaltic magmatism in the Payenia volcanic province, Argentina

Benjamin H Chilson-Parks^{1*}, F. Calabozo², A. E. Saal¹, Z. Wang³, S. Mallick¹, F.A. Frey⁴

¹Brown University, Providence, Rhode Island, United States

²Universidad Nacional de Río Negro, General Roca, Argentina

³The City College of New York, New York, New York, United States

⁴Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

***email: Benjamin_Chilson-Parks@brown.edu**

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0.) Abstract

We report whole-rock major and trace element concentrations and Sr-, Nd-, Hf-, and Pb-isotope ratios and olivine phenocryst high-precision oxygen-isotope ratios in a suite of 34 alkaline basalts and 1 basaltic trachyandesite from the Payenia volcanic province (central Argentina, 34.5- 38°S). A substantial portion of this basaltic volcanism bears an intraplate geochemical signature, the origin of which is debated. Payenia samples have Nd and Hf isotope values that diverge below the mantle array (i.e., $\Delta\epsilon_{\text{Hf}}$ values as low as -2.8). $\delta^{18}\text{O}_{\text{VSMOW}}$ values of olivine phenocrysts from Payenia basalts vary from 4.84 to 5.39‰, a range that covers and extends below the range of normal mantle $\delta^{18}\text{O}$ values. The lowest $\delta^{18}\text{O}_{\text{oli}}$ values are from lavas in the Buta Ranquil area, which show evidence of mixing with differentiated magma sourced from the Tromen stratovolcano. Primitive basalts from other regions of Payenia show negative correlations for $\delta^{18}\text{O}_{\text{oli}}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values and correlations of $\delta^{18}\text{O}_{\text{oli}}$ versus trace element ratios indicative of arc signature (e.g., Ba/Nb). We suggest these isotopic and trace element variations reflect the contribution of metasomatized subcontinental lithospheric mantle (SCLM) in the Payenia melt source. We present a simple forward model of cumulate formation and melting within the SCLM that predicts the observed lava compositions. Variations in $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ suggest that the age of the SCLM cumulate is 150-200 Ma, which coincides with the development of the proto-Pacific Andean arc and the breakup of Gondwana. Variations in $\delta^{18}\text{O}_{\text{oli}}$ values from modeled cumulate-derived melts indicate that cumulate formation represents a mechanism that can fractionate oxygen isotopes even when the melt forming the cumulate has a $\delta^{18}\text{O}$ value normal for ambient upper mantle. Therefore, a slab component

depleted in ^{18}O relative to the upper mantle, as is commonly invoked in low- $\delta^{18}\text{O}$ arc lavas, is not required to explain the compositional diversity of Payenia lavas.

1.) Introduction

The Payenia volcanic province (34-38°S) represents the northernmost extent of back-arc volcanism of the Andean Southern Volcanic Zone (SVZ) and some of the most voluminous Cenozoic volcanic activity in South America (Ramos and Folguera, 2011). Covering roughly 40,000 km², Payenia comprises over 800 cinder cones, shield volcanoes, and stratovolcanoes (Bertotto et al., 2006) (Figure 1). Previous investigations into the source of alkaline basalts in Payenia noted that their chemical and isotopic compositions display a variable degree of arc signature (Germa et al., 2010; Gudnason et al., 2012; Hernando et al., 2014; Jacques et al., 2013; Kay et al., 2006; Kay et al., 2013; Pallares et al., 2016; Søgner and Holm, 2013; Søgner et al., 2013; Søgner et al., 2015a; Stern et al., 1990).

Such chemical diversity occurs throughout the SVZ back-arc. Stern et al. (1990) categorized this chemical diversity into two groups. “Transitional” basalts represent back-arc basalts that, relative to volcanic front basalts, exhibit similar but less dramatic enrichments in large-ion lithophile elements (LILEs) versus high field-strength elements (HFSEs). Alternatively, “cratonic” basalts have intraplate-like trace element patterns, with enrichments in highly incompatible trace elements, and lack high (arc-like) LILE/HFSE ratios. Stern et al. (1990) also noted that in the basaltic back-arc plateaus of the SVZ south of Payenia, transitional basalts erupted along the western margins of the plateaus, closer to the magmatic arc, while cratonic basalts erupted farther from the volcanic front. Transitional basalts are thought to represent melting of the mantle wedge with a weaker

slab fluid flux than beneath the volcanic front and/or melting of mantle contaminated by subducted material earlier in the Cenozoic. Erupting farther from the volcanic front, cratonic basalts would instead represent the lower-degree melting of variably enriched asthenosphere and/or sub-continental lithospheric mantle (SCLM). A similar weakening of arc signature with increasing distance from the volcanic front has been documented in basalt compositions from other continental arc settings, such as the Cascades and Mexico (Johnson et al., 2009; Rowe et al., 2009). For instance, in Mexico, the olivine-hosted melt inclusions of alkali basalts that erupted far from the volcanic front exhibit low volatile contents, HFSE enrichments, and slightly lower $\delta^{18}\text{O}_{\text{oli}}$ values than those of melt inclusions from closer to the magmatic arc (Johnson et al., 2009).

Although the chemical diversity of Payenia basalts have been previously characterized, there remains a debate concerning the mechanisms that cause the variation between transitional and cratonic compositions. Regarding the origin of the cratonic signature in Payenia, some authors explain it as a reflection of the melting of a mixed peridotite-pyroxenite asthenospheric source (Søager and Holm, 2013; Søager et al., 2013; Søager et al., 2015a; Søager et al., 2015b). They suggest that this asthenospheric source upwelled beneath Payenia during the steepening of the subducting Nazca plate, which followed a Late Miocene-Early-Pliocene episode of transient slab shallowing and compressional tectonics (Kay et al., 2006). Alternatively, previous authors proposed that heating and melting of the sub-continental lithospheric mantle (SCLM) is responsible for the cratonic signature in Payenia lavas (Jacques et al., 2013; Kay et al., 2013; Søager et al., 2018). Contribution of metasomatized SCLM was proposed to explain the trace element and isotopic characteristics of small eruptive centers adjacent to the Villarica volcano in the central SVZ (Hickey-Vargas et al., 2016b).

These possibilities serve as the hypotheses tested by the geochemical dataset we present in this study. We report new whole-rock major and trace element concentrations and Sr, Nd, Hf, and Pb isotope contents and olivine phenocryst $\delta^{18}\text{O}$ values of 35 lavas sampled from the Payenia volcanic province. We identify multiple petrological processes that acted on the Payenia lavas, from a two-stage process of magma differentiation and mixing within the crust near Tromen Volcano to the melting of the metasomatized SCLM controlling the compositional variation in the mafic lavas from the Payenia region. We test this hypothesis by presenting a model quantifying the effect of the melting of the metasomatized SCLM on the geochemical character of Payenia magmatism.

2.) Methods

We analyzed whole-rock powders for major and trace element concentrations and Sr, Nd, Pb, and Hf isotope contents, and olivine phenocrysts for oxygen isotope ratios. Whole-rock major element oxide concentrations were measured by X-ray fluorescence (XRF) spectrometry at the University of Massachusetts, Amherst, and at Washington State University. For all reported samples except MEN-026 and VEJ-041, whole-rock major element oxides (SiO_2 , TiO_2 , Al_2O_3 , FeO^{T} , CaO , MgO , MnO , K_2O , Na_2O , and P_2O_5) and some trace elements (Cr, V, Ni, Zn, and Ga) were measured at the University of Massachusetts, Amherst by an automated Siemens XRF spectrometer. Measurement precision in all measurements yielded <2% RSD (2σ) for duplicated sample analyses except for MnO (<3%) and Na_2O ($\leq 6\%$). Cr, V, Ni, Zn, and Ga concentrations were also measured by XRF, yielding significantly higher standard deviations, especially for Ni concentrations that are <50 ppm in some samples.

For samples MEN-026 and VEJ-041, XRF analyses of the same set of major and trace elements were performed at the Peter Hooper GeoAnalytical Lab, Washington State University by a ThermoARL Advant'XP+ sequential XRF spectrometer. Sample preparation, analytical procedure, and accuracy and precision is detailed in Johnson et al. (1999). To monitor instrumental drift, analyses of GSP2, BCR-1, and AGV-2 standards were performed every 24-48 hours, with a precision of 0.1-0.5% RSD. Analyses of duplicate beads made from the same unknown sample whole-rock powder had a reproducibility of <1% RSD for all major elements, except FeO^T (<1.4%). For the trace elements measured by XRF, duplicate reproducibility was <10%, except for Ga (<15%).

For all samples, the remaining trace elements (Sc, Rb, Sr, Y, Zr, Nb, Cs, REE, Th, U, Hf, Ta, Pb) were measured by inductively coupled plasma-mass spectrometry (ICP-MS) using an Agilent 7700 quadrupole mass spectrometer at WSU, on Li-tetraborate fused beads. Reproducibility over the course of the analyses was assessed by repeatedly measuring the compositions of an international rock standard (BCR-2, n=54), an in-house standard (TED, n=33) as unknowns among the samples. Precision yielded <5% RSD (2σ) for most elements except for Pb in BCR-2 (<8%) and Cs in TED (<12%). In addition to monitoring trace element reproducibility with the BCR-2 and TED standards, trace element concentrations of an alkaline basalt sample from the Nevado volcanic field were measured five times during the course of the analyses, yielding <6% RSD (2σ) for most elements except for Pb (<28%) and Sc (<8%).

Sr, Nd, Hf, and Pb isotopic compositions were measured on a Thermo Scientific Neptune Plus MC-ICP-MS at the Mass Spectrometer Analytical Facility, Brown University. Sr, Nd and Hf were introduced in the plasma using a PFA nebulizer with a flow rate of ~70 $\mu\text{l}/\text{min}$ coupled with a glass spray chamber, while Pb was introduced with an

APEX-IR introduction system to enhance the sensitivity. The mass spectrometer was equipped with an H-skimmer cone and H-sampler cone. The baseline measurement was taken at -0.5 amu. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were corrected for instrumental mass fractionation using an $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$, respectively, with an exponential law. Pb solution was spiked with NBS SRM-997 Tl standard prior to analysis with a Pb/Tl = 4 to correct for the mass fractionation using an exponential law with $^{203}\text{Tl}/^{205}\text{Tl} = 0.418922$. Sr, Nd, and Hf were measured at 200 ppb concentration whereas Pb was measured at 75 ppb concentration level. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios of samples are reported relative to the NBS SRM 987 standard with $^{87}\text{Sr}/^{86}\text{Sr} = 0.71024$, the JNd-i standard with $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$ and the JMC-475 standard with $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$, respectively. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are reported relative to the NBS 981 standard with $^{206}\text{Pb}/^{204}\text{Pb} = 16.9356$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4891$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7006$ (Todt et al., 1996). The internal precision is 5-10 ppm for Sr and Nd, 20-45 ppm for Pb and 20-30 ppm for Hf, while the external precision over the course of two years is 27 ppm for Sr (2σ , n=75), 29 ppm for Nd (2σ , n=104), 39 ppm for Hf (2σ , n=89) and 100 ppm for Pb isotopes (2σ , n=75). Procedure blanks were <50 pg for Sr and Pb and <30 pg for Nd and Hf. The USGS reference material BCR-2 and BIR-1 were processed during the sample preparation and measured with the same instrument set up, data for both are in agreement with the range reported in GeoRem database.

Oxygen isotope analyses of olivine phenocrysts were measured by the infrared-laser fluorination technique (ILFT) at Yale University, using previously described methods (Eiler et al., 1996). During analysis, measurements of standards UWG (Gore Mountain garnet from New York) and KHX-1 (Kilbourne Hole olivine from New Mexico) were

interspersed with measurements of unknown samples. Results for the standards are UWG-2 = $5.77 \pm 0.14\text{‰}$ (n=16) and KHX-1 = $5.20 \pm 0.13\text{‰}$ (n=38), which are within the analytical uncertainty of accepted values of UWG (5.80‰) and KHX-1 (5.25‰) (Eiler et al., 2000a; Eiler et al., 2000b; Valley et al., 1995; Wang et al., 2011). All standard deviations refer to 1σ of long-term reproducibility of raw measurements. All $\delta^{18}\text{O}$ values for unknown samples on a given day were corrected by the difference between measured and accepted values for standards on that day. For samples with duplicated measurements, standard deviations typically were $<0.1\text{‰}$.

Details of sample preparation are in the supplementary material.

3.) Results

Hereafter, we refer to three areas of the Payenia volcanic province (Figure 1). The Tromen-Buta Ranquil (TBR) area represents the eruptive centers at the Buta Ranquil locality and the Tromen stratovolcano. The south-central (SC) area is comprised of the Llancanelo, Payún Matrú, Auca Mahuida, and Río Colorado volcanic fields. The Nevado-Diamante (ND) area contains the Nevado volcanic field and isolated eruptive centers near the back-arc stratovolcano Cerro Diamante.

3.1) Major and trace element concentrations

Major and trace element concentrations are reported in Table 1. Samples range in composition from basalt to basaltic trachyandesite within the alkaline compositional field (Figure 2). All but six samples in this study are nepheline-normative according to the CIPW norm classification: two ND samples and four TBR samples are hypersthene-normative (Table 1). MgO concentrations for the samples varies from 5 to 12 wt.% and SiO₂ concentrations vary from 46.0 to 52.5 wt.%, except for hy-normative basaltic

trachyandesite sample 27-5, taken from a flow on the northeastern flank of the Tromen volcano, which has $\text{SiO}_2=55.4$ wt.% (Figure 3). This compositional range is similar to what was previously reported for Payenia samples (Hernando et al., 2014; Jacques et al., 2013; Søager et al., 2013). Relative to lavas from the transitional SVZ (TSVZ) at the same latitude, the lavas from the Payenia volcanic province range to lower SiO_2 , Al_2O_3 , higher FeO^T , CaO , TiO_2 , P_2O_5 , and slightly higher Na_2O and K_2O at a given MgO content (Figure 3).

A comparison of lavas from the different areas within Payenia show that ND lavas have higher MgO contents than those from TBR and SC areas. Sample 27-5, sourced from Tromen volcano, exhibits major element concentrations typical of TSVZ lavas, while other TBR lavas span a range in major element concentrations between Tromen and SC lavas.

The trace element concentrations of representative samples from each area in Payenia are shown in Figure 4. Trace element patterns of lavas from ND and TBR areas show the closest resemblance to primitive (> 5 wt. % MgO) TSVZ lavas, with typical arc signature (high LILE/HFSE ratios), but with relatively smaller Nb, Ta, and Ti negative anomalies. The trace elements of SC area lavas lack a prominent arc signature; their trace element patterns more closely resemble trace element patterns of cratonic lavas (Stern et al., 1991), which lack depletions in Nb, Ta, and Ti relative to elements of similar incompatibilities.

3.2) Sr-Nd-Pb-Hf isotopes of whole-rock powders

Newly obtained Sr-Nd-Pb-Hf isotope ratios are reported in Table 1 and Figure 5. Data cover a similar range to what has been previously reported for Payenia lava samples (Holm et al., 2016; Holm et al., 2014; Jacques et al., 2013; Kay et al., 2006; Kay et al., 2013; Saal, 1994; Søager and Holm, 2013; Søager et al., 2013; Søager et al., 2015a). The

$^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for Payenia lavas are negatively correlated (Figure 5A) and overlap with values reported for TSVZ lavas (Davidson et al., 1987; Harmon et al., 1984; Hickey et al., 1986; Hildreth and Moorbath, 1988; Tormey et al., 1995). Both, Payenia and volcanic front lavas, have $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios intermediate between those reported for the Discovery and Shona segments of the southern Mid-Atlantic Ridge (MAR) (Douglass et al., 1999) and Chile trench sediments. East Pacific Rise (EPR) MORBs (Gale et al., 2013 and references therein) yield significantly higher $^{143}\text{Nd}/^{144}\text{Nd}$ and lower $^{87}\text{Sr}/^{86}\text{Sr}$ values than those for Andean volcanics.

$^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are positively correlated (Figure 5B), however, Payenia lavas generally have lower $^{176}\text{Hf}/^{177}\text{Hf}$ at similar $^{143}\text{Nd}/^{144}\text{Nd}$ ratios than those from TSVZ lavas and trench sediments. Payenia lavas display a range in $^{176}\text{Hf}/^{177}\text{Hf}$ ratios that extend from values similar to the Nd-Hf isotope mantle array (Chauvel et al., 2008) to values below the array (i.e., $\Delta\epsilon_{\text{Hf}} < 0$) at a given $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. Payenia lavas with the most radiogenic Nd and Hf trend towards and overlap with Nd and Hf isotope values of the Discovery- and Shona-influenced Mid-Atlantic Ridge (MAR) MORBs. East Pacific Rise (EPR) MORBs yield higher $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios than Andean volcanics. The two hypersthene-normative samples from the ND area have lower $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ and higher $^{86}\text{Sr}/^{87}\text{Sr}$ values than the nepheline-normative samples from the same area.

Pb isotopes for Payenia volcanic province and TSVZ lavas show strong positive correlations extending between values for Discovery- and Shona-influenced MAR MORBs and those for Chile trench sediments (Figure 5C-D). SC area lavas have the least radiogenic Pb compositions in Payenia, which overlap with the range of isotope values of Discovery-Shona MAR MORBs (Douglass et al., 1999). ND and TBR samples span a range in

$^{206}\text{Pb}/^{204}\text{Pb}$ values between SC sample values and TSVZ lava and trench sediment values. TBR lava compositions fall along a similar linear trend, $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, while ND area samples generally have slightly lower $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values than TBR samples. EPR MORB samples occur along the Northern Hemisphere Reference Line (Hart, 1984), which has significantly lower $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values at a given $^{206}\text{Pb}/^{204}\text{Pb}$ value than the Andean samples.

3.3) *Oxygen isotopes of olivine phenocrysts*

The $\delta^{18}\text{O}$ values of olivine from Payenia volcanic province lavas range from 4.84‰ to 5.39‰ (Table 1). The $\delta^{18}\text{O}_{\text{oli}}$ values recorded for TBR samples (4.84-5.01‰) extend to values lower than previously reported for $\delta^{18}\text{O}_{\text{oli}}$ values in Payenia (5.02-5.42‰; Jacques et al., 2013), which overlaps with normal values for mantle olivine (5.0-5.4‰; Eiler, 2001; Matthey et al., 1994). Figure 6 demonstrates a link between the eruption location of the Payenia lavas and $\delta^{18}\text{O}_{\text{oli}}$ values: the lowest $\delta^{18}\text{O}_{\text{oli}}$ values in Payenia occur in samples from the TBR area, intermediate $\delta^{18}\text{O}_{\text{oli}}$ values in SC samples (4.97-5.27‰), and relatively high $\delta^{18}\text{O}_{\text{oli}}$ values in ND samples (5.23-5.39‰). Although the $\delta^{18}\text{O}_{\text{olivine}}$ values of TSVZ lavas span a similar range (4.88-5.52‰, Jacques et al., 2013) to that of our measurements, they lack a clear trend in the spatial distribution of $\delta^{18}\text{O}_{\text{oli}}$ variation (Figure 6). TSVZ lava samples that were identified by Jacques et al. (2013) as erupted from isolated satellite cones do not represent endmember $\delta^{18}\text{O}_{\text{oli}}$ values, and TVSZ $\delta^{18}\text{O}_{\text{oli}}$ values do not clearly vary with proxies for magmatic differentiation (e.g., MgO, SiO₂). When compared to $\delta^{18}\text{O}_{\text{oli}}$ values from other continental arc settings, Payenia lavas display a range similar to Central American lavas (4.6-5.7‰; Eiler et al. 2005), while covering the lower extent of the $\delta^{18}\text{O}_{\text{oli}}$ range observed in Kamchatka (5.1-7.4‰; Auer et al., 2009), Mexico (5.3-6.6‰; Straub et al., 2015), and the Cascades (4.7-6.1‰; Martin et al., 2011).

4.) Discussion

4.1) *Compositional variations in the TBR area*

Isotopic and trace element characteristics of our samples indicate that the source of the SC lavas was less influenced by subduction-related processes than the sources of ND and TBR lavas. While this variability in arc signature is consistent with previous insights that identify heterogeneous Payenia melt sources (e.g., Jacques et al., 2013; Søger et al., 2013), TBR lavas exhibit distinctive compositional traits, such as low $\delta^{18}\text{O}_{\text{oli}}$ values, dominantly hy-norm major element compositions, and high Zr/Sm ratios (Figures 7, S1). These characteristics signify a distinct petrologic history from other Payenia lavas. Because TBR lavas erupted close to the Tromen stratovolcano and have a broad range in major element concentrations, we discuss the potential impact of Tromen magmatic differentiation on TBR lava compositions.

Among TBR area samples, major element concentrations vary systematically along linear trends between the Hy-normative basaltic trachyandesite Tromen sample 27-5 and the sole ne-normative basalt from the TBR area, Buta Ranquil sample 27-4 (Figures 2-3). Trace element patterns for TBR lavas also display a substantial range in trace element patterns. Hy-norm sample 27-5 has a relatively strong arc signature, whereas Ne-norm sample 27-4 has generally lower trace element concentrations and the weakest arc signature among TBR area samples (Figure 7A). Trace element concentrations of TBR samples can be explained by a two-endmember mixing of an evolved, hy-norm Tromen sample 27-5 and a ne-norm Buta Ranquil basalt 27-4. Mixtures of 20-40% of the hy-norm endmember closely resemble trace element concentrations of the three hy-norm Buta Ranquil lavas,

suggesting that they represent mixing of a relatively evolved, hy-norm magma with a more primitive, ne-norm magma.

This trend is also reflected in the isotopic characteristics of the TBR lavas. Although Tromen sample 27-5 does not have the lowest $\delta^{18}\text{O}_{\text{oli}}$ value, it is below the normal mantle olivine range and within 0.1‰ of $\delta^{18}\text{O}_{\text{oli}}$ values of hy-norm Buta Ranquil lavas, while sample 27-4 has the highest $\delta^{18}\text{O}_{\text{olivine}}$ value from the TBR area (Figure 6). 27-5 also has the highest $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios in the area, and Buta Ranquil samples decrease in Pb isotope ratios to those of sample 27-4, which has the lowest radiogenic Pb contents in the TBR area, similar to Pb isotope contents of the ne-norm SC area lavas (Figure 5C-D). Overall, this compositional relationship between Tromen and Buta Ranquil lavas indicates that the hy-norm, arc-related signal present in these lavas is linked to the magma source of the Tromen stratovolcano, while the ne-norm non-arc-related signal is associated with a source similar to that of SC area alkaline basalts.

The extent of differentiation of the Tromen mixing endmember may also cause the distinctive Zr/Sm and low $\delta^{18}\text{O}_{\text{oli}}$ values of TBR samples. The Zr/Sm value of sample 27-5 is significantly higher than those of the more primitive Payenia lavas we report (Zr/Sm = 42 for 27-5 versus Zr/Sm = 19-32 for ND and SC area samples). Other Payenia lavas with Zr/Sm > 40 are intermediate to felsic lavas erupted from the Payún Liso stratovolcano and the Payún Matrú and Auca Mahuida shield volcanoes (Espanon et al., 2014; Germa et al., 2010; Hernando et al., 2014; Kay et al., 2013; Pallares et al., 2016; Søger et al., 2013). These lavas exhibit a positive correlation between Zr/Sm and SiO_2 concentration. Lavas with $\text{SiO}_2 \sim 55$ wt.% have Zr/Sm < 40, and lavas with $\text{SiO}_2 > 70$ wt.% have Zr/Sm > 100 (Figure 7B), highlighting the relationship between extent of magmatic differentiation and Zr/Sm. The mineral most likely to cause this variation in Zr/Sm is apatite. For andesitic

melts, Zr and Hf have $D_{\text{apatite/melt}} < \sim 1$, while for trace elements that have a similar incompatibility to Zr and Hf during mantle melting (e.g., Sm, Nd, Eu) have $D_{\text{apatite/melt}} > \sim 10$ (Fujimaki, 1986; Watson and Green, 1981). Therefore, as apatite precipitates from the melt, the melt Zr/Sm is expected to increase. Additionally, Zr/Sm increases in lavas from the Tromen, Payún Matrú, and Auca Mahuida volcanoes over the same range of SiO_2 concentrations (from ~ 50 -70 wt.%) that sees a decrease in P_2O_5 from ~ 1 to < 0.1 wt.% (Figure 7C). Because P_2O_5 decreases systematically as Zr/Sm increases in evolved Payenia lavas, and because apatite partitions Sm from Zr and Hf, we propose that apatite crystallization increased Zr/Sm in Tromen lavas. Hy-norm Buta Ranquil lavas subsequently inherited elevated Zr/Sm when Tromen-sourced magma mixed with ne-norm Buta Ranquil magma, an explanation consistent with variations in SiO_2 , P_2O_5 , and Zr/Sm.

As differentiation progresses to intermediate compositions, $\delta^{18}\text{O}_{\text{oli}}$ values are expected to decrease (Bindeman et al., 2004; Bucholz et al., 2017; Eiler, 2001). This decrease in $\delta^{18}\text{O}_{\text{oli}}$ is primarily due to the magnitude of melt-olivine oxygen isotope fractionations increasing as temperature decreases along the LLD. Modeling studies and natural sample suites representative of closed-system differentiation demonstrate the relationship between temperature and olivine oxygen isotope contents (Bucholz et al., 2017 and references therein).

Lacking sufficient constraints on the temperatures and extents of crystallization experienced by Tromen magmas along a LLD, we applied the experimental data of a hydrous, hy-norm basaltic melt fractionally crystallizing at 0.7 GPa (Nandedkar et al., 2014) to ascertain the magnitude of the decrease in $\delta^{18}\text{O}_{\text{oli}}$ imposed by the differentiation of Tromen magmatism. From these experiments, the lowest-temperature melt from which olivine crystallizes ($T=1070^\circ\text{C}$, $\sim 25\%$ extent of crystallization) $\delta^{18}\text{O}_{\text{oli}}$ decreased by

~0.2‰ relative to the $\delta^{18}\text{O}_{\text{oli}}$ value of the first olivine to crystallize on the LLD. While most of the Payenia lava samples from this study have major element compositions suggesting minimal differentiation, Tromen sample 27-5 has major element concentrations that indicate that this lava experienced significantly more differentiation than other samples from the area (Figures 2-3). If 27-5 ($\delta^{18}\text{O}_{\text{oli}}=4.93\text{‰}$) experienced a similar differentiation history to the experimental liquids of Nandedkar et al. (2014), the parental melt of 27-5 would have an equilibrium $\delta^{18}\text{O}_{\text{oli}}$ of ~5.1 ‰, a value within the lower extent of the normal mantle $\delta^{18}\text{O}_{\text{oli}}$ values.

Therefore, characteristics of the Tromen-Buta Ranquil area lavas reflect a two-step process. Initially, lavas from Tromen stratovolcano underwent shallow-level fractional crystallization including apatite, increasing magma Zr/Sm to values greater than those of primitive Payenia lavas. Decreasing temperatures during differentiation would increase the magnitude of melt-olivine oxygen isotope fractionation, allowing olivine to crystallize in Tromen melts with $\delta^{18}\text{O}$ values below the normal mantle $\delta^{18}\text{O}_{\text{oli}}$ range. Subsequently, differentiated Tromen magma mixed with more primitive, ne-norm magma in Buta Ranquil, erupting as hy-norm basalts.

4.2) The geochemical variability of ND and SC area lavas

The significant variability in the radiogenic and oxygen isotope contents of ND and SC area lavas demonstrate that closed system fractional crystallization is not responsible for the geochemical signals present in these lavas (Figures 5, XX). Therefore, geochemical variation of ND and SC lavas cannot be explained by the differentiation and mixing processes that can explain the origin of the hy-norm TBR lavas, nor can these variations reflect the melting of a homogeneous source. Rather, the compositional variations in the ND and SC lavas appear to reflect processes related to a heterogeneous melt source,

producing the negative trends in Nd and Hf isotopes versus $\delta^{18}\text{O}_{\text{oli}}$ values (Figure 8A). While each sample group covers a similar range of Nd and Hf isotope ratios, the ND samples form an array subparallel to, but at higher $\delta^{18}\text{O}_{\text{oli}}$ values than, those of SC area samples (Figure 8A). SC samples with the most radiogenic Nd and Hf have $\delta^{18}\text{O}_{\text{oli}}$ values that extend below the normal range for mantle olivine (5.0‰). Assimilation-fractional crystallization (AFC) processes involving continental crust are unlikely to be the cause of the low $\delta^{18}\text{O}_{\text{oli}}$ values and relatively radiogenic Nd and Hf isotopes, since continental crust tends to be enriched in ^{18}O and unradiogenic in Nd and Hf relative to mantle lithologies (Simon and Lécuyer, 2005; Vervoort et al., 1999). A potential indication of the heterogeneous source components affecting ND and SC lavas is given by the comparison of whole-rock Mg# and $\delta^{18}\text{O}_{\text{oli}}$ values: SC area lavas have relatively low Mg# values and $\delta^{18}\text{O}_{\text{oli}}$ values while ND area samples range from high Mg# and intermediate $\delta^{18}\text{O}_{\text{oli}}$ values to lower Mg# and high $\delta^{18}\text{O}_{\text{oli}}$ values (Figure 8B). Although previous work argues that crustal contamination affected ND lavas (Søager et al., 2013), all of our ND samples have $\delta^{18}\text{O}_{\text{oli}}$ values within the mantle range, high MgO and low SiO_2 concentrations, indicative of their primitive character. We note that the hy-norm ND lavas represent the samples with low Mg# and high $\delta^{18}\text{O}_{\text{oli}}$ values. While this may also reflect AFC processes, this would represent a small minority of the basalts in this region. Furthermore, there remains the possibility that these hy-norm lavas, which have high-MgO contents and trace element patterns similar to ne-norm ND lavas, may reflect mantle melting processes involving lower pressures and/or a wetter mantle source than ne-norm lavas (Kinzler and Grove, 1992; Kushiro, 1968; Stolper, 1980).

4.2.1) The influence of subducted slab-derived inputs

The role of slab derived material must be considered in the petrogenesis of ND and SC lavas, given that ND and SC lavas resemble VF lavas in their Sr and Nd isotope contents (Figure 5). Moreover, the trace element contents indicative of subduction inputs, such as high LILE/HFSE ratios and positive Sr anomalies in primitive mantle-normalized trace element patterns, are a common feature of most Payenia lavas (Figure 4). Although ND area lavas have higher LILE/HFSE ratios, many SC lavas do exhibit negative Nb-Ta and Ti anomalies, suggesting that the SC lava source was influenced by subduction inputs, but to a lesser extent than ND lavas. As has been argued for transitional basalts in other back-arc settings (Johnson et al., 2009; Rowe et al., 2009; Stern et al., 1990), Payenia basalts with arc-like trace element and isotopic compositions may reflect flux melting, but with less fluxing than in the mantle wedge beneath the VF. However, ND area basalts with strong arc signature erupted farther from the trench than SC area lavas with considerably weaker arc signature (Figure 1), which indicates that some other process may be responsible for the arc signature in ND lavas. In addition, VF lavas have more radiogenic Hf contents than Nd and SC lavas (Figure 5B). Pb isotope trends also do not represent a continuous decrease in slab-derived source inputs from the VF to ND to SC area samples. Although the compositions of SC and ND area samples trend toward the high $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ values of VF lavas, ND area samples trend to lower $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values at lower $^{206}\text{Pb}/^{204}\text{Pb}$ than values for SC area (Figure 5C-D). Given these distinctions in Pb, Nd and Hf isotope contents, Payenia lava compositions cannot be explained by melting of a homogeneous mantle with variable input from the subducting slab.

Direct melting of the subducting slabs is also unlikely given the Pb isotopic composition of the Payenia lavas. We would expect any slab-derived melt to impose an

isotopic signature that resembles oceanic basalts from Pacific upper mantle, but Pb isotope patterns show that Payenia lavas have distinctly higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at similar $^{206}\text{Pb}/^{204}\text{Pb}$ values compared to EPR MORBs, nor do they form linear arrays in Pb-Pb isotope space that trend toward EPR MORBs. This observation would not support the possibility of an EPR MORB-related source such as a melt of the subducted slab. Likewise, EPR MORB and Chile trench sediments have higher $^{176}\text{Hf}/^{177}\text{Hf}$ than Payenia basalts, indicating that these potential source components are not responsible for the $\Delta\epsilon_{\text{Hf}} < 0$ character of Payenia lavas. Slab and sediment melts would also be expected to inherit an enrichment in ^{18}O from their source relative to normal mantle oxygen isotope content. Because Payenia basalts have $\delta^{18}\text{O}$ values within the normal mantle $\delta^{18}\text{O}_{\text{oli}}$ range, and because their $\delta^{18}\text{O}_{\text{oli}}$ increase with decreasing $^{176}\text{Hf}/^{177}\text{Hf}$, the influence of slab and/or sediment melts on Payenia basalt $\delta^{18}\text{O}$ values are expected to be negligible. Additionally, adakitic lavas, which are thought to represent melting of the subducted slab and sediments (Castillo, 2012), have not been found in or near Payenia.

4.2.2) *The influence of SCLM metasomatism*

The inverse correlations between $\delta^{18}\text{O}_{\text{oli}}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values, as well as the negative deviation of the ND and SC lavas from the Hf-Nd isotope mantle array (i.e., $\Delta\epsilon_{\text{Hf}} < 0$) (Figure 5B), suggest a common process affecting their melt source. Moreover, trace element indicators of arc signature (e.g., Ba/Nb, Pb/Ce, U/Nb) correlate positively with $\delta^{18}\text{O}_{\text{oli}}$ (Figure 8C-E), and thus exhibit a similar negative correlation with $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios. Compared to the group of SC lavas, ND lavas generally have higher values in arc signature-indicative trace element ratios and $\delta^{18}\text{O}_{\text{oli}}$ values at less negative $\Delta\epsilon_{\text{Hf}}$ values (Figure 9). These variations indicate that among all Payenia samples, mantle source composition varies from weaker arc signature, lower $\delta^{18}\text{O}$, and negative $\Delta\epsilon_{\text{Hf}}$

to arc-like trace element content, higher $\delta^{18}\text{O}$ values, and near-zero to positive $\Delta\epsilon_{\text{Hf}}$ values. However, within each group of ND and SC area lavas, we observe a weak negative correlation between $\Delta\epsilon_{\text{Hf}}$ and Ba/Nb, Pb/Ce, and U/Nb.

These variations imply two dimensions of variability in ND and SC lava compositions. One dimension represents increasing arc signature with increasing $\Delta\epsilon_{\text{Hf}}$. The other represents increasing arc signature with constant or decreasing $\Delta\epsilon_{\text{Hf}}$. Two dimensions of variability is consistent with three source components controlling SC and ND lava compositions: one with arc signature and $\Delta\epsilon_{\text{Hf}} = \sim 0$, a second with no arc signature and negative $\Delta\epsilon_{\text{Hf}}$, and a third with arc signature and negative $\Delta\epsilon_{\text{Hf}}$. These characteristics are consistent with the three endmembers identified using Mg# versus $\delta^{18}\text{O}_{\text{oli}}$ (Figure 8B). Of these three components, we assume one component must represent an asthenospheric melt source. Because volcanic front lavas near Payenia fall along the Hf-Nd mantle array, the likely component to represent the sub-Payenia mantle wedge is the endmember with arc signature and $\Delta\epsilon_{\text{Hf}} = \sim 0$. In addition to an asthenospheric source component, there remain two source components with negative $\Delta\epsilon_{\text{Hf}}$, which are not easily explained by heterogeneities in the asthenosphere. HIMU OIBs also exhibit negative $\Delta\epsilon_{\text{Hf}}$ values (Stracke et al., 2005), but Payenia lavas do not exhibit Pb isotope trends that reflect significant input from a source with $^{206}\text{Pb}/^{204}\text{Pb} > 19.5$ and $^{208}\text{Pb}/^{204}\text{Pb} > 39.5$.

A potential cause for these compositional variations in Payenia lavas is the melting of the metasomatized SCLM. Metasomatic enrichment of the SCLM can be caused by low-degree asthenospheric melts that percolate through the SCLM and precipitate veins of cumulates consisting of anhydrous (e.g., clinopyroxene, garnet, olivine) and hydrous (e.g., amphibole, phlogopite) mineral phases (Foley, 1992). The presence of a phlogopite (+/-

hornblende)-bearing veined cumulate melt was also proposed by S ager et al. (2018) for the Payenia lavas based on major and trace element compositions of olivine-hosted melt inclusions in from the SC area. Alkaline basalts from Patagonia bear mantle xenoliths containing amphibole, phlogopite and apatite, evidence of modal metasomatism (Aliani et al., 2009; Bjerg et al., 2005; Scambelluri et al., 2009). Modeling and experimental studies have shown that the melting of veined cumulates yields major and trace element compositions resembling alkaline lavas from oceanic and continental settings (Condamine and M dard, 2014; Pilet et al., 2011; Pilet et al., 2008; Sorbadere et al., 2013).

Melting metasomatic cumulates also can impart distinctive isotopic characteristics to alkaline lavas. Given sufficient timescales (~ 0.15 Gyr), parent-daughter ratios of radiogenic isotope systems in metasomatized lithosphere can yield isotopic signatures that differ considerably from MORB values, trending toward EM-1 and HIMU endmembers, which are known for having negative $\Delta\epsilon_{\text{Hf}}$ values (Panter et al., 2006; Pilet et al., 2011). The crystallization and melting of veined cumulates in the SCLM also may affect the oxygen isotope contents of alkaline basalts. Pyroxenes from SCLM xenoliths in the Colorado Plateau have been characterized by anomalously low $\delta^{18}\text{O}$ values relative to unmetasomatized mantle (Perkins et al., 2006). In metasomatized peridotite xenoliths from the Kaapvaal craton, intergranular or neoblastic secondary mineral grains have lower $\delta^{18}\text{O}$ values than the porphyroclastic relic grains, whose $\delta^{18}\text{O}$ values are closer to the “average mantle” range (Zhang et al., 2000). Low $\delta^{18}\text{O}$ signatures in arc lavas are likely caused by either closed-system fractional crystallization as the system evolves along a liquid line of descent (LLD, Bucholz et al. (2017)) or the contribution of slab-derived low- $\delta^{18}\text{O}$ fluids to the melt source, as have been attributed to low $\delta^{18}\text{O}_{\text{oli}}$ values from Nicaraguan arc basalts (Eiler et al., 2005). However, amphibole, clinopyroxene, and garnet, which constitute the

major phases in metasomatized SCLM that contribute to the generation of alkaline basalts, retain lighter oxygen isotopes relative to the parent melt during fractional crystallization at temperatures typical of the SCLM. We expect the low- $\delta^{18}\text{O}$ character of minerals precipitated during SCLM metasomatism to cause low- $\delta^{18}\text{O}$ melts formed during cumulate anatexis.

In light of these trends, we test the possibility that SCLM metasomatism consists of two compositional endmembers: one representing cumulates crystallized from subduction-related parent melt with high trace element arc signature and $\delta^{18}\text{O}$ and another representing cumulates crystallized from a parent melt sourced from ambient upwelling asthenosphere with low $\delta^{18}\text{O}$. Because melts derived from these cumulates have isotope contents significantly below the Nd-Hf isotope mantle array, we propose that the formation age of these cumulates is old enough to significantly decouple the isotopic composition of the cumulates in the lithosphere prior to the generation and eruption of Payenia lavas. In the following sections, we describe and discuss forward model calculations that simulate the generation of SCLM-derived melts, their mixing with asthenospheric melts, and their compositional resemblance to Payenia lavas.

4.2.3) Modeling SCLM cumulate formation and melting

We test the hypothesis that ND and SC lavas represent melts formed from the metasomatized SCLM by presenting a forward model to explain the major and trace element and Nd, Hf, and O isotope contents of Payenia lavas as a consequence of veined cumulates forming in the SCLM, which then melt and mix with an asthenospheric melt. We assume that two types of cumulate-derived melt compositions contribute to Payenia. Given their variable arc signature, we assume that one cumulate endmember formed from melts generated from melting enriched depleted-MORB mantle (EDMM), and the second

crystallized from melts generated from the mantle wedge with an isotopic signature similar to that of TSVZ lavas. The asthenospheric melt that would mix with these cumulate derived melts would likely have some arc signature in its trace element contents due to the back-arc setting of Payenia. Also, its Nd and Hf isotope contents would plot along the mantle array, at $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values between those of volcanic front lavas and those of Shona-influenced MORBs. For the intents of this model, the ND area sample 19-10 composition that satisfies these criteria and represents the asthenospheric melt that mixes with the cumulate-derived melts.

Using assumed major, trace, and Nd, Hf, and O isotopic compositions of two asthenospheric sources (Table 2) and the melt-mineral trace element partition coefficients compilation of Pilet et al. (2011), we employed the alphaMELTS interface of pHMELTS (Asimow et al., 2004; Smith and Asimow, 2005) to model the formation and melting of SCLM cumulates. We performed this model in five steps: 1.) low-degree asthenospheric parent melts are formed isobarically at 2.5 GPa, 2) these parent melts undergo isobaric fractional crystallization at 1.5 GPa until they reach a temperature of 1000°C, 3) cumulates experience 100-200 million years of isotopic ingrowth, 4) these cumulates undergo isobaric batch melting at 1.5 GPa, and 5) cumulate-derived melts, at variable extents of melting, mix with each other and an asthenospheric melt to represent the range of lava compositions observed in Payenia samples. In order to evaluate the compositional range produced from mixing between an asthenospheric melt, an EDMM-type cumulate melt, and an arc-type cumulate melt, we calculated 2000 mixture compositions by randomly determining the mixing proportions of each endmember and then determining the weighted average of the compositions in these proportions. For each cumulate melt endmember, the extent of

melting was also randomly determined for a given mixing iteration. Model results are presented in Tables 2 and 3 and Figures 8, 10, 11, and 12.

To track O-isotope evolution during the crystallization and subsequent melting of the SCLM cumulate, we employed the methods of Bucholz et al. (2017). We use the outputs from pHMELTS (temperature, melt fraction, liquid major element concentrations, and crystallizing and residual mineral phase proportions) to determine $\Delta^{18}\text{O}_{\text{melt-cumulate}}$ values during crystallization and melting of SCLM cumulates (see supplementary information).

4.2.4) EDMM-type cumulate

For the modeled cumulate endmember composition that would be sourced from upper mantle [samples?] lacking arc signature, we assumed the parent melt was formed as a low-degree melt of EDMM. Major element contents of the EDMM source are values for depleted MORB Mantle (DMM) reported in Workman and Hart (2005), and mantle trace element concentrations were adopted from EDMM values also reported in Workman and Hart (2005). We assume $\text{H}_2\text{O}=600$ ppm, which approximates estimates of EDMM water contents constrained by previous investigations of MORB glasses and melt inclusions (Dixon et al., 2002; Shimizu et al., 2016). To establish the Hf and Nd isotope values of this EDMM-type mantle source, we adopted the Nd and Hf isotope contents of sample 19-10 which has $\Delta\epsilon_{\text{Hf}} = \sim 0$ and is assumed to represent the composition of the asthenospheric melt endmember. Present-day average $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values of the EDMM-type mantle source (Table 3), in conjunction with Sm/Nd and Lu/Hf ratios of EDMM, were used to correct for the assumed 100-200 m.y. of isotopic ingrowth in the EDMM-type mantle source. These corrected $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values were then used as initial isotope contents of the cumulate at the time of crystallization.

Using these assumptions for the EDMM-type mantle source composition, we calculated the composition of a 1% partial melt formed isobarically at 2.5 GPa, a pressure that would occur at or below the base of the SCLM in northern Patagonia, according to the maximum equilibration depths calculated for mantle xenoliths sampled from the southeastern margin of Payenia (Bertotto et al., 2013). We assumed $\delta^{18}\text{O}=5.7\text{‰}$ for EDMM-type parent melt, the average value of MORBs (Ito et al., 1987). Using this result as the starting composition for fractional crystallization, we then calculated the isobaric LLD at 1.5 GPa and the fayalite-magnetite-quartz (FMQ) f_{O_2} buffer. To form the crystal EDMM-type SCLM cumulate, we aggregated all fractionated crystal compositions that formed over the temperature range of 1295-980°C. We expect these cumulate formation conditions to represent northern Patagonian SCLM based on constraints offered by the compositions of mantle xenoliths erupted on the eastern margin of Payenia in the Agua Poca locality (Bertotto et al., 2013).

4.2.5) *Arc-type cumulate*

For the arc-type cumulate endmember composition, we assumed that parent melt formed in a mantle wedge environment analogous to the present-day mantle wedge beneath the volcanic front of the TSVZ. To determine the present the Hf and Nd isotope values of this arc-type mantle source, we first determined the average of $^{143}\text{Nd}/^{144}\text{Nd}$ values from primitive (>5 wt.% MgO) TSVZ lavas (data from references listed in the caption of Figure 5). Using this $^{143}\text{Nd}/^{144}\text{Nd}$ value, we estimated the corresponding $^{176}\text{Hf}/^{177}\text{Hf}$ value on the Nd-Hf mantle array according to the formulation of Chauvel et al. (2008). We use this approximation because Nd and Hf isotopes of TSVZ lavas occur close to the mantle array and because the available dataset of $^{176}\text{Hf}/^{177}\text{Hf}$ values for TSVZ lavas is limited and presumably less representative of the total isotopic range of TSVZ lavas compared to the

$^{143}\text{Nd}/^{144}\text{Nd}$ dataset. To constrain trace element concentrations in the modeled mantle wedge, we used trace element concentrations of primitive trachybasalt sample 126008 (Søager et al., 2013) from the neighboring Infiernillo area (Figure 1), which has a strong arc signature (e.g., $\text{Ba}/\text{Nb} = 54$, $\text{Pb}/\text{Ce} = 0.17$). To calculate the mantle wedge source concentration, we assumed the trachybasalt sample 126008 formed as a 5% nonmodal batch melt of garnet lherzolite. We assume a garnet-bearing lithology for this lava sample because of its depletion in HREEs relative to MREEs (e.g., $(\text{Sm}/\text{Yb})_{\text{N}} = 3.92$), a trait characteristic of residual garnet in its melt source. The melt reaction used in this calculation, $8 \text{ olivine} + 81 \text{ clinopyroxene} + 30 \text{ garnet} = 100 \text{ melt} + 19 \text{ orthopyroxene}$, was adopted from Walter (1998), and the modal assemblage of the garnet lherzolite was assumed to be 59 wt.% olivine, 19 wt.% orthopyroxene, 11 wt.% clinopyroxene, and 11wt.% garnet. These modal proportions were determined by Pilet et al. (2011) as the modal proportions of garnet peridotite with the bulk major element composition of DMM (Workman and Hart, 2005), which we adopt as the major element composition of the mantle wedge. The resulting trace element composition of the arc-type mantle source was used to reverse Nd and Hf isotope ingrowth in the mantle wedge and determine the isotopic composition of the parent melt that formed the arc-type endmember cumulate. We assume a H_2O concentration of 2000 ppm in the modeled mantle wedge. This concentration represents a lower bound for the source water contents estimated for the sub-SVZ mantle based on olivine-hosted melt inclusion compositions reported in Weller and Stern (2018).

This mantle wedge source composition was batch melted to 3% at 2.5 GPa to form the melt from which the arc-type SCLM cumulate would form (Table 2). We assigned to this parent melt a $\delta^{18}\text{O}$ value of 6.0‰ to reflect the enrichment in ^{18}O during interaction with material derived from sediments and upper oceanic crust in the subducted slab, as is

observed in the compositions of volcanic front melts from the SVZ (Hickey-Vargas et al., 2016a). We employed the same methods of calculating the compositions of the aggregated cumulate and the cumulate-derived melt as used for the EDMM-type cumulate and its cumulate-derived melt.

4.2.6) Model results and implications

Modeled compositions of asthenosphere source, asthenospheric melt, SCLM cumulate, and cumulate-derived melt are presented in Table 2. The mineral assemblage of both compositional end-member cumulates consists of olivine, clinopyroxene, garnet, hornblende, phlogopite, and apatite. The EDMM-type cumulate bears larger proportions of hornblende (20 wt.% in the EDMM-type versus 9 wt.% in the arc-type) and phlogopite (7 wt.% in the EDMM-type versus 2 wt.% in the arc-type), which is likely a consequence of the higher alkali concentrations of the EDMM-type parent melt that resulted from the lower degree of mantle melting relative to the arc-type parent melt. These differences in modal abundances also mean that phlogopite is consumed in the EDMM-type cumulate at a higher degree of melting ($F=28\%$) than in the arc-type cumulate $F=7\%$. We do not expect these results to represent the differences in modal abundances that would necessarily arise from crystallizing a melt from the mantle wedge melt versus a melt from ambient upper mantle melt. Rather, this is more likely an outcome of the simplified assumptions made in this model (i.e., a single asthenospheric melt composition for each endmember, which crystallizes at a constant pressure in the SCLM) and the thermodynamic constraints on phlogopite and amphibole stability of the pHMELTS algorithm. Nonetheless, the cumulate mineral assemblages for both endmembers resemble estimates from geochemical modeling, experiments, and petrological observations of lithospheric veined cumulates (Pilet et al., 2011 and references therein).

Trace element patterns and concentrations and Nd, Hf, and O isotope contents of the modeled melt mixtures resemble those of SC and ND area samples in concentration and pattern (Figures 8, 10). Modeled trace element patterns reproduce the positive P and Sr anomalies common among Payenia lavas, as well as the prominent negative Nb-Ta anomalies of ND area lavas and the Modeled melt mixtures with a large abundance of the arc-type cumulate high Ba/Nb and $\delta^{18}\text{O}_{\text{oli}}$, intermediate U/Nb and Pb/Ce, and low Mg# and $^{177}\text{Hf}/^{176}\text{Hf}$ of ND area lavas. Mixtures with a large abundance of the EDMM-type cumulate reproduce the low Ba/Nb, $\delta^{18}\text{O}_{\text{oli}}$, U/Nb and Pb/Ce and low Mg# and $^{177}\text{Hf}/^{176}\text{Hf}$ values of SC area lavas. Arc-type cumulate melts exhibit considerably larger range in trace element ratios than EDMM-type cumulates. Despite this variability, the ND area lava compositions most closely resemble the Mg#, Ba/Nb, U/Nb and Ba/K values of arc-type cumulate melts formed from a source that has residual phlogopite. This common trait may indicate that melting conditions, at least for the arc-type cumulate, remain cooler than the temperature of phlogopite-out, which would occur at $\sim 1300^\circ\text{C}$ at 1.5 GPa based on melting experiments of phlogopite-bearing peridotite (Condamine et al., 2016). Furthermore, the trace element ratios indicative of arc signature (Ba/Nb, Pb/Ce, and U/Nb) are low for low-degree melts of the arc-type cumulate compared to values for volcanic front lavas. This relationship indicates that the process of forming and melting SCLM cumulates potentially dilutes the arc signature inherited by cumulate-derived melts, a possibility that has not been closely considered in investigations of the chemical diversity of continental basalts.

We also find it notable that the EDMM-type cumulate melts reproduce the relatively low $\delta^{18}\text{O}_{\text{oli}}$ values of SC area lavas as a result of mineral-melt oxygen isotope fractionation. This effect has largely been ignored as a potential mechanism for lowering the $\delta^{18}\text{O}_{\text{oli}}$ values of basaltic magmas. Instead, previous studies have attributed low- $\delta^{18}\text{O}_{\text{oli}}$

values measured in subduction-related basalts to the contribution of low- $\delta^{18}\text{O}$ fluids released from portions of the subducting slab that underwent high-temperature ($>350^\circ\text{C}$) hydrothermal alteration prior to subduction (Eiler et al., 2005; Martin et al., 2011). While $\delta^{18}\text{O}_{\text{oli}}$ values that are several tenths of a permil below the normal mantle olivine range may require a low- $\delta^{18}\text{O}$ input into the melt source, our model does not use such an input to yield modeled melts with $\delta^{18}\text{O}_{\text{oli}} = \sim 5.0\text{‰}$ instead of the expected value of $\sim 5.2\text{‰}$ in MORB olivine. In our model calculations, the fractionation of oxygen isotopes between the asthenospheric melt and the clinopyroxene, amphibole, and garnet formed in the cumulate is $\sim -0.3 - -0.5\text{‰}$. When these phases melt, they impart lower $\delta^{18}\text{O}_{\text{oli}}$ values to the modeled melts on a similar scale. This model demonstrates that the mineral phases involved in SCLM cumulate formation and melting can significantly influence the oxygen isotope content of the mafic melts they generate even when the melt that forms these cumulates has a MORB-like $\delta^{18}\text{O}$ value.

In order for the cumulate-derived melts to inherit the low $\delta^{18}\text{O}_{\text{oli}}$ values, oxygen must diffuse at a sufficiently slow rate to prevent the surrounding peridotite in the SCLM from significantly influencing the $\delta^{18}\text{O}$ signature inherited by the melt. Given that the characteristic length scale of diffusion equals the square root of the product of diffusion rate and time (i.e., $L=(D*t)^{0.5}$), oxygen would be expected to diffuse $\sim 3 \times 10^{-5} \mu\text{m}$ in olivine at 1000°C in 200 m.y. using the diffusion rate constraints of Costa and Chakraborty (2008), essentially preserving the $\delta^{18}\text{O}$ signature of the metasomatized SCLM melt source until Payenia melt generation. Likewise, melting and eruption would occur fast enough to avoid influence of the $\delta^{18}\text{O}$ signature of refractory SCLM. U-series isotopic disequilibria in young SVZ lavas have constrained magma transfer from mantle wedge to surface to take

~10,000 years (Sigmarsson et al., 2002), whereas oxygen would be expected to diffuse $\sim 1 \times 10^{-5}$ μm in olivine at 1300°C in this interval.

The Nd and Hf isotope ingrowth trends of EDMM- and arc-type cumulates show that an isotopic ingrowth duration of 150-200 m.y. matches or exceeds the most negative $\Delta\epsilon_{\text{Hf}}$ values of Payenia lavas (Figure 11, Table 3). These results suggest that the metasomatism that generated both endmember cumulate compositions dates to ~150-200 Ma. Over the same timescale, the arc-type cumulate achieves a larger deviation from the mantle array and lower $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values than the EDMM-type cumulate, which is consistent with the weak negative trend between $\Delta\epsilon_{\text{Hf}}$ and arc signature trace element ratios within the ND and SC sample groups (Figure 9).

The model we present employs a simplification of the mineral assemblages that control Nd and Hf isotope ingrowth in the asthenosphere and metasomatized SCLM. In particular, the ingrowth of radiogenic Hf is highly sensitive to the presence of garnet: because garnet is enriched in HREEs, it has significantly higher Lu/Hf than other mineral phases considered in our model. A larger abundance of residual garnet in the asthenosphere would cause more rapid ingrowth of radiogenic Hf, in which case the present-day asthenosphere evolved from significantly lower $^{176}\text{Hf}/^{177}\text{Hf}$ values for a given time in the past. Similarly, if a SCLM cumulate contains a large abundance of garnet, it will ingrow radiogenic Hf at a fast rate, limiting the decoupling of SCLM cumulate $^{176}\text{Hf}/^{177}\text{Hf}$ values from those of its asthenospheric source. If the SCLM cumulates related to Payenia lavas contained less garnet and/or their asthenospheric melt source contained more garnet, the cumulates would ingrow less ^{177}Hf , and the negative $\Delta\epsilon_{\text{Hf}}$ values of the Payenia lava source would be caused by more recent SCLM metasomatism.

The polybaric differentiation of a metasomatic agent in the SCLM, which we do not consider in our model, may offer a mechanism for limiting garnet in the SCLM melt source. As was proposed by Pilet et al. (2011), a low-degree, volatile-rich melt that ascends through the lithosphere would precipitate anhydrous phases (e.g., clinopyroxene, garnet) before forming veins rich in amphibole and phlogopite. The garnet-rich base of the SCLM, which would ingrow an abundance of radiogenic Hf, could be eroded or delaminated prior to the melting of the shallower, hydrous phase-abundant portion of the SCLM, which would ingrow little radiogenic Hf. Melts generated in this scenario would require shorter timescales to develop negative $\Delta\epsilon_{\text{Hf}}$ values and thus more recent episodes of SCLM metasomatism. More refined modeling is required to test the validity of this scenario.

Major element concentrations of the modeled melts are compared to Payenia lava compositions in Figure 12. Melts formed from each endmember cumulate exhibit trends of increasing MgO, CaO, and FeO^{T} concentrations and decreasing SiO_2 , Al_2O_3 , and Na_2O with increasing degree of melting. Similar trends occur in results from experimental studies of melts from amphibole- and clinopyroxene-bearing mafic cumulates at 1-1.5 GPa (Pilet et al., 2008). Our model results yield lower SiO_2 and CaO and higher Al_2O_3 concentrations than the experimental results. This difference may result from the presence of garnet in the modeled cumulates, whereas garnet is absent from starting assemblages used in the experiments of Pilet et al. (2008). In addition to modeling melting of pure cumulate, we calculated the melt compositions produced by melting a hybrid of 50 wt.% of endmember cumulate with 50 wt.% of a hypothetical harzburgite composition that would form the refractory portion of the SCLM hosting the veined cumulates (Table 3, see Supplementary Material for additional details). While most major element concentrations are comparable between melts of pure cumulate and of cumulate and harzburgite, SiO_2 concentrations are

~5% higher than those in melts formed from pure cumulate for both cumulate endmembers and more closely resemble the SiO₂ concentrations of Payenia basalts and the aforementioned experimental melts. This modification is consistent with the hypothesis that intraplate alkali magmas range in composition from silica-undersaturated nephelinites to alkali basalts because of interaction with the peridotite surrounding veined cumulates. Silica enrichment by ~4-5 wt.% has been demonstrated by the melts produced from hornblendite-peridotite melting experiments (Pilet et al., 2008). If Payenia lavas represent cumulate-derived melts that interacted with the refractory harzburgitic portions of the SCLM, either by melt-rock reaction or by mixing with peridotite-derived melts, we assume this process would have minimal effect on the Nd and Hf isotope signature and trace element pattern of the melt, because the incompatible trace element budget of an orthopyroxene and olivine-dominant lithology is expected to be highly depleted relative to the trace element budget of the cumulate mineral assemblages. While the interaction with surrounding peridotite may influence the oxygen isotope content of the cumulate-derived melt, additional modeling is required to quantify this effect.

4.3) Potential geological processes behind the melting of SCLM in the Payenia region

While these model results demonstrate that the melting of SCLM cumulates can cause much of the chemical diversity of basaltic Payenia lavas, we must also consider potential causes behind the melting of SCLM cumulates. The simplest explanation for the melting of SCLM would involve lithospheric thinning and heating from upwelling asthenosphere. A likely cause for lithospheric thinning and heating beneath Payenia is the inflow of hot asthenosphere beneath Payenia during the Plio-Quaternary episode of slab steepening and regional extension (Kay et al., 2006; Ramos and Folguera, 2011). Geophysical observations show that in the present-day mantle beneath Payenia, an

anomaly of low seismic velocity and high electrical conductivity currently occupies the shallow asthenosphere (Burd et al., 2014; Gilbert et al., 2006), which may signify a thermal anomaly responsible for the heating and melting of veined cumulates in the SCLM.

We also consider why the ingrowth of radiogenic Nd and Hf in our modeled cumulate compositions would require 150-200 million years to experience the isotopic ingrowth necessary to deviate as far from the Nd-Hf mantle array as the Nd-Hf isotope contents of Payenia lavas. This time period coincides with the ~180 Ma timing of the breakup of the Gondwana supercontinent, during which the Payenia region of South America rifted from and Africa to open the South Atlantic Ocean (Franzese et al., 2003; Ramos, 1999; Ramos, 2005). During the same period, along the western margin of Patagonia, subduction of the proto-Pacific plate initiated Andean arc magmatism (Gordon and Ort, 1993; Haller and Lapido, 1980; Lizuain, 1999). These two tectonic events would generate significant quantities of mantle melts in the Payenia region, of which a portion would represent adiabatic decompression during rifting, and other mantle melts would represent the hydrous flux melting that formed the Jurassic Andean arc. The expected compositional variation expected from this variety of mantle melts, one with arc signature and the other without, is consistent with the two types of metasomatic agents used to form SCLM cumulates in the model presented here.

5. Conclusions

The major and trace element and isotopic results presented in this study suggest that veined cumulates in the SCLM provide a viable, significant melt source for Payenia basalts. SCLM metasomatism and cumulate formation occurred as early as 150-200 Ma, a consequence of the proto-Pacific convergent margin in northern Patagonia and the breakup

of Gondwana. Isotopic ingrowth of veined cumulates differed from peridotitic mantle, imparting distinctive Nd and Hf isotope values to Payenia melts.

Geochemical trends related to differentiation in both the metasomatized SCLM and the Tromen stratovolcano magmatic system underscore the possibility that back-arc basalts can acquire low $\delta^{18}\text{O}_{\text{oli}}$ values not only from ^{18}O -depleted fluids released from the downgoing slab, but also from the oxygen isotope fractionations that occur during fractional crystallization and cumulate formation in SCLM. Therefore, when considering alkaline basalts generated from or interacting with metasomatized SCLM, we find it prudent to consider the potential for differentiation to cause systematic variations in oxygen isotope contents, regardless of whether high- or low- $\delta^{18}\text{O}$ recycled material contributes to SCLM metasomatism or melt generation.

SUPPLEMENTARY MATERIAL

Sample Preparation

We obtained major and trace element concentrations and Sr, Nd, Pb and Hf isotope ratios on whole-rock powders of each sample. We produced these powders by manually crushing the plastic-wrapped rock samples with a hammer. We then washed the freshly crushed chips with distilled water and dried them overnight at 80°C. The cleaned chips were then ground to a fine powder using an agate shatter box.

Prior to Sr, Nd, Pb and Hf isotope analyses, about 1 g of sample whole-rock powders are leached with 6N double distilled HCl for about 1 hour on the hot plate at 100°C and rinsed with distilled water (18 M Ω) three times. During each rinsing step samples were centrifuged to ensure the complete removal of any residual acid. After drying the leached samples, about 100 mg of powder was dissolved in a double distilled HF (3): HNO₃ (1)

mixture. Pb is separated first from the matrix using AG1-X8 (100-200 mesh, BIO-RAD) resin and then Hf using Ln resin (Eichrom). The remaining matrix is passed through TRU-spec resin (Eichrom) to separate Rb-Sr from REE. Rb-Sr fraction is then passed through Sr-spec resin (Eichrom) to get a clean Sr fraction and REE fraction is passed through Ln resin (Eichrom) to get a clean Nd fraction.

Prior to $\delta^{18}\text{O}$ measurement by ILFT, olivine grains that bore little or no inclusions or alteration were handpicked from chips of rock sample under a binocular microscope. Olivine grains were then carefully crushed to separate and remove any remaining inclusions or alteration. 1.5 - 2 mg of crushed pieces of olivine were collected for each ILFT analysis.

Calculation of $\Delta^{18}\text{O}_{\text{melt-cumulate}}$ values

$\Delta^{18}\text{O}_{\text{melt-cumulate}}$ values used in melt-cumulate oxygen isotope fractionation modeling are from the $\Delta^{18}\text{O}_{\text{quartz-mineral}}$ compilation of Bucholz et al. (2017), with the addition of the $\Delta^{18}\text{O}_{\text{quartz-pyrope}}$ parameterization from Zheng (1993). $\Delta^{18}\text{O}_{\text{melt-mineral}}$ values, which were weighted by mineral proportion in the fractionating/residual crystal assemblage to calculate $\Delta^{18}\text{O}_{\text{melt-cumulate}}$, were determined by approximating the melt composition as a mixture of CIPW-normative minerals, as has been the accepted practice in previous efforts to model $\delta^{18}\text{O}$ variations during fractional crystallization (Bindeman et al., 2004; Bucholz et al., 2017; Eiler, 2001), despite the inability to account for any potential effect the water content of the melt may have on $\Delta^{18}\text{O}_{\text{melt-mineral}}$ values.

Consideration of apatite in the SCLM cumulate formation and melting model

Our model makes a minor modification to the asthenospheric melt compositions that precipitate the SCLM cumulates in order to better account for the presence of apatite in the cumulate assemblage. We make this modification because of the presence of apatite

in metasomatic veins in Patagonian mantle xenoliths (Aliani et al., 2009; Bjerg et al., 2005) and the prevalence of positive P anomalies in the primitive mantle-normalized trace element patterns of Payenia lavas (Figure 4). In accordance with this reasoning, we increased the asthenospheric melt P_2O_5 concentration by 0.2 wt. % for the parent melt of arc-type cumulate to ensure that apatite crystallizes and influences the composition of the cumulate.

Modeling the melting of a cumulate-harzburgite hybrid assemblage

In order to assess the influence the surrounding peridotite has on melting of the veined cumulates in the SCLM, we performed equilibrium melting calculations of the EDMM- and arc-type cumulate compositions described in sections 4.2.4 and 4.2.5, respectively, combined with a refractory harzburgite composition in a 50-50 mixture. The composition of the harzburgite used in this mixture is presented in Table 2. Assuming that the veined cumulate would dominate the trace element signature of this hybrid composition, the hybrid has half the concentration of trace elements as the 100% cumulate melt source. As was performed with the 100% cumulate compositions, compositions of melts derived from the hybrid compositions were calculated assuming batch isobaric melting at 1.5 GPa.

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FIGURE CAPTIONS

Figure 1-1. A) Tectonic map of the Nazca-South America plates showing mid-ocean ridges (red lines), fracture zones (black lines) and subduction zones (orange lines with triangles). The black square marks the region displayed in part B. Velocity and convergence direction of the Nazca-South American plates taken from Kendrick et al. (2003). Abbreviations: CR: Chile Ridge, EPR: East Pacific Rise, MAR: Mid-Atlantic Ridge, TSVZ: Transitional Southern Volcanic Zone. B). Simplified geologic map of the Payenia volcanic province, with locations of samples presented in this work. Note that the Payún Matrú volcanic field extends to the east and west of the Payún Matrú volcano.

Figure 1-2. Total alkali-silica diagram (TAS, Le Bas et al., 1986) of the Payenia and volcanic front samples. Black dashed line separates the alkaline (above the line) from the subalkaline fields (MacDonald and Katsura, 1964). Payenia literature data represented by a smaller symbol size than those for data reported in this study. Payenia literature data from Germa et al. (2010); Gudnason et al. (2012); Hernando et al. (2014a); Jacques et al. (2013); Kay et al. (2006); Kay et al. (2013); Pallares et al. (2016); Søgner and Holm (2013); Søgner et al., (2013); Søgner et al., (2015a); Stern et al. (1990). TSVZ volcanic front literature data from Davidson et al. (1988); Dungan et al. (2001); Ferguson et al. (1992); Holm et al. (2014); Jacques et al. (2013); Rodríguez et al. (2007); Ruprecht et al. (2012); Sellés et al. (2004); Tormey et al. (1995).

Figure 1-3. Major element concentrations, in weight percent, of Payenia samples reported in this study and TSVZ samples from literature. Symbols and literature data are the same as in Figure 1-2.

Figure 1-4. Primitive mantle-normalized trace element concentrations of 3 representative high- MgO (>6.9 wt.%) Payenia lavas and the volcanic front lava (CL196 from Jacques et al. (2013)). Normalization values from McDonough and Sun (1995).

Figure 1-5. A) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$, B) $^{176}\text{Hf}/^{177}\text{Hf}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$, C) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$, and D) $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$. Error bars are 2-sigma standard deviation external reproducibility. For Pb isotopes, error bars are smaller than symbol size. Chile trench sediments are from Lucassen et al. (2010) and Jacques et al. (2013). EPR MORB data taken from the compilation of Gale et al. (2013). MORB data from the Discovery and Shona segments of the southern Mid-Atlantic Ridge (MAR) taken from Douglass et al. (1999) and Andres et al. (2002). Payenia and TSVZ sample symbols same as in Figure 1-1; literature TSVZ and Payenia data from Jacques et al. (2013). Grey dashed Northern Hemisphere Reference Line (NHRL) in the Pb-Pb plots from Hart (1984). The green line representing the mantle array in the Nd-Hf plot from Chauvel et al. (2008). Other symbols and literature data are the same as in Figure 1-2.

Figure 1-6. $\delta^{18}\text{O}_{\text{Olivine}}$ values versus longitude of Payenia lavas reported in this study. Error bars are 1-sigma standard deviation.

Figure 1-7. A.) Primitive mantle-normalized trace element diagram showing T-BR area lavas compared with two-member mixing calculations between Buta Ranquil sample 27-4 (~1% nepheline normative) and the basaltic trachyandesite sample 27-5 from Tromen (~16% hypersthene normative). Primitive mantle values from McDonough and Sun (1995).

SiO₂ versus B.) P₂O₅ and C.) Zr/Sm. Red triangles represent evolved (MgO<4 wt.%) lavas from the Payun Liso stratovolcano and the Payun Matru, and Auca Mahuida shield volcanoes from literature data sources mentioned in Figure 1-2. Grey triangles represent SVZ volcano compositions from Turner et al. (2016). Other symbols same as in Figure 1-2.

Figure 1-8. Cartesian plots comparing Mg#, trace element ratios, and O and Hf isotope contents for Payenia samples and model results from section 4.2. Purple symbols and lines represent model results for the melt of the EDMM-type cumulate and black symbols and lines represent modeled melts of arc-type cumulate. Light blue square represents sample 19-10, which was used as the asthenospheric melt composition in melt mixing calculations. Payenia symbols and corresponding literature data same as in Figure 1-2. Modeled ¹⁷⁶Hf/¹⁷⁷Hf values represent 150 million years of isotopic ingrowth.

Figure 1-9. Cartesian plots comparing $\Delta\epsilon_{\text{Hf}}$ versus trace element ratios, and O isotope contents for Payenia. Sample symbols are the same as in Figure 1-2.

Figure 1-10. Primitive mantle-normalized trace element diagram displaying model results versus representative Payenia sample compositions. Red lines represent samples from the SC area, and Blue lines represent samples from the ND area. Grey lines represent all 2000 random mixtures between the asthenospheric melt (sample 19-10), the modeled melts of the EDMM-type cumulate, and the modeled melts of the arc-type cumulate. Black lines are selected modeled melt mixtures that resemble representative Payenia melt compositions.

Figure 1-11. $^{176}\text{Hf}/^{177}\text{Hf}$ vs. $^{143}\text{Nd}/^{144}\text{Nd}$ of modeled isotopic ingrowth estimates and natural samples from Payenia, TSVZ volcanic front, MORB samples from the Shona and Discovery MAR segments, and the mantle Nd-Hf isotope array (symbols same as in Figure 1-5. Black lines: ingrowth trends of the arc-type cumulate component; purple lines: ingrowth trends of the EDMM-type cumulate component: Empty stars: present-day isotopic values for mantle sources of the modeled asthenospheric melts that crystallize the cumulates; filled stars: initial isotopic values of the modeled cumulates inherited from their mantle source; crosses: present-day isotopic values of modeled cumulates calculated as ingrowth from the time of cumulate formation at 100, 150, and 200 Ma.

Figure 1-12. Major element concentrations of modeled melts from SCLM cumulates compared with Payenia samples. Cumulate- harzburgite mixtures represent 50% cumulate and 50% depleted harzburgite mixture (see results in Table 1-3). Hourglass symbols represent experimental melts from Pilet et al. (2008). Payenia sample symbols same as in Figure 1-2.

FIGURES

Figure 1-1.

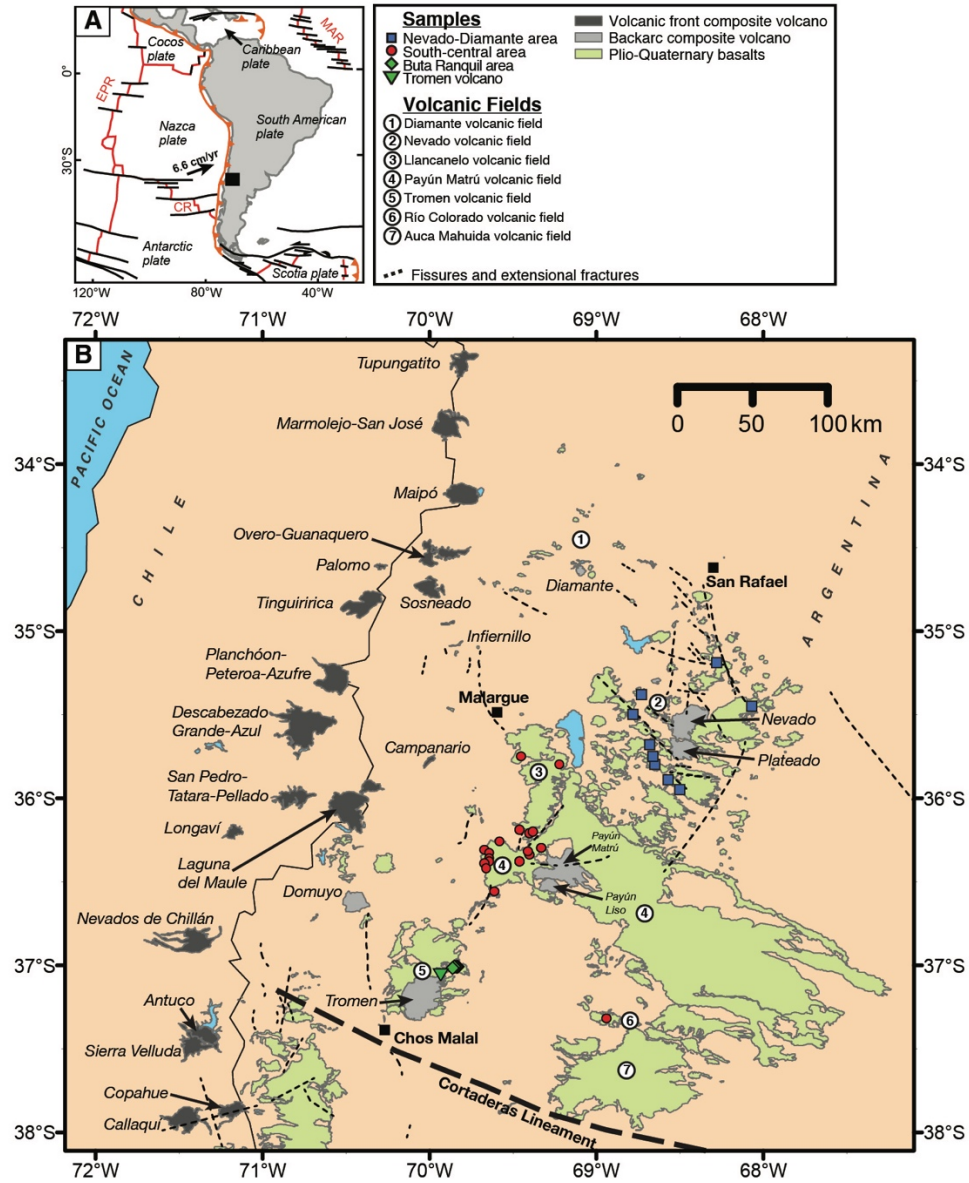


Figure 1-2.

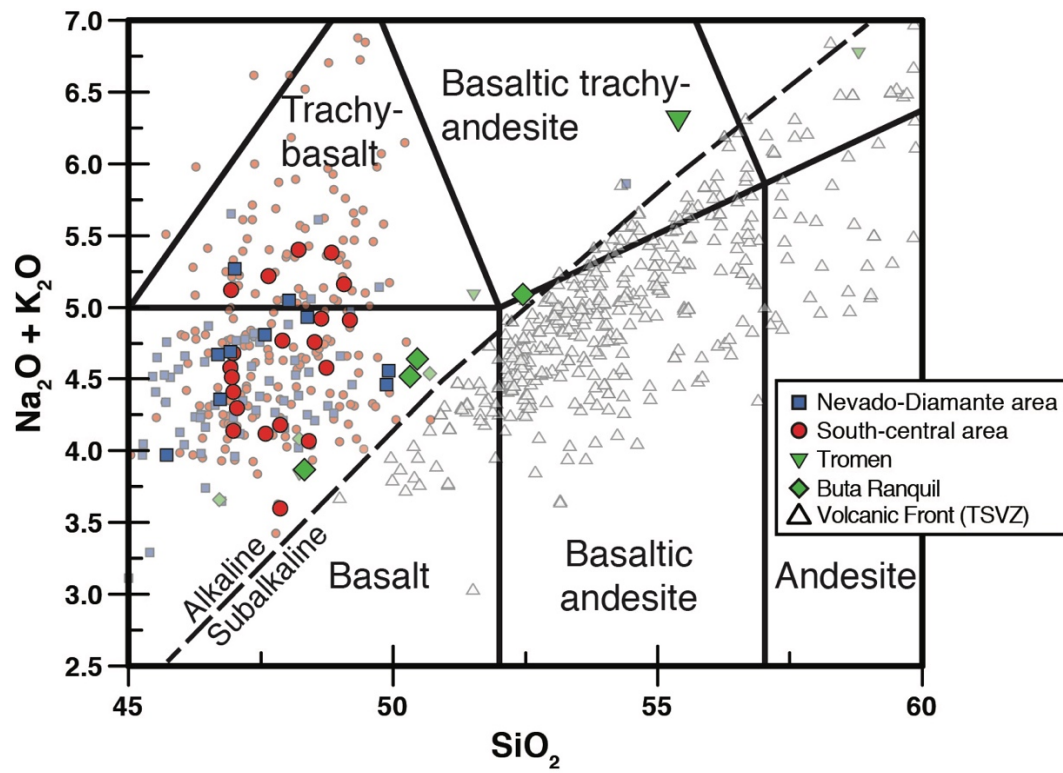


Figure 1-3.

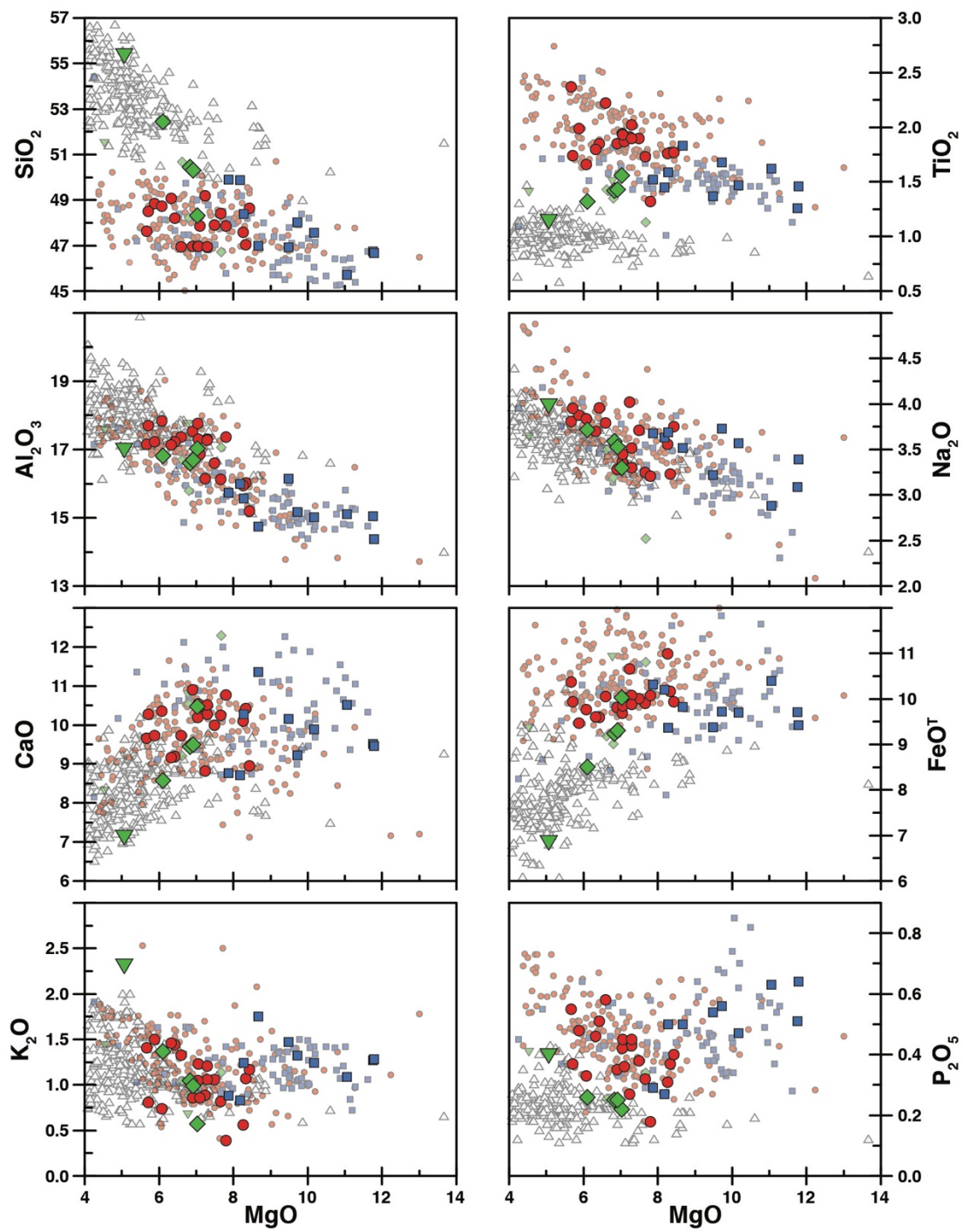


Figure 1-4.

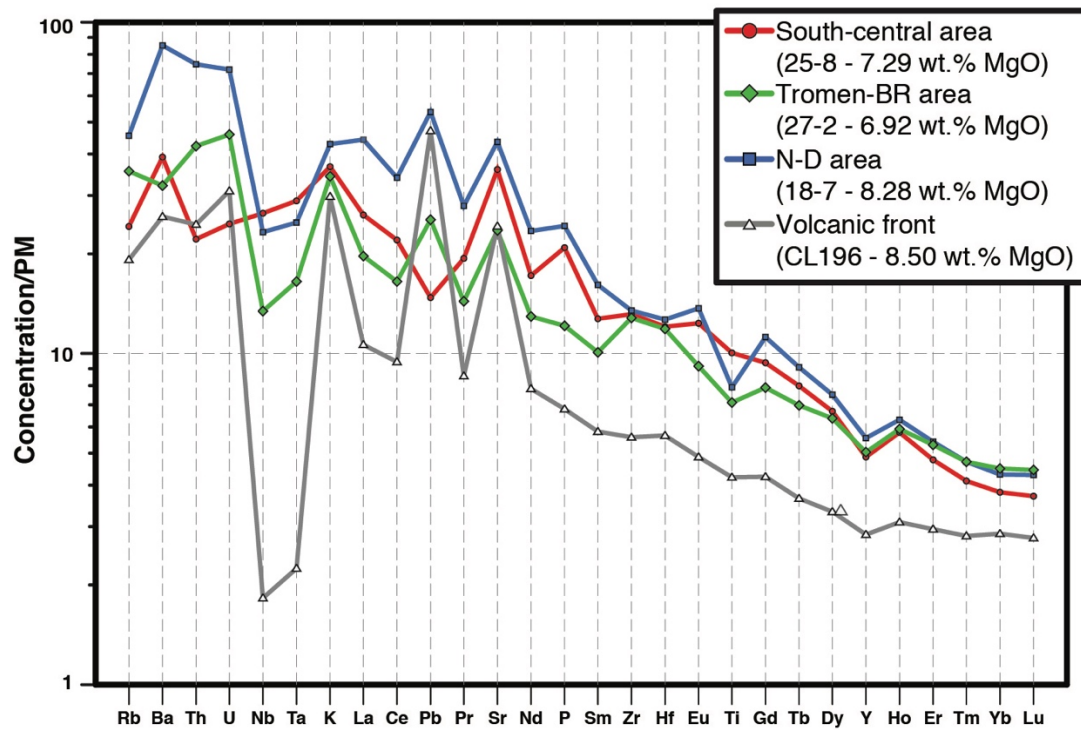


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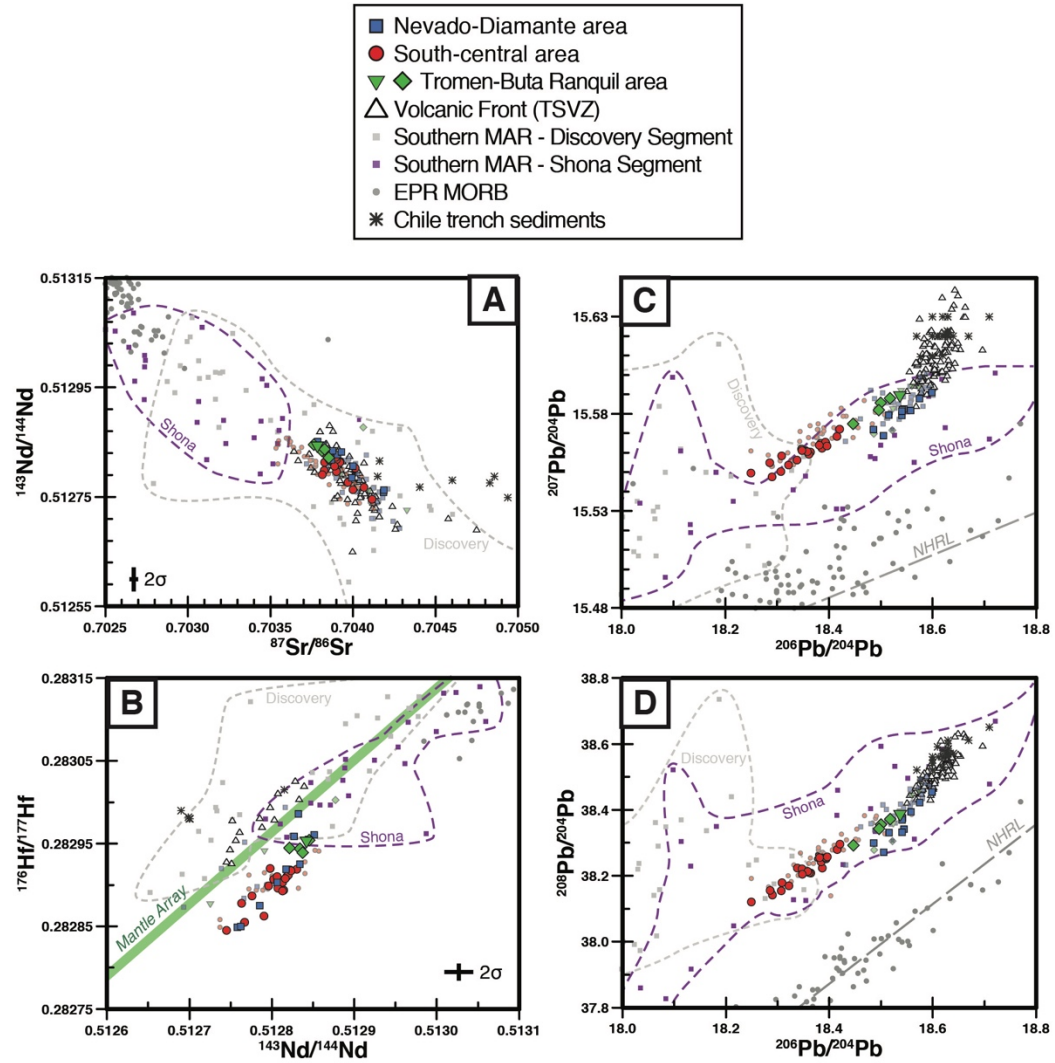


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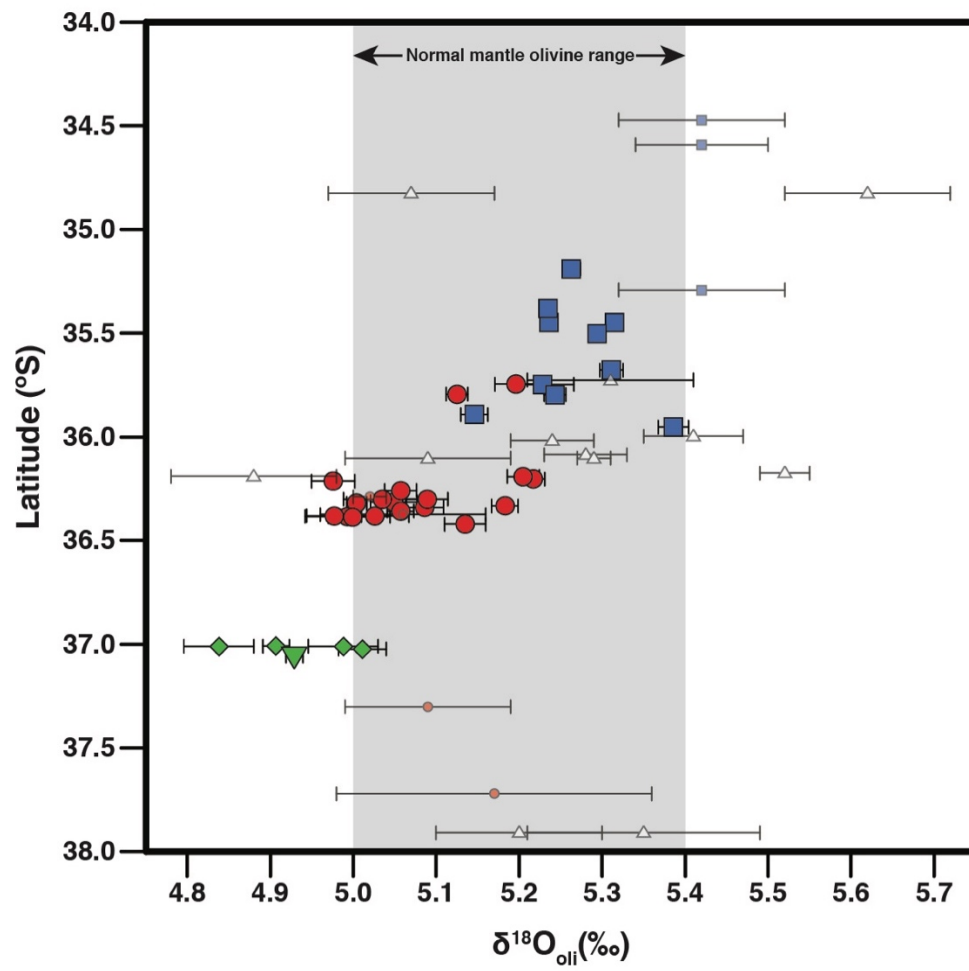


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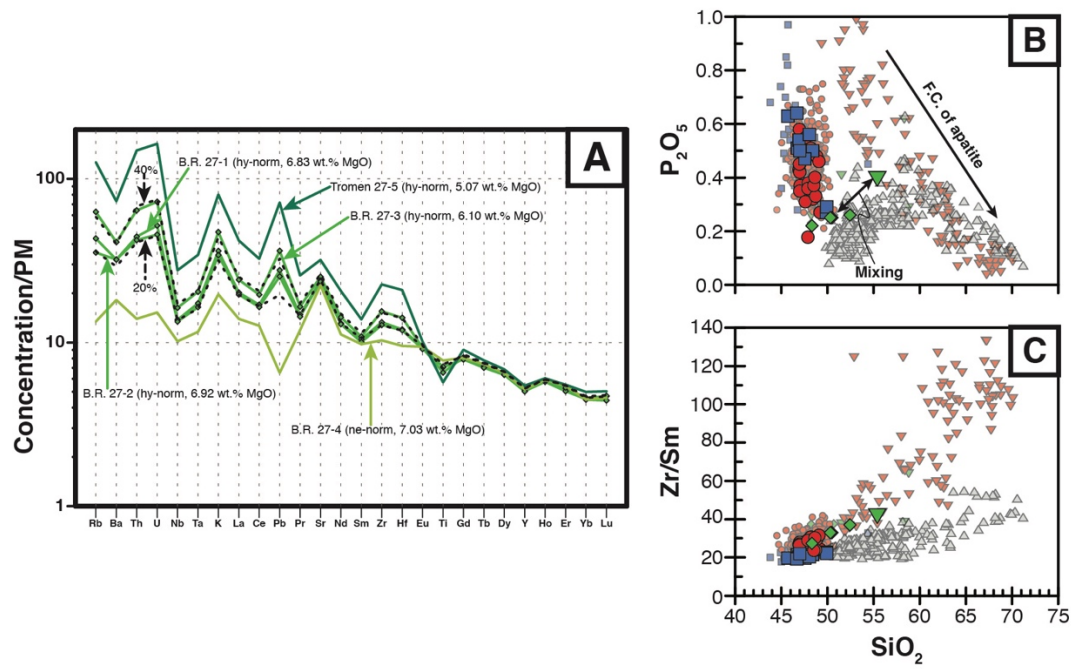


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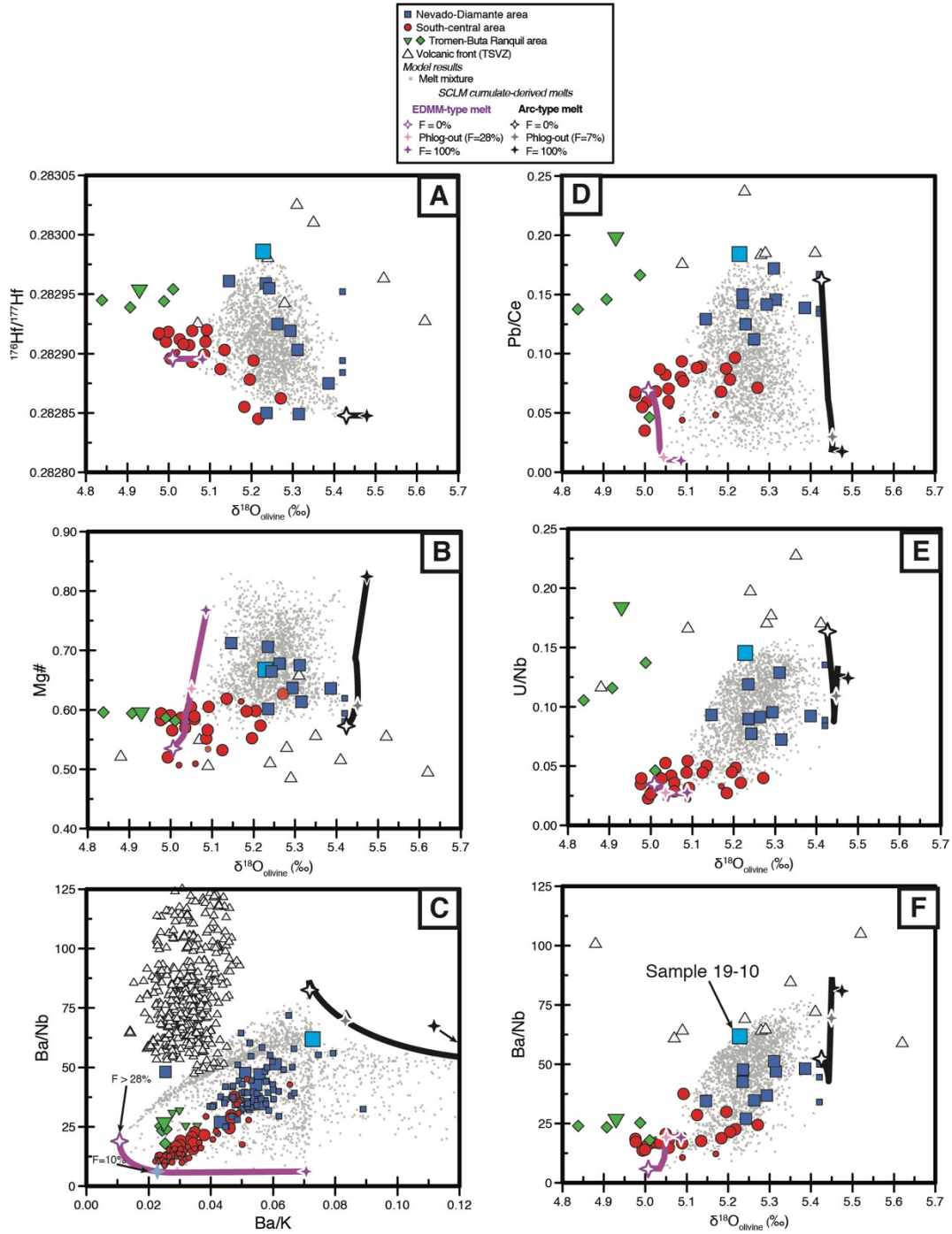


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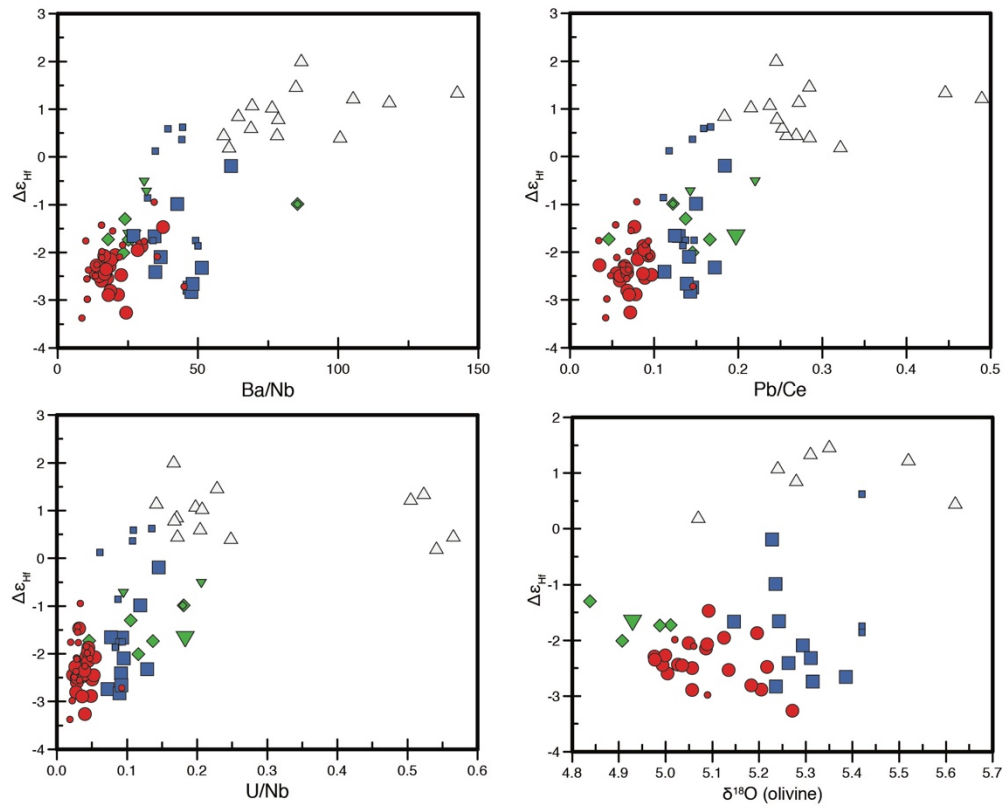


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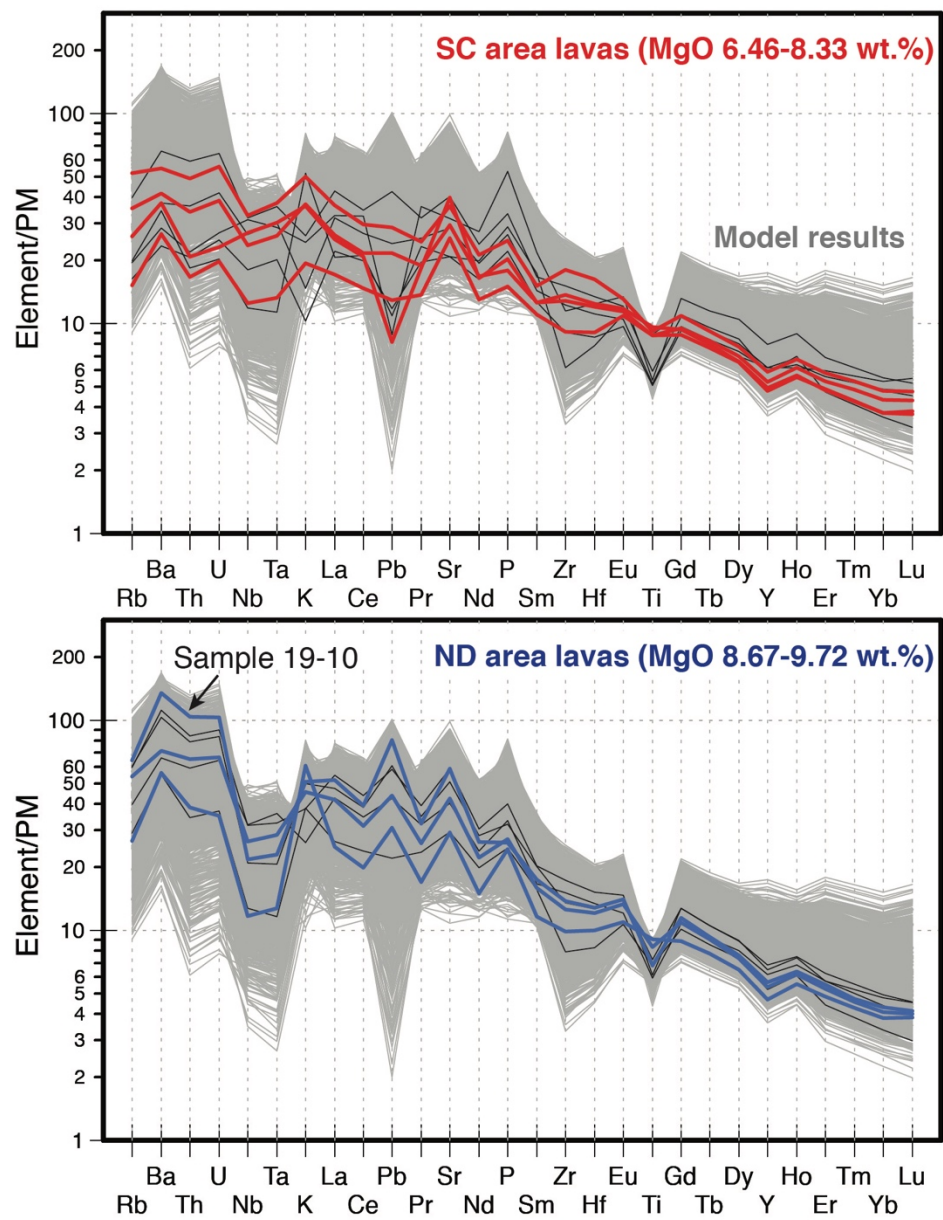


Figure 1-11.

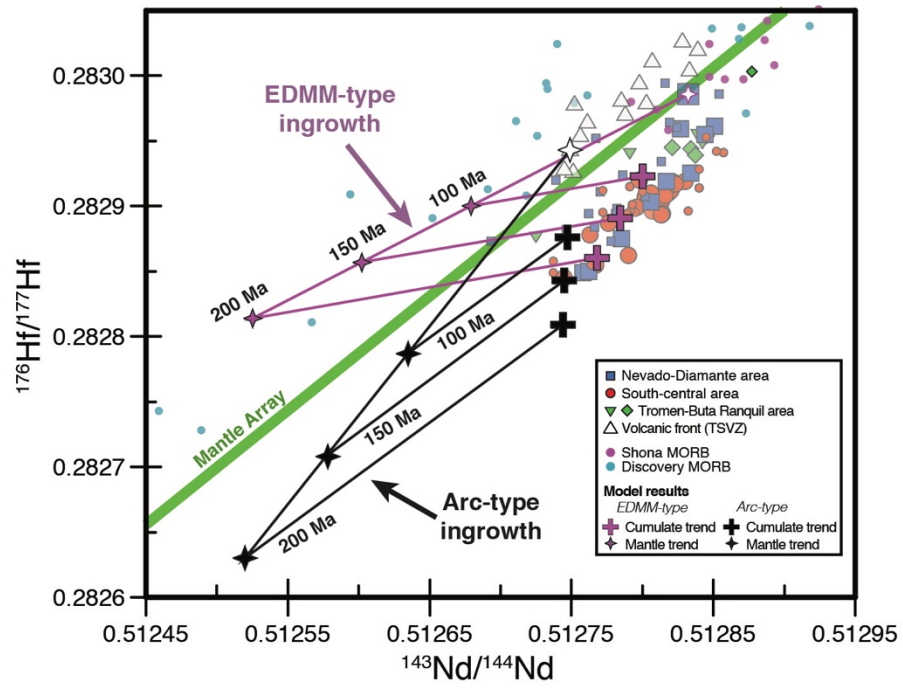
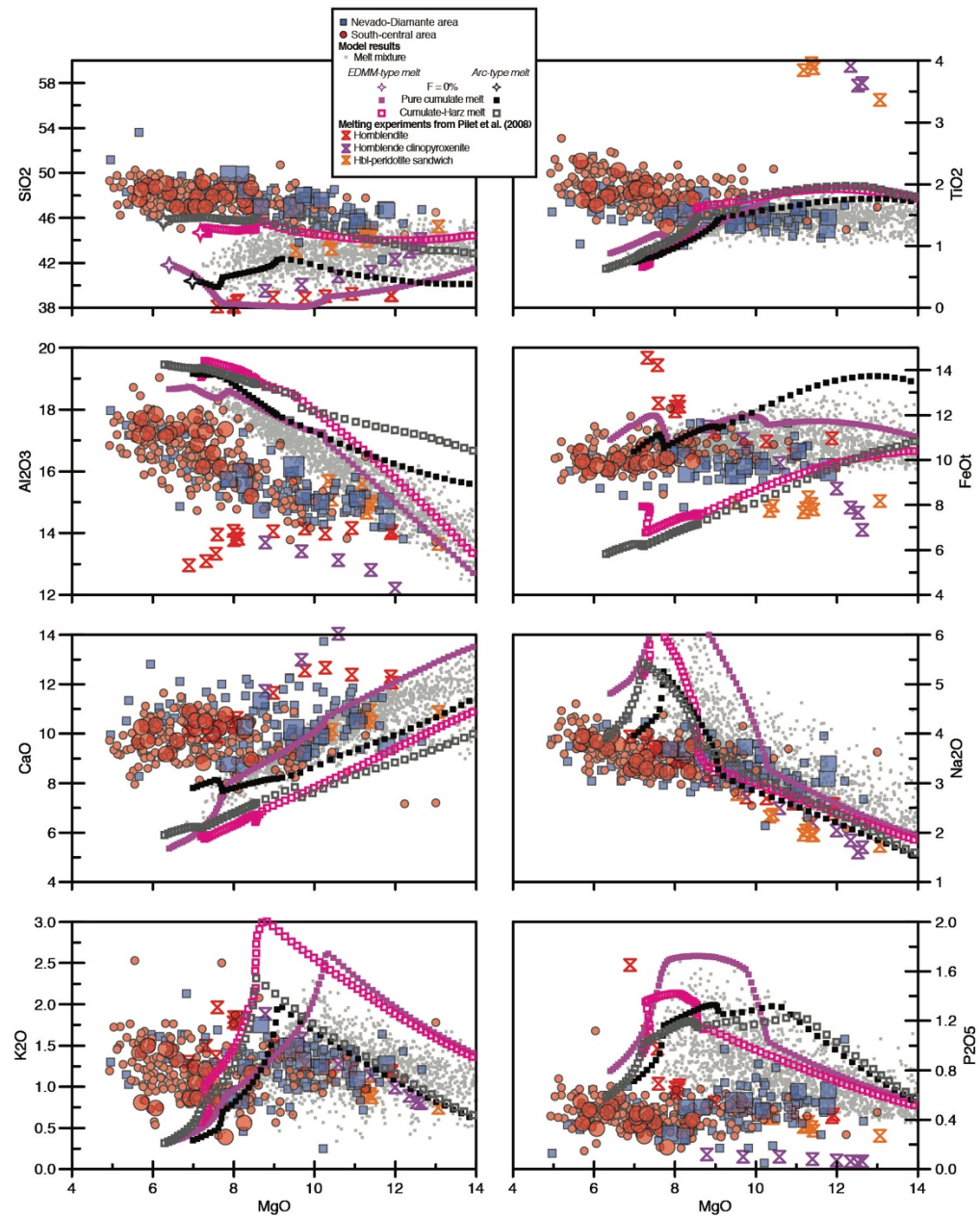


Figure 1-12.



TABLES

Table 1-1.

Table 1. Sample locations, major and trace element concentrations, and Sr, Nd, Pb, Hf, and O isotope contents.														
Sample ID	15-3	16-4	16-5	18-7	19-6	19-7	19-8	19-10	19-11	20-2	21-6	21-8	22-5	23-1
Area	N-D	N-D	N-D	N-D	N-D	N-D	N-D	N-D	N-D	N-D	S-C	S-C	S-C	S-C
Volcanic Fiel	Nevado	Nevado	Nevado	Nevado	Nevado	Nevado	Nevado	Nevado	Nevado	Nevado	Llan.	Llan.	P.M.	P.M.
Latitude (°W)	35.19	35.45	35.45	35.50	35.89	35.95	35.85	35.75	35.68	35.38	35.75	35.80	36.31	36.34
Longitude (°E)	68.28	68.07	68.07	68.78	68.57	68.50	68.65	68.66	68.68	68.73	69.45	69.22	69.67	69.40
Major elements (wt. %)														
SiO2	45.72	49.87	49.91	48.38	46.68	47.00	48.03	46.92	47.57	46.73	48.73	48.51	48.41	48.84
TiO2	1.62	1.45	1.52	1.59	1.46	1.83	1.68	1.37	1.47	1.26	1.66	1.74	1.73	1.99
Al2O3	15.10	16.00	15.74	15.56	14.38	14.74	15.17	16.15	15.01	15.04	17.84	17.70	16.13	17.23
Fe2O3T	11.55	11.34	11.47	10.41	10.47	10.92	10.81	10.42	10.78	10.79	10.85	11.05	11.01	10.52
FeOT														
CaO	10.51	8.71	8.76	10.27	9.46	11.35	9.22	10.16	9.89	9.51	10.35	10.27	10.25	9.73
MgO	11.05	8.18	7.87	8.28	11.79	8.67	9.72	9.49	10.17	11.76	6.07	5.71	7.66	5.88
MnO	0.19	0.16	0.17	0.17	0.17	0.17	0.17	0.19	0.17	0.18	0.16	0.16	0.17	0.16
K2O	1.09	0.83	0.88	1.24	1.28	1.75	1.32	1.47	1.24	1.27	0.74	0.81	0.82	1.50
Na2O	2.88	3.63	3.68	3.69	3.39	3.52	3.73	3.22	3.57	3.09	3.84	3.95	3.25	3.88
P2O5	0.63	0.27	0.29	0.50	0.64	0.50	0.56	0.54	0.47	0.51	0.33	0.37	0.32	0.48
Total	100.32	100.42	100.29	100.08	99.74	100.44	100.41	99.92	100.34	100.12	100.54	100.27	99.74	100.20
Mg#	69.04	62.72	61.55	64.96	72.41	64.92	67.69	67.98	68.74	71.75	56.60	54.66	61.87	56.57
Mg# calculated assuming Fe3+/(Total Fe)=0.15.														
CIPW Norm														
Quartz														
Albite	14.04	30.83	31.34	21.33	15.60	18.01	16.63	10.97	21.49	16.28	26.47	26.15	25.98	24.79
Anorthite	25.08	24.94	23.87	22.27	25.28	21.24	20.29	19.22	20.73	23.48	29.30	28.26	27.25	25.26
Orthoclase	6.66	5.06	5.41	7.62	9.14	7.62	7.89	10.55	8.03	7.75	4.48	4.95	5.01	9.06
Nepheline	5.67			5.45	6.41	6.66	6.69	10.26	5.51	5.41	3.30	4.06	0.98	4.45
Diopside	18.93	13.75	14.79	21.06	18.08	20.32	18.61	27.70	17.58	16.83	16.59	17.09	18.13	16.66
Hypersthene		1.44	0.71											
Olivine	22.43	18.05	17.74	15.70	19.24	19.78	23.16	14.18	19.69	24.16	13.53	12.86	16.11	12.51
Ilmenite	3.09	2.76	2.90	3.04	2.63	2.80	2.81	3.48	3.21	2.41	3.16	3.32	3.32	3.80
Magnetite	2.52	2.48	2.51	2.28	2.28	2.35	2.30	2.38	2.36	2.36	2.37	2.42	2.42	2.30
Apatite	1.46	0.62	0.67	1.18	1.25	1.10	1.50	1.16	1.31	1.18	0.76	0.85	0.74	1.11
Zircon	0.03	0.02	0.02	0.03	0.03	0.02	0.03	0.02	0.03	0.03	0.02	0.03	0.02	0.04
Chromite	0.09	0.06	0.05	0.05	0.06	0.08	0.10	0.08	0.07	0.11	0.02	0.02	0.05	0.02
CIPW norm calculated assuming Fe3+/(Total Fe)=0.15.														
Trace elements (ppm)														
Sc	29.4	19.9	20.6	24.3	22.8	24.8	23.0	25.0	27.0	23.9	25.0	26.4	29.2	26.6
V*	234	175	159	195	198	221	195	225	210	226	185	203	207	219
Cr*	430	265	235	242	437	354	307	290	348	503	96	79	249	98
Ni*	214	139	119	132	276	139	188	146	192	284	39	31	89	47
Zn*	94	103	88	86	83	95	99	92	88	83	94	91	92	83
Ga*	19.1	21.2	22.5	19.6	17.4	21.0	19.5	19.9	18.6	18.6	20.8	22.2	21.4	21.0
Rb	20.9	16.8	16.6	27.3	33.6	16.0	32.5	38.8	29.0	32.1	13.7	15.6	13.2	27.8
Sr	793	577	577	866	902	582	843	1172	802	863	613	667	541	657
Y	24.3	21.3	20.8	23.9	22.3	20.2	23.2	24.4	22.3	22.0	21.9	23.4	21.9	25.0
Zr	130	110	107	141	131	104	132	144	123	125	121	130	121	180
Nb	14.6	8.2	7.8	15.3	17.2	7.7	17.5	14.4	12.2	13.5	9.6	11.0	11.2	19.7
Cs	1.31	0.25	0.50	0.92	1.37	0.51	1.13	2.38	1.32	1.04	0.54	0.59	0.41	1.07
Ba	506	384	373	563	594	370	471	888	627	576	286	314	231	377
La	26.02	17.22	16.51	28.70	31.57	16.20	27.08	33.72	26.49	27.48	14.48	16.42	13.43	22.25
Ce	53.57	34.93	33.72	56.89	61.59	33.32	52.67	65.74	52.37	53.03	32.29	36.29	29.85	47.79
Pr	6.99	4.56	4.35	7.09	7.63	4.30	6.59	8.16	6.60	6.52	4.38	4.95	4.08	6.26
Nd	29.29	19.30	18.73	29.28	31.13	18.78	27.79	32.92	27.54	26.43	19.46	21.53	18.40	26.17
Sm	6.61	4.83	4.79	6.54	6.74	4.73	6.46	7.10	6.26	5.84	5.05	5.50	4.91	6.11
Eu	2.15	1.68	1.64	2.11	2.14	1.69	2.06	2.16	2.04	1.84	1.79	1.88	1.78	2.03
Gd	6.11	5.00	4.79	6.10	6.03	4.83	5.94	6.25	5.87	5.26	5.05	5.57	5.15	5.93
Tb	0.92	0.78	0.76	0.90	0.88	0.77	0.90	0.92	0.87	0.80	0.78	0.85	0.81	0.91
Ho	0.51	0.45	0.47	0.56	0.48	0.43	0.49	0.57	0.54	0.44	0.45	0.46	0.49	0.54
Yb	0.97	0.86	0.85	0.94	0.90	0.83	0.92	0.95	0.89	0.86	0.88	0.94	0.92	1.02
Er	2.55	2.15	2.17	2.55	2.37	2.12	2.31	2.33	2.23	2.30	2.41	2.34	2.32	2.54
Tm	0.35	0.31	0.29	0.32	0.30	0.29	0.31	0.32	0.30	0.31	0.31	0.33	0.32	0.35
Yb	2.01	1.77	1.72	1.90	1.79	1.69	1.80	1.90	1.74	1.81	1.84	1.95	1.82	2.08
Lu	0.310	0.266	0.261	0.290	0.263	0.262	0.273	0.284	0.270	0.285	0.275	0.298	0.282	0.319
Hf	3.46	2.96	2.89	3.58	3.25	2.83	3.42	3.62	3.28	3.16	3.10	3.35	3.26	4.36
Ta	0.87	0.48	0.47	0.92	1.00	0.47	1.05	0.85	0.73	0.81	0.56	0.65	0.71	1.27
Pb	6.01	5.08	4.82	8.05	7.95	4.62	6.57	12.10	9.01	7.95	2.82	3.20	2.46	3.83
Th	4.62	3.30	3.23	5.94	6.12	3.06	5.20	8.24	6.45	6.02	1.57	1.82	1.72	3.10
U	1.33	0.59	0.70	1.46	1.60	0.71	1.35	2.09	1.57	1.61	0.43	0.49	0.47	0.88
* Indicates trace element concentrations measured by XRF														
Isotopes														
143Nd/144Nd	0.512834	0.512758	0.512762	0.512817	0.512851	0.512785	0.512844	0.512832	0.512806	0.512772	0.512763	0.512776	0.512802	0.512796
2SE	0.000006	0.000005	0.000005	0.000005	0.000006	0.000010	0.000005	0.000005	0.000006	0.000005	0.000006	0.000007	0.000007	0.000005
76Hf/76Sr	0.703878	0.704188	0.704189	0.703871	0.703788	0.703994	0.703820	0.703933	0.704001	0.703907	0.704001	0.703972	0.704016	0.703903
2SE	0.000008	0.000008	0.000008	0.000008	0.000008	0.000007	0.000007	0.000008	0.000009	0.000011	0.000010	0.000008	0.000007	0.000009
176Hf/177Hf	0.282925	0.282849	0.282850	0.282919	0.282961	0.282875	0.282955	0.282986	0.282903	0.282959	0.282878	0.282887	0.282907	0.282899
2SE	0.000010	0.000008	0.000007	0.000008	0.000006	0.000005	0.000005	0.000005	0.000009	0.000005	0.000006	0.000006	0.000004	0.000008
206Pb/204Pb	18.4662	18.5448	18.5407	18.5417	18.5408	18.5053	18.5159	18.5896	18.5754	18.5582	18.3815	18.3965	18.4205	18.3475
2SE	0.0004	0.0004	0.0004	0.0003	0.0003	0.0004	0.0003	0.0005	0.0004	0.0005	0.0004	0.0004	0.0003	0.0003
155Sm/149Sm	15.5719	15.5625	15.5793	15.5621	15.5814	15.5689	15.5774	15.5910	15.5878	15.5819	15.5639	15.5655	15.5721	15.5619
2SE	0.0004	0.0004	0.0004	0.0003	0.0003	0.0003	0.0003	0.0004	0.0004	0.0004	0.0003	0.0003	0.0003	0.0003
208Pb/204Pb	38.2998	38.3412	38.3311	38.3744	38.3689	38.2711	38.3300	38.4529	38.4214	38.3940	38.2543	38.2570	38.2955	38.2203
2SE	0.0010	0.0010	0.0010	0.0007	0.0007	0.0011	0.0007	0.0010	0.0011	0.0011	0.0010	0.0009	0.0010	0.0009
δ18O_VSMOW ‰	5.263	5.315	5.236	5.294	5.146	5.386	5.243	5.228	5.311	5.235	5.196	5.125	5.049	5.086
2SE	0.011	0.010	0.009	0.008	0.016	0.018	0.013	0.038	0.014	0.009	0.025	0.013	0.028	0.023

Table 1-1.

23-14	24-1A	24-1B	25-1	25-2	25-4	25-5	25-7	25-8*	25-9	25-10	25-11	26-1	26-3	VEJ-041
S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C	S-C
P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.
36.32	36.38	36.38	36.30	36.30	36.21	36.26	36.33	36.36	36.38	36.19	36.20	36.39	36.42	36.56
69.41	69.46	69.46	69.33	69.33	69.40	69.58	69.64	69.64	69.64	69.46	69.38	69.67	69.66	69.61
48.94	48.98	46.95	49.07	48.21	46.98	48.21	47.91	46.92	47.64	47.58	47.74	46.98	47.05	47.86
2.22	1.93	1.90	1.80	1.85	1.85	1.85	1.90	2.02	2.37	1.76	1.73	1.94	1.77	1.32
17.36	17.31	17.28	17.14	17.23	17.53	17.23	16.60	17.30	17.15	15.94	16.45	17.77	16.03	17.36
11.17	10.95	10.98	10.68	10.67	10.90	10.67	11.12	11.20	11.53	12.21	10.74	10.77	11.30	
														10.08
9.73	10.54	10.52	9.17	9.19	10.90	9.19	10.00	10.27	9.66	10.10	9.88	10.20	10.42	10.77
6.60	7.06	7.30	6.33	6.42	6.91	6.42	7.49	7.29	5.67	8.26	7.53	7.05	8.33	7.80
0.17	0.16	0.17	0.17	0.17	0.16	0.17	0.17	0.16	0.17	0.17	0.18	0.16	0.17	0.17
1.33	1.23	1.21	1.46	1.44	0.86	1.44	1.06	1.06	1.41	0.56	1.46	1.05	1.07	0.39
3.79	3.45	3.30	3.70	3.96	3.28	3.96	3.71	3.52	3.81	3.56	3.60	3.36	3.23	3.21
0.58	0.45	0.45	0.46	0.51	0.35	0.51	0.38	0.43	0.55	0.31	0.51	0.42	0.37	0.18
99.88	100.06	100.04	99.97	99.63	99.72	99.63	100.35	100.18	99.94	100.43	99.81	99.70	99.73	99.15
57.95	60.04	60.78	58.01	58.39	59.65	58.39	61.08	60.26	53.40	61.18	62.04	60.40	63.21	61.88
21.24	18.91	19.08	27.21	24.01	20.83	24.65	20.70	24.76	22.63	20.30	23.80	21.58	19.57	24.25
26.60	28.28	28.92	26.00	25.95	24.64	25.21	30.83	25.24	25.58	28.41	25.70	30.58	26.32	32.00
8.06	7.46	7.35	8.83	3.37	8.81	8.78	5.26	8.73	6.39	6.39	8.51	6.39	6.50	2.36
6.05	5.67	4.90	2.36	3.40	5.36	4.99	4.00	4.94	4.85	5.26	4.75	3.90	4.37	1.66
15.16	17.65	17.09	13.94	18.37	17.66	14.54	17.75	14.50	17.89	16.52	15.86	14.69	19.25	16.88
14.77	14.82	15.51	14.73	18.07	15.77	14.67	14.63	14.69	15.64	15.72	12.97	15.70	17.17	17.40
4.28	3.89	3.84	3.45	3.36	3.32	3.56	3.55	3.56	3.63	3.86	4.55	3.73	3.39	2.52
2.45	2.40	2.41	2.34	2.67	2.36	2.35	2.40	2.35	2.43	2.45	2.53	2.37	2.49	2.45
1.35	1.06	1.04	1.07	0.71	1.19	1.19	0.81	1.19	0.89	1.01	1.28	0.99	0.86	0.41
0.04	0.03	0.03	0.04	0.02	0.02	0.04	0.02	0.03	0.03	0.03	0.04	0.03	0.03	0.02
0.02	0.03	0.03	0.03	0.06	0.05	0.03	0.03	0.03	0.04	0.04	0.02	0.03	0.06	0.03
25.6	28.9	28.3	23.7	23.4	27.9	28.1	28.7	25.9	25.5	26.4	22.1	23.4	29.6	31.4
213	229	224	197	208	221	208	199	219	233	204	171	203	223	200
77	138	141	158	154	152	154	185	182	85	278	210	157	255	157
51	67	76	66	76	70	76	75	73	36	105	89	73	110	93
92	88	90	91	90	82	90	81	82	87	102	98	85	90	76
21.4	20.8	19.8	21.1	21.1	20.5	21.1	21.3	19.7	21.2	21.5	20.4	19.9	19.8	17.6
20.6	22.0	21.5	32.2	31.2	14.6	12.6	14.7	14.5	19.7	9.1	15.8	15.6	21.2	4.5
812	761	740	644	720	658	619	575	715	763	506	516	794	585	420
25.5	23.7	22.3	24.8	25.3	21.9	22.3	24.0	20.9	26.2	20.6	20.2	21.3	22.7	23.1
181	156	149	188	189	121	130	162	138	187	96	111	144	134	102
24.2	18.1	17.5	21.0	21.5	12.9	13.6	15.4	17.4	23.7	8.2	11.4	17.9	15.5	4.1
0.57	0.77	0.78	1.29	1.21	0.50	0.44	0.41	0.36	0.52	0.33	0.32	0.42	0.84	0.10
379	306	302	349	361	239	246	290	258	322	176	258	248	274	154
23.48	19.16	19.00	23.01	23.61	14.34	14.99	17.07	16.97	21.63	11.06	12.30	16.29	17.03	7.66
50.07	41.61	41.31	47.97	49.43	32.24	33.10	37.75	36.88	46.83	24.68	27.42	34.97	36.32	18.36
6.50	5.45	5.51	6.17	6.21	4.40	4.45	5.05	4.92	6.09	3.48	3.83	4.67	4.79	2.67
28.15	23.74	23.71	25.47	26.55	19.67	20.16	22.24	21.50	27.08	16.28	17.52	20.68	20.99	12.71
6.65	5.78	5.61	5.96	6.15	5.00	5.21	5.51	5.17	6.71	4.49	4.60	5.13	5.10	3.53
2.29	1.96	1.90	1.99	2.02	1.79	1.86	1.96	1.90	2.31	1.68	1.72	1.82	1.76	1.33
6.26	5.68	5.37	5.74	5.92	5.19	5.38	5.42	5.10	6.50	4.80	4.75	5.12	5.18	4.06
0.96	0.88	0.82	0.89	0.91	0.80	0.82	0.87	0.79	1.02	0.76	0.75	0.79	0.82	0.70
5.45	5.03	4.84	5.17	5.21	4.61	4.70	5.12	4.51	5.82	4.42	4.31	4.47	4.71	4.40
1.03	0.97	0.90	0.98	1.01	0.89	0.92	0.96	0.86	1.08	0.83	0.80	0.85	0.92	0.91
2.59	2.44	2.24	2.54	2.55	2.24	2.33	2.48	2.09	2.73	2.14	2.07	2.11	2.32	2.52
0.35	0.33	0.31	0.35	0.36	0.31	0.31	0.35	0.28	0.37	0.29	0.28	0.29	0.33	0.37
2.07	1.91	1.84	2.12	2.11	1.81	1.83	2.05	1.68	2.17	1.66	1.67	1.66	1.91	2.23
0.315	0.285	0.280	0.335	0.317	0.276	0.278	0.305	0.251	0.322	0.248	0.247	0.259	0.293	0.353
4.36	3.83	3.69	4.63	4.59	3.20	3.40	3.85	3.41	4.47	2.57	2.96	3.53	3.41	2.54
1.49	1.14	1.11	1.35	1.39	0.79	0.85	0.96	1.07	1.48	0.49	0.70	1.12	0.97	0.26
2.97	2.84	2.79	4.48	4.29	2.09	2.33	2.56	2.21	2.58	1.93	2.65	1.23	3.24	1.41
2.50	2.26	2.26	4.22	3.88	1.52	1.72	1.48	1.76	2.23	1.32	1.56	1.66	2.70	0.59
0.69	0.71	0.69	1.14	1.13	0.45	0.49	0.42	0.50	0.54	0.40	0.41	0.47	0.78	0.13
0.512807	0.512820	0.512823	0.512806	0.512816	0.512820	0.512813	0.512767	0.512830	0.512818	0.512814	0.512745	0.512822	0.512813	0.512798
0.000006	0.000006	0.000005	0.000005	0.000007	0.000005	0.000008	0.000006	0.000005	0.000006	0.000006	0.000004	0.000007	0.000006	0.000006
0.703894	0.703853	0.703844	0.703890	0.703861	0.703864	0.703922	0.704070	0.703873	0.703903	0.703923	0.704117	0.703898	0.703829	0.703828
0.000009	0.000008	0.000006	0.000009	0.000009	0.000009	0.000011	0.000007	0.000007	0.000009	0.000007	0.000007	0.000009	0.000007	0.000011
0.282896	0.282912	0.282917	0.282910	0.282908	0.282916	0.282893	0.282855	0.282919	0.282910	0.282894	0.282845	0.282918	0.282903	0.282920
0.000006	0.000005	0.000003	0.000008	0.000005	0.000009	0.000006	0.000007	0.000005	0.000005	0.000006	0.000004	0.000004	0.000007	0.000009
18.3221	18.3612	18.3588	18.3931	18.3939	18.3647	18.3846	18.2491	18.3076	18.2905	18.3866	18.3363	18.3088	18.4155	18.2858
0.0006	0.0011	0.0007	0.0003	0.0005	0.0004	0.0004	0.0004	0.0003	0.0005	0.0004	0.0006	0.0003	0.0004	0.0005
15.5537	15.5593	15.5608	15.5655	15.5655	15.5604	15.5649	15.5496	15.5504	15.5477	15.5624	15.5562	15.5584	15.5584	15.5549
0.0006	0.0011	0.0006	0.0003	0.0004	0.0004	0.0004	0.0004	0.0003	0.0004	0.0003	0.0006	0.0003	0.0003	0.0005
38.1692	38.2086	38.2120	38.2542	38.2513	38.2075	38.2418	38.1203	38.1542	38.1403	38.2230	38.2229	38.1785	38.2787	38.1554
0.0015	0.0027	0.0017	0.0008	0.0011	0.0011	0.0011	0.0009	0.0009	0.0011	0.0010	0.0016	0.0009	0.0008	0.0011
5.004	5.026	4.977	5.089	5.035	4.976	5.057	5.183	4.993	5.205	5.217	4.999	5.135	5.092	
0.012	0.041	0.033	0.025	0.047	0.026	0.019	0.016	0.016	0.051	0.019	0.014	0.029	0.025	0.018

Table 1-1.

MEN-026	27-1	27-2	27-3	27-4	27-5
S-C	Tromen	Tromen	Tromen	Tromen	Tromen
R.C.	Buta Ranquill	Buta Ranquill	Buta Ranquill	Buta Ranquill	Tromen
37.32	37.01	37.01	37.01	37.02	37.06
68.94	69.83	69.84	69.85	69.86	69.93
48.64	50.46	50.32	52.45	48.32	55.39
1.77	1.42	1.43	1.32	1.56	1.15
15.20	16.60	16.69	16.81	17.03	17.02
	10.27	10.35	9.46	11.15	7.64
9.94					
8.95	9.44	9.50	8.58	10.47	7.15
8.43	6.83	6.92	6.10	7.03	5.07
0.16	0.16	0.16	0.15	0.17	0.13
1.17	1.05	0.99	1.37	0.57	2.32
3.75	3.59	3.53	3.72	3.30	3.99
0.40	0.25	0.25	0.26	0.22	0.40
98.41	100.06	100.13	100.23	99.81	100.24
64.01	60.80	60.91	60.04	59.49	60.72
					0.09
26.43	30.61	30.06	31.60	26.71	33.85
21.35	26.21	26.89	25.21	30.31	21.65
7.21	6.34	6.00	8.25	3.42	13.93
3.11				0.79	
17.18	15.85	15.55	13.09	17.04	9.41
	1.34	2.01	9.75		16.22
17.85	14.02	13.86	6.84	15.68	0.00
3.41	2.72	2.73	2.52	3.00	2.18
2.43	2.25	2.27	2.07	2.45	1.67
0.94	0.59	0.58	0.61	0.52	0.92
0.03	0.03	0.03	0.03	0.02	0.05
0.06	0.04	0.04	0.03	0.03	0.03
21.2	27.0	27.5	23.0	30.4	18.8
206	192	197	174	219	133
273	192	187	144	155	124
176	69	73	57	61	57
95	78	77	75	85	68
18.8	19.0	19.5	18.7	19.3	17.4
21.4	26.0	21.3	37.7	8.1	75.9
603	476	468	502	446	636
21.3	21.8	21.6	22.3	22.2	23.4
161	140	134	163	108	238
18.3	9.1	8.8	10.7	6.7	18.2
0.62	1.19	0.78	1.70	0.27	3.75
447	212	212	271	120	481
18.63	13.08	12.74	15.68	9.05	27.21
38.33	28.47	27.61	32.83	21.19	54.45
5.00	3.75	3.65	4.21	3.02	6.53
21.63	16.37	16.17	17.84	14.03	25.84
5.33	4.24	4.09	4.41	3.97	5.63
1.82	1.44	1.41	1.43	1.45	1.56
5.19	4.30	4.29	4.40	4.39	4.91
0.80	0.70	0.69	0.71	0.73	0.77
4.55	4.30	4.29	4.32	4.40	4.62
0.84	0.86	0.88	0.87	0.88	0.90
2.18	2.21	2.32	2.29	2.38	2.42
0.29	0.33	0.32	0.33	0.33	0.35
1.74	1.99	1.98	2.03	1.98	2.20
0.258	0.319	0.299	0.317	0.311	0.344
3.74	3.41	3.36	4.02	2.70	5.93
1.13	0.64	0.61	0.75	0.43	1.27
2.74	4.15	3.80	5.46	0.98	10.75
2.11	3.52	3.36	5.10	1.11	11.86
0.73	1.05	0.93	1.47	0.31	3.33
0.512790	0.512837	0.512821	0.512834	0.512845	0.512842
0.000008	0.000006	0.000005	0.000005	0.000009	0.000004
0.703816	0.703829	0.703855	0.703814	0.703765	0.703785
0.000007	0.000009	0.000008	0.000007	0.000007	0.000007
0.282862	0.282939	0.282945	0.282944	0.282954	0.282953
0.000003	0.000007	0.000006	0.000007	0.000006	0.000002
18.3484	18.5005	18.4964	18.5180	18.4465	18.5370
0.0005	0.0003	0.0004	0.0004	0.0005	0.0004
15.5611	15.5858	15.5820	15.5881	15.5749	15.5893
0.0003	0.0003	0.0003	0.0003	0.0005	0.0004
38.2035	38.3551	38.3427	38.3715	38.2918	38.3848
0.0013	0.0007	0.0009	0.0008	0.0012	0.0008
5.271	4.907	4.838	4.988	5.011	4.929
0.028	0.016	0.042	0.042	0.029	0.010

Table 1-2.

Table 2. Starting compositions and results for the SCLM cumulate formation and melting model.

[illegible]

a- Major elements from data compilation reported in WORKMAN and HART (2005)
b- Trace elements from EDMA composition reported in WORKMAN and HART (2005)
c- Trace elements represent source composition of 5% bathonoidal melt that would have produced the trace element composition of Fritsenite sample 120008 reported in SAGER ET AL. (2013)

Table 1-3.

Table 3. Parent-daughter isotope ratios and Nd and Hf isotope ratios involved in ingrowth calculations for Shona-type and Arc-type asthenospheric sources and SCLM cumulates.

Shona-type asthenosphere

	$^{143}\text{Sm}/^{144}\text{Nd}$	$^{176}\text{Lu}/^{177}\text{Hf}$			
	0.235	0.046			
	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{176}\text{Hf}/^{177}\text{Hf}$	ϵ_{Nd}	ϵ_{Hf}	$\Delta\epsilon_{\text{Hf}}$
Today	0.512832	0.282986	7.10	3.79	-0.20
At 100 Ma	0.512679	0.282900	4.06	0.79	1.52
At 150 Ma	0.512602	0.282857	2.54	-0.71	2.38
At 200 Ma	0.512525	0.282814	1.02	-2.20	3.25

Shona-type cumulate

	$^{143}\text{Sm}/^{144}\text{Nd}$	$^{176}\text{Lu}/^{177}\text{Hf}$			
	0.012	0.186			
	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{176}\text{Hf}/^{177}\text{Hf}$	ϵ_{Nd}	ϵ_{Hf}	$\Delta\epsilon_{\text{Hf}}$
At 100 Ma	0.512800	0.282923	4.87	3.17	-1.44
At 150 Ma	0.512784	0.282891	3.76	2.86	-2.06
At 200 Ma	0.512768	0.282860	2.64	2.54	-2.69

Arc-type asthenosphere

	$^{143}\text{Sm}/^{144}\text{Nd}$	$^{176}\text{Lu}/^{177}\text{Hf}$			
	0.175	0.084			
	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{176}\text{Hf}/^{177}\text{Hf}$	ϵ_{Nd}	ϵ_{Hf}	$\Delta\epsilon_{\text{Hf}}$
Today	0.512749	0.282943	2.17	5.60	0.86
At 100 Ma	0.512635	0.282787	-0.06	0.06	-1.13
At 150 Ma	0.512578	0.282708	-1.18	-2.72	-2.13
At 200 Ma	0.512520	0.282630	-2.30	-5.50	-3.13

Arc-type cumulate

	$^{143}\text{Sm}/^{144}\text{Nd}$	$^{176}\text{Lu}/^{177}\text{Hf}$			
	0.171	0.048			
	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{176}\text{Hf}/^{177}\text{Hf}$	ϵ_{Nd}	ϵ_{Hf}	$\Delta\epsilon_{\text{Hf}}$
At 100 Ma	0.512747	0.282876	2.12	3.23	-1.43
At 150 Ma	0.512745	0.282843	2.10	2.04	-2.57
At 200 Ma	0.512744	0.282809	2.07	0.85	-3.72

CHAPTER 2

The major, trace, and volatile elements of olivine-hosted melt inclusions from the back-arc of the Andean Southern Volcanic Zone (34°-38°S)

Benjamin H Chilson-Parks^{1*}, A. E. Saal¹, F. Calabozo², E. Hauri³, S. Mallick¹

¹Brown University, Providence, Rhode Island, United States

²Universidad Nacional de Río Negro, General Roca, Argentina

³Carnegie DTM, Washington, D.C., United States

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0.) Abstract

We report here the volatile (H_2O , CO_2 , F, Cl), major, and trace element contents of silicate melt inclusions (MIs) and embayments, as well as the major and trace element contents of their olivine phenocryst hosts, for three basaltic tephra that erupted in back-arc of the Andean Transitional Southern Volcanic Zone (TSVZ, 34-38°S).

One tephra from the Auca Mahuida (AM) volcanic field has melt inclusions with 1) low H_2O (<1 wt.%) and S (<2000 ppm) and high CO_2 (as high as 2000 ppm) concentrations, 2) intraplate-like trace element contents, and 3) MORB-like $\text{Fe}^{3+}/\Sigma\text{Fe}$ values (~ 0.20) calculated from olivine-melt V partitioning. F, Cl, and trace element contents indicate that the AM melt source consists of a melt contribution from metasomatic cumulates in the subcontinental lithospheric mantle (SCLM) related to an EDMM-type metasomatic agent.

In contrast, MIs from tephra in the Loncopué and Diamante localities have 1) H_2O concentrations as high as 3.5-4 wt.%, 2) arc-like trace element patterns (e.g., depletion in Nb and enrichment in Pb), 3) enrichments in S, Cl, and F and 4) arc-like $\text{Fe}^{3+}/\Sigma\text{Fe}$ values (0.22-0.35). The large range in H_2O content in Loncopué and Diamante MIs may in part be caused by degassing, but low- H_2O , high- CO_2 Diamante MIs cannot be a consequence of the degassing of magma with homogeneous H_2O content. Although these traits demonstrate a strong arc signature in Loncopué and Diamante glasses, the major, trace element, and volatile content of Diamante MIs resemble the characteristics of a melt formed from SCLM cumulates that were themselves formed from a metasomatic agent with a strong arc signature.

The high Ni contents of AM and Diamante olivines (~ 1000 -2500ppm) indicate melting of either a pyroxenitic source or a peridotitic source that experienced large thermal

variations between melting and phenocryst formation. The lower Ni contents in Loncopué olivines are consistent with Loncopué melts originating in the peridotitic mantle wedge. These patterns in MI compositions demonstrate that despite their compositional differences, Diamante and AM MIs both reflect melt contributions from metasomatized SCLM.

1.) Introduction

Volatiles play an important role in the petrogenesis and evolution of subduction zone magmas. Nonetheless, ambiguity still surrounds the dominant processes behind fluid transfer from slab to mantle wedge, subsequent melt generation, and the behavior of volatiles in magmas as they ascend, crystallize, and erupt through the lithosphere. Previous works debate the important mechanisms behind subduction zone melt petrogenesis, whether it be flux melting, which involves slab-derived volatiles (primarily H₂O) lowering the solidus of the mantle wedge (e.g., Grove et al., Kelley et al., 2006; Stolper and Newman, 1994), or adiabatic decompression melting (e.g., Kohut et al., 2006; Plank and Langmuir, 1988; Sisson and Bronto, 1998).

Olivine-hosted melt inclusions (MIs) represent an effective means of evaluating the volatile contents and primitive compositions of subduction zone magmas and their mantle sources. MIs are parcels of melt that have been enclosed in a host crystal due to irregularities in crystal growth (Roedder, 1979). MIs are commonly trapped at pressures exceeding the pressure of eruption, with the host crystal acting as a pressure vessel, curbing the effects of degassing on the volatile contents of the melt. In addition, sample suites of olivine-hosted MIs often display a chemical and isotopic variability comparable to the range of chemical and isotopic compositions observed in global datasets of whole-rock

lava compositions. (e.g., Kent., 2008; Saal et al., 1998). These traits enable MIs to provide information about the pre-eruptive volatile contents of magmas and about heterogeneities and processes affecting subduction zone magma petrogenesis.

A setting that merits such an investigation is the Transitional Southern Volcanic Zone (transitional SVZ or TSVZ, ~34°S-38°S) of the Andean magmatic arc. The back-arc region of the TSVZ, which contains the Payenia volcanic province and the basalts erupted in the Loncopué graben, contains over 800 Plio-Quaternary monogenetic cinder cones, fissure eruptions, silicic calderas, and stratovolcanoes. It is one of the most volcanically productive regions of South America since the Pliocene (Ramos and Folguera, 2011; Varekamp et al., 2010; Völker et al., 2011). The predominantly basaltic volcanism of the TSVZ back-arc is not only voluminous but also chemically diverse. Some lavas exhibit whole-rock chemical and isotopic traits that resemble lavas from the TSVZ volcanic front, such as enrichments of large-ion lithophile elements (LILEs) relative to high field strength elements (HFSEs), while other basalts exhibit traits akin to intraplate basalts, which lack high LILE/HFSE ratios, but nonetheless have enrichments in highly incompatible trace elements relative to MORBs (e.g., Chilson-Parks et al., in prep; Jacques et al., 2013, Søager et al. 2013). These studies have found that the basalts with the strongest arc signature tend to occur in Loncopué and northern and southeastern Payenia, whereas the basalts with the strongest intraplate signature occur in central and southeastern Payenia. Earlier findings from compositions of Payenia olivine-hosted MIs show enrichments in S, Cl and F in northern Payenia MIs, which were deemed a consequence of increased contribution of slab-derived fluids in the mantle wedge beneath northern Payenia. Although previous work on TSVZ back-arc basalts have made progress in identifying and characterizing certain

aspects of their chemical diversity, this work lacks a consensus on the origin of the chemical diversity of basalts that erupted within close proximity to one another.

In the central and southern SVZ back-arc ($\sim 38^{\circ}$ - 46° S), a stronger trace element and isotopic arc signature occurs in basalts that erupted closer to the trench, while a stronger intraplate signature occurs in basalts farther from the trench (e.g., Stern et al., 1990). The more complex relationship between location and basalt composition in the TSVZ back-arc may reflect several possible factors. These possibilities may involve unique variations in (1) the abundance of slab-derived contributions in the mantle source, (2) the proportions of sediment melts versus fluids in the slab input, (3) the degree of melting experienced by the mantle source, (4) the importance of decompression-induced melting versus flux melting, (5) the variable melting of heterogeneities residing in the mantle wedge, and (6) the variable melting of continental crust and/or subcontinental lithospheric mantle (SCLM).

These petrogenetic factors can be better understood by the investigation of olivine-hosted MIs from the TSVZ back arc, given the preservation of primitive major and trace element concentrations and volatile contents. This study is the first study to report H_2O , CO_2 , S, F, and Cl contents and major and trace element concentrations of olivine-hosted MIs from the TSVZ back-arc. We use MI-bearing tephra sampled at different distances from the trench in order to assess the chemical diversity of TSVZ back-arc basalts and how it relates to the mantle sources and processes that control the petrogenesis of TSVZ back-arc basalts.

2.) Descriptions of sample localities, sample petrography, and whole-rock compositions

2.1) Sample localities

Melt inclusion-bearing tephtras were sampled from the Loncopué, Diamante, and Auca Mahuida, areas of the TSVZ back- arc. Sample 011510-181, hereafter referred to as the Loncopué sample, is from a lapilli and coarse ash deposit on Cerro Morado in the northern Loncopué graben. The Loncopué graben is a NW-SE oriented, 270 km-long depression situated between the Andean magmatic arc to the west, the Agrio fold and thrust belt to the east, and the Payenia province to the northeast. Extension occurring in Loncopué has been linked to slab steepening that followed an episode of late Miocene shallow subduction in the TSVZ (Folguera et al., 2010; Kay et al., 2006). The compositions of primitive basalts ($\text{MgO} > 5 \text{ wt.}\%$) from Loncopué exhibit a clear arc signature, given their depletions in HFSE (Nb, Ta, and Ti) and enrichments in Rb, Ba, Pb, and Sr (Rojas Vera et al., 2014; Varekamp et al., 2010).

Sample 011910-188, hereafter referred to as the Diamante sample, is from a deposit of fine lapilli and stratified ash at a monogenetic cone near the Diamante Volcano in the northern extent of the Payenia province. Basaltic lavas from the monogenetic centers near Diamante Volcano exhibit a strong trace element and isotopic arc signature, which may reflect the contribution of subduction-derived material to their mantle melting source, and/or the contribution of mantle metasomatized by a melt with arc-like trace element signature (Chilson-Parks et al., *in prep*; Holm et al., 2016). This region of Payenia is bounded by the thrust faults of the San Rafael Block to the east, the Andean foothills to the west, and the Pampean flat slab region to the north. The basalts near Diamante erupted in the Middle-Late Pleistocene (Folguera et al., 2009; Gudnason et al., 2012; Kay et al., 2006).

Sample AUC-035, hereafter referred to as the Auca Mahuida sample, is from a lapilli deposit within the Aguada de Lustre locality of the Auca Mahuida volcanic field in the southern extent of the Payenia province. The Auca Mahuida volcanic field is comprised

of E-W trending parasitic cones that erupted over the Auca Mahuida shield volcano, which represents the only shield volcano in the TSVZ back-arc (Kay et al., 2006; Llambías et al., 2010). Radiometric dating of Auca Mahuida lavas constrain its volcanism to <1.8 Ma (Pallares et al., 2016), and the basalts from this volcanic field exhibit intraplate-like trace element signatures (Jacques et al., 2013; Kay et al., 2006; Kay et al., 2013; Pallares et al., 2016). We note that AUC-035 is the rare occurrence in this region of a hypersthene-normative basalt. However, hypersthene consists of only ~1.5% of its CIPW norm, and trace element and isotope contents do not otherwise distinguish this sample from other Auca Mahuida basalts (chapter 3).

2.2) Sample petrography

Using photomicrographs taken of the samples prior to polishing and mounting in indium, we estimated the dimensions of vapor bubbles, melt inclusions, and, if present, any crystal grains contained within inclusions (Figure 1). MIs that exhibited spherical or rhomboidal morphologies represent those considered primary (i.e., coeval with the growth of the olivine grain), and are thus more likely to preserve the melt compositions prior to eruption and degassing. The abundance of melt inclusions in the Diamante and Loncopué samples is relatively limited, with most olivine grains hosting one or two MIs. Conversely, olivine grains from the AM sample often bear several MIs per grain, with one olivine crystal containing over 20 MIs. AM olivine grains may have captured more MIs per olivine grain due to the AM sample experiencing relatively rapid crystal growth of dendritic olivine crystals or rapid crystal growth following an earlier episode of differential mineral dissolution (Kent, 2008 and references therein) .

Vapor bubbles were identified in ~28% of all observed melt inclusions. In most bubble-bearing inclusions, the bubble constitutes <8% of the inclusion volume. These

bubbles form during decompression of the inclusion. Post-entrapment bubble growth can result from the difference in thermal contraction between the inclusion and the host crystal during cooling and post-entrapment crystallization of the mineral host (Roedder, 1979). Bubble growth can also be triggered by the pressure decrease associated with the diffusion of significant H₂O from the inclusion into the mineral host, which can decrease pressure and the solubility of CO₂ in the melt enough to form a vapor phase (Gaetani et al., 2012). In ~13% of the bubble-bearing inclusions, the bubble is 8-24% of the inclusion volume. The proportionally larger bubbles may not have formed during decompression within the host crystal, but instead during degassing prior to entrapment within the host crystal. Available observations cannot distinguish between these possibilities, although shrinkage bubbles are unlikely to occupy >15% of the inclusion volume since basaltic liquids are not expected to contract to such a degree (Lange and Carmichael, 1987).

Crystals also occur within and/or adjacent to MIs (Figure 1). These crystals are most commonly spinel, which are opaque and cubic. Tabular grains of plagioclase are also present. As is the case for vapor bubbles, available petrographic observations provide limited insight into whether the crystals formed prior to or after the entrapment of the MIs within the olivine host. Further analysis of crystals that are spatially associated with MIs must be conducted to further elucidate their influence on MI compositions.

2.3) Whole-rock compositions

Whole-rock major and trace element contents were measured using the XRF and ICP-MS methods described in the previous chapter. Measurements were performed on the AM MI sample itself, while the Diamante and Loncopué MI-bearing samples exhibited a degree of alteration that prevented their analysis. Instead, Diamante sample 011910-192 (located ~1000 meters from 011910-188), and Cerro Morado sample 011510-179 (located

~300 meters from 011510-181) were measured for their whole-rock compositions as the respective equivalents to the Diamante and Loncopué MI-bearing samples. Major and trace element concentrations are reported in Table 1 and primitive mantle-normalized trace element concentrations are presented in Figure 2. Analytical methods for data in Table 1 are reported in chapter 3. All three samples have $\text{MgO} > 6 \text{ wt.}\%$; the Diamante sample is the only nepheline-normative sample, and the Loncopué sample is the only calc-alkaline sample. Despite these differences in major element compositions, samples from Diamante and Loncopué both have trace element patterns indicative of a subduction-influenced melt source (e.g. high Ba/Nb , K/Nb and Sr/Nd and low Ce/Pb and Ti/Gd). The Loncopué sample is more depleted in incompatible trace elements than the Diamante sample, which suggests that the Loncopué mantle underwent a relatively high degree of melting or came from a more depleted melt source composition. The whole-rock trace element pattern of the AM sample differs from the Diamante and Loncopué patterns in that it lacks depletions in Nb, Ta, and Ti, and has a negative Th and Pb anomaly. All three samples exhibit similarly high Ba/Th and Sr/Nd ratios.

3.) Methods

3.1) Sample Preparation

Melt inclusion-bearing olivine phenocrysts were identified and sorted by first hand-grinding samples of vitreous scoria. For each sample, 200-500 olivine phenocrysts were handpicked under binocular microscope. To expose the melt inclusions, polishing of olivine phenocrysts took place by mounting a group of phenocrysts in Crystalbond resin on glass slides. Once inclusions in an individual phenocryst were polished and exposed, the phenocryst was removed from the resin, rinsed with acetone in an ultrasonic bath

several times (until the remainder of the resin was removed), and inserted in 1-inch circular mounts of indium metal.

3.2) Volatile and trace element concentrations by ion probe

Volatile element (H_2O , CO_2 , Cl, F, S) concentrations were measured using a Cameca nanoSIMS 50L and a Cameca IMS 6F at the Department of Terrestrial Magnetism (DTM). Each analysis of volatile elements used a 300-second presputter period with a 20-30- μm raster prior to counting time of 200 seconds. Volatile element measurements by nanoSIMS employed a primary beam of Cs^+ at 8 kV and 10-15 nA with a secondary extraction voltage of -8 kV (the Cs beam energy is +16 keV). Analytical detection limits were <0.5 ppm for F, S, and Cl, and 4-5 ppm for H_2O and CO_2 . We achieved an average analytical precision ($\pm 2\sigma$) of 2-6% for all volatile elements. The precision reported represents the average of the relative standard deviation of replicated analyses (10) of standard glass D52-5 during different day-long sessions within 5 months of each other.

Trace element (P, K, Ti, V, Cr, Mn, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb, Hf, Pb, Th, U) concentrations were measured using a Cameca IMS 6F at DTM. These analyses employed a primary beam of O^- at -12.5 kV and 15 nA, with an extraction voltage of 10kV (the O beam energy was -22.5 keV). Analytical detection limits were 50-60 ppm for Sc, 0.1-0.8 ppm for P, K, and Ti, and <0.05 ppm for the other trace elements. For standard glass 519-4-1, we achieved average analytical precision ($\pm 2\sigma$) of <14% for all trace elements except for Pb ($2\sigma=30\%$). Each analysis of trace elements used a 300-second presputter period with a 20-30- μm raster prior to counting time of ~1100 seconds.

3.3) Major element concentrations by electron probe

Major element analysis of basaltic glass and olivine host crystals was performed with the Brown University Cameca SX-100 electron microprobe. Operating conditions of

the instrument were 15 kV voltage, 10 nA current and a 5-micron-diameter, defocused beam. Counting times were 30 seconds for on peak and half that time for backgrounds for all elements except Na, which was counted for 20 seconds. The data were calculated using the PAP correction procedures (Pouchou and Pichoir, 1991). One-sigma standard deviations are <1% for major elements and 3–8% for minor elements. Standards used for the basaltic glass analysis included USGS AGV-2 andesite glass (Si); USGS BIR-1G Iceland basalt glass (Al, Ca); synthetic Fo97 forsterite, University of Rhode Island (Mg); Rockport, Massachusetts fayalite, NMNH 85,276 (Fe); Amelia albite, Purdue University (Na); rhodonite, AMNH 104738 (Mn); synthetic orthoclase OR-1, AMNH (K); synthetic rutile, Brown University, (Ti); Ni metal SPI 02751-AB44 Metal Standards Serial AF (Ni); magnesiochromite, synthetic (Cr), and berlinite, synthetic, AMNH G. Harlow (P). The electron microprobe is equipped with extra-large diffracting crystals (LTAP, LLIF, LPET) that generate about five times the count rate of standard-sized diffracting crystals. Extra-large crystals were used in the analysis of Mg, Mn, Fe, Ti, Na, Ni, Cr, and P. Standard-sized crystals were used for Si, Al, Ca, and K. Na and K were analyzed using a loss routine to account for any volatilization of the elements under the beam. USGS Columbia River basalt BCR-2G was used as reference standard.

3.4) Olivine trace element concentrations by laser ablation ICP-MS

Because the dimensions of the majority of our MI samples were smaller than an acceptable laser spot size (~50 μm), we only employed laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to measure minor and trace element concentrations of olivine host grains. Measurements were performed at Brown University using a Photon-Machines Analyte G2 Laser in conjunction with a Thermo X-series-2 quadrupole ICP-MS. Samples were ablated by a 193-nm excimer (ArF) laser with a fluence

of 3.75 J/cm² and a 10 Hz repeat rate at 50% energy. Ablation duration lasted 30 seconds, which was preceded by 30 seconds of background. In order to maximize signal, a laser spot size of 110 µm was used, unless the polished surface of an olivine grain could not accommodate this size, in which case a spot size of 110-85 µm was used. All data was calibrated against glass standards from the USGS (BIR-1G, BCR-2G, BHVO-2G) and the Max Planck Institute (KL2-G, ML3B-G, StHs6/80-G, GOR132-G, T1-G, ATHO-G; (Jochum et al., 2006). We used ²⁵Mg as an internal standard. Calibration curves were linear for all reported elements to R²>0.99, except for Zn and Ga (R²>0.98). Treated as an unknown, replicate analyses (n=12) of standard glass 519-4-1 (Fine and Stolper, 1986) yielded <15% RSD (2 sigma) for all reported elements, and the average concentrations of these replicate analyses were <10% different from preferred values.

3.5) Correction of La, Ce and Gd concentrations

A subset of glass trace element compositions from Loncopué and Diamante exhibited anomalously high concentrations for La, Ce, and Gd that were deemed to be an artefact of analytical conditions, given that these apparent enrichments did not relate to other geochemical variables in any clear manner. Corrections were made to these values according to their expected placement on a primitive mantle (PM)-normalized REE diagram. Gd concentration was calculated as the geometric average of the PM-normalized (McDonough and Sun, 1995) concentrations of Sm and Dy (i.e., $Gd = 0.544 \text{ ppm} * (Sm_{PM} * Dy_{PM})^{1/2}$). Corrected Ce concentrations were calculated using the geometric slope formed by the PM-normalized concentrations of Pr and Nd (i.e., $Ce = 0.1.675 \text{ ppm} * (Pr_{PM}^2 / Nd_{PM})$). Lastly, corrected La concentrations were calculated using the slope formed by the PM-normalized concentrations of Ce and Pr (i.e., $La = 0.648 \text{ ppm} * (Ce_{PM}^2 / Pr_{PM})$). Compositions affected by these corrections are indicated in Table 3.

3.6) Correction for post-entrapment crystallization

When considering MI compositions, a correction must be made to account for any additional post-entrapment crystallization (PEC) of olivine. The MI composition as analyzed represents the composition of the melt inclusion in equilibrium with the portion of the olivine crystal adjacent to the inclusion rather than with the olivine composition that originally trapped the melt (e.g., Danyushevsky et al., 2002). Because FeO^{T} concentrations of MIs were similar to those of embayments and the whole-rock, the Fe-loss that would reflect diffusive exchange between MIs and their host olivine during cooling (Danyushevsky et al., 2000) is not expected to have had a significant effect of MI compositions in these samples. To correct the melt inclusion composition to what was in equilibrium with the host olivine, we use the average compositions of each olivine host crystal (Table 2) to perform a calculation that adds the composition of the host olivine crystal back to the melt composition in 0.1% increments until the melt composition is in equilibrium with this host olivine composition. We define this equilibrium with a constant $K_{\text{D}}^{\text{ol-liq}}(\text{Fe}^{2+}/\text{Mg}) = 0.3$ (Putirka, 2008). We use the oxidation state determined for the melts in each of the three samples in order to constrain the proportions of ferric versus ferrous Fe in the MIs. Based on oxidation state constraints from olivine-melt V partitioning (see section 4.5), we determine that the AM glasses have $\text{Fe}^{3+}/\Sigma\text{Fe}=0.20$, Diamante glasses have $\text{Fe}^{3+}/\Sigma\text{Fe}=0.32$, and the Loncopué glasses have $\text{Fe}^{3+}/\Sigma\text{Fe}=0.24$.

MI compositions were corrected for up to 28% olivine addition, but on average, 12% olivine addition was required for Diamante MIs, 4%, for Loncopué MIs, and 4% for AM MIs (Table 3). Some melt inclusions required little olivine addition or minor olivine subtraction, which reflect melt compositions that were already close to equilibrium with their olivine host crystals. Corrected volatile and trace element concentrations were

calculated by multiplying the measured concentrations by the dilution factor derived from the percentage of olivine added or subtracted for this correction (i.e., % dilution = 100- % olivine added or subtracted).

3.7) Correction for vapor bubble formation

Vapor bubbles are enriched in volatile elements that exsolve from the melt phase and can sequester 40-90% of the CO₂ contents of the melt inclusion (Moore et al., 2015; Wallace et al., 2015). Therefore, the measured volatile contents of a bubble-bearing melt inclusion can substantially underrepresent the CO₂ and H₂O concentrations of the melt. The corrected H₂O and CO₂ concentrations of a bubble-bearing melt inclusion were constrained using 1) the inclusion and bubble dimensions and the crystal dimensions (if crystals are present), 2) the measured H₂O and CO₂ concentrations of the melt inclusion, 3) the calculated pressure of vapor saturation, 4) the molar proportions of H₂O and CO₂ modeled to occur in the vapor bubble at these P-T conditions, 5) the calculated density of glass for each MI composition, and 6) a representative value of the glass transition temperature. Using the equation of state for an ideal gas ($PV=nRT$), these inputs constrain the amounts of H₂O and CO₂ contained in the vapor bubble. The H₂O and CO₂ contents of the bubble are lastly added to the measured H₂O and CO₂ concentrations to determine the concentrations of these volatile species in the melt inclusion prior to the formation of the vapor bubble.

The temperature used in the equation of state represents the glass transition temperature (T_g). T_g values were adopted from the experimental results of Giordano et al. (2005). $T_g = 505\text{ }^{\circ}\text{C}$ (778 K) determined for a basaltic melt with 1.64 wt.% H₂O was applied to Diamante and Loncopué MIs, and $T_g = 571\text{ }^{\circ}\text{C}$ (844 K) determined for a basaltic melt with 0.64 wt.% H₂O was applied to AM MIs. Vapor saturation pressures, as well as the

mole fractions of H₂O and CO₂ in the vapor, were then estimated for MIs by applying PEC-corrected SiO₂, H₂O, and CO₂ concentrations to the H₂O-CO₂ solubility model of Dixon et al. (1995). Glass density values for each MI, which were used to constrain the mass of the MI, were estimated based on the PEC-corrected major element and H₂O concentrations of the MIs and the calculated pressure and temperature of the trapped inclusion prior to bubble formation. Values for dV/dT, dV/dP, and molar volumes of major element oxides and H₂O were taken from Lange and Carmichael (1987), Lange (1997), and Ochs and Lange (1999).

4.) Results

4.1) Olivine host phenocryst compositions

We compare the range in olivine host crystal compositions represented by their forsterite content ($Fo = Mg/(Mg+Fe)$ in mole %) to the Mg# values of corresponding melt inclusions in Figure 3. The compositions displayed in Figure 3 and reported in Table 2 represent the olivine compositions for each grain that were averaged from at least 2 microprobe analyses. Diamante olivines (n=24) have the highest and most variable observed Fo contents (82.89-87.66), Loncopué (n=25) olivines have intermediate and the least variable values (80.11-82.64), and Auca Mahuida olivines (n=29) have the lowest Fo contents (78.91-81.84). While analyzed Mg# values for AM and Loncopué embayments resemble values for AM and Loncopué MIs, Diamante embayments (average $Mg\# = 0.47 \pm 0.14$ 2 σ), have lower Mg# values than Diamante MIs (average $Mg\# = 0.56 \pm 0.07$ 2 σ).

Ni concentrations are the lowest in Loncopué olivines (55-1120 ppm), while AM (1100-1965 ppm) and Diamante olivines (1022-2263 ppm) have similar Ni contents (Figure 4). Within individual grains, Diamante olivines on average yield larger compositional variations in Fo content (an average intragranular range of ~1.8) and Ni

concentration (average 720 ppm) than the olivine populations from the Loncopué (average intragranular Fo content range of 1.2 and Ni concentration range of 580 ppm) and AM samples (average Fo content range of 0.9 and Ni concentration range of 493 ppm). The inter- and intragranular variability in Fo content and Ni concentration displayed by Diamante olivines may reflect a broader range of differentiation preserved in Diamante sample than what was preserved by the olivine populations from the Loncopué or AM samples.

4.2) Major elements

Analyzed and PEC-corrected major element concentrations in the MIs and embayments are reported in Table 3 and Figures 5 and 6. As displayed in Figure 5, Diamante MIs have basanitic alkali and silica contents, while Loncopué and AM MIs are basaltic and trachybasaltic. Brandt et al. (2017) also identified basanitic olivine-hosted melt inclusions from the Diamante area of Payenia, although these had similar silica content ($\text{SiO}_2=45\text{-}48$ wt.%) at higher alkali content than other Payenia MIs. The olivine phenocrysts that host these MIs also have similarly high Fo-contents ($\text{Fo}_{85}\text{-}\text{Fo}_{88}$). The mostly alkaline composition of MIs from all three samples differs from the predominantly subalkaline composition of MIs from SVZ lavas (see references in the caption of Figure 5). AM whole-rock and embayment major element concentration ranges overlap with ranges of MI compositions, although AM embayments have higher FeO^T at similar MgO concentrations than AM MIs. Loncopué embayments have lower MgO and Al_2O_3 and higher SiO_2 , TiO_2 , and FeO^T concentrations than Loncopué MIs (Figure 6). Diamante embayments have lower MgO concentrations than Diamante MIs or whole-rock samples, as well as higher lower CaO and Al_2O_3 and higher SiO_2 , TiO_2 , FeO^T , Na_2O , K_2O and P_2O_5 than Diamante MIs. Liquid lines of descent (LLDs) were calculated for each locality using

the MELTS algorithm for comparison with the analyzed glass and whole-rock data (Ghiorso and Sack, 1995; see caption of Fig. 6 for modeling details). The calculated LLDs follow the trends in AM glass and whole-rock compositions, as well as Diamante whole-rock compositions, whereas the variability of the Diamante glass and the Loncopué whole-rock and glass major element concentrations do not track neatly along the LLD calculated for Loncopué, indicating that some other mechanism is needed to account for this variability.

4.3) *Trace elements*

Melt inclusion and embayment trace element compositions are presented in Figure 7 and Table 3. PM-normalized (McDonough and Sun, 1995) trace element patterns (Figure 7) show that Diamante samples have the most enriched trace element concentrations, especially Rb, Ba, Th, and U. Diamante and Loncopué compositions have an arc signature demonstrated by their positive anomalies for Pb and Sr, and negative anomalies for Nb and Ti, while AM compositions resemble those of intraplate basalts in their lack of a positive Pb anomaly and negative Nb and Ti anomalies.

Although glasses from Loncopué and Diamante both have arc signature, Loncopué glasses differ from Diamante and Auca Mahuida glasses in their more variable trace element patterns. Loncopué glasses have a greater range than Diamante glasses for Pb/Ce (2-18 for Loncopué versus 3-6 for Diamante). Loncopué glasses also on average have lower and less variable Ba/Nb values than Diamante glasses (49 ± 15 2σ) versus Ba/Nb = 70 ± 29 for Diamante.

Comparing La/Nb and Ba/Nb values (Figure 8a) shows that the narrow range of La/Nb and the relatively elevated Ba/Nb values of Diamante glasses resembles those of Chile trench sediments (Jacques et al., 2013; Lucassen et al., 2010), whereas Loncopué

glass compositions have similar La/Nb values at slightly lower Ba/Nb values. The negative correlation of Th/La and Sm/La among these glasses (Figure 8b) resembles the linear mantle-sediment mixing arrays formed by arc lava compositions (Plank, 2005), such that Diamante glass compositions most closely resemble Chile trench sediment compositions with high Th/La and low Sm/La. Loncopué glasses have a weaker sediment signature. AM glass compositions reflect a mantle source with little direct contribution from recycled sediments (i.e., low Th/La), similar to MORBs.

Although both Loncopué Sr enrichments lack a clear systematic relation to the LREE variations described above, two different Sr anomalies can be seen among both Loncopué MI and embayment trace element patterns. Compositions of Loncopué MIs and embayments can be divided into two groups: a high-Sr/Nd group ($\text{Sr/Nd} > 43$) and low-Sr/Nd group ($\text{Sr/Nd} < 30$). These two groups exhibit distinct major element characteristics: the high-Sr/Nd group glasses are higher in Al_2O_3 and CaO and lower in SiO_2 , TiO_2 , FeO^T , MgO, K_2O , and P_2O_5 than the low-Sr/Nd group. Moreover, PM-normalized trace element patterns reveal that high-Sr/Nd Loncopué glasses have lower concentrations of incompatible trace elements. A similar dichotomy between large and small positive Sr anomalies exists for Diamante embayments, whereas all Diamante MIs all exhibit large Sr anomalies. However, high-Sr and low-Sr Diamante embayments do not have differences in their major element concentrations that can be identified with the available data.

4.4) Volatiles

PEC-corrected volatile concentrations show that Diamante and Loncopué MIs have a similar range in H_2O concentrations (0.67-3.54 wt.% for Diamante, 0.42-3.87 wt.% for Loncopué), while AM MIs are restricted to lower H_2O concentrations (0.06-0.72 wt.%). PEC-corrected CO_2 concentrations for Diamante (37-2545 ppm) and Auca Mahuida MIs

(37-1913 ppm) range to significantly higher values than those for Loncopué MIs (5-637 ppm) (Figure 9a).

The results of the bubble correction are presented in Table 4 and Figure 9b. This correction increases CO₂ by a greater proportion than H₂O, which is expected given that CO₂ exsolves into vapor from the melt more readily than H₂O. Bubble-corrected CO₂ concentrations of melt inclusions are augmented by as much as an order of magnitude, whereas H₂O concentrations increase by as much as 21%, while most increase by <5%. Maximum bubble-corrected CO₂ concentrations are 26,993 ppm for Auca Mahuida, 25,796 ppm for Diamante, and 10,759 ppm for Loncopué. Given this significant modification to volatile contents, we acknowledge that many factors can affect the uncertainty of this correction, such as the measurement of the spatial dimensions of the inclusion, bubble, and crystal, the analytical uncertainty of the major and volatile element concentrations, and the uncertainty of calculating the pressure and temperature conditions assumed for this correction. We vary these parameters in order to estimate the maximum and minimum values for corrected H₂O and CO₂ concentrations, which yields a larger uncertainty for CO₂ concentrations than for H₂O concentrations. Details of our uncertainty estimations are presented in Table 4.

S, Cl and F concentrations are highest in Diamante MIs, intermediate in Loncopué MIs, and lowest in Auca Mahuida MIs (Figure 10)—a result that is consistent with trace element contents in demonstrating the relatively strong arc signature of Diamante MIs among the sample suite. These values in S, Cl, and F are also high relative to MIs from other arc settings, the highest of which come from the Central American Volcanic Arc and the Cascades (Ruscitto et al., 2010; Sadofsky et al., 2008). The S concentrations of these lavas are 367-6583 ppm in Diamante glasses, 123-4175 ppm for Loncopué, and 85-1462

ppm for Auca Mahuida. Cl concentrations are 1557-3091 ppm in Diamante glasses, 989-2284 ppm for Loncopué, and 50-263 for Auca Mahuida. F concentrations are 810-1303 ppm in Diamante glasses, 380-1174 ppm for Loncopué, and 109-477 ppm for Auca Mahuida. While Diamante and Loncopué MIs have F/Cl ratios that are similar to those of MIs from arc lavas ($F/Cl \sim 0.5$, Figure 11), AM MIs have significantly higher F/Cl ratios of ~ 2 , which represents the upper bounds for F/Cl values observed in arc lava MIs, of which lavas MIs from the Mexican-Central American Arc and the SVZ have similarly high F/Cl values (see references listed in caption of Figure 10). And although Cl and F concentrations span a similar range among MIs and embayment glasses from each sample, S concentrations are lower in matrix/embayment glasses than in MIs. Among each sample, S and CO_2 exhibit positive correlations, with the clearest trend shown by the AM MIs. In general, the MIs from the two samples with an arc signature, Diamante and Loncopué, are consistently more enriched in H_2O , S, Cl, and to a lesser extent F relative to AM MIs.

4.5) Oxidation state constraints using $D_V^{olivine/melt}$

Constraining the oxidation state experienced by the observed melt composition allows us to determine proportions of Fe^{3+} and Fe^{2+} , which we use to correct for the effects of pre- and post-entrapment crystallization. Additionally, knowledge of the oxidation state of MIs allows us to consider the redox-sensitive speciation of S, which affects S solubility (Jugo, 2009), and the conditions of mantle melting experienced during primary melt generation. In order to determine the oxygen fugacity of the observed melts, we use an oxybarometer parameterized from the partitioning of V between olivine and melt. V partitioning reflects changes in f_{O_2} because V^{2+} , V^{3+} , V^{4+} , and V^{5+} occur in magmas according to proportions determined by f_{O_2} . Likewise, V compatibility in olivine is greatest for V^{3+} and decreases for V at higher oxidation states, which occur at higher f_{O_2} . Thus,

$D_V^{\text{olivine/melt}}$ decreases with increasing f_{O_2} . We apply the expression of Canil (2002) to our PEC-corrected melt V concentrations and the olivine V concentrations measured by LA-ICP-MS to determine f_{O_2} in log units relative to the fayalite-magnetite-quartz (FMQ) buffer (Figure 12, Table 5). We then apply the expression of Kress and Carmichael (1991) in order to determine the $Fe^{3+}/\Sigma Fe$ ratios of the observed melts. Our results indicate that Diamante melts have the highest f_{O_2} values ($\Delta FMQ+1.2-2.4$), Loncopué melts have intermediate f_{O_2} values ($\Delta FMQ +1.0-1.4$), and AM melts have the lowest f_{O_2} values ($\Delta FMQ+0.12-0.76$). These results equate to $Fe^{3+}/\Sigma Fe > \sim 0.22$ for Diamante and Loncopué melts, and $Fe^{3+}/\Sigma Fe < \sim 0.22$ for AM melts. We note that the oxidized nature of Diamante and Loncopué melts overlaps with values for the most oxidized arc magmas ($Fe^{3+}/\Sigma Fe \sim 0.30$), (Brounce et al., 2014; Kelley and Cottrell, 2009), whereas the reduced nature of the AM melts more closely resembles values for MORBs and back arc basin basalts (Kelley and Cottrell, 2009). The f_{O_2} range of our three samples also overlaps with previous estimations for other Payenia MIs ($\Delta FMQ+0.6-2.8$, (Brandt et al., 2017), which were determined using the olivine-spinel oxybarometer of Ballhaus et al. (1990).

5.) Discussion

5.1) Pressure-temperature conditions of entrapment

In order to estimate the pressure of vapor saturation experienced by the observed MIs, multiple volatile solubility models are available for application to basaltic magmas (e.g. Dixon et al., 1995; Ghiorso and Gualda, 2015; Papale et al., 2006). While some of these models are calibrated for a wider range of magma compositions, we have applied the model of Dixon et al. (1995) to our suite of MI compositions, which is calibrated for tholeiitic basalts. Despite the alkaline nature of our MI compositions, we deem it an

appropriate model for placing general constraints on the saturation pressures experienced by the sample suite. To test the role of alkalinity, in our pressure estimates, we compared these results with those from the SolEx model, which is calibrated for melt alkali content. Differences between the results from the Dixon et al (1995) model and SolEx were less than 0.2 kbar and were also not systematically higher or lower with increasing alkalinity. Therefore, the Dixon et al. (1995) model yields sufficient results for the purposes of our interpretations. For PEC-corrected MI compositions, model calculations indicate that these samples experienced degassing from as deep as 4-5 kbar whereas Loncopué MIs would have degassed from depths <2 kbar.

Bubble-corrected CO₂ and H₂O concentrations, when applied to the vapor solubility model of Dixon et al. (1995), yield significantly higher estimations of vapor saturation pressure. Maximum saturation pressure estimates are ~9 kbar (~27 km depth) for Loncopué, 8 kbar (23 km depth) for Diamante, and 16 kbar (49 km depth) for AM. The depths these pressures represent are near or potentially below the Moho in this region, according to estimates from geophysical observations (Gilbert et al., 2006; Tassara and Echaurren, 2012; Wagner et al., 2005). If we apply the lower bounds of our uncertainty estimates for the vapor bubble correction of H₂O and CO₂ concentrations (Table 3), saturation pressure estimates are reduced to ~4 kbar for Loncopué and Diamante and ~8 kbar for AM.

A potential cause for the high estimations of CO₂ concentrations (and thus high saturation pressures) may be that many MIs do not bear post-entrapment shrinkage bubbles, but bubbles formed by pre-entrapment vapor exsolution processes. Although vapor bubbles with volumes >~5% of the MI volume have been suggested to represent pre-entrapment bubbles (Lowenstern, 2015), we observe no clear correlation between bubble-corrected

CO₂ concentrations and bubble volume. We require further investigation in order to verify the validity of this method of correcting H₂O and CO₂ concentrations to account for the presence of a shrinkage bubble. Because of the large uncertainties in the vapor bubble correction, we regard the PEC-corrected H₂O and CO₂ concentrations as conservative estimates.

The temperature sensitivity of olivine-liquid Fe-Mg exchange can be used to determine equilibrium temperatures experienced by MIs at entrapment. We apply olivine host major element concentrations and PEC-corrected MI major element and water concentrations to the geothermometer presented as equation 4 in Putirka et al. (2007), using the saturation pressures determined using the model from Dixon et al. (1995). Temperature estimates are 1086-1198°C for Loncopué MIs, 1116-1189°C for Diamante MIs, and 1133-1206°C for AM MIs. These crystallization temperatures overlap with the estimates of Søger et al. (2015) using the spinel-olivine thermometer of Wan et al. (2008) for tephras from the southern Payenia volcanic province (1155-1243°C).

5.2) Mantle source constraints from olivine compositions

Given that AM and Diamante olivines are enriched in Ni relative to Loncopué olivines, this relationship may reflect differences in mantle source lithology or differences in the thermal history of these melts. Previous studies of olivine phenocryst compositions have argued that olivine from intraplate basalts often has higher Ni and Fe/Mn than those predicted for olivine crystallized from melts sourced from normal peridotite (Herzberg, 2010; Sobolev et al., 2005). Peridotite mineral assemblages are dominated by olivine, in which Ni is more compatible and Mn is less compatible than in pyroxene (Beattie, 1993), leading to the inference that high-Ni and Fe/Mn olivine reflects the melting of a pyroxenite source lithology rather than an olivine-bearing peridotite.

Alternatively, additional studies have demonstrated that other factors can control Ni and Mn variations in olivine. Experimental evidence has shown that Ni contents of olivine crystallized from a primitive melt are sensitive to conditions separate from the Ni content of the mantle source. Wang and Gaetani (2008) report that an olivine-saturated, SiO₂-rich partial melt of eclogite melt mixed with a primitive Hawaiian tholeiite will crystallize Ni-rich olivine due to an increase in $D_{\text{Ni}}^{\text{oli/melt}}$ with melt polymerization, despite the moderate Ni content of this melt mixture. Other experiments have shown that for a constant composition with moderate Ni content, $D_{\text{Ni}}^{\text{oli/melt}}$ increases significantly with decreasing temperature, such that Ni-rich olivine crystallizes at low temperatures from a primitive melt generated from a high-temperature peridotitic source (Matzen et al., 2013).

Previously, Søgner et al. (2015) cited the enrichment of Ni and depletion of Mn in olivine phenocrysts in Payenia basalts as evidence for melt petrogenesis from a peridotite-pyroxenite mixture of sub-Payenia asthenosphere. However, more recent work has shown that the geochemical and isotopic character (e.g., negative Δ_{EHf} and low $\delta^{18}\text{O}_{\text{Olivine}}$) of Payenia basalts reflects the melting of metasomatized SCLM (Søgner et al., 2018, Chilson-Parks, in prep). Thus, the Ni enrichment of AM and Diamante olivines may reflect 1) the melting of high-Ni, pyroxenitic veins in the SCLM and/or 2) high-temperature partial melting during lithospheric heating and interaction with asthenospheric melts, which would be followed by the low-temperature crystallization of these olivine phenocrysts.

On the other hand, Loncopué olivines, with Ni contents almost exclusively in the range of compositions expected from peridotite melting, were probably not significantly affected by a pyroxenitic source and/or these thermal variations.

5.3) Effects of secondary processes on melt inclusion volatile contents

5.3.1) H₂O and CO₂ behavior

Multiple secondary processes that affect melt inclusion compositions must be assessed before using MI volatile contents to constrain the volatile budget of their mantle source. Two such processes, post-entrapment crystallization and vapor bubble formation, were considered in previous sections. Although estimates of entrapment pressures indicate that some MIs from all three samples were entrapped in mid-to-lower crustal conditions, each sample exhibits significant variability in H₂O and CO₂ contents (Figure 9). Because CO₂ exsolution is highly sensitive to pressure conditions, magmatic degassing will deplete the melt in CO₂, and to a lesser degree H₂O, as MIs are entrapped at decreasing pressures during melt ascent. Most of the AM MIs conform to its expected degassing trajectory, for which CO₂ would be depleted nearly completely before H₂O begins to decrease significantly.

In contrast, Diamante and Loncopué MIs have a larger range of H₂O concentrations. A possible explanation behind this dispersion of H₂O concentrations involves the diffusion of H⁺ from the melt inclusion (Bucholz et al., 2013; Chen et al., 2011; Gaetani et al., 2012; Hauri, 2002; Lloyd et al., 2013; Massare et al., 2002; Portnyagin et al., 2008). To test whether the concentration of H₂O is controlled by H⁺ diffusion rather than mixing between magmas with variable slab-derived inputs, we considered the relationship between variations in PEC-corrected H₂O content of Diamante MIs and trace element concentration ratios indicative of arc signature. Arc signature-indicative trace element ratios do not systematically vary with H₂O among these compositions and have values of Pb/Ce > 0.15 and Ba/Nb > 50 (except for one Diamante MI, which has Ba/Nb = 32 and H₂O = 2.95 wt.%). Loncopué MI compositions also lack clear trends between arc signature and H₂O concentrations. Thus, the consistently low CO₂ concentrations of Loncopué MIs (all but two MIs have CO₂ < 500 ppm) may reflect some combination of the

degassing of relatively low- CO_2 melt and H^+ diffusion. Overall, the consistency of the arc signature-related trace element ratios of Diamante and Loncopué MIs indicates that magma mixing among melts with variable slab-derived inputs is an unlikely cause of their range in H_2O concentrations.

If diffusion did decrease the H_2O concentration of these MIs, the loss of H^+ could have occurred over short timescales (day-hours). This may have occurred if the host olivine crystal was surrounded by an H_2O -poor matrix melt, which would have imposed a large compositional gradient and a high diffusion rate (Portnyagin et al., 2008). Most Diamante and Loncopué embayments have $\text{H}_2\text{O} < 0.5$ wt.%. This MI-embayment H_2O difference is comparable to the MI-matrix H_2O gradient in the experiments of Portnyagin et al. (2008), which demonstrate that MIs can undergo changes of ~ 2.5 wt.% H_2O over 2 days at 2 kbar and 1140°C , conditions similar to those determined as the entrapment conditions of the embayments (see section 5.1). Pre-entrapment mixing of variably degassed melts may have also caused the dispersion of H_2O concentrations at elevated CO_2 .

Two observations would suggest that our observed MIs experienced rapid ascent. First, embayment Mg# values are not in equilibrium with adjacent olivine grains in all three samples, indicative of timescales that were short enough to prevent Fe-Mg exchange between olivine grains and their magma host. Second, although embayment CO_2 concentrations are lower than CO_2 concentrations of most MIs, some concentrations reach values as high as ~ 100 - 290 ppm in AM and Loncopué embayments. Using the saturation pressures predicted by the Dixon et al. (1995) model, magmas from Loncopué and AM ascended fast enough for the embayments to maintain the CO_2 solubility the melt experienced at depths of ~ 1 - 2 km. Previous work has used fine-scale H_2O concentration profiles in olivine-hosted melt embayments to constrain diffusion-based ascent rates

(Ferguson et al., 2016; Lloyd et al., 2014), an approach we can pursue in the future to quantify the ascent rates experienced by these samples, and to better understand whether these ascent rates represent reasonable timescales for H^+ diffusion.

5.3.2) *S behavior*

Degassing and the saturation of sulfides or sulfates are expected to control S systematics in olivine-hosted MIs. S concentrations for MIs from each of the three samples show increases in S with CO_2 concentration (Figure 10), indicating that the degassing also caused depletions in S. For Diamante and Loncopué MIs, S does not vary systematically with H_2O (Figure 10), although a positive correlation exists for AM MIs. For AM MIs with $CO_2 < 500$ ppm (which equate to saturation pressures $< \sim 1$ kbar), S concentrations decrease more dramatically with decreasing CO_2 , which may reflect the more efficient partitioning of S into vapor at the low pressures experienced by low- CO_2 MIs.

In addition to degassing, oxidation state is another significant control on S solubility (Jugo et al., 2005a, b). Diamante MIs have S concentrations as high as the highest S concentrations observed in MIs from arc lavas from the Aleutians (Figure 10), which reflects the high f_{O_2} in arc magmas and the Diamante and Loncopué MIs. Experimental evidence shows that in basaltic melts, S is more soluble as a sulfate than as a sulfide, and that sulfate is stable at $\Delta FMQ > \sim +1.8$ (Jugo et al., 2005b), which is generally the case for the observed compositions based on our f_{O_2} constraints (Table 6).

To estimate the expected sulfur content at the sulfide saturation (SCSS) of the samples, we used the sulfide saturation model of Fortin et al. (2015), which considers the major element and H_2O content of the melt, as well as the pressure (determined at CO_2 - H_2O vapor saturation as mentioned above), and the temperature (determined using olivine-melt equilibrium as mentioned above) of the MIs. Calculated values for SCSS are

compared to measured S contents in Figure 13a. We see that SCSS ranges from ~1000 – 2000 ppm for our samples, and that most MIs from Diamante and Loncopué are sulfide supersaturated (i.e., $SCSS < \text{measured S}$), whereas AM MIs are sulfide undersaturated (i.e., $SCSS > \text{measured S}$) or at sulfide saturation. The undersaturated character of the AM MIs resembles SCSS trends in MORB glasses (Shimizu et al., 2016), which are also relatively reduced. SCSS estimates (also calculated using the model of Fortin et al. (2015)) for MIs sampled nearby in Payenia also yield much lower SCSS values (also ~1000-2000 ppm) compared to most of their measured S concentrations (Brandt et al., 2017). Although this model predicts the presence of sulfides in the Diamante and Loncopué samples, we currently lack detailed petrographic observations of sulfides in these samples.

The Fortin et al. (2015) model likely overestimates SCSS in our samples due to its assumption that the sulfide in equilibrium with silicate melt is pure FeS. Cu and Ni can reach concentrations of ~5-16 wt.% in MORB glass-hosted sulfides (Patten et al., 2013). The presence of significant Ni and Cu in the sulfide melt lowers the activity of FeS and stabilizes sulfide melt at lower SCSS compared to sulfides of pure FeS (e.g., (Smythe et al., 2017)). The SCSS model of Smythe et al. (2017) does consider Ni and Cu contents in its determination of SCSS; however, we presently do not have measurements of Ni or Cu for our samples or any compositional information regarding sulfides present in our samples. Nonetheless, the constraints on SCSS determined using the Fortin et al. (2015) model provide a conservative estimate of the number of our reported glass compositions that are saturated in sulfides. The positive correlation between $Fe^{3+}/\Sigma Fe$ and maximum S concentrations observed from each locality, a feature shared with other Payenia MIs (Brandt et al., 2017), indicates that f_{O_2} controls the sulfur contents of our samples (Figure 13b).

5.3.3) *F and Cl behavior*

F and Cl concentrations of MIs and embayments are expected to be less sensitive to degassing than H₂O, CO₂, or S concentrations. Previous studies have shown that for MIs with H₂O <~4 wt.%, Cl is not expected to undergo significant degassing (Webster et al., 1999). Accordingly, F and Cl concentrations do not exhibit strong correlations with H₂O or CO₂, except for a slight decrease in Cl with decreasing H₂O in AM MIs. For the AM and Loncopué samples, embayment and MI F and Cl concentrations are similar; whereas Diamante embayments are enriched in F relative to Diamante MIs. Such relationships are not predicted to reflect degassing. Neither is the positive correlation between Cl concentrations and Ba/Nb values of Loncopué and Diamante glasses (Figure 14a). This relationship suggests that Cl contents in Diamante and Loncopué glasses are controlled by slab-derived Cl enrichment in their melt source. Similarly, most Diamante and Loncopué MIs form a positive correlation between S and Cl (Figure 14b), indicating that the enrichment of S in Diamante and Loncopué melts was also caused by slab-derived inputs. The comparison of S and Cl also highlights the effects of degassing on S concentrations of MIs. The ~1500 ppm variation of S in AM MIs at near-constant Cl suggests that S degassed from AM MIs. In contrast, the majority of MIs from Diamante and Loncopué form a clear positive correlation between Cl and S, and represent the upper bounds of S concentrations observed in MIs from Payenia and the SVZ volcanic front.

Given the minimally degassed nature of glass halogen contents, the high F/Cl ratios of AM glasses (Figure 11a) may reflect melt source heterogeneity. The distinct behavior of halogens in AM glasses is also demonstrated by the comparison between F/Cl and H₂O/K₂O (Figure 11b): AM MIs have low H₂O/K₂O for their high F/Cl values, as well as a negative correlation between these two ratios. A similar relationship exists between F/Cl

and H₂O/Ce values (Figure 11c) for which AM MIs have H₂O/Ce=17-227, Loncopué and Diamante MIs have H₂O/Ce=95-1329, and the typical MORB range is H₂O/Ce=140-400 (Shimizu et al., 2016). F/Cl values reported for other Payenia MIs cover a similar range as the F/Cl values reported in this work.

These variations in F/Cl may reveal important information about the melt source of the AM MIs. Because AM MIs have a narrow range of H₂O concentrations, variation in K₂O and Ce concentrations causes the variation of H₂O/K₂O—notable given the similar partitioning behavior of K, Ce, and H₂O during mantle melting (Hauri et al., 2006). Thus, K is enriched in AM MIs relative to H₂O with increasing F/Cl in AM MIs. Given that F is significantly more compatible in amphibole and phlogopite than Cl (Chevychelov et al., 2008; Van den Bleeken and Koga, 2015), the consumption of these mineral phases during melting would impart high F/Cl and K to a melt. This increase in K with F/Cl is not expected to arise from normal mantle melting, given that F and Cl are both incompatible in garnet, pyroxene, and olivine, and Cl is more incompatible in these minerals than F (Dalou et al., 2014). Olivine-hosted, high-K MIs from the Trans-Mexican Volcanic Belt (blue triangles in Figure 9) also exhibit similarly high F/Cl = ~2—a feature of these melts that was interpreted to represent the melting of a phlogopite-bearing mantle source (Vigouroux et al., 2008). These observations are consistent with the melting of metasomatized SCLM, which has been posited to play a role in the petrogenesis of Payenia basalts (Søager et al., 2018; Chilson-Parks et al. *in prep*). Hence, the variations in H₂O/K₂O and F/Cl displayed by AM MIs may reflect variable amounts of hydrous metasomatic phases being melted in the AM mantle source.

Additional volatile and trace element modeling is needed to test expected F/Cl variations during melting of metasomatized SCLM as other factors may control melt F/Cl

rations besides the presence of amphibole and/or phlogopite in the melt source. During flux melting in the mantle wedge, slab-derived fluids are expected to enrich the melt in Cl relative to F, because seawater has a ~20,000x enrichment in Cl relative to F (Straub and Layne, 2003). The low F/Cl ratios of arc MIs is an indicator of this slab-fluid derived signature, and experiments show that higher degrees of isobaric hydrous melting, even with amphibole in the source lithology, decreases F/Cl of the melt (Dalou et al., 2014). Diamante and Loncopué MIs, which have $F/Cl < 1$, resemble other arc MIs in exhibiting the halogen contents of a melt derived from a source fluxed or metasomatized by slab fluids. The extent to which AM MIs reflect melting of a source with hydrous phases rather than one with merely a weaker contribution of low-F/Cl slab fluids must be better resolved.

5.4) Processes and source components responsible for TSVZ back-arc mantle melting

High LILE/HFSE ratios, enrichments in H₂O, S, Cl and F, and high Fe^{3+}/Fe ratios clearly demonstrate that Diamante and Loncopué MIs have a strong arc signature. However, important compositional differences exist between these two MI suites. We consider these differences to assess how subduction-related processes imparted an arc signature to the Loncopué and Diamante melt sources.

One of the clearest distinctions between Diamante and Loncopué MIs is the basanitic composition of Diamante MIs versus the basaltic (both alkaline and subalkaline) composition of most Loncopué MIs (Figure 3). Basanitic Diamante MIs are >3 wt.% lower in silica than MIs from the SVZ volcanic front. The low-silica character of Diamante MIs is not an expected trait of continental arc basalts: globally, almost no primitive ($Mg\# > 50$) continental arc lavas have $SiO_2 < 45$ wt.%, while mafic arc magmas nonetheless have a similar H₂O content (~4 wt.%) to Diamante MIs (Kelemen et al., 2003; Plank et al., 2013).

If source composition is similar between Loncopué and Diamante, the chemical character of Diamante MIs may result from a lower degree of melting at greater depths relative to the Loncopué source. This possibility is consistent with the relatively high concentrations of highly incompatible trace element concentrations of Diamante MIs (Figure 7). A similar difference in trace element patterns was noted between back-arc SVZ basalts and volcanic front SVZ basalts as an indication that SVZ basalts represent lower degrees of mantle melting with increasing distance from the trench (Stern et al., 1990). Diamante MIs also have steeper REE patterns than Loncopué MIs, indicative of residual garnet in their mantle source, and thus lower-degree and/or deeper melting at depths of garnet stability.

These variations merit the consideration of the primary melt compositions of Diamante and Loncopué MIs. To estimate primary melt compositions (Table 3), we fractionation-corrected MI compositions back to equilibrium with mantle olivine (Fo_{90} , Stolper and Newman, 1994). As in the approach of the PEC correction, we added 0.1% increments of olivine to MI compositions until equilibrium with Fo_{90} is attained. The amount of dilution from this olivine addition was used to proportionally dilute trace and volatile element contents. Fo_{90} -correction required as much as 24% and as little as 5% olivine addition, and on average 19% was required. These amounts of olivine addition are similar to the results of Weller and Stern (2018) for primary melt compositions of olivine-hosted MIs from the SVZ volcanic front.

A useful indicator of variations in melting is the content of elements that behave incompatibly during partial melting but are generally unmodified by slab-derived inputs. HFSEs such as Ti, Zr, Hf, and Nb are not mobile in aqueous fluids at 4 GPa (Kessel et al., 2005). Instead, they are expected to remain in the residual rutile of a subducted, dehydrated

slab (Ryerson and Watson, 1987). Therefore, we presume that the HFSE budget of the mantle wedge is unmodified by slab-derived inputs, and that the TiO_2 content of melts generated from the mantle wedge are not directly sensitive to variable contribution from slab-derived inputs. These assumptions have been made in previous investigations of the primary melt compositions of olivine-hosted MIs from subduction zone settings (Kelley et al., 2006; Kelley et al., 2010). The decreasing $\text{TiO}_{2(\text{Fo90})}$ with increasing $\text{H}_2\text{O}_{(\text{Fo90})}$ of subduction-related MIs is consistent with H_2O content controlling the extent of melting in the mantle wedge. To test this relationship in the SVZ back-arc, Figure 15 compares Fo_{90} -corrected concentrations of HFSEs to H_2O . Since Nb is more incompatible than Zr, a higher-degree of melt would have higher Zr/Nb. Loncopué MIs exhibit higher Zr/Nb than Diamante MIs, both of which have higher Zr/Nb than AM MIs. This pattern is consistent with slab input controlling the degree of mantle melting and causing the Loncopué source to melt the most. However, a comparison between $\text{TiO}_{2(\text{Fo90})}$ and $\text{H}_2\text{O}_{(\text{Fo90})}$ concentrations does not display a clear negative correlation between Loncopué and Diamante MIs. Among Loncopué MIs, a weak negative correlation may be observed between $\text{H}_2\text{O}_{(\text{Fo90})}$ versus $\text{TiO}_{2(\text{Fo90})}$ and $\text{H}_2\text{O}_{(\text{Fo90})}$ versus Zr/Nb, $\text{TiO}_{2(\text{Fo90})}$. $\text{H}_2\text{O}_{(\text{Fo90})}$ values for Loncopué MIs are similar to values for SVZ volcanic front MIs?]. In contrast, Diamante and AM MIs exhibit no clear trends in these comparisons and have distinctly higher $\text{TiO}_{2(\text{Fo90})}$ values than Loncopué and SVZ volcanic front MIs, despite similar $\text{H}_2\text{O}_{(\text{Fo90})}$ in Diamante MIs. This lack of correlation may be influenced by diffusive loss of H^+ , but this process would not explain why Diamante MIs have such similar $\text{TiO}_{2(\text{Fo90})}$ concentrations to AM MIs. Thus, Loncopué MIs, with their low $\text{TiO}_{2(\text{Fo90})}$ concentrations and high Zr/Nb values, may represent higher-degree melts than Diamante and AM MIs. Nevertheless, the high

$\text{TiO}_{2(\text{Fo}90)}$ and $\text{H}_2\text{O}_{(\text{Fo}90)}$ concentrations of Diamante MIs cannot be explained as lower-degree melts of the same mantle source that generated the Loncopué MIs.

Furthermore, other compositional differences between Loncopué and Diamante MIs do not support the notion that Diamante and Loncopué MIs represent variable fluxing of a homogeneous mantle source. If this was the case, we would expect Loncopué MIs to represent a higher degree of melting and have a stronger arc signature. Instead, Diamante MIs exhibit higher Ba/Nb, Th/La, and $\text{Fe}^{3+}/\Sigma\text{Fe}$ than Loncopué glasses (Figures 8 and 12). These traits imply a stronger arc signature in the Diamante melt source. Similarly, the Loncopué and Diamante sample localities are situated at similar distances from the trench (408 km for Diamante versus 380 km for Loncopué), which implies that the scenario of slab input and degree of melting decreasing with increasing distance from the trench cannot explain their differences. In contrast, the AM sample, which exhibits an intraplate signature in its trace element and volatile contents, is considerably farther (540 km) from the trench.

These observations imply that the unique compositions of Diamante glasses require a more complex explanation than flux melting of the same mantle wedge composition that would generate the Loncopué MIs. Continental contamination is unlikely to have caused the arc signature of Diamante glasses given their low SiO_2 concentrations and the high (i.e., mantle-like) Fo contents of their olivine host phenocrysts (Figure 2). The comparison of Th/La and Sm/La ratios shows a strong affinity between Diamante MIs and Chile trench sediment compositions (Figure 8), which may imply a relatively sediment-rich slab input in the Diamante source. Alternatively, the sediments contributing to the Loncopué source may have lower Th/La than sediments in the Diamante source. Chile trench sediment samples were taken from similar latitudes (i.e., similar along-strike position in the arc) as the Loncopué and Diamante samples (Jacques et al., 2013; Lucassen et al., 2010; Plank,

2014), and exhibit no clear trends in chemical variation with along-trench position. Therefore, Diamante MIs may reflect a more sediment-rich slab input than Loncopué MIs, while any variation in subducted sediment compositions between the two sample locations is unlikely.

Even if sediments do contribute to the Diamante source, a sediment-rich slab input cannot explain other compositional characteristics. Diamante MIs exhibit a weak increase in Ba/Nb with decreasing $\text{SiO}_2(\text{F}_{0.90})$, a relationship not predicted by an increase in sediment-rich slab-inputs (Figure 16). Diamante MIs also have higher Ba/K₂O and Rb/K₂O ratios than Loncopué and AM MIs (Figure 16). Phlogopite and amphibole represent potential controls on the LILE budget of Diamante MIs given that phlogopite, and to a lesser extent amphibole, represent Ba- and Rb-rich phases. These characteristics are consistent with the possibility that Diamante MIs reflect the melting of metasomatized SCLM, a process that was previously argued for alkali basalts erupted in the Payenia volcanic province (Søager et al., 2018; Chilson-Parks et al., *in prep*). Basanites from continental settings have been shown to carry metasomatized SCLM xenoliths to the surface and have also been associated with the melting of metasomatized lithosphere (Frey and Green, 1974; Furman and Graham, 1999; Thompson et al., 2005). Melting experiments performed at 1.5 GPa demonstrate that nephelinitic to basanitic melts have also been shown to form from hornblendite and clinopyroxene hornblendite, which are lithologies representative of veined cumulates formed in the lithospheric mantle. Chilson-Parks et al. (*in prep*) used geochemical modeling results to demonstrate that the melts of SCLM cumulates contribute to Payenia magmatism. Chilson-Parks et al. (*in prep*) also demonstrate that SCLM cumulates can inherit a trace element arc signature from a mantle wedge-derived parent melt. In turn, melts of arc-type SCLM cumulates were shown to exhibit this arc signature

as well. Figure 16 compares the model results of Chilson-Parks et al. (*in prep*) to SVZ MI compositions. Using the composition of a hydrous cumulate crystallized from a melt with a strong arc signature, modeled melts at degrees at or above the point of biotite consumption have Ba/K₂O and Rb/K₂O ratios that match the highest values of Diamante MIs at similar silica contents. The modeled arc-type SCLM cumulate melts also reproduce the high Ba/Nb and H₂O_(F090) values of Diamante MIs, which indicates that Diamante MIs predominantly reflect the melting of metasomatized SCLM that inherited its arc signature from a metasomatic agent generated in the mantle wedge. This hypothesis is not mutually exclusive with the influence of a sediment-rich, high-Th/La slab input in the Diamante source. We note that Loncopué MIs also exhibit a negative correlation between Ba/Nb and SiO₂. This may indicate that arc-type cumulates also contribute melt to the Loncopué source, but in a smaller proportion than in the Diamante source.

Comparisons between these MI compositions and modeled SCLM cumulate-derived melts add support to hypothesis that two cumulate endmembers are present in the Payenia melt source, one with a strong arc signature and one that originates from upper mantle that lacks this arc signature. As mentioned in section 5.3, AM MI compositions may also represent the melting of veined cumulates in the SCLM, specifically cumulates that lack the arc signature present in the Diamante source. Both AM and Diamante olivine phenocrysts have Ni concentrations that are enriched relative to predicted for peridotite-derived magmas (Figure 3). As mentioned in section 5.2, this common feature may reflect melts from a pyroxenitic source component, or melts formed from the high-temperature melting of a peridotitic source and the subsequent low-temperature crystallization of the olivine phenocrysts in that melt. Either scenario could apply to the melting of metasomatized SCLM, given that the cumulates are likely to be clinopyroxene-rich and

cumulate-derived melts would form during lithospheric heating and interact with ascending asthenospheric melts.

Figure 16 also displays trends in melt compositions modeled for a melt from an EDMM-type cumulate composition. AM MIs display a weaker trend toward the lower Ba/Nb, Ba/K₂O, and Rb/K₂O values of the modeled EDMM-type cumulate melts, although AM MIs have lower H₂O_(F090) and SiO₂ concentrations than the modeled melts. The H₂O content of the modeled EDMM-type cumulate melt only decreases below 1 wt.% at degrees of melting > ~70%, which essentially suggests that this cumulate composition would need to be completely melted in order to reproduce the H₂O content of the AM MIs. Experimental melts from veined cumulate analogs (e.g., hornblendite, amphibole wehrlite, phlogopite peridotite) yield similarly high H₂O contents in melts of hydrous cumulates at high degrees of melting (Condamine and Médard, 2014; Médard et al., 2005; Pilet et al., 2008; Sorbadere et al., 2013). H₂O enrichment in these experimental melts is a consequence of the starting material, which is representative of metasomatized lithosphere, having H₂O contents that match or exceed the highest H₂O concentrations of AM MIs (e.g. clinopyroxene hornblendite has 0.76 wt.-% H₂O in the study of Pilet et al., 2008). The high H₂O contents of melts from metasomatic cumulates, regardless of whether they are derived from subduction related melts, indicates that this enrichment is a consequence of the hydrous mineral assemblages being melted in the SCLM as opposed to the water contents of their parental metasomatic agent. Asthenospheric melts that would metasomatize the SCLM can be rich in H₂O and CO₂ as long as they are low-degree partial melts of upper mantle with typical H₂O and CO₂ contents (Dasgupta et al., 2007). Therefore, the resemblance between Diamante MIs and the modeled arc-type cumulate melts suggests that the enrichment in H₂O in Diamante MIs may largely come from a hydrous SCLM

cumulate source. In contrast, the Loncopué MIs, which exhibit considerably less resemblance to cumulate-derived melt compositions, and Fo_{90} -corrected TiO_2 and H_2O contents, similar to SVZ volcanic front compositions, implies that the enrichment in volatiles in Loncopué MIs was inherited directly from the fluxed mantle wedge.

Differences between the H_2O content of AM MIs and modeled melts may be a consequence of AM melts reacting with surrounding peridotite during ascent through the SCLM, or of mixing with less volatile-rich asthenospheric melts. Either process would likely dilute the volatile contents of the melts, and the melting of orthopyroxene would also enrich melts in SiO_2 from nephelinites or basanites to alkali basalts (an increase in SiO_2 by ~4-5 wt.%), as is demonstrated by peridotite-hornblendite sandwich melting experiments (Pilet et al., 2008).

The high CO_2 contents of AM MIs, which may be on the order of multiple weight percent based on bubble correction estimates, may also play an important role in their petrogenesis. CO_2 content in the SCLM is not taken into account in the modeling of Chilson-Parks et al. (*in prep*), yet carbonated mantle xenoliths have been identified in the SVZ back-arc (Gorring and Kay, 2000; Laurora et al., 2001). Consideration of a CO_2 -saturated mantle source would have significant implications on the P-T conditions necessary for aggregating metasomatic cumulates in the SCLM. Within the pressure range of TSVZ SCLM (~1-2 GPa, based on xenolith thermobarometry results of Bertotto et al., 2013 and geophysical observations of Tassara and Echaurren, 2012), the solidus of carbonated peridotite is expected to plateau (Harry and Leeman, 1995). As a result, the crystallization of CO_2 -rich melts would occur within a narrow depth range in the lithosphere. Observations of seismic discontinuities at mid-lithospheric depths have been attributed to such a layer of hydrous phase-rich cumulates (Selway et al., 2015). If

metasomatic cumulates form this seismic discontinuity, it may have formed due to the SCLM geotherm intersecting with this carbonated peridotite solidus plateau over a limited depth range. Such a phenomenon would freeze SCLM metasomatism as a concentrated layer of hydrous phases that is identifiable in the seismic structure of the SCLM, as was postulated by Hopper and Fischer (2015). Consideration of the role of CO₂ in cumulate melting is necessary for refining our estimates of volatile contents in cumulate-derived melts and for clarifying whether melts of SCLM cumulates are likely to generate the enrichment in CO₂ exhibited by AM and Diamante MIs.

6.) Conclusions

These findings demonstrate that the well-documented chemical diversity of alkaline basalts in the SVZ back-arc is also reflected in the major, trace, and volatile element contents of olivine-hosted MIs and embayments. These variations in melt inclusion and olivine phenocryst compositions also indicate that the basaltic volcanism in the AM, Diamante, and Loncopué localities cannot be sourced from the same mantle source. Variations in trace element arc signature and primary H₂O and TiO₂ contents also demonstrate that degree of melting in the TSVZ back-arc mantle is not directly a function of amount of slab-derived input, given that Diamante MIs display a stronger arc signature and lower Zr/Nb values than Loncopué MIs. Instead, AM and Diamante MIs may both be in part derived from metasomatized SCLM. The origin of the SCLM source may differ between the AM and Diamante sources, such that metasomatic cumulates in the Diamante source would be more oxidized, inherit high Cl/F values from Cl-rich slab inputs, and have a stronger trace element arc signature pattern. Such variation between melts from these two regions signifies the presence of least two types of metasomatic cumulates in the TSVZ back-arc

SCLM, and that SCLM cumulates minimally influence the Loncopué mantle source, which yields primary melts that resemble SVZ volcanic front primary melts.

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FIGURE CAPTIONS

Figure 2-1. Transmitted light photomicrograph of an MI in olivine #35 of the Diamante sample, displaying a shrinkage bubble and crystal.

Figure 2-2. Primitive mantle- normalized trace element diagram of the whole-rock compositions of the MI-bearing tephra sample from Auca Mahuida and of the lava samples from Diamante and Loncopué that are proximal to the MI-bearing tephra sample in these localities. Normalizing values from McDonough and Sun (1995).

Figure 2-3. Forsterite (Fo) content in olivine host phenocrysts versus Mg# of MIs. Faded symbols have Mg# values uncorrected for post-entrapment crystallization (PEC) of olivine. Solid symbols have PEC-corrected Mg# values. Black solid line represents a constant $K_D^{ol-liq}(Fe^{2+}/Mg) = 0.3$, which was used for the PEC correction, while the dashed lines represent ± 0.03 . Stars represent Mg# values of the whole-rock compositions of the MI-bearing samples, with the expected Fo content of equilibrium olivine. Note that the majority of the uncorrected values have lower Mg# values than predicted by $K_D^{ol-liq}(Fe^{2+}/Mg)=0.3$, meaning that these compositions required olivine “addition” to correct for PEC.

Figure 2-4. Olivine Ni versus Fo contents. Fields for olivines from peridotite- and pyroxenite-derived magmas from Herzberg (2010), and for olivines from a peridotite-pyroxenite source from Gazel et al. (2012).

Figure 2-5. TAS diagram, displaying the rock classifications of Le Bas et al. (1986). Grey triangles represent MI compositions from the SVZ volcanic front (Bouvet de Maisonneuve et al., 2012; Pioli et al., 2015; Watt et al., 2013; Weller and Stern, 2018; Witter et al., 2004). Small black squares represent previously reported MI compositions from the Payenia volcanic province (Brandt et al., 2017; Søger et al., 2018).

Figure 2-6. Major element concentrations (in wt.%) of reported embayment and PEC-corrected MI compositions and whole-rock lavas from the same volcanic fields as the MI-bearing samples. Dashed lines represent modeled liquid lines of descent, of the highest-MgO lava compositions from each volcanic field (sample CL393 from Auca Mahuida, EPO-056 from Diamante, and 010910-149 from Loncopué). CL393 data from Søager et al. (2015). LLDs were calculated using MELTS, assuming isobaric fractional crystallization at 1 kbar, f_{O_2} =FMQ+1, and parental magma H₂O = 0.7 wt.% for Auca Mahuida, 3% for Diamante, and 4% for Loncopué.

Figure 2-7. Primitive mantle- normalized trace element and REE diagrams of whole-rock, embayment, and PEC-corrected MI compositions. Bold lines represent the whole-rock trace element patterns from Figure 2-2, dashed lines represent embayments, and thin lines represent MIs. Normalizing values from McDonough and Sun (1995).

Figure 2-8. A.) La/Nb versus Ba/Nb and B.) Sm/La versus Th/La. SVZ data from same sources listed in Figure 2-4. Chile trench sediment data from (Jacques et al., 2013; Lucassen et al., 2010). MORB glass data from PetDB.

Figure 2-9. H₂O versus CO₂ concentrations for A) embayments and PEC-corrected MI compositions, and B) MIs with bubbles, which were corrected for H₂O and CO₂ exsolution into a coexisting bubble. Isobars and isopleths calculated using VolatileCalc (Newman and Lowenstern, 2002).

Figure 2-10. S, Cl, and F concentrations versus PEC-corrected H₂O and CO₂ concentrations. MORB data source same as in Figure 2-8. Dark triangles represent SVZ volcanic front MIs (same sources as in Figure 2-2). Light grey triangles represent arc MIs from the Aleutians (Rasmussen et al., 2018; Zimmer et al., 2010), Cascades (Le Voyer et al., 2010; Ruscitto et al., 2010; Ruscitto et al., 2011; Walowski et al., 2016), Central America (Benjamin et al., 2007; Lloyd et al., 2013; Portnyagin et al., 2014; Roggensack, 2001; Roggensack et al., 1997; Sadofsky et al., 2008; Wade et al., 2006; Walker et al., 2003), Kamchatka (Gurenko et al., 2005; Portnyagin et al., 2007), and Mexico (Cervantes and Wallace, 2003; Johnson et al., 2008; Johnson et al., 2009; Roberge et al., 2009).

Figure 2-11. A) F versus Cl, B) F/Cl versus H₂O/K₂O and C) F/Cl versus H₂O/Ce. Sample symbols the same as in Figure 2-10.

Figure 2-12. Embayment and PEC-corrected MI V concentrations versus A) olivine host V concentrations and B) Fe³⁺/ΣFe. Lines of constant f_{O_2} (and $D_V^{oli/melt}$) were determined using the calibration from Canil (2002). Fe³⁺/ΣFe values were determined from f_{O_2} using the expression of Kress and Carmichael (1991).

Figure 2-13. Embayment and PEC-corrected MI S content versus A) sulfur content at sulfide saturation (SCSS) and B) Fe³⁺/ΣFe. SCSS determined using the model of Fortin et al. (2015).

Figure 2-14. Embayment and PEC-corrected MI Cl content versus A) Ba/Nb and B) S content. Literature data sources same as in Figure 2-10.

Figure 2-15. Relations for TSVZ back-arc MIs between Zr/Nb and Fo₉₀-corrected TiO₂ and H₂O concentrations, in weight percent. Sample symbols same as in Figure 2-10. Values for SVZ volcanic front lavas (grey triangles) from Watt et al. (2013) and Weller and Stern (2018).

Figure 2-16. Fo₉₀-corrected SiO₂ versus Rb/K₂O, Ba/K₂O, Ba/Nb, and Fo₉₀-corrected H₂O concentrations, in weight percent, for TSVZ back arc MIs, as compared to the modeled compositions of melts derived from metasomatic cumulates in the SCLM. Purple lines and symbols represent melts of a cumulate crystallized from melt of EDMM-type affinity, and black lines and symbols represent melts of a cumulate crystallized from a melt with arc signature. Additional modeling details can be found in Chilson-Parks et al. (*in prep*).

FIGURES

Figure 2-1.



Figure 2-2.

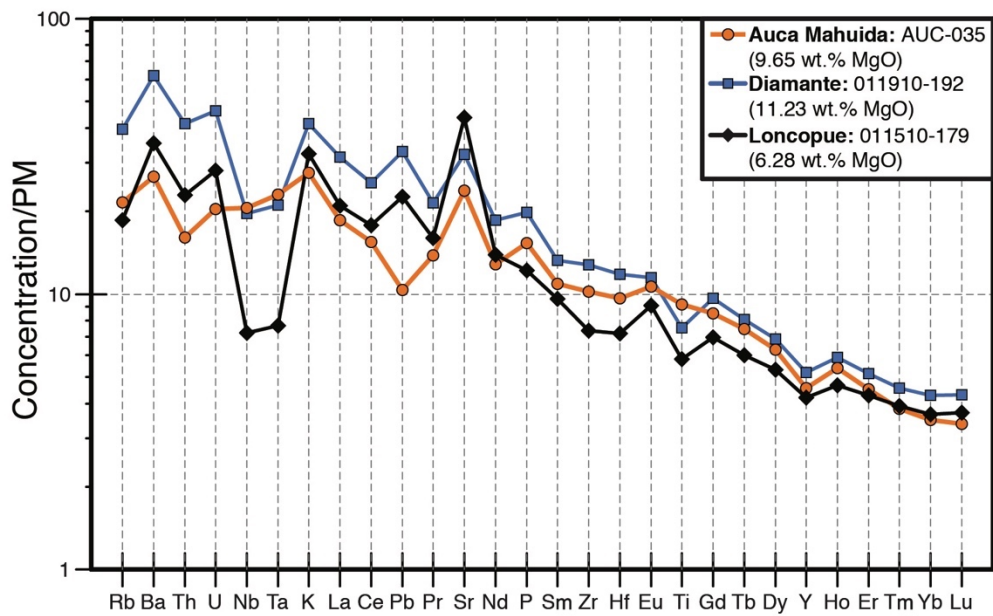


Figure 2-3.

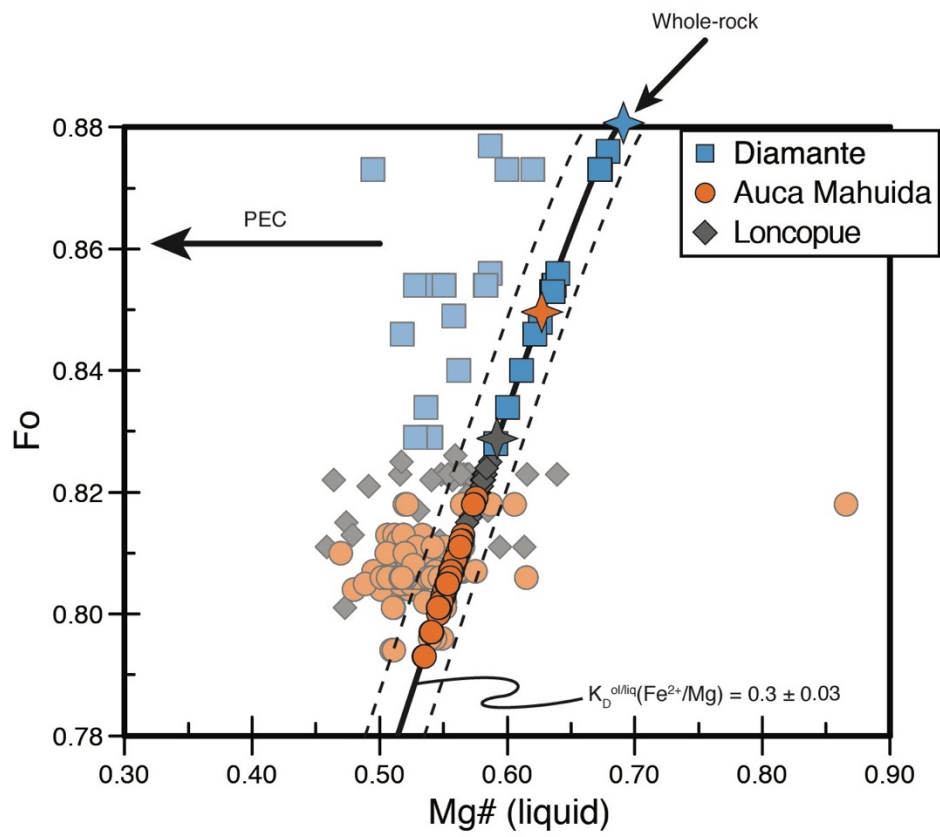


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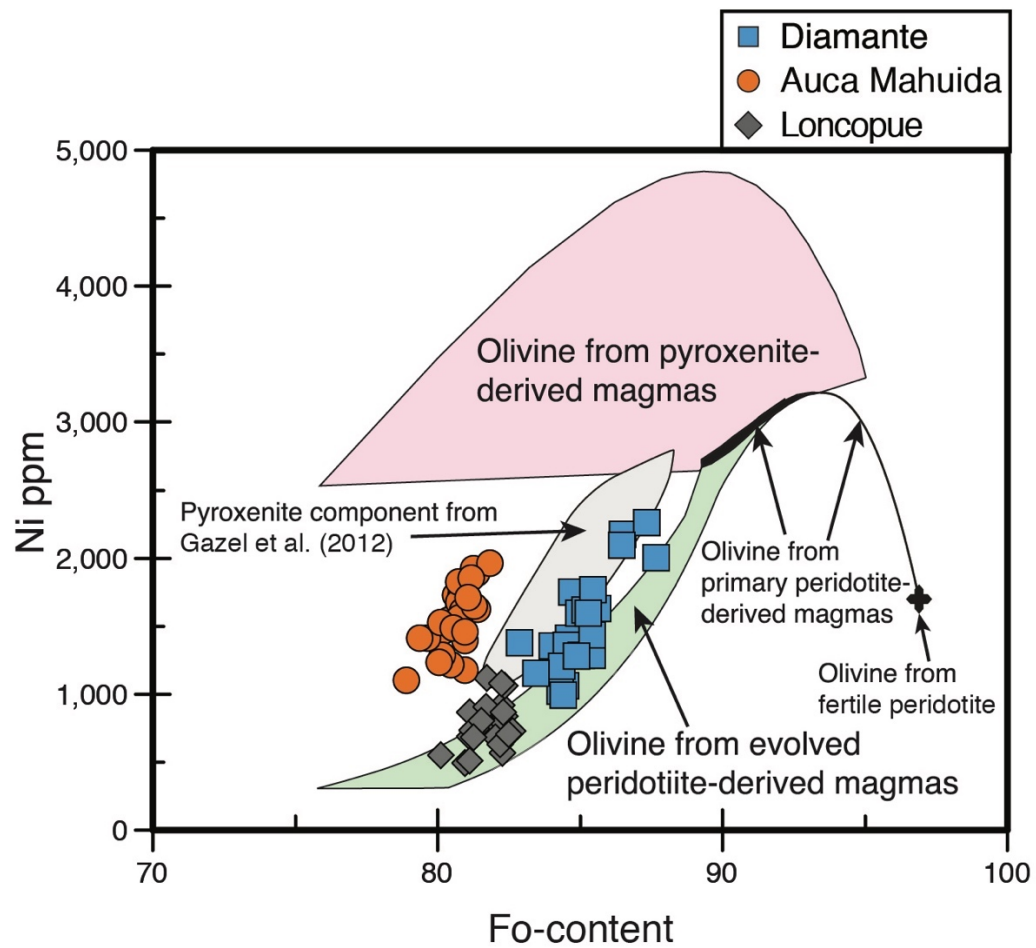


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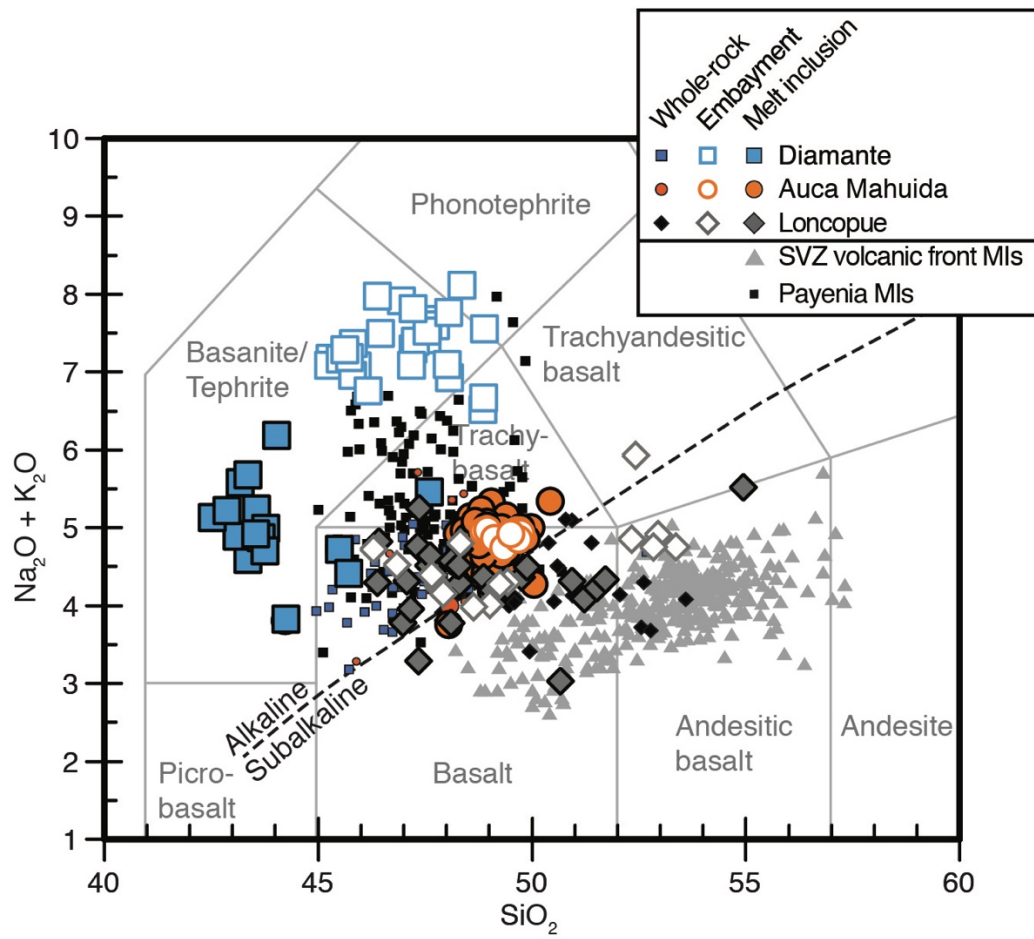


Figure 2-6.

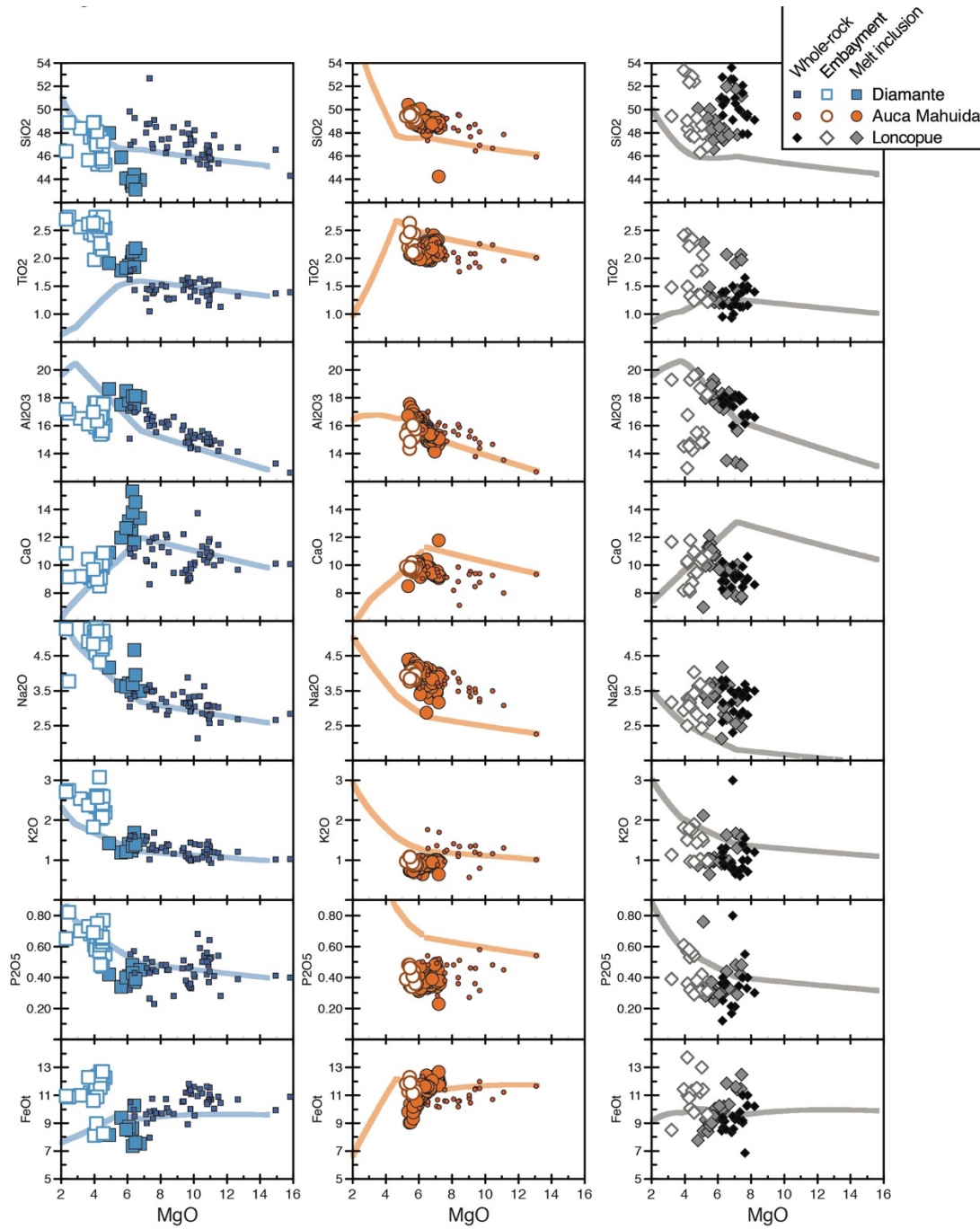


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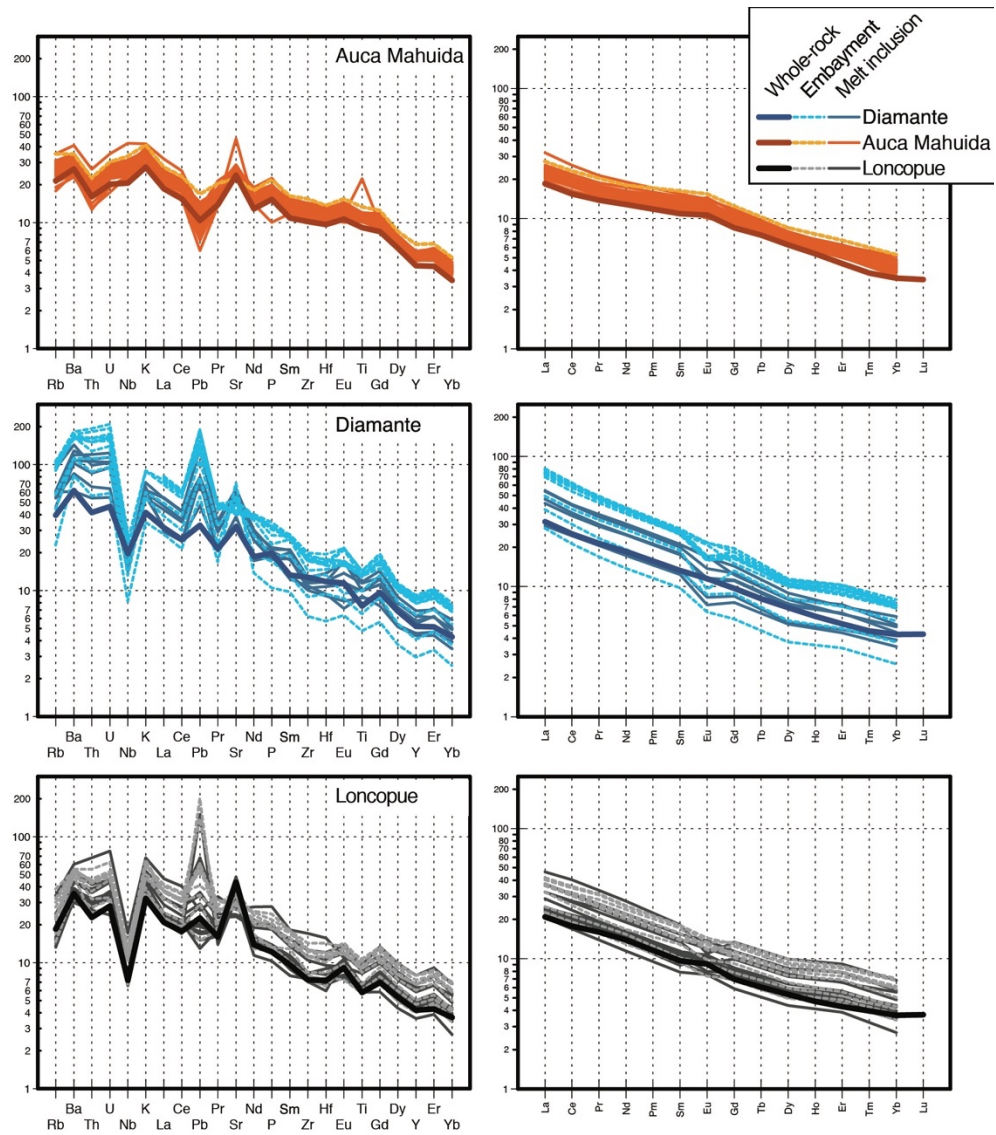


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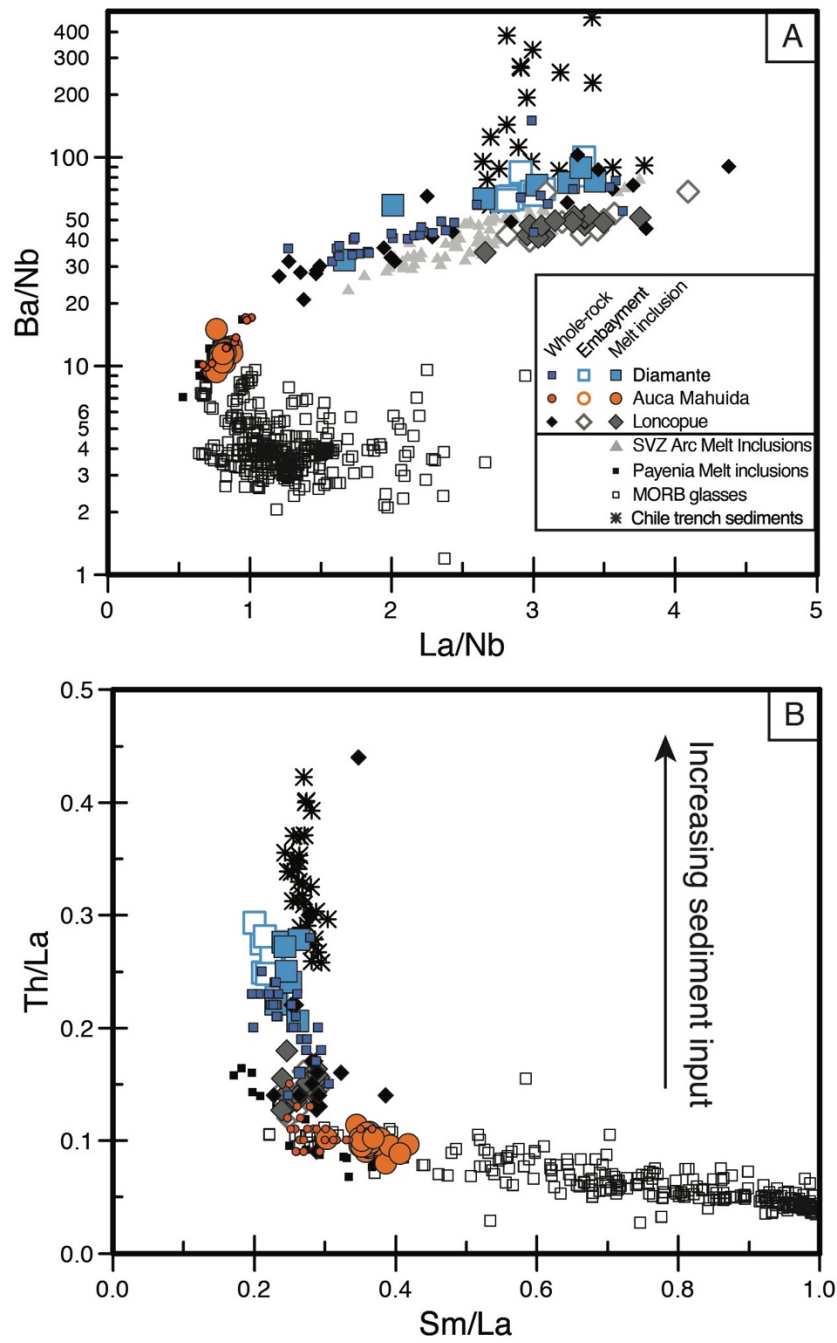


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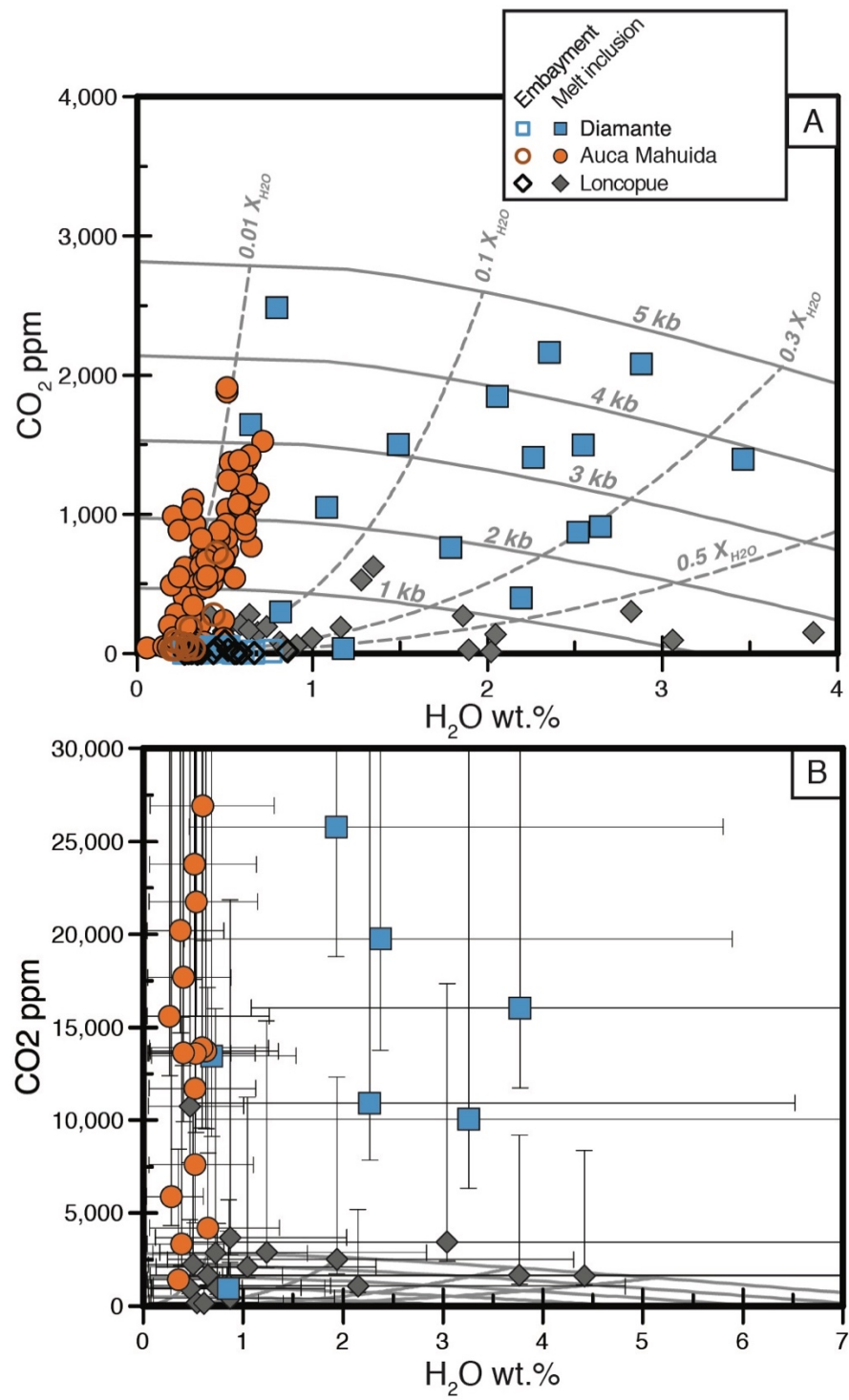


Figure 2-10.

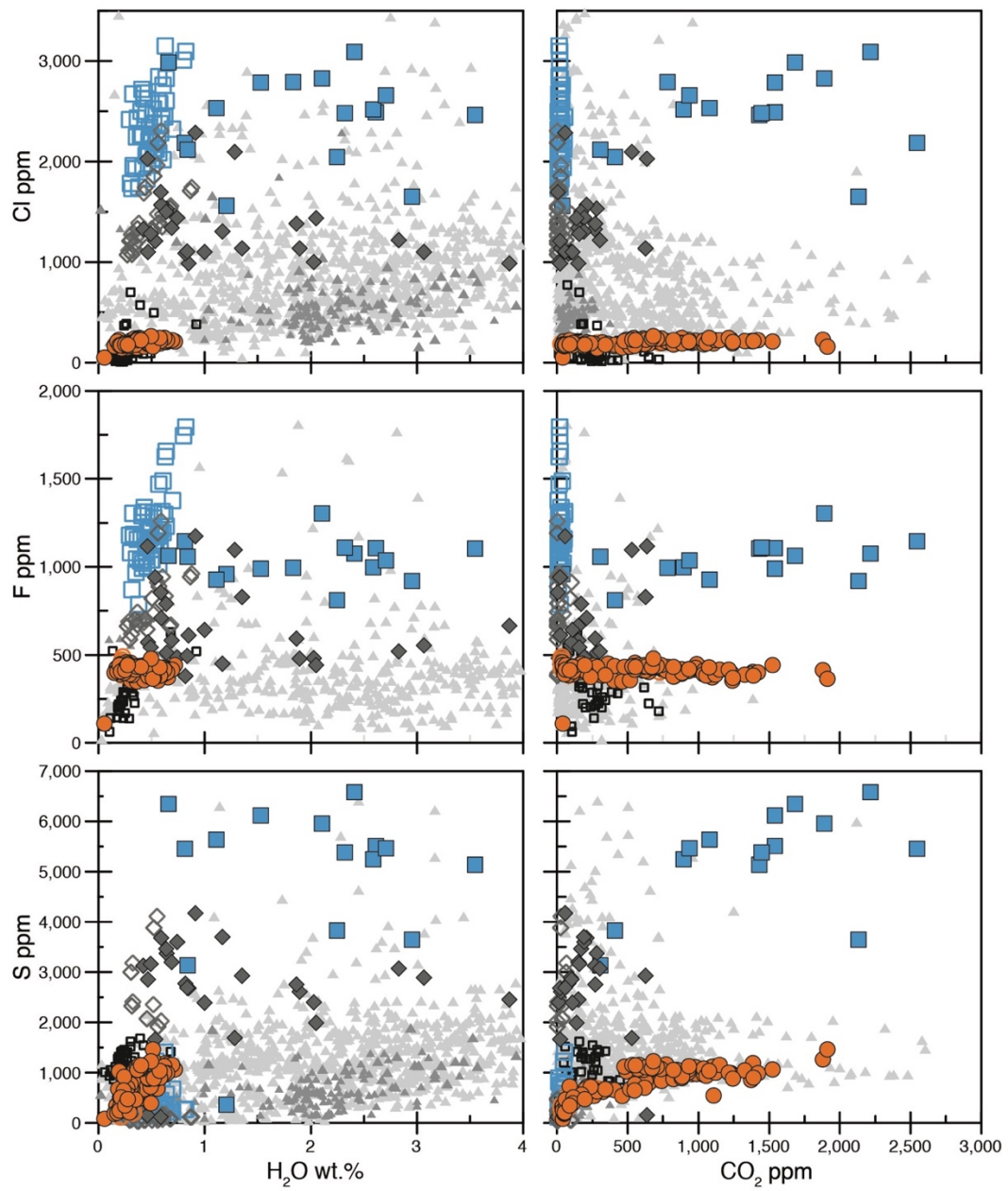


Figure 2-11.

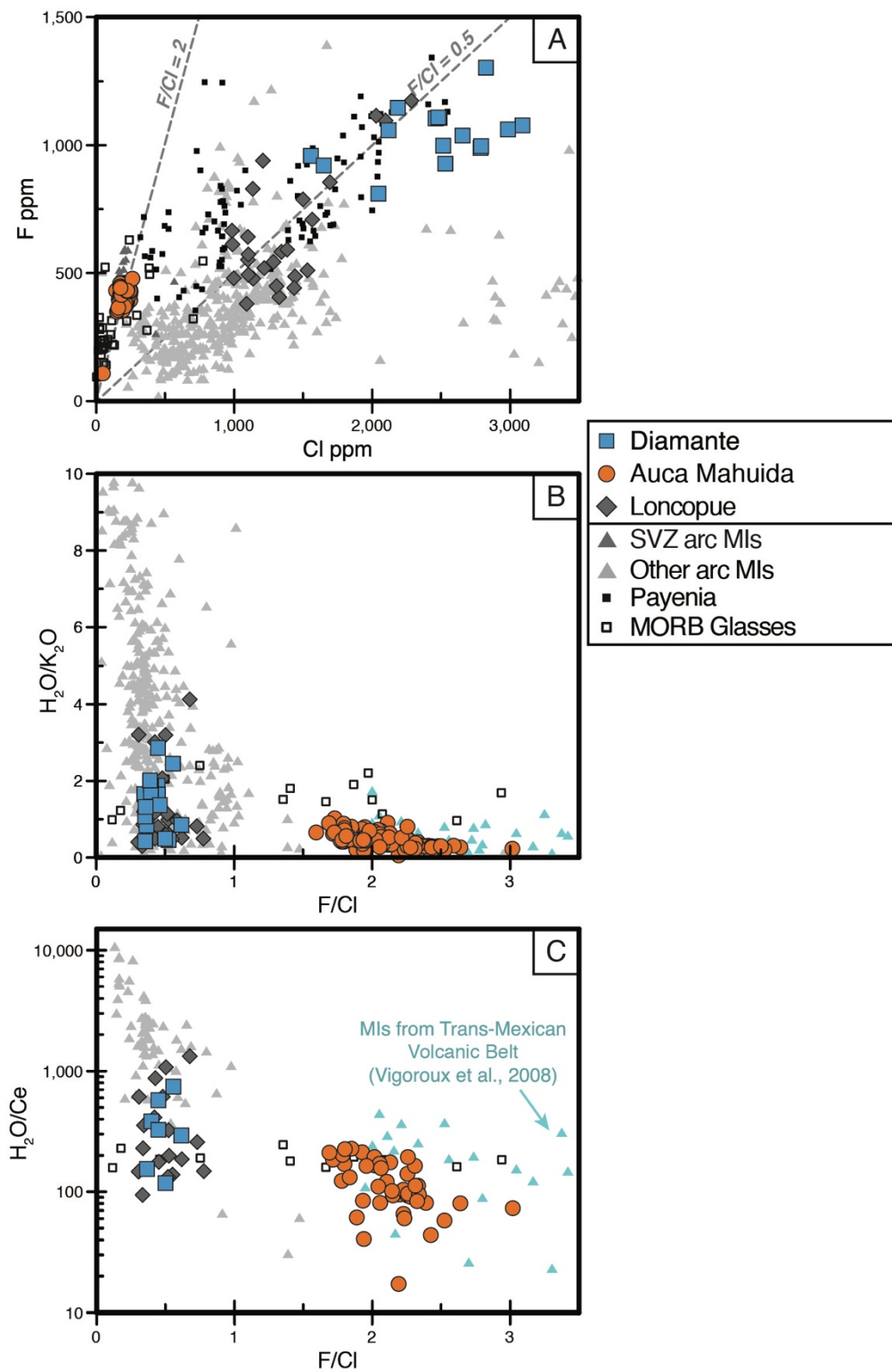


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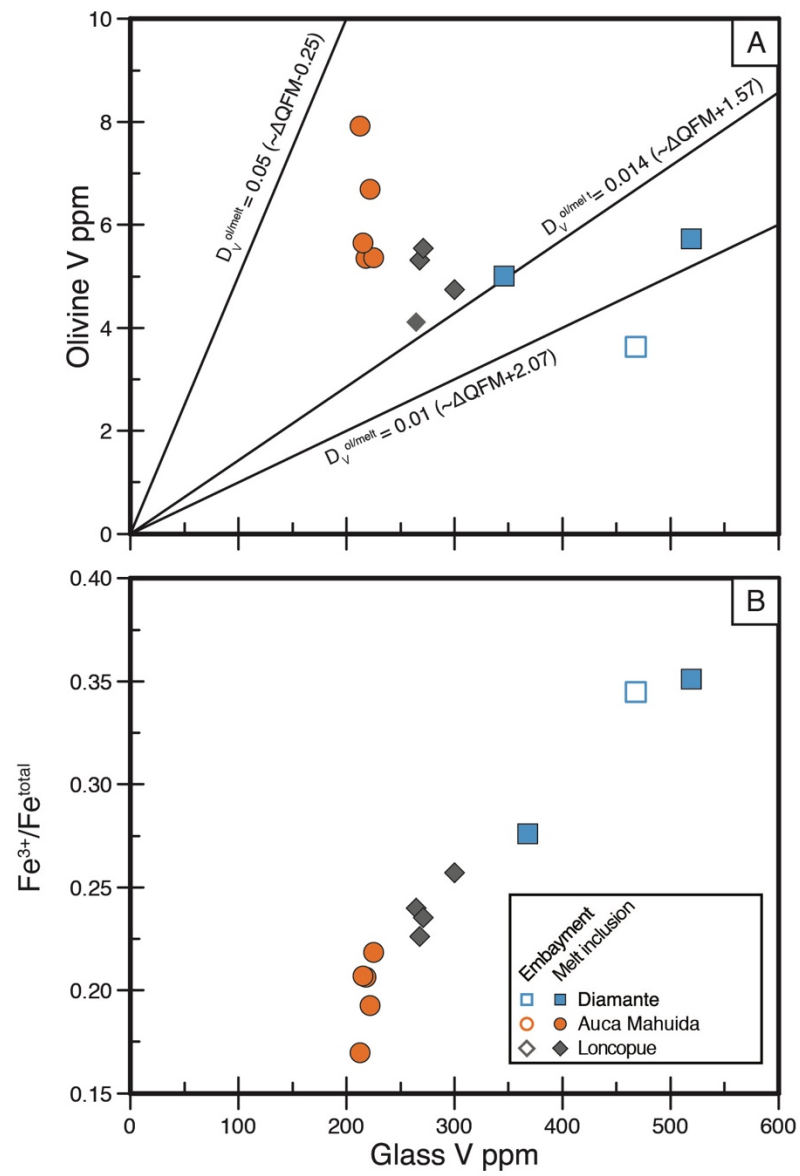


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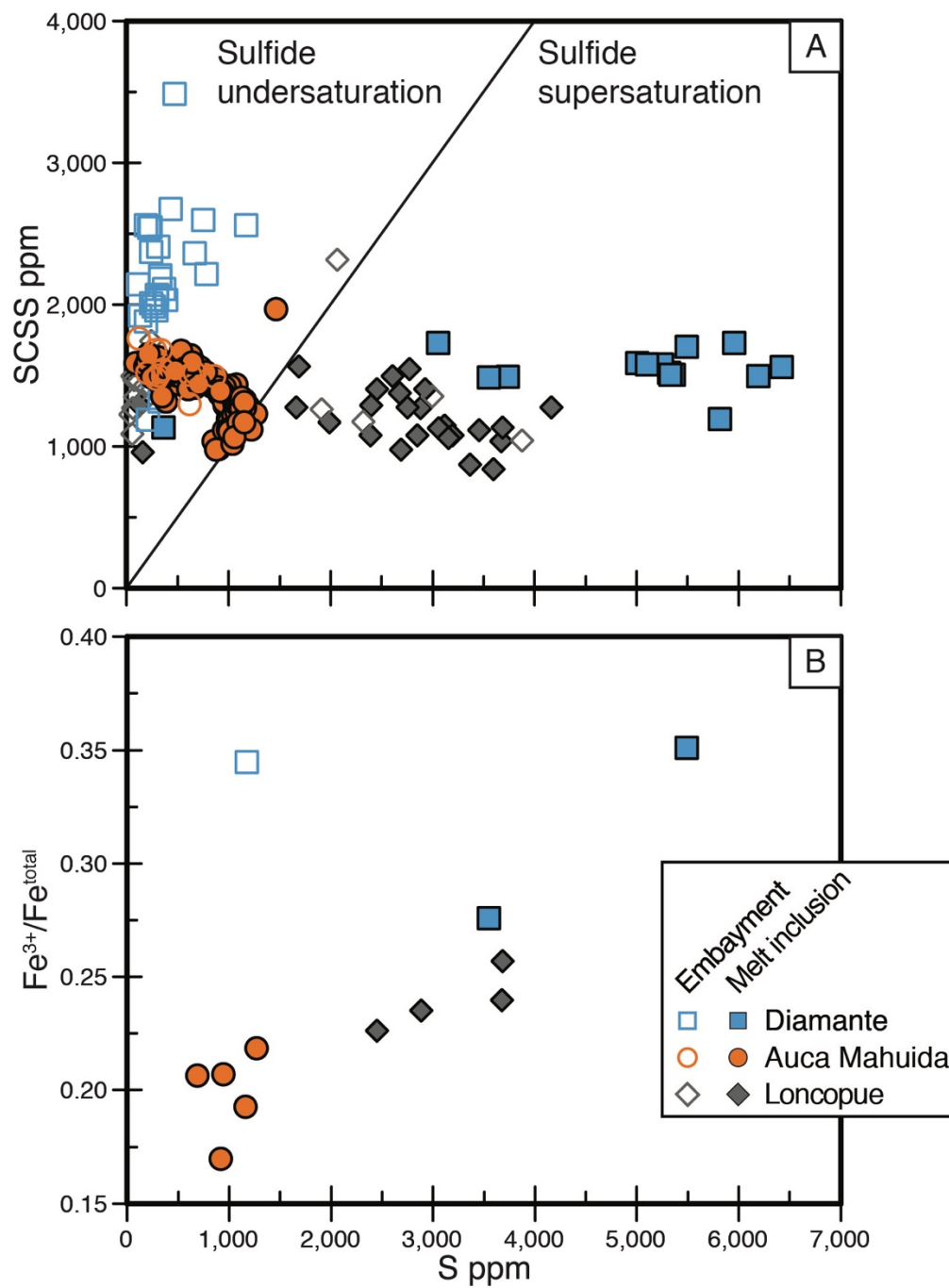


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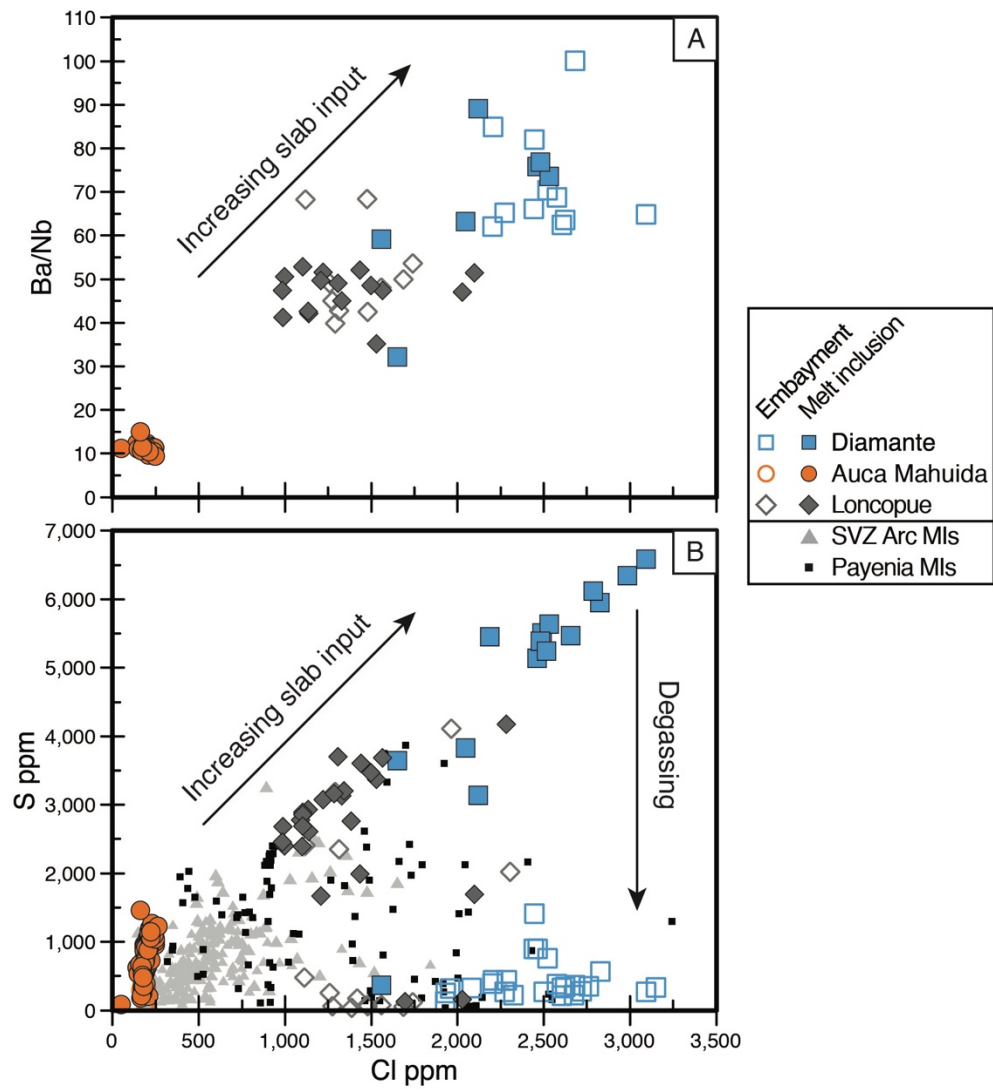


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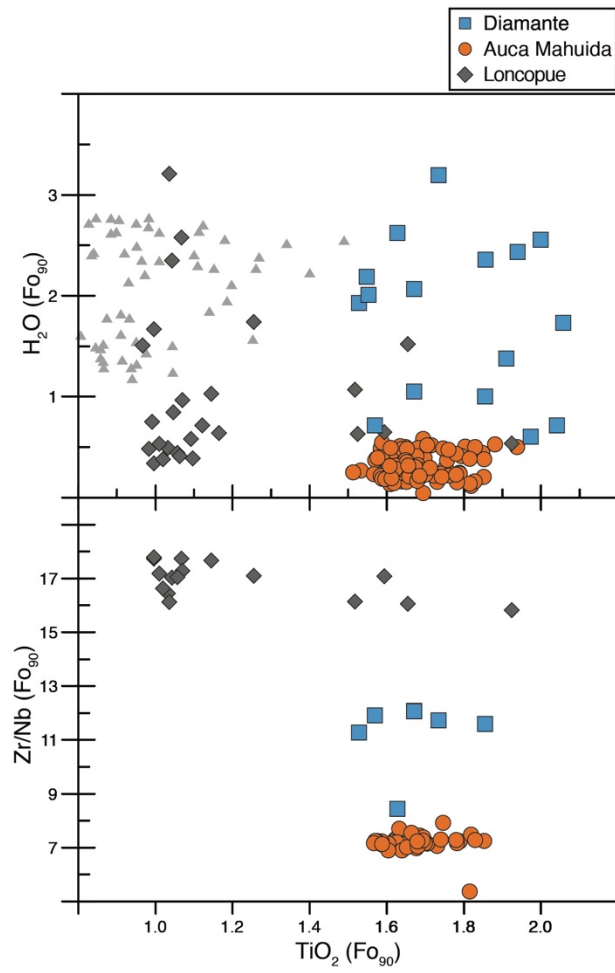
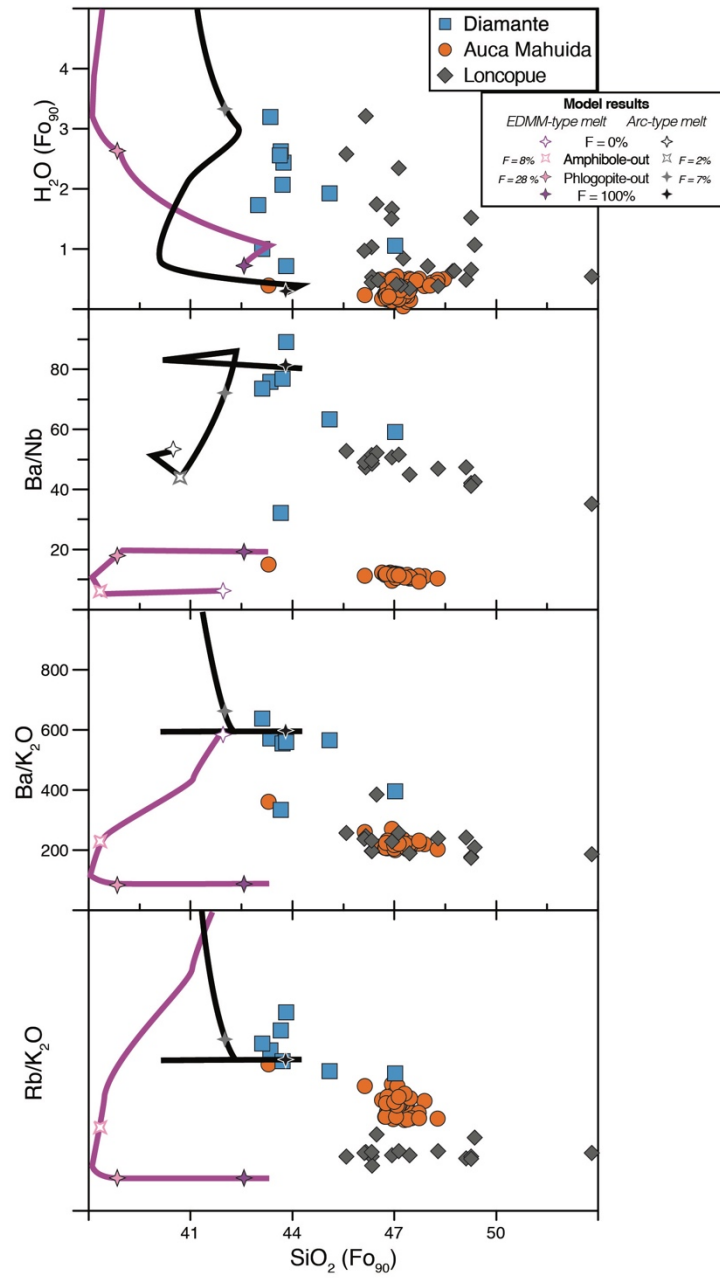


Figure 2-16.



TABLES

Table 2-1.

Table 1. Whole-rock compositions of the MI-bearing samples or their nearby proxies.

Sample ID	011910-192	AUC-035	011510-179
Volcanic Field	Diamante	Auca Mahuida	Loncopué
Locality	Diamante	Aguada Lustre	Cerro Morado
Latitude (°S)	-34.6189	-37.7012	-37.7535
Longitude (°W)	-69.0632	-68.8578	-70.6623
Type	Lava	Tephra	Dyke
Age (Ma)	<1	~1	~1
Major elements (wt.%)			
SiO ₂	47.78	48.08	49.48
TiO ₂	1.520	1.845	1.167
Al ₂ O ₃	14.94	14.78	18.06
FeO _T	10.04	11.5	8.66
CaO	10.01	8.77	10.22
MgO	11.23	9.65	6.28
MnO	0.171	0.166	0.16
K ₂ O	1.2	0.8	0.93
Na ₂ O	3.06	3.19	3.15
P ₂ O ₅	0.409	0.316	0.251
Total	100.35	99.09	98.36
Mg#	0.691	0.627	0.592
CIPW Norm			
Ne	3.81	-	-
Ol	21.46	19.92	10.06
Di	18.9	14.42	13.58
Hy	-	1.82	4.87
Qtz	-	-	-
Trace elements (ppm)			
Sc	28.58	21.67	29.66
V	240.52	188.86	269.95
Cr	527.41	312.91	69.07
Ni	233.18	214.7	35.08
Zn	81.06	104.07	80.77
Rb	23.78	12.95	11.11
Sr	640.12	472.19	870.58
Y	22.34	19.62	18.08
Zr	134.25	107.23	77.2
Nb	12.89	13.54	4.77
Cs	0.86	0.39	0.18
Ba	408.79	175.82	233.07
La	20.4	12.04	13.56
Ce	42.42	25.86	29.81
Pr	5.44	3.52	4.06
Nd	23.22	16.06	17.37
Sm	5.38	4.42	3.9
Eu	1.77	1.64	1.4
Gd	5.26	4.63	3.79
Tb	0.8	0.74	0.6
Dy	4.63	4.24	3.59
Ho	0.88	0.8	0.7
Er	2.26	1.98	1.88
Tm	0.31	0.26	0.27
Yb	1.89	1.54	1.62
Lu	0.29	0.23	0.25
Hf	3.34	2.73	2.04
Ta	0.78	0.85	0.28
Pb	4.95	1.56	3.39
Th	3.3	1.28	1.82
U	0.94	0.41	0.57
Cu	51.14	51.89	31.22
Ga	17.05	19.88	19.03

Table 2-2.

Table 2. Averages of olivine host crystal compositions, analyzed by EPMA.

EPMA		MgO	SiO2	CaO	FeO	NiO	Al2O3	Cr2O3	Total	Fo	
Olivine #	spots per grain										
011510-181 n=25 Loncopué											
oi3	5	42.28	39.17	0.18	18.72	0.07	0.01	0.01	100.43	80.11	
oi4	5	43.29	39.33	0.18	16.85	0.09	0.04	0.01	99.79	82.08	
oi5	4	43.91	39.69	0.19	16.90	0.09	0.03	0.02	100.83	82.25	
oi8	4	43.35	39.45	0.17	17.27	0.14	0.03	0.03	100.43	81.73	
oi9	4	42.73	39.34	0.19	17.93	0.06	0.02	0.01	100.28	80.95	
oi10	4	44.52	40.49	0.18	17.11	0.07	0.03	0.01	102.39	82.27	
oi11	3	43.73	39.72	0.18	16.81	0.12	0.03	0.01	100.60	82.26	
oi12	2	44.90	41.27	0.19	17.16	0.14	0.03	0.00	103.68	82.35	
oi13	3	43.62	39.73	0.17	16.67	0.11	0.04	0.03	100.38	82.35	
oi15	5	44.17	40.04	0.18	17.00	0.10	0.03	0.02	101.54	82.25	
oi16	5	42.29	38.94	0.19	17.52	0.11	0.01	0.01	99.07	81.13	
oi18	3	44.33	40.37	0.18	17.10	0.10	0.03	0.00	102.12	82.21	
oi19	4	42.55	39.28	0.20	17.64	0.09	0.02	0.02	99.79	81.13	
oi20	4	43.70	39.72	0.18	16.77	0.10	0.03	0.01	100.51	82.29	
oi21	4	43.24	39.95	0.22	17.93	0.07	0.02	0.01	101.44	81.13	
oi27	3	43.22	39.00	0.18	16.87	0.09	0.00	0.01	99.36	82.04	
oi28	4	43.72	39.71	0.18	16.82	0.14	0.02	0.01	100.58	82.25	
oi30	4	42.33	38.85	0.18	16.89	0.12	0.02	0.01	98.39	81.71	
oi32	3	43.79	39.59	0.19	16.93	0.08	0.02	0.01	100.62	82.18	
oi33	4	44.51	40.20	0.17	16.67	0.09	0.02	0.03	101.69	82.64	
oi34	3	41.97	38.53	0.18	17.32	0.09	0.04	0.00	98.15	81.20	
oi35	4	43.60	39.73	0.20	16.73	0.11	0.03	0.00	100.40	82.29	
oi36	4	43.13	39.32	0.18	17.41	0.10	0.01	0.02	100.15	81.54	
oi37	3	44.30	40.25	0.17	16.77	0.09	0.01	0.02	101.62	82.49	
oi38	3	42.54	38.95	0.19	17.48	0.09	0.03	0.01	99.28	81.26	
011910-188 n=24 Diamante											
oi1	4	45.19	39.94	0.18	14.78	0.14	0.02	0.02	100.26	84.50	
oi2	4	45.33	39.96	0.13	14.60	0.22	0.01	0.03	100.28	84.70	
oi3	5	45.29	39.87	0.19	14.69	0.18	0.03	0.01	100.26	84.61	
oi5	3	45.27	39.88	0.16	14.30	0.20	0.01	0.02	99.84	84.95	
oi6	4	45.64	40.14	0.21	13.96	0.21	0.04	0.02	100.19	85.36	
oi10	4	44.75	39.59	0.20	15.16	0.17	0.01	0.02	99.90	84.03	
oi12	4	45.00	39.97	0.22	14.93	0.13	0.01	0.01	100.26	84.31	
oi13	4	47.39	40.20	0.19	11.89	0.26	0.02	0.04	99.97	87.66	
oi15	3	45.68	39.80	0.19	14.17	0.21	0.01	0.02	100.07	85.17	
oi16	3	45.13	39.80	0.19	14.72	0.17	0.02	0.02	100.06	84.53	
oi18	4	45.79	40.02	0.21	13.70	0.21	0.02	0.03	99.96	85.63	
oi19	4	45.54	39.73	0.19	13.82	0.23	0.02	0.03	99.54	85.45	
oi21	4	43.88	39.35	0.21	16.15	0.18	0.01	0.02	99.79	82.89	
oi26	6	44.78	39.72	0.19	14.82	0.15	0.02	0.01	99.69	84.35	
oi30	3	45.37	39.74	0.23	14.23	0.16	0.02	0.01	99.77	85.04	
oi31	3	45.52	39.86	0.20	13.85	0.16	0.03	0.01	99.63	85.42	
oi32	4	45.45	39.98	0.19	13.83	0.18	0.03	0.05	99.70	85.42	
oi35	6	45.60	40.00	0.19	13.97	0.20	0.01	0.02	99.99	85.30	
oi40	7	45.11	39.67	0.22	14.32	0.16	0.02	0.02	99.53	84.89	
oi41	3	44.63	39.63	0.21	14.71	0.13	0.01	0.02	99.33	84.40	
oi44	3	46.09	39.85	0.15	12.82	0.28	0.03	0.04	99.25	86.50	
oi54	3	44.24	39.35	0.11	15.65	0.15	0.02	0.01	99.53	83.44	
oi55	5	46.77	40.11	0.20	12.08	0.29	0.01	0.02	99.48	87.34	
oi57	3	46.27	40.08	0.15	12.88	0.27	0.01	0.04	99.69	86.47	
AUC-035 n=29 Auca Mahuida											
oi1	3	42.31	39.12	0.26	18.13	0.22	0.04	0.02	100.09	80.62	
oi3	17	42.39	39.37	0.23	18.03	0.21	0.02	0.03	100.28	80.74	
oi5	3	43.20	39.51	0.22	17.64	0.24	0.01	0.03	100.85	81.36	
oi6	6	42.15	39.25	0.26	18.35	0.20	0.02	0.02	100.24	80.37	
oi10	3	42.62	39.37	0.25	17.85	0.21	0.04	0.03	100.36	80.98	

Table 2-2 (continued).

oi11	5	42.04	39.03	0.28	18.51	0.19	0.04	0.05	100.14	80.19
oi14	4	42.48	39.19	0.22	17.81	0.15	0.05	0.03	99.93	80.96
oi15	3	42.62	39.25	0.20	18.03	0.22	0.03	0.03	100.37	80.83
oi16	10	42.49	39.40	0.26	18.07	0.21	0.03	0.03	100.48	80.74
oi18	6	42.33	39.07	0.27	18.33	0.16	0.03	0.03	100.21	80.46
oi20	4	42.73	39.42	0.24	17.57	0.25	0.05	0.04	100.30	81.26
oi21	3	42.30	38.98	0.18	18.65	0.16	0.01	0.02	100.31	80.17
oi22	4	42.44	39.23	0.25	18.21	0.19	0.03	0.02	100.36	80.60
oi23	4	42.43	39.35	0.26	18.06	0.23	0.05	0.04	100.43	80.73
oi26	8	43.13	39.34	0.24	17.06	0.25	0.03	0.03	100.08	81.84
oi28	5	42.87	39.31	0.23	17.72	0.24	0.04	0.04	100.43	81.17
oi29	3	43.19	39.16	0.22	17.59	0.21	0.04	0.04	100.45	81.39
oi30	4	41.58	39.15	0.27	18.95	0.18	0.05	0.03	100.21	79.64
oi32	4	42.71	39.29	0.26	17.91	0.18	0.02	0.02	100.39	80.96
oi34	4	42.36	39.38	0.26	17.85	0.21	0.03	0.03	100.11	80.88
oi35	6	42.45	39.19	0.28	18.01	0.20	0.04	0.04	100.20	80.78
oi36	5	42.84	39.59	0.23	17.57	0.21	0.03	0.04	100.51	81.30
oi37	4	41.60	39.12	0.17	19.29	0.18	0.02	0.02	100.39	79.36
oi38	5	41.98	39.16	0.22	18.58	0.19	0.02	0.03	100.18	80.11
oi40	8	42.85	39.24	0.25	17.83	0.22	0.02	0.01	100.41	81.08
oi41	3	40.93	38.82	0.16	19.50	0.14	0.00	0.01	99.56	78.90
oi42	3	41.92	38.88	0.23	18.61	0.16	0.03	0.03	99.86	80.05
oi43	19	42.22	39.03	0.28	18.17	0.19	0.03	0.03	99.95	80.55
oi44	7	42.83	39.22	0.24	17.95	0.19	0.03	0.02	100.49	80.97

Table 2-3.

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Table 2-3 (continued).

[illegible]

Table 2-3 (continued).

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
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Table 2-3 (continued).

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Table 2-4.

Table 4. Details of the correction of MI H2O and CO2 concentrations for the presence of a vapor bubble.

Sample	PEC-corr. H2O wt. %	PEC-corr. CO2 ppm	P(calc) bars	XCO2 in vapor	XH2O in vapor	T (K)	MI volume (m ³)	Bubble volume (m ³)	Crystal volume (m ³)	MI density (g/m ³)	Final H2O wt. %	Final CO2 ppm
011510-181 Loncopué												
181-o13-2	0.844	21.71	114	0.410	0.591	1444	3.30E-14	1.15E-15	0E+00	2.63E+06	0.857	248.92
181-o11-1	0.687	152.36	202	0.758	0.244	1400	5.80E-15	3.82E-16	0E+00	2.65E+06	0.706	158.01
181-o113-1	3.863	150.24	1694	0.097	0.904	1375	6.64E-14	2.14E-15	0E+00	2.52E+06	0.473	958.62
181-o116-3	0.815	81.40	238	0.735	0.267	1471	1.95E-13	1.56E-14	0E+00	2.64E+06	0.843	1988.74
181-o119-1	0.459	634.91	1341	0.984	0.016	1407	8.91E-13	2.85E-14	0E+00	2.65E+06	0.463	6218.61
181-o119-2	2.919	303.06	1309	0.359	0.641	1359	7.38E-13	1.72E-14	0E+00	2.55E+06	2.941	1970.98
181-o120-1	3.059	95.09	1120	0.080	0.920	1365	1.15E-13	7.24E-15	0E+00	2.55E+06	3.461	949.69
181-o120-2	0.462	102.58	185	0.895	0.106	1401	1.21E-12	2.24E-14	0E+00	2.66E+06	0.464	540.21
181-o127-1	0.635	171.38	252	0.842	0.160	1408	2.82E-13	7.24E-15	0E+00	2.65E+06	0.641	940.86
181-o128-1	0.739	193.63	467	0.887	0.114	1369	2.45E-14	1.80E-16	0E+00	2.61E+06	0.742	642.30
181-o128-2	2.044	138.40	625	0.268	0.733	1364	7.15E-14	1.44E-15	0E+00	2.60E+06	2.100	639.37
181-o130-1	1.161	189.04	364	0.598	0.402	1397	9.27E-14	4.19E-15	0E+00	2.63E+06	1.200	1602.53
181-o132-1	0.532	22.11	55	0.509	0.494	1433	2.48E-13	5.58E-15	0E+00	2.66E+06	0.535	109.01
181-o133-2	0.833	56.59	188	0.649	0.353	1385	2.19E-13	7.24E-15	0E+00	2.63E+06	0.846	640.48
181-o135-1	0.996	110.08	281	0.643	0.357	1392	4.42E-14	1.77E-15	0E+00	2.63E+06	1.020	1153.58
181-o135-2	0.489	158.07	267	0.916	0.084	1403	5.70E-14	1.77E-15	0E+00	2.65E+06	0.493	1234.04
181-o137-1	0.584	5.40	40	0.183	0.822	1442	4.89E-13	4.16E-14	0E+00	2.66E+06	0.598	81.41
181-o138-1	1.859	270.04	801	0.533	0.467	1405	6.06E-15	1.13E-16	0E+00	2.60E+06	1.901	1425.62
011910-188 Diamante												
188-o13-1	2.879	2078.77	2364	0.512	0.488	1394	1.10E-13	2.57E-15	4.50E-15	2.58E+06	3.042	6261.73
188-o113-1	2.058	1846.94	2053	0.726	0.274	1389	1.69E-13	7.24E-15	0E+00	2.60E+06	2.203	11195.29
188-o118-2	0.645	1643.59	1037	0.948	0.053	1422	1.57E-14	6.97E-16	0E+00	2.68E+06	0.658	7704.36
188-o131-1	1.490	1501.48	1130	0.710	0.290	1433	4.36E-14	4.85E-15	0E+00	2.66E+06	1.698	13874.22
188-o154-1	0.818	297.96	279	0.714	0.287	1462	2.83E-12	3.35E-14	0E+00	2.67E+06	0.823	617.27
188-o155-2	2.643	913.74	1482	0.364	0.636	1404	2.24E-13	2.24E-14	4.91E-15	2.58E+06	3.208	8802.74
188-o155-3	1.790	761.82	876	0.487	0.513	1423	9.46E-14	8.18E-15	7.68E-16	2.63E+06	2.015	5986.19
AUC-035 Auca Mahuida												
auc035-o13-11	0.644	1422.18	2818	0.983	0.017	1405	4.09E-13	1.77E-15	0E+00	2.64E+06	0.645	3129.68
auc035-o14-1	0.350	59.34	131	0.922	0.081	1460	1.37E-12	6.54E-14	6.4E-14	2.68E+06	0.353	839.14
auc035-o16-2	0.620	1213.96	2448	0.982	0.018	1417	1.89E-13	4.19E-15	0E+00	2.64E+06	0.625	8740.88
auc035-o26-2	0.580	1388.25	2752	0.986	0.014	1406	7.22E-13	1.41E-14	0E+00	2.63E+06	0.584	8988.46
auc035-o26-6	0.520	1244.54	2493	0.988	0.012	1413	1.19E-13	4.19E-15	0E+00	2.64E+06	0.526	13614.12
auc035-o135-4	0.511	1912.70	1305	0.975	0.025	1455	2.43E-13	8.18E-15	0E+00	2.73E+06	0.517	7613.09
auc035-o138-1	0.248	89.57	199	0.976	0.026	1451	1.54E-12	5.24E-13	6.4E-14	2.68E+06	0.258	9071.10
auc035-o140-6	0.578	1073.87	2189	0.983	0.017	1414	2.77E-13	1.41E-14	0E+00	2.64E+06	0.589	16617.40
auc035-o143-2	0.393	672.11	1246	0.988	0.012	1425	5.71E-13	3.35E-14	0E+00	2.66E+06	0.399	10743.39
auc035-o143-3	0.381	531.88	988	0.986	0.014	1431	3.39E-13	4.19E-15	0E+00	2.66E+06	0.382	2199.99
auc035-o143-7	0.493	681.93	1436	0.983	0.017	1433	1.18E-13	8.18E-15	0E+00	2.65E+06	0.503	14329.51
auc035-o143-10	0.367	824.67	1704	0.992	0.008	1418	1.68E-13	8.18E-15	0E+00	2.66E+06	0.371	12405.58
auc035-o143-15	0.359	556.66	1180	0.987	0.013	1428	7.03E-13	3.35E-14	0E+00	2.66E+06	0.404	8296.29
auc035-o143-21	0.277	194.96	384	0.984	0.017	1462	1.01E-12	6.54E-14	0E+00	2.68E+06	0.279	3484.25
Errors												
Lower limit (higher density +0.1 kg/m³, higher T +100K, smaller bubble 20%, larger inclusion 20%, smaller crystal 20%, lower concentration 15 and 10% for C and H respectively)												
181-o13-2	0.759	18.46	114	0.410	0.591	1544	5.84E-14	5.89E-16	0.00E+00	2.73E+06	0.763	77.66
181-o111-1	0.619	129.50	202	0.758	0.244	1500	1.05E-14	1.95E-16	0.00E+00	2.75E+06	0.623	494.40
181-o113-1	3.477	127.71	1694	0.097	0.904	1475	1.17E-13	1.10E-15	0.00E+00	2.62E+06	3.557	337.68
181-o116-3	0.734	69.19	238	0.735	0.267	1571	3.55E-13	7.99E-15	0.00E+00	2.74E+06	0.741	551.85
181-o119-1	0.413	539.67	1341	0.984	0.016	1507	1.57E-12	1.36E-14	0.00E+00	2.75E+06	0.414	1997.52
181-o119-2	2.538	257.60	1309	0.359	0.641	1459	1.30E-12	8.78E-15	0.00E+00	2.65E+06	2.569	693.43
181-o120-1	2.753	80.83	1120	0.080	0.920	1465	2.08E-13	3.71E-15	0.00E+00	2.65E+06	2.855	298.27
181-o120-2	0.416	87.20	185	0.895	0.106	1501	2.12E-12	1.15E-14	0.00E+00	2.76E+06	0.416	202.33
181-o127-1	0.572	145.68	252	0.842	0.160	1508	4.96E-13	3.71E-15	0.00E+00	2.75E+06	0.573	347.19
181-o128-1	0.666	164.59	467	0.887	0.114	1469	4.25E-14	9.20E-17	0.00E+00	2.71E+06	0.666	283.30
181-o128-2	1.840	117.64	625	0.268	0.733	1464	1.25E-13	7.36E-16	0.00E+00	2.70E+06	1.855	248.96
181-o130-1	1.045	160.68	364	0.598	0.402	1497	1.65E-13	2.14E-15	0.00E+00	2.73E+06	1.055	525.62
181-o132-1	0.479	18.79	55	0.509	0.494	1533	4.34E-13	2.85E-15	0.00E+00	2.76E+06	0.480	41.63
181-o133-2	0.750	48.10	188	0.649	0.353	1485	3.88E-13	3.71E-15	0.00E+00	2.73E+06	0.753	200.01
181-o135-1	0.897	93.57	281	0.643	0.357	1492	7.86E-14	9.05E-16	0.00E+00	2.73E+06	0.903	363.85
181-o135-2	0.440	134.36	267	0.916	0.084	1503	1.01E-13	9.05E-16	0.00E+00	2.75E+06	0.441	415.03
181-o137-1	0.526	4.59	40	0.183	0.822	1542	8.95E-13	2.13E-14	0.00E+00	2.76E+06	0.530	26.04
181-o138-1	1.673	229.53	801	0.533	0.467	1505	1.06E-14	5.79E-17	0.00E+00	2.70E+06	1.684	533.33
Higher limit (lower d -0.1, lower T -100, larger bubble 20%, smaller inclusion 20%, larger crystal 20%, higher concentration 15 and 10% for C and H respectively)												
188-o13-1	2.591	1766.95	2364	0.512	0.488	1494	1.98E-13	1.32E-15	2.30E-15	2.68E+06	2.633	2831.90
188-o113-1	1.852	1569.90	2053	0.726	0.274	1489	3.02E-13	3.71E-15	0.00E+00	2.70E+06	1.890	3985.32
188-o118-2	0.580	1397.05	1037	0.948	0.053	1522	2.79E-14	3.57E-16	0.00E+00	2.78E+06	0.584	2965.47
188-o131-1	1.341	1276.26	1130	0.710	0.290	1533	8.13E-14	2.48E-15	0.00E+00	2.76E+06	1.393	4339.47
188-o154-1	0.736	253.27	279	0.714	0.287	1562	4.94E-12	1.72E-14	0.00E+00	2.77E+06	0.737	337.92
188-o155-2	2.378	776.68	1482	0.364	0.636	1504	4.20E-13	1.15E-14	2.52E-15	2.68E+06	2.517	2711.05
188-o155-3	1.611	647.55	876	0.487	0.513	1523	1.74E-13	4.19E-15	3.93E-16	2.73E+06	1.667	1953.86
Errors												
auc035-o13-11	0.580	1208.86	2818	0.983	0.017	1505	7.10E-13	9.05E-16	0.00E+00	2.74E+06	0.580	1662.54
auc035-o14-1	0.315	50.44	131	0.922	0.081	1560	2.53E-12	3.35E-14	3.28E-14	2.78E+06	0.316	245.93
auc035-o16-2	0.558	1031.87	2448	0.982	0.018	1517	3.32E-13	2.14E-15	0.00E+00	2.74E+06	0.559	3008.23
auc035-o26-2	0.522	1180.01	2752	0.986	0.014	1506	1.27E-12	7.24E-15	0.00E+00	2.73E+06	0.523	3177.92
auc035-o26-6	0.468	1057.86	2493	0.988	0.012	1513	2.10E-13	2.14E-15	0.00E+00	2.74E+06	0.469	4275.58
auc035-o135-4	0.460	1625.79	1305	0.975	0.025	1555	4.30E-13	4.19E-15	0.00E+00	2.83E+06	0.461	3115.13
auc035-o138-1	0.224	76.14	199	0.976	0.026	1551	3.37E-12	2.68E-13	3.28E-14	2.78E+06	0.226	1967.94
auc035-o140-6	0.520	912.79	2189	0.983	0.017	1514	4.97E-13	7.24E-15	0.00E+00	2.74E+06	0.523	4913.77
auc035-o143-2	0.354	571.30	1246	0.988	0.012	1525	1.03E-12	1.72E-14	0.00E+00	2.76E+06	0.355	3152.25
auc035-o143-3	0.343	452.10	988	0.986	0.014	1531	5.92E-13	2.14E-15	0.00E+00	2.76E+06	0.343	893.53</

Table 2-4 (continued).

181-oi3-2	0.928	24.97	114	0.410	0.591	1344	1.55E-14	1.99E-15	0.00E+00	2.53E+06	0.983	958.71
181-oi11-1	0.756	175.21	202	0.758	0.244	1300	2.50E-15	6.60E-16	0.00E+00	2.55E+06	0.840	6589.47
181-oi13-1	4.250	172.78	1694	0.097	0.904	1275	3.14E-14	3.71E-15	0.00E+00	2.42E+06	5.520	3491.37
181-oi16-3	0.897	93.61	238	0.735	0.267	1371	8.07E-14	2.70E-14	0.00E+00	2.54E+06	1.029	8958.80
181-oi19-1	0.505	730.14	1341	0.984	0.016	1307	4.24E-13	4.58E-14	0.00E+00	2.55E+06	0.520	23417.37
181-oi19-2	3.101	348.52	1309	0.359	0.641	1259	3.57E-13	2.96E-14	0.00E+00	2.45E+06	3.591	7042.21
181-oi20-1	3.365	109.35	1120	0.080	0.920	1265	5.03E-14	1.25E-14	0.00E+00	2.45E+06	5.152	3915.06
181-oi20-2	0.508	117.97	185	0.895	0.106	1301	5.91E-13	3.88E-14	0.00E+00	2.56E+06	0.516	1847.00
181-oi27-1	0.699	197.09	252	0.842	0.160	1308	1.36E-13	1.25E-14	0.00E+00	2.55E+06	0.723	3290.58
181-oi28-1	0.813	222.68	467	0.887	0.114	1269	1.23E-14	3.10E-16	0.00E+00	2.51E+06	0.822	1951.30
181-oi28-2	2.249	159.16	625	0.268	0.733	1264	3.49E-14	2.48E-15	0.00E+00	2.50E+06	2.472	2151.69
181-oi30-1	1.277	217.39	364	0.598	0.402	1297	4.23E-14	7.24E-15	0.00E+00	2.53E+06	1.442	6200.82
181-oi32-1	0.585	25.42	55	0.509	0.494	1333	1.20E-13	9.63E-15	0.00E+00	2.56E+06	0.599	371.59
181-oi33-2	0.916	65.07	188	0.649	0.353	1285	1.04E-13	1.25E-14	0.00E+00	2.53E+06	0.970	2460.87
181-oi35-1	1.096	126.59	281	0.643	0.357	1292	2.05E-14	3.05E-15	0.00E+00	2.53E+06	1.195	4484.63
181-oi35-2	0.538	181.78	267	0.916	0.084	1303	2.70E-14	3.05E-15	0.00E+00	2.55E+06	0.554	4567.83
181-oi37-1	0.643	6.21	40	0.183	0.822	1342	2.00E-13	7.19E-14	0.00E+00	2.56E+06	0.717	408.45
181-oi38-1	2.045	310.54	801	0.533	0.467	1305	2.97E-15	1.95E-16	0.00E+00	2.50E+06	2.209	4880.19
188-oi3-1	3.167	2390.58	2364	0.512	0.488	1294	4.76E-14	4.45E-15	7.78E-15	2.48E+06	3.895	21072.78
188-oi13-1	2.264	2123.98	2053	0.726	0.274	1289	7.79E-14	1.25E-14	0.00E+00	2.50E+06	2.872	41477.76
188-oi18-2	0.709	1890.12	1037	0.948	0.053	1322	7.17E-15	1.20E-15	0.00E+00	2.58E+06	0.767	27444.12
188-oi31-1	1.640	1726.70	1130	0.710	0.290	1333	1.65E-14	8.38E-15	0.00E+00	2.56E+06	2.700	65088.58
188-oi54-1	0.900	342.65	279	0.714	0.287	1362	1.41E-12	5.79E-14	0.00E+00	2.57E+06	0.920	1579.19
188-oi55-2	2.907	1050.80	1482	0.364	0.636	1304	8.14E-14	3.88E-14	8.49E-15	2.48E+06	5.916	43063.97
188-oi55-3	1.969	876.10	876	0.487	0.513	1323	3.75E-14	1.41E-14	1.33E-15	2.53E+06	3.066	26306.06
auc035-oi3-11	0.709	1635.51	2818	0.983	0.017	1305	2.07E-13	3.05E-15	0.00E+00	2.54E+06	0.713	8151.11
auc035-oi14-1	0.385	68.24	131	0.922	0.081	1360	5.46E-13	1.13E-13	1.11E-13	2.58E+06	0.399	3849.44
auc035-oi16-2	0.682	1396.06	2448	0.982	0.018	1317	9.19E-14	7.24E-15	0.00E+00	2.54E+06	0.704	31379.70
auc035-oi26-2	0.638	1596.49	2752	0.986	0.014	1306	3.53E-13	2.44E-14	0.00E+00	2.53E+06	0.655	31701.51
auc035-oi26-6	0.572	1431.22	2493	0.988	0.012	1313	5.56E-14	7.24E-15	0.00E+00	2.54E+06	0.597	52407.93
auc035-oi35-4	0.562	2199.60	1305	0.975	0.025	1355	1.15E-13	1.41E-14	0.00E+00	2.63E+06	0.586	25505.31
auc035-oi38-1	0.273	103.01	199	0.976	0.026	1351	7.37E-14	9.05E-13	1.11E-13	2.58E+06	0.669	361747.46
auc035-oi40-6	0.636	1234.95	2189	0.983	0.017	1314	1.25E-13	2.44E-14	0.00E+00	2.54E+06	0.682	67985.22
auc035-oi43-2	0.433	772.93	1246	0.988	0.012	1325	2.52E-13	5.79E-14	0.00E+00	2.56E+06	0.455	44903.24
auc035-oi43-3	0.419	611.66	988	0.986	0.014	1331	1.69E-13	7.24E-15	0.00E+00	2.56E+06	0.423	7090.39
auc035-oi43-7	0.543	784.22	1436	0.983	0.017	1333	5.04E-14	1.41E-14	0.00E+00	2.55E+06	0.587	62403.07
auc035-oi43-10	0.403	948.37	1704	0.992	0.008	1318	7.59E-14	1.41E-14	0.00E+00	2.56E+06	0.420	50367.20
auc035-oi43-15	0.439	640.16	1180	0.987	0.013	1328	3.19E-13	5.79E-14	0.00E+00	2.56E+06	0.457	33552.87
auc035-oi43-21	0.304	224.20	384	0.984	0.017	1362	4.40E-13	1.13E-13	0.00E+00	2.58E+06	0.315	14841.87

Table 2-5.

Table 5. Olivine and MI V concentrations and fO₂ and Fe³⁺/Fe^T constraints using the expressions from Canil (2002) and Kress and Carmichael (1991).

Sample_Olivine#	Fo averaged V, MI (ppm)	V, ol (ppm)	D(V)ol/melt	log(fO2)	ΔFMQ	Fe3+/FeT	
011510-181 Loncopué							
181_oli12	82.35	264	4.11	0.016	-7.47	1.44	0.240
181_oli13	82.35	268	5.32	0.020	-8.34	1.03	0.226
181_oli20	82.29	271	5.54	0.020	-8.53	1.02	0.235
181_oli30	81.71	300	4.75	0.016	-7.76	1.40	0.257
Average						1.22	0.240
1 std. dev.						0.23	0.013
011910-188 Diamante							
188_oli3	84.61	368	6.29	0.017	-7.84	1.21	0.351
188_oli32	85.42	519	5.73	0.011	-6.79	1.91	0.276
188_oli35	85.30	468	3.63	0.008	-4.83	2.43	0.345
Average						1.85	0.324
1 std. dev.						0.61	0.042
AUC-035 Auca Mahuida							
AUC-035_oli15	80.83	218	5.35	0.025	-7.71	0.76	0.206
AUC-035_oli32	80.96	225	5.36	0.024	-7.85	0.69	0.218
AUC-035_oli34	80.88	215	5.64	0.026	-7.91	0.61	0.207
AUC-035_oli42	80.05	222	6.69	0.030	-8.32	0.41	0.193
AUC-035_oli44	80.97	213	7.92	0.037	-8.32	0.12	0.170
Average						0.52	0.199
1 std. dev.						0.26	0.019

Table 2-6.

[illegible]

Table 2-6 (continued).

	2017										2018										2019										2020										2021										2022										2023										2024										2025										2026										2027										2028										2029										2030										2031										2032										2033										2034										2035										2036										2037										2038										2039										2040										2041										2042										2043										2044										2045										2046										2047										2048										2049										2050										2051										2052										2053										2054										2055										2056										2057										2058										2059										2060										2061										2062										2063										2064										2065										2066										2067										2068										2069										2070										2071										2072										2073										2074										2075										2076										2077										2078										2079										2080										2081										2082										2083										2084										2085										2086										2087										2088										2089										2090										2091										2092										2093										2094										2095										2096										2097										2098										2099										2100										2101										2102										2103										2104										2105										2106										2107										2108										2109										2110										2111										2112										2113										2114										2115										2116										2117										2118										2119										2120										2121										2122										2123										2124										2125										2126										2127										2128										2129										2130										2131										2132										2133										2134										2135										2136										2137										2138										2139										2140										2141										2142										2143										2144										2145										2146										2147										2148										2149										2150										2151										2152										2153										2154										2155										2156										2157										2158										2159										2160										2161										2162										2163										2164										2165										2166										2167										2168										2169										2170										2171										2172										2173										2174										2175										2176										2177										2178										2179										2180										2181										2182										2183										2184										2185										2186										2187										2188										2189										2190										2191										2192										2193										2194										2195										2196										2197										2198										2199										2200										2201										2202										2203										2204										2205										2206										2207										2208										2209										2210										2211										2212										2213										2214										2215										2216										2217										2218										2219										2220										2221										2222										2223										2224										2225										2226										2227										2228										2229										2230										2231										2232										2233										2234										2235										2236										2237										2238										2239										2240										2241										2242										2243										2244										2245										2246										2247										2248										2249										2250										2251										2252										2253										2254										2255										2256										2257										2258										2259										2260										2261										2262										2263										2264										2265										2266										2267										2268										2269										2270										2271										2272										2273										2274										2275										2276										2277										2278										2279										2280										2281										2282										2283										2284										2285										2286										2287										2288										2289										2290										2291										2292										2293										2294										2295										2296										2297										2298										2299										2300										2301										2302										2303										2304										2305										2306										2307										2308										2309										2310										2311										2312										2313										2314										2315										2316										2317										2318										2319										2320										2321										2322										2323										2324										2325										2326										2327										2328										2329										2330										2331										2332										2333										2334										2335										2336										2337										2338										2339										2340										2341										2342										2343										2344										2345										2346										2347										2348										2349										2350										2351										2352										2353										2354										2355										2356										2357										2358										2359										2360										2361										2362										2363										2364										2365										2366										2367										2368										2369										2370										2371										2372										2373										2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Table 2-6 (continued).

[illegible]

Table 2-6 (continued).

[illegible]

Table 2-6 (continued).

1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2423	2424	2425	2426	2427	2428	2429	2430	2431	2432	2433	2434	2435	2436	2437	2438	2439	2440	2441	2442	2443	2444	2445	2446	2447	2448	2449	2450	2451	2452	2453	2454	2455	2456	2457	2458	2459	2460	2461	2462	2463	2464	2465	2466	2467	2468	2469	2470	2471	2472	2473	2474	2475	2476	2477	2478	2479	2480	2481	2482	2483	2484	2485	2486	2487	2488	2489	2490	2491	2492	2493	2494	2495	2496	2497	2498	2499	2500	2501	2502	2503	2504	2505	2506	2507	2508	2509	2510	2511	2512	2513	2514	2515	2516	2517	2518	2519	2520	2521	2522	2523	2524	2525	2526	2527	2528	2529	2530	2531	2532	2533	2534	2535	2536	2537	2538	2539	2540	2541	2542	2543	2544	2545	2546	2547	2548	2549	2550	2551	2552	2553	2554	2555	2556	2557	2558	2559	2560	2561	2562	2563	2564	2565	2566	2567	2568	2569	2570	2571	2572	2573	2574	2575	2576	2577	2578	2579	2580	2581	2582	2583	2584	2585	2586	2587	2588	2589	2590	2591	2592	2593	2594	2595	2596	2597	2598	2599	2600	2601	2602	2603	2604	2605	2606	2607	2608	2609	2610	2611	2612	2613	2614	2615	2616	2617	2618	2619	2620	2621	2622	2623	2624	2625	2626	2627	2628	2629	2630	2631	2632	2633	2634	2635	2636	2637	2638	2639	2640	2641	2642	2643	2644	2645	2646	2647	2648	2649	2650	2651	2652	2653	2654	2655	2656	2657	2658	2659	2660	2661	2662	2663	2664	2665	2666	2667	2668	2669	2670	2671	2672	2673	2674	2675	2676	2677	2678	2679	2680	2681	2682	2683	2684	2685	2686	2687	2688	2689	2690	2691	2692	2693	2694	2695	2696	2697	2698	2699	2700	2701	2702	2703	2704	2705	2706	2707	2708	2709	2710	2711	2712	2713	2714	2715	2716	2717	2718	2719	2720	2721	2722	2723	2724	2725	2726	2727	2728	2729	2730	2731	2732	2733	2734	2735	2736	2737	2738	2739	2740	2741	2742	2743	2744	2745	2746	2747	2748	2749	2750	2751	2752	2753	2754	2755	2756	2757	2758	2759	2760	2761	2762	2763	2764	2765	2766	2767	2768	2769	2770	2771	2772	2773	2774	2775	2776	2777	2778	2779	2780	2781	2782	2783	2784	2785	2786	2787	2788	2789	2790	2791	2792	2793	2794	2795	2796	2797	2798	2799	2800	2801	2802	2803	2804	2805	2806	2807	2808	2809	2810	2811	2812	2813	2814	2815	2816	2817	2818	2819	2820	2821	2822	2823	2824	2825	2826	2827	2828	2829	2830	2831	2832	2833	2834	2835	2836	2837	2838	2839	2840	2841	2842	2843	2844	2845	2846	2847	2848	2849	2850	2851	2852	2853	2854	2855	2856	2857	2858	2859	2860	2861	2862	2863	2864	2865	2866	2867	2868	2869	2870	2871	2872	2873	2874	2875	2876	2877	2878	2879	2880	2881	2882	2883	2884	2885	2886	2887	2888	2889	2890	2891	2892	2893	2894	2895	2896	2897	2898	2899	2900	2901	2902	2903	2904	2905	2906	2907	2908	2909	2910	2911	2912	2913	2914	2915	2916	2917	2918	2919	2920	2921	2922	2923	2924	2925	2926	2927	2928	2929	2930	2931	2932	2933	2934	2935	2936	2937	2938	2939	2940	2941	2942	2943	2944	2945	2946	2947	2948	2949	2950	2951	2952	2953	2954	2955	2956	2957	2958	2959	2960	2961	2962	2963	2964	2965	2966	2967	2968	2969	2970	2971	2972	2973	2974	2975	2976	2977	2978	2979	2980	2981	2982	2983	2984	2985	2986	2987	2988	2989	2990	2991	2992	2993	2994	2995	2996	2997	2998	2999	3000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																												

CHAPTER 3

The Miocene-Quaternary chemical diversity of mafic volcanism in the Andean Transitional Volcanic Zone (34°-38°S): new spatio-temporal constraints on the signature of metasomatized subcontinental lithospheric mantle

Benjamin H Chilson-Parks^{1*}, A. E. Saal¹, F. Calabozo², S. Mallick¹, J. Blusztajn³, A. Wulff⁴, F.A. Frey⁵

¹Brown University, Providence, Rhode Island, United States

²Universidad Nacional de Río Negro, General Roca, Argentina

³Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, United States

⁴Western Kentucky University, Bowling Green, Kentucky, United States

⁵Massachusetts Institute of Technology, Cambridge, Massachusetts, United States

***email: Benjamin_Chilson-Parks@brown.edu**

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0.) Abstract

The transitional Southern Volcanic Zone (TSVZ) in South America represents a region of uniquely voluminous basaltic volcanism formed during the Cenozoic. Back-arc volcanism that has occurred in the TSVZ constitutes a geochemically diverse suite of alkaline volcanic products, the petrological origins of which have been proposed to reflect contributions from the melts of metasomatic cumulates that reside in the subcontinental lithospheric mantle. This study presents new major and trace element and Sr, Nd, Pb and Hf isotope and Ar-Ar age data from a sample suite of 179 lavas and tephras from the TSVZ with the goal of more clearly resolving the geochemical signature of metasomatized SCLM in the TSVZ mantle source. Using geochemical data reported here and in previously published studies of TSVZ volcanism, we employ a principal component analysis (PCA) to identify variations and endmembers present in the incompatible trace element (ITE) and radiogenic isotope contents of mafic TSVZ volcanism. PCA results indicate that while the contributions of slab-derived materials explain most of the variance in ITE and isotope variations, TSVZ back-arc samples with weakest slab input also exhibit patterns that reflect the melting of amphibole and/or phlogopite—phases that would be associated with veined cumulated in the SCLM. PCA results also show a close resemblance between samples exhibiting this SCLM signature and the compositions of melt pockets associated with hydrous mineral assemblages in Patagonian mantle xenoliths. The TSVZ lavas that show the strongest affinity to melt pockets date to the Early Miocene and Plio-Quaternary, suggesting that the SCLM cumulate signature has persisted for at least 24 million years. Most of these lavas occur between 69° and 70°W, but other lavas with this geochemical affinity have erupted along the northeastern and southeastern margins of the back-arc region. The Pleistocene Cerro de la Laguna basanite has anomalously low silica contents,

LILE and HFSE-enriched trace element contents, and MORB-like Hf and Nd isotope contents, which distinguish it from other back-arc lavas as a low-degree melt of a SCLM cumulate source with residual amphibole and/or phlogopite. These results add support to the role of metasomatized SCLM as a significant contributor to melt generation in a continental back-arc setting.

1.) Introduction

The subcontinental lithospheric mantle (SCLM) represents the melt-depleted keel of a continental plate that is cooler and more rigid than the underlying convecting asthenosphere (e.g., Hawkesworth et al., 1999). Xenoliths that sample SCLM show that the SCLM are compositionally modified by the metasomatic fluids and/or melts that move through it (e.g., Pearson et al., 2014 and references therein). Metasomatism can not only enrich SCLM in incompatible trace elements, but also modify its modal assemblage by precipitating such phases as amphibole, phlogopite, clinopyroxene, and apatite. Much of this metasomatism likely occurs when low-degree, volatile-enriched melts percolate and crystalize (e.g., Bodinier et al., 1987; Harte et al., 1993; Nielson and Wilshire, 1993; Nielson and Noller, 1987; Wilshire, 1987). The presence of these crystallized products of metasomatism lowers the temperature necessary for melting to occur within the SCLM. At upper mantle pressures (1.5-3 GPa), anhydrous harzburgite will melt at >1400°C (Parman and Grove, 2004), whereas peridotite containing amphibole and/or phlogopite is expected to have a solidus at 1150-1200°C (Condamine and Médard, 2014; Condamine et al., 2016; Pilet et al., 2008; Sorbadere et al., 2013). Therefore, if metasomatized SCLM experiences heating- and/or decompression-induced melting, the consumption of metasomatic phases will have the strongest influence on the composition of the melt. Previous workers have

postulated that the melting of veined cumulates formed during SCLM metasomatism plays an important role in the generation of alkaline magmas in continental and oceanic settings (Dai et al., 2014; Foley, 1992; Halliday et al., 1995; Ma et al., 2011; Mayer et al., 2014; Panter et al., 2006; Pilet, 2015; Pilet et al., 2011; Pilet et al., 2008).

The back-arc of the Andean Southern Volcanic Zone (SVZ) represents a continental setting where widespread Cenozoic alkaline volcanism has taken place. Since the Jurassic, this region of South America has experienced the opening of the southern Atlantic Ocean to the east and the development of the proto-Pacific convergent margin to the west (Franzese and Spalletti, 2001; Ramos, 1999; Rapela et al., 1998; Rapela et al., 2005), during which periods of mafic magmatism have occurred and are expected to have metasomatized the SCLM. Moreover, mantle xenoliths from this region show evidence of metasomatism, both in their enriched trace element patterns and the presence of amphibole and phlogopite (Bertotto et al., 2013; Bjerg et al., 2005; Bjerg et al., 2009; Laurora et al., 2001; Rivalenti et al., 2007). Nonetheless, the petrogenetic link between SCLM metasomatism and alkali basalt volcanism in the SVZ back-arc has remained ambiguous.

In this study, we aim to resolve this ambiguity in the Transitional SVZ (TSVZ, ~34°S-38°S (Figure 1), where some of the most voluminous basaltic SVZ magmatism has occurred in the SVZ over the Cenozoic (Ramos and Folguera, 2011). We present new major and trace element, Sr-Nd-Pb-Hf isotope, and Ar-Ar age data for over 180 predominantly basaltic samples from the TSVZ, the majority of which represent monogenetic eruption centers in the back-arc. With the addition of this new geochemical dataset, there exists major and trace element concentration and isotope content data available for hundreds of additional TSVZ lavas, which permit a statistically-driven characterization of the different components contributing to the TSVZ mantle source.

2.) Geologic background

In the TSVZ region, the subducting slab of the Nazca plate, aged at ~ 25 Ma (Tebbens et al., 1997), is bounded by the Mocha fracture zone to the north and the Valdivia fracture zone to the south. Overlying sediments on the subducting Nazca plate are predominantly terrigenous material transported by river from the western Andes (Lamy et al., 1998), and include hemipelagic clays and turbiditic sands (Völker et al., 2008).

Magmatism in the TSVZ back-arc dates back to at least the Upper Cretaceous (Kay et al., 2006a). By ~ 27 Ma, volcanic front lavas in the Chilean Cordillera Principal developed calc-alkaline & tholeiitic magmatism with strong arc signature, as represented by the Abanico and Farellones formations, which previous workers suggest developed coeval with the development of extensional intra-arc basins (Charrier et al., 2002; Kay et al., 2005). Lower Miocene alkali basaltic volcanism developed in the TSVZ back-arc in the Fortunoso, Palaoco, Huantraico, la Matancilla, and Punta del Agua areas (Dyhr et al., 2013a; Dyhr et al., 2013b; Kay and Copeland, 2006). The prevalence of intraplate trace element signatures in the basalts of these areas coincided with lithospheric extension and a normal angle of subduction. At ~ 18 Ma, arc volcanism began to expand east into the TSVZ back-arc, causing widespread high-K, calc-alkaline volcanism with arc-like trace element patterns. Within the period of 8-4 Ma, volcanism expanded hundreds of kilometers east of the trench, as far as Sierra de Chachahuén at $\sim 37^\circ\text{S}$, Plateado volcano at $\sim 35.5^\circ\text{S}$, and the Diamante volcano at $\sim 34.5^\circ\text{S}$ (Folguera et al., 2009; Kay et al., 2006b; Litvak et al., 2015; Ramos et al., 2014). This expansion of arc volcanism is attributed to a transient episode of shallow slab subduction in the late Miocene-early Pliocene TSVZ (Kay et al., 2006a; Kay and Copeland, 2006; Ramos et al., 2014; Spagnuolo et al., 2012).

Subsequently, this shallow subduction episode was followed by the alkali basaltic volcanism of the Plio-Quaternary Payenia volcanic province, which coincided with the development of an extensional tectonic regime (Kay et al., 2006a; Llambías et al., 2010; Ramos and Folguera, 2011). Previous studies of Payenia lava petrogenesis document a range in the geochemical signal of slab-derived materials (e.g., Bertotto et al., 2009, Kay et al., 2013, Søgner et al., 2013, 2015a, Søgner and Holm, 2013, Jacques et al., 2013), such that lavas from the Nevado-Diamante (ND) area of Payenia in the north and the Tromen-Buta Ranquil (TBR) area of Payenia in the south have the strongest arc signature in their trace element patterns and isotope contents. The volcanism of the south-central (SC) area of Payenia (consisting of the Llanquanelo, Payún Matrú, Río Colorado, and Auca Mahuida volcanic fields) have weaker arc signature, with compositions that more closely resemble intraplate basalts.

While some previous studies attributed the intraplate signature of Payenia basalts to the melting of a hybridized peridotite-pyroxenite asthenosphere (Søgner and Holm, 2013; Søgner et al., 2013; Søgner et al., 2015a; Søgner et al., 2015b), other work proposed contributions from metasomatized SCLM as a melt source of Patagonian intraplate basalts, as well as monogenetic eruptive centers within the volcanic front of the Andean magmatic arc (Chilson-Parks et al., *in prep*; Gorrington et al., 2003; Hickey et al., 1986; Hickey-Vargas et al., 2016; Jacques et al., 2013; Kay et al., 2013; Søgner et al., 2018). Most recently, Chilson-Parks et al. (*in prep*) has shown that in addition to generating Payenia basalts with an intraplate signature, Payenia lavas with an arc signature can be attributed the melting of SCLM cumulates formed from an asthenospheric melt with arc signature. This arc-type cumulate signature is also identified in basanitic olivine hosted melt inclusions from the Diamante area of Payenia (chapter 2). What remains unresolved is whether this cumulate

signature is present in Miocene TSVZ back-arc lavas. Forward approaches to predicting the composition of melts of metasomatic cumulate include geochemical modeling (e.g., Chilson-Parks et al., *in prep*, Pilet et al., 2011), melting experiments (e.g., Condamine and Medard, 2014, Medard et al., 2006, Pilet et al., 2008, Sorbadere et al., 2013), and observation of natural mantle rocks. The most direct observations we have of these melts are parcels of glass preserved interstitially in the metasomatic veins of mantle xenoliths. In the SVZ back-arc, vitrified melt pockets associated with amphibole and/or phlogopite in mantle xenoliths have been identified in the Gobernador Gregores locality (Aliani et al., 2009; Gorrington and Kay, 2000; Laurora et al., 2001; Scambelluri et al., 2009). These melt pockets have been analyzed for their major and trace element contents, to which we can compare the compositions of mafic TSVZ lavas. These available data and lingering uncertainties prompt our investigation, which aims to evaluate the geochemical signature SCLM melting among the mafic ($\text{MgO} > 5 \text{ wt.}\%$) volcanism of the Miocene-Quaternary TSVZ.

3.) Analytical methods and literature data sources

3.1) Major and trace elements

Whole-rock major element oxide concentrations were measured by X-ray fluorescence (XRF) spectrometry at the University of Massachusetts, Amherst, and at Washington State University. Samples analyzed in each lab are indicated in Table 1. At UMass, whole-rock major element oxides (SiO_2 , TiO_2 , Al_2O_3 , FeO^T , CaO , MgO , MnO , K_2O , Na_2O , and P_2O_5) and some trace elements (Cr, V, Ni, Zn, and Ga) were measured by an automated Siemens XRF spectrometer. Measurement precision in all measurements yielded $<2\%$ RSD (2σ) for duplicated sample analyses except for MnO ($<3\%$) and Na_2O

($\leq 6\%$). Cr, V, Ni, Zn, and Ga concentrations were also measured by XRF, yielding significantly higher standard deviations, especially for Ni concentrations that are < 50 ppm in some samples.

XRF analyses of the same set of major and trace elements were performed at the Peter Hooper GeoAnalytical Lab, Washington State University by a ThermoARL Advant'XP+ sequential XRF spectrometer, which operated at 60 kV and 60 mA. Sample preparation, analytical procedure, and accuracy and precision is detailed in Johnson et al. (1999). To monitor instrumental drift, analyses of GSP2, BCR-1, and AGV-2 standards were performed every 24-48 hours, with a precision of 0.1-0.5% RSD. Analyses of duplicate beads made from the same unknown sample whole-rock powder had a reproducibility of $< 1\%$ RSD for all major elements, except FeO^T ($< 1.4\%$). For the trace elements measured by XRF, duplicate reproducibility was $< 10\%$, except for Ga ($< 15\%$). Statistics of duplicate analysis precision and detection limits (2 sigma) of the GeoAnalytical Lab XRF are reported in Table 2a.

For all samples, the remaining trace elements (Sc, Rb, Sr, Y, Zr, Nb, Cs, REE, Th, U, Hf, Ta, Pb) were measured by inductively coupled plasma-mass spectrometry (ICP-MS) using an Agilent 7700 quadrupole mass spectrometer at WSU on Li-tetraborate fused beads. Reproducibility over the course of the analyses was assessed by repeatedly measuring the compositions of an international rock standard (BCR-2, $n=54$), an in-house standard (TED, $n=33$) as unknowns among the samples. Precision yielded $< 5\%$ RSD (2σ) for most elements except for Pb in BCR-2 ($< 8\%$) and Cs in TED ($< 12\%$). In addition to monitoring trace element reproducibility with the BCR-2 and TED standards, trace element concentrations of an alkaline basalt sample from the Nevado volcanic field were measured five times during the course of the analyses, yielding $< 6\%$ RSD (2σ) for most elements

except for Pb (<28%) and Sc (<8%). Reproducibility over the course of the analyses was assessed by repeatedly measuring the compositions of an international rock standard (BCR-2, n=54) and an in-house standard (TED, n=33) as unknowns among the samples. Precision yielded <5% RSD (2σ) for most elements except for Pb in BCR-2 (<8%) and Cs in TED (<12%). Statistics of duplicate analysis precision and detection limits (2 sigma) of the GeoAnalytical Lab ICP-MS are reported in Table 2b.

3.2) *Sr, Nd, Pb, and Hf isotopes*

The Sr, Nd, Hf, and Pb isotopic compositions of reported samples are presented in Table 3. The majority of the reported isotope data were measured at the Mass Spectrometer Analytical Facility, Brown University. A subset of samples was analyzed for Sr, Nd, and Pb isotope contents by TIMS at the Massachusetts Institute of Technology and another subset by MC-ICP-MS at the Woods Hole Institution of Oceanography.

Sr, Nd, and Pb isotope chemistry and measurements at MIT consisted of the following procedure. Powdered samples were first dissolved in HF+HNO₃ and HCl in Teflon beakers on a hotplate. Prior to column chemistry, aliquots of Sr, Nd, and Pb for each sample were dissolved in 3.5N HNO₃, 3N HCL, and 1.1N HBr, respectively. Sr was isolated and collected using Sr-spec^R resin on a Teflon microcolumn, and the REE fraction was collected using standard cation chromatography. Sm and Nd fractions were collected using a HDEHP-on-Teflon column after the methods of White and Patchett (1984). The Pb fraction was collected using standard HBr techniques. Analyses were conducted using single Ta filaments for Sr isotopes and triple and single Re filaments for Nd and Pb isotopes, respectively, on a VG Sector 54 TIMS. Sr and Nd analyses occurred in dynamic multicollector mode and Pb analyses in static multicollector mode. ⁸⁷Sr/⁸⁶Sr and ¹⁴³Nd/¹⁴⁴Nd ratios were corrected for instrumental mass fractionation to ⁸⁸Sr/⁸⁶Sr =

0.1194 and $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$, respectively, with an exponential law. Replicated measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ standard NBS-987, with accepted value of 0.71024, yielded an average of 0.7102410 ± 0.000009 (2σ , $n = 35$). Replicated measurements of the $^{143}\text{Nd}/^{144}\text{Nd}$ standards La Jolla Nd and AMES Nd, with the accepted value of 0.512115, yielded averages of 0.511847 ± 0.000010 (2σ , $n = 25$) and 0.511906 ± 0.000010 (2σ , $n = 41$), respectively. Pb isotope analyses were corrected 0.12%/amu for instrumental mass fractionation determined from replicate analyses of standard NBS-SRM-981. Error for Pb analyses is 0.05%/amu (i.e., 0.10% for $^{207}\text{Pb}/^{204}\text{Pb}$, 0.15% for $^{208}\text{Pb}/^{204}\text{Pb}$, and 0.20% for $^{208}\text{Pb}/^{204}\text{Pb}$) due to fractionation correction uncertainty. The standard deviation of measurements during one run for each sample (i.e., internal precision) is less than the standard deviation of all the measurements of the standard sample (i.e., external precision), with the exception of the internal precision of $^{208}\text{Pb}/^{204}\text{Pb}$ being 0.40%.

Details of the analytical techniques used to measure the Sr, Nd, and Pb isotope data collected on the Thermo Scientific Neptune MC-ICP-MS at WHOI can be found in Workman et al. (2004) and Hart et al. (2002).

For the analyses conducted at Brown, isotope data was collected on a Thermo Scientific Neptune Plus MC-ICP-MS. Sr, Nd and Hf were introduced in the plasma using a PFA nebulizer with a flow rate of ~ 70 $\mu\text{l}/\text{min}$ coupled with a glass spray chamber, while Pb was introduced with an APEX-IR introduction system to enhance the sensitivity. The mass spectrometer was equipped with an H-skimmer cone and H-sampler cone. The baseline measurement was taken at -0.5 amu. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, and $^{176}\text{Hf}/^{177}\text{Hf}$ ratios were corrected for instrumental mass fractionation to $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$, respectively, with an exponential law. Pb solution was spiked with NBS SRM-997 Tl standard prior to analysis with a Pb/Tl

= 4 to correct for the mass fractionation using an exponential law with $^{203}\text{Tl}/^{205}\text{Tl} = 0.418922$. Sr, Nd, and Hf were measured at 200 ppb concentration whereas Pb was measured at 75 ppb concentration level.

Replicated measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ standard NBS-987, with accepted value of 0.71024, yielded an average of 0.710246 ± 0.000019 (2σ , $n = 75$). Replicated measurements of the $^{143}\text{Nd}/^{144}\text{Nd}$ standard JNd-I, with the accepted value of 0.512115, yielded an average of 0.512093 ± 0.000015 (2σ , $n = 104$). Replicated measurements of the $^{176}\text{Hf}/^{177}\text{Hf}$ standard JMC-275, with the accepted value of 0.282160, yielded an average of 0.282152 ± 0.000011 (2σ , $n = 89$). Replicated measurements of the standard NBS 981 for $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$, which have accepted values of ratios are reported relative to the 16.9356, 15.4891, 36.7006, respectively (Todt et al., 1996), yielded averages of 16.9329 ± 0.0009 , 15.4864 ± 0.0009 , 36.6828 ± 0.0030 (2σ , $n = 75$), respectively. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios are reported relative to the NBS 981 standard with $^{206}\text{Pb}/^{204}\text{Pb} = 16.9356$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4891$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7006$ (Todt et al., 1996). $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and Pb isotope ratios of samples are reported relative to the NBS SRM 987, JNd-i, JMC-475, and NBS 981 standards, respectively.

The internal precision is 5-10 ppm for Sr and Nd, 20-45 ppm for Pb and 20-30 ppm for Hf, while the external precision over the course of two years is 27 ppm for Sr (2σ , $n=75$), 29 ppm for Nd (2σ , $n=104$), 39 ppm for Hf (2σ , $n=89$) and 100 ppm for Pb isotopes (2σ , $n=75$). Procedure blanks were <50 pg for Sr and Pb and <30 pg for Nd and Hf. The USGS reference material BCR-2 and BIR-1 were processed during the sample preparation and measured with the same instrument set up, data for both are in agreement with the range reported in GeoRem database.

3.3) *Ar-Ar ages*

Dating using the $^{40}\text{Ar}/^{39}\text{Ar}$ method was conducted for 27 total samples in two separate analytical labs (Table 4). 24 groundmass samples were dated at the National Taiwan University. Samples were initially grounded, and fresh, phenocryst-free chips of groundmass were sieved in the size range of 140-250 μm . Chips were sonicated in distilled water and then dried, after which the freshest chips that lacked any visible alteration were hand-collected. On September 10, 2010, the samples and biotite standard LP-6 (Odin and Collaborators, 1982) were irradiated at the VT-C position in the THOR reactor in Taiwan. To monitor the neutron flux in the reactor, 3 6-10 mg aliquots of LP-6 were stacked together with the samples in each irradiation package that measured $\sim 9\text{cm}$ in length. Following irradiation, standards and samples were incrementally heated over the temperature range of 400°C - 1500°C in a double vacuum Mo resistance oven and an all-metal gas extraction system. The extracted gas was analyzed with a VG3600 mass spectrometer in the Department of Geosciences of National Taiwan University (<http://argonlab.gl.ntu.edu.tw/>). J-values were calculated using the Ar composition of biotite standard LP-6 with an $^{40}\text{Ar}/^{39}\text{Ar}$ age of 128.4 ± 0.2 Ma, which was calibrated using the age of from the Fish Canyon tuff, assuming that it has the same age as Fish Canyon sanidine, which has an age of 28.02 ± 0.28 Ma (Renne et al., 1998). Ages were determined from Ar isotope content after making corrections for mass discrimination, interference from other nuclear reactions, procedural blanks, and atmospheric Ar contamination. Integrated ages were then calculated as the summed heights of the peaks of each heating step. Errors were calculated from the square root of the sum of the squares in the error of the peaks at each heating step. Additional details of the analytical methods are available in Lo et al. (2002).

Three groundmass samples were dated in the Argon Geochronological Lab at Oregon State University. Groundmass chip crushing, sieving, cleaning, hand-picking, and leaching protocols can be found on <http://geochronology.coas.oregonstate.edu/>. Samples were irradiated in the OSU Radiation Center in the TRIGA experimental reactor. Reactor neutron flux was monitored using multiple standard samples (Mmhb-1 hornblende, FCT-3 biotite, TCR sanidine). Incremental heating age determinations were analyzed on a single collector Mass Analyser Products (MAP) Model 215-50 mass spectrometer. Details of analytical procedures, as well as the calculations and corrections used to determine sample ages, can be found in Duncan and Al-Amri (2013).

3.4) Literature data sources and sample groups

For the sake of simplicity, I list here the sample groups that I will be referring to in the following sections, as well as the literature references for previously reported geochemical data that will be considered in the following sections .

Nevado-Diamante (ND) area of Payenia

(Bertotto et al., 2009; Holm et al., 2016; Jacques et al., 2013; Murray, 2013; Søgner et al., 2013; Søgner et al., 2015a)

South-central (SC) area of Payenia

Llancanelo

(Dyhr et al., 2013a; Espanon et al., 2014a; Jacques et al., 2013; Søgner et al., 2013; Søgner et al., 2015a),

Payún Matrú

(Espanon et al., 2014a; Germa et al., 2010; Hernando et al., 2014; Jacques et al., 2013; Pasquarè et al., 2008; Søgner and Holm, 2013; Søgner et al., 2013),

Auca Mahuida and Río Colorado

(Bertotto et al., 2009; Jalowitzki et al., 2008; Kay et al., 2013; Pallares et al., 2016; Søager and Holm, 2013)

Tromen-Buta Ranquil (TBR) area of Payenia

(Jacques et al., 2013; Søager et al., 2013; Søager et al., 2015a)

Cerro de la Laguna

(Bertotto et al., 2009; Jalowitzki et al., 2008).

Miocene TSVZ back-arc

Palaoco and Fortunoso

(Dyhr et al., 2013a),

Huantraico and la Matancilla

(Dyhr et al., 2013b).

TSVZ volcanic front

(Davidson et al., 1988; Dungan et al., 2001; Ferguson et al., 1992; Holm et al., 2014; Jacques et al., 2013; Rodríguez et al., 2007; Ruprecht et al., 2012; Sellés et al., 2004; Tormey et al., 1995).

SVZ back-arc melt pockets from mantle xenoliths

(Aliani et al., 2009; Laurora et al., 2001; Scambelluri et al., 2009)

4.) Petrography

Mineral textures in the samples reported in this study are predominantly porphyritic and range from intergranular to subophitic with olivine, plagioclase, and clinopyroxene present as phenocrysts in variable proportions. The matrix is typically made up of plagioclase, clinopyroxene, and opaque phases.

Regarding the petrographic characteristics of specific localities in the study area, the two samples (16-1 and 16-2) from the Punta del Agua locality have olivine phenocrysts, some of which are > 0.7 mm, that exhibit extensive alteration to iddingsite. Other ND area samples have either olivine-dominant phenocryst assemblages or plagioclase- and clinopyroxene-dominant phenocryst assemblages. Quartz xenocrysts were identified in several ND area samples (16-1, 16-2, 18-7, 19-8, 27-150384, 83066, and 6-110384) and exhibit resorption, as most have clinopyroxene coronae. However, field observations indicate that quartz xenocrysts originated from quartzite exposed at the surface. These samples also do not show any clear distinctions in their chemical or isotopic composition that would indicate significant quartzite assimilation. These observations suggest that quartz xenocrysts were entrained in lavas at the surface during eruption.

Samples from Infiernillo are relatively phenocryst-poor, and some samples contain amphibole phenocrysts.

Llancanelo volcanic field lavas have similar petrographic traits to other Payenia lavas, and lack iddingsite. Sample 21-6 also contains a quartz xenocryst.

Payún Matrú volcanic field lavas exhibit olivine and plagioclase as dominant phenocryst phases, with some samples lacking clinopyroxene phenocrysts. Sample 22-5 contains a hornblende tonalite xenolith. Samples 25-10 and 26-2 are notable for containing more segregated vesicles than basalts from other localities. Río Colorado volcanic field lavas are dominated by olivine phenocrysts, with holocrystalline matrix textures.

Auca Mahuida samples contain matrix textures that range from holocrystalline in lavas to vitreous in tephra. Vesiculated and/or fractured samples contain zeolites and carbonates. Quartz xenocrysts have also been identified in some samples.

Samples from the TBR area show more compositional variability than samples from other Payenia localities. The most mafic lavas, such as those from Cochiquito and Barrancas, have olivine-dominant phenocryst assemblages, while more evolved TBR samples have a greater abundance of plagioclase and clinopyroxene phenocrysts.

Cerro de la Laguna sample CLA-009 contains peridotite xenoliths, as well as olivine and orthopyroxene xenocrysts. Olivine is the dominant phenocryst phase with clinopyroxene, plagioclase, apatite and other opaque phases in the matrix.

Lavas from volcanic front localities (Cerro Azul, Los Hornitos, and Nicanor) have olivine as the dominant phenocryst phase. Cerro Azul also has some clinopyroxene phenocrysts within a trachytic matrix texture. The Los Hornitos sample represents a fresh, thick lapilli scoria with some olivine-hosted melt inclusions in a primarily vitreous matrix.

5.) Results

5.1) Major elements

Samples reported in this study are mostly alkaline basalts and alkaline trachybasalts according to the classification of Le Bas et al. (1986) (Figure 2). In contrast, volcanic front lavas with $\text{MgO} > 5 \text{ wt.}\%$ from this region are subalkaline basalts, trachybasalts, basaltic andesites and basaltic trachyandesites. Samples from Cerro de la Laguna have distinctly low- SiO_2 compositions in the basanite field, with $>11\%$ nepheline in their CIPW norm assemblages. Similarly, lavas from Miocene localities Palaoco, La Matancilla, and Punta del Agua contain $>10\%$ nepheline in their CIPW norm assemblages.

Samples from SC Payenia and Nevado volcanic fields are predominantly nepheline-normative. Hypersthene-normative samples from these localities consist of six samples from the ND area (46, 16-4, 16-5, 16-6, 18-2, and CCH-005, with 0.6-5.4%

hypersthene and sample JAU-053, with 14% hypersthene) and two from the SC area (22-4 in the Llancanelo volcanic field, with 2.8% hypersthene sample AUC-035 in the Auca Mahuida volcanic field, with 1.5% hypersthene), all of which are alkaline basalts and trachybasalts. All reported samples from the volcanic front are hypersthene-normative ($>11.5\%$). Lavas from the Tromen-Buta Ranquil area display variable silica and alkali content and consist of both alkaline and subalkaline and nepheline- and hypersthene-normative compositions.

Intermediate and evolved back-arc lavas have been sampled from the Auca Mahuida and Payún Matrú calderas in the SC area (see external references in section 3.4) and the Malal Negro eruptive center (samples 22-1, 22-2, and 22-3, this study). Because of the evolved nature of the Malal Negro samples, they are not considered in our interpretations about the geochemical character of the TSVZ mantle source. These samples follow the differentiation trend of an alkali-rich magmas and range from trachybasalt to trachyte. The two Tromen samples 27-5 and 27-7 are a basaltic trachyandesite and a trachyandesite, respectively, and are both alkaline.

Back-arc lava major element variations generally follow trends indicative of magmatic differentiation: with decreasing MgO concentration, SiO₂, TiO₂, Al₂O₃, K₂O, and Na₂O concentrations increase (Figure 3). In contrast, FeO^T decreases moderately and, CaO and P₂O₅ concentrations do not vary with changing MgO. Much of the variation in major element content at MgO > 5 wt. % is similar to major element variations expected from olivine fractionation, as estimated by a 1 kb isobaric liquid line of descent calculated from the MELTS algorithm (Ghiorso and Sack, 1995). Most samples have MgO < 11 wt.%, lavas with MgO > 11 wt.% have Mg# > 75 , which is greater than the Mg# of primary mantle-derived melts (Mg# = 68-72, Roeder and Emslie, 1970) and likely a consequence

of olivine accumulation. Among separate localities within the back-arc, ND samples tend to have high MgO concentrations. Additionally, at MgO concentrations similar to other back-arc lavas, ND lavas have lower Al₂O₃ and TiO₂ concentrations. ND lavas also have a wider range of CaO, Na₂O and P₂O₅ than is predicted to result from olivine fractionation. Hy-norm ND samples have higher SiO₂, lower TiO₂, lower CaO and CaO/Al₂O₃, and lower K₂O than ne-norm Nevado samples.

Miocene samples closely resemble the major element concentrations of younger back-arc lavas, except for exhibiting lower Al₂O₃ concentrations at similar MgO concentrations. The Two early Miocene samples from the Punta del Agua locality (samples 16-1 and 16-2, reported in this study), exhibit similar

Although back-arc lavas tend to be more MgO-rich than volcanic front sample compositions, when compared at similar MgO concentrations back-arc lavas tend to have lower SiO₂, higher TiO₂, FeO^T, Na₂O, K₂O, and P₂O₅ concentrations. Samples from the Tromen-Buta Ranquil area tend to have major element compositions intermediate between those of other back-arc lavas and volcanic front lavas, such that the Tromen samples have high SiO₂ and low TiO₂, CaO, FeO^T, and MgO concentrations similar to volcanic front lavas. Nepheline normative sample 27-4 from Buta Ranquil has the low SiO₂ and high TiO₂, CaO, FeO^T and MgO of other Payenia lavas. This variation in major elements of TBR lavas likely reflects a mixing relationship between a differentiated hy-norm Tromen magma source and a primitive, ne-norm magma source (see Chilson-Parks et al., *in prep*).

5.2) Compatible Trace Elements

Back-arc samples comprise positive correlations between Ni, Cr and MgO concentrations for MgO > 4%, and these trends resemble predicted olivine fractionation trends. At MgO <~7 wt.%, Sc and V concentrations and CaO/Al₂O₃ both decrease--trends

which are likely caused by clinopyroxene fractionation. At similar MgO concentrations to other back-arc samples, SC area and Miocene lavas exhibit higher concentrations of Ni, Cr, and Zn and lower V and Sc.

5.3) Incompatible trace elements

Primitive mantle-normalized trace element patterns of selected TSVZ lavas are compared in Figure 4. As noted from previous work, back-arc lavas at similar MgO concentrations exhibit significant variability in trace element patterns, ranging from patterns akin to those of intraplate basalts, with low U/Nb, Ba/Nb, and Pb/Ce, to patterns that reflect a stronger arc signature. Despite these differences, a common feature of Miocene and Plio-Quaternary basalts and trachybasalts from all back-arc localities is positive Sr and P anomalies.

Both hy- and ne-norm samples from the ND area have a relatively strong arc signature among Plio-Quaternary back-arc samples, as indicated by an enrichment in Rb, Ba, Th, and U, a negative Nb-Ta anomaly, and a positive Pb anomaly. The two hy-norm Tromen samples also exhibit a trace element arc signature, but at higher incompatible trace element concentrations. This trait may be a consequence of the differentiated character of this sample, as well as a negative Ba anomaly and positive Zr-Hf anomaly. Some SC area Payenia samples exhibit a less pronounced arc signature (e.g. Llancanelo sample 21-4, Figure 4), while others lack a negative Nb-Ta anomaly and have a negative Pb anomaly. These features that are indicative of an intraplate trace element signature (e.g. Auca Mahuida sample PM1, Figure 4).

Among Miocene samples, younger (~8 Ma) lavas have a stronger arc signature than Early Miocene lavas (Dyhr et al., 2013a). Miocene lavas with an intraplate signature are enriched in highly incompatible trace elements relative to Plio-Quaternary lavas with an

intraplate signature. Early Miocene lavas are characterized by a prominent positive Ba anomaly and a negative U-Th anomaly. These trace element patterns are similar among Early Miocene basalts from the Punta del Agua, Fortunoso and La Matancilla localities.

Melt pockets in mantle xenoliths from Gobernador Gregores (GG) (Laurora et al., 2001; Scambelluri et al., 2009) have trace element patterns that resemble an exaggerated version of the trace element patterns of Early Miocene lavas, with moderate-to-dramatic enrichments in Nb and Ta, positive Ba and Sr anomalies, and enrichments in K, LREEs and MREEs relative to TSVZ lava. GG melt pockets also have negative U-Th anomalies, and those with extreme Nb-Ta enrichments also exhibit negative Zr-Hf and Ti anomalies.

5.4) Sr, Nd, Pb and Hf Isotopes

Volcanic front and back-arc samples exhibit essentially the same range in Sr and Nd isotope contents (Figure 5A). Low $^{87}\text{Sr}/^{86}\text{Sr}$ and high $^{143}\text{Nd}/^{144}\text{Nd}$ values of TSVZ lavas overlap with MORBs from the Discovery- and Shona-affiliated segments of the Mid-Atlantic Ridge and neighboring aseismic ridges. Among back-arc samples, Cerro de la Laguna lavas have the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 0.7030) and highest $^{143}\text{Nd}/^{144}\text{Nd}$ values (~ 0.5129). Hy-norm ND area basalt sample JAU-053 has the highest $^{87}\text{Sr}/^{86}\text{Sr}$ and lowest $^{143}\text{Nd}/^{144}\text{Nd}$ of TSVZ lavas. Other hy-norm ND lavas also extend towards higher $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{143}\text{Nd}/^{144}\text{Nd}$ values than ne-norm ND lavas. The high- $^{87}\text{Sr}/^{86}\text{Sr}$ and low- $^{143}\text{Nd}/^{144}\text{Nd}$ values of TSVZ lavas overlaps with values for Chile trench sediments (Jacques et al., 2013; Lucassen et al., 2010) and EM-1 type OIBs (data taken from GEOROC, <http://georoc.mpch-mainz.gwdg.de/georoc/>).

All samples have greater $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values than the Northern Hemisphere reference line (NHRL, Figure 5B-C; Hart, 1984). Volcanic front samples have Pb isotope contents that closely resemble those of Chile trench sediments and have greater

$^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ than back-arc samples. The majority of the back-arc samples constitute linear trends $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$, which suggests mixing controls the Pb isotopic variability of the back-arc samples. The back-arc Pb isotope array, which is generally subparallel to the NHRL for both $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$, does not trend toward Pb isotope contents of Pacific MORBs, indicating that Pacific upper mantle did not influence the melt source of mafic magmatism in this area, as has been previously noted (Jacques et al., 2013; S ager and Holm, 2013). Similarly, Pb isotope contents of back-arc samples do not trend toward the high- $^{208}\text{Pb}/^{204}\text{Pb}$ isotope contents of EM-1 OIBs. Instead, this array trends between the more radiogenic values of the volcanic front lavas and Chile trench sediments and less radiogenic South Atlantic MORBs with Discovery and Shona isotopic affinities.

In this array, ND and TBR samples tend to have relatively radiogenic Pb and SC area and Miocene lavas generally have the least radiogenic Pb of the back-arc. Infiernillo samples have highly radiogenic Pb isotope contents that equal and exceed those of volcanic front and trench sediment samples. Huantraico samples have less $^{208}\text{Pb}/^{204}\text{Pb}$ at similar $^{206}\text{Pb}/^{204}\text{Pb}$ to the back-arc array, and Cerro de la Laguna sample CLA-009 has less $^{207}\text{Pb}/^{204}\text{Pb}$ at similar $^{206}\text{Pb}/^{204}\text{Pb}$ to the back-arc array, as indicated by $\Delta 7/4 = 5$, the lowest value of the sample suite.

While Lower Miocene lavas share a similar range in $^{206}\text{Pb}/^{204}\text{Pb}$ Pb with SC area Payenia samples, SC samples tend to have lower $^{208}\text{Pb}/^{204}\text{Pb}$ (i.e., lower $\Delta 8/4$, Figure 5D). Nevado, Buta Ranquil, and Tromen samples also have lower $\Delta 8/4$ values ($\Delta 8/4=27-38$, except Nevado sample 24, with $\Delta 8/4=54$) than those of SC area Payenia samples ($\Delta 8/4=\sim 35-47$). This difference in $\Delta 8/4$ between back-arc localities highlights the trend of

Nevado samples toward a lower low- $^{208}\text{Pb}/^{204}\text{Pb}$ mixing endmember than that of the SC area Payenia samples.

Comparing the Nd and Hf isotope contents of volcanic front and back-arc samples reveals a clear distinction between these two groups (Figure 5D). While they generally overlap in their range of $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, volcanic front lavas have higher $^{176}\text{Hf}/^{177}\text{Hf}$ ratios than most back-arc samples. This positions the volcanic front $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ values along and above the Nd-Hf isotope mantle array (Chauvel et al., 2008), such that $\Delta\epsilon_{\text{Hf}} = 0-2$ for these samples. Back-arc samples have Nd and Hf isotope contents along and below the mantle trend ($\Delta\epsilon_{\text{Hf}} = -4-0$), forming an array roughly subparallel to the field of volcanic front values. SC area lavas tend to have lower $\Delta\epsilon_{\text{Hf}}$ values than samples from the ND and TBR areas. Miocene Punta del Agua sample 16-1 has the largest negative deviation from the mantle array ($\Delta\epsilon_{\text{Hf}} = -4$).

5.5) *Ar-Ar ages*

$^{40}\text{Ar}/^{39}\text{Ar}$ ages for 27 samples from the TSVZ back-arc are presented in Table 4. For samples from the SC area of Payenia, plateau ages range from ~2.3 Ma to 0.1 Ma in the Payún Matrú volcanic field 1.8 to 0.5 Ma in the Llanquanelo volcanic field and an age of 732 ka for Río Colorado sample MOR-021. These ages are comparable to previous ages of lavas from the 373 ka Pampas Onduladas flow (Espanon et al., 2014b), as well as the Auca Mahuida volcanic field (2.03 - 0.99 Ma, Kay et al., 2013; Rossello et al., 2002) and the Río Colorado volcanic field (2.26 - 0.34 Ma, Kay et al., 2006a; Gudnason et al., 2012).

ND and TBR area samples show larger ranges, with ND lavas dating to 3.1-0.5 Ma (except for sample 19-7 dating to 6.7 Ma), and TBR dating to 2.9-0.9 Ma (except for sample 26-12 dating to 5.8 Ma). Cerro de la Laguna sample dates to 354 ka, in stark contrast with the previous estimation of a Miocene age of eruption (Bertotto et al., 2009), which was

based on lithostratigraphic observations. Except for one ~6 Ma age from each area, these dates constrain magmatism to the last ~3 Ma in the ND and TBR areas, which is similar to constraints for SC area lavas.

Early Miocene sample 16-1 from the Punta del Agua locality has an age of 23.4 Ma, which is comparable to the Early Miocene ages of basalts from the Fortunoso area (20.8 Ma, Dyhr et al., 2013a) and the La Matancilla area (24.2-21 Ma, Dyhr et al., 2013b). We take note of this similarity in age even though Punta del Agua basalts erupted along the eastern margin of the TSVZ back arc, ~150 km northeast of the Fortunoso lava flows and ~175 km northeast of La Matancilla.

Other Miocene lavas, which erupt from the Fortunoso, Palaoco, and Huantraico areas, erupted significantly later (17.9-17.6 Ma for Huantraico and 8.6-7.5 Ma for Fortunoso and Palaoco, Dyhr et al., 2013a; Dyhr et al., 2013b).

6.) Discussion

6.1) The role of fractional crystallization and crustal contamination in the composition of TSVZ lavas

Prior to making interpretations regarding the mantle source characteristics of TSVZ volcanism, we first account for the influence of shallow level processes, such as fractional crystallization and crustal contamination, on sample compositions. Petrographic observations show olivine, plagioclase and clinopyroxene in variable amounts as phenocrysts, meaning that these phases may have affected compositions during fractional crystallization. By considering only data that have MgO>5 wt.%, we have minimized the possibility that clinopyroxene and plagioclase fractionation significantly modified the primitive characteristics of the trace element contents we investigate. Furthermore, lavas

that have $\text{MgO} > 5\%$ generally conform to major element concentration patterns that are consistent with fractionation dominated by olivine, which would have the general effect of enriching lavas in all incompatible trace elements in similar proportions, maintaining incompatible trace element ratio values. V and Sc concentrations do display a positive correlation with CaO, an expected outcome of clinopyroxene fractionation given the compatible behavior of V and Sc in clinopyroxene (Hart and Dunn, 1993). Although this may demonstrate that clinopyroxene fractionation may affect TSVZ lavas, this process is assumed to have little effect on the highly incompatible trace element contents of TSVZ lavas discussed below.

Because TSVZ volcanism erupted through > 35 km of continental crust (Gilbert et al., 2006), the role of crustal contamination must also be considered. The majority of samples reported in this study have high MgO concentrations (> 5 wt.%), meaning that these samples probably did not experience significant contamination by felsic crustal material. Nonetheless, if crustal contamination occurred to such a limited degree that it did not modify major element concentrations, variations in trace element ratios and isotope contents may give a better indication of this possibility.

A possible exception are hy-norm ND lavas, which exhibit higher SiO_2 , lower TiO_2 , lower CaO and $\text{CaO}/\text{Al}_2\text{O}_3$, and lower K_2O than ne-norm Nevado samples, as well as lower $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ values. The intermediate to felsic igneous complexes of the Permian-Triassic Choiyoi Group comprise a large portion of the crystalline basement in our study region (Kleiman and Japas, 2009; Llambías et al., 2003; Rocha-Campos et al., 2011), making it a potential assimilant in Cenozoic TSVZ magmatism. However, evolved ($\text{SiO}_2 > 70\%$) Choiyoi samples exhibit low Ti/Gd and high Pb/Ce, U/Nb, K/La, and Ba/Rb ratios--traits not present in ND lava compositions.

Nevertheless, the differences between hy-norm and ne-norm ND lavas may suggest different melting conditions: experimental evidence shows that lower melting pressures can yield hy-norm lavas (Kinzler and Grove, 1992; Kushiro, 1968; Stolper, 1980). If hy-norm compositions reflect lower melting temperatures, they may also reflect AFC processes associated with the nearby Nevado stratovolcano. Søger et al. (2013) proposed that ND lavas experienced as much as 70% contamination by plagioclase-bearing mafic lower continental crust (LCC). They noted that high Ba/Th, Nb/U, and Eu/Eu* values in ND lavas trend toward the global average composition of LCC (Rudnick and Gao, 2014). These authors also attributed enrichments in Ba, K, Sr, and Eu to the contribution of plagioclase to the melts. 70% assimilation of LCC would be expected to substantially increase SiO₂ and produce intermediate to felsic magmas, which are not present in the ND sample suite.

Another detail that lessens the possibility of substantial plagioclase assimilation or interaction concerns the typically ¹⁸O-enriched character of LCC xenoliths relative MORBs (Kempton and Harmon, 1992). While ND area $\delta^{18}\text{O}_{\text{olivine}}$ values are high relative to those of other back-arc samples (see results of Chilson-Parks et al., *in prep*), these values are within the range expected of normal mantle olivine $\delta^{18}\text{O} = 5.0\text{-}5.4\text{ ‰}$ (Eiler, 2001; Matthey et al., 1994), and thus do not show the magnitude of ¹⁸O enrichment predicted by the amount of LCC contamination determined] by Søger et al. (2013). Mafic LCC xenoliths of the nearby Mesoproterozoic Precordillera (Kay et al., 1996) have significantly higher Pb/Ce and Sm/Nd and lower Nb/Ta values than ND samples. Additionally, when ¹⁴³Nd/¹⁴⁴Nd values are compared to Sm/Nd ratios of Nevado samples, ND sample isotope contents do not form a clear binary mixing trend toward Precordillera xenolith isotope contents.

Therefore, if some crustal contaminant did influence the compositions of hy-norm ND samples, its composition has not yet been clearly identified. Because hy-norm ND lavas maintain primitive major element contents (e.g., $\text{MgO} > 7.4 \text{ wt.}\%$ and $\text{SiO}_2 < 52.7 \text{ wt.}\%$), the amount of crustal material that would have contaminated the ND source would have to be small. The close resemblance of trace element patterns of ne-norm and hy-norm ND samples also complicates efforts to characterize a potential contaminant. For the broader suite of samples with $\text{MgO} > 5 \text{ wt.}\%$, the lack of correlations between major elements and isotope contents and relevant trace element ratios suggests negligible influence from crustal contaminants.

6.2) Evaluating mantle source endmembers using principal component analysis

Assuming that crustal-level processes have minimal effect on the compositions of TSVZ samples with $\text{MgO} > 5 \text{ wt.}\%$, we can use the compositions of such samples to ascertain the nature of the mantle source controlling geochemical variations present across the TSVZ. Towards the goal of better identifying source heterogeneities present in the mantle, we have used principal component analysis (PCA) to evaluate the trace element and isotope systematics of primitive ($> 5\% \text{ MgO}$) lavas from the volcanic front and back-arc of the TSVZ. Previous studies of geochemical datasets have used PCA to understand better the petrogenesis of basaltic lavas on regional and global scales (Allègre et al., 1987; Allègre et al., 1995; Saal et al., 2001). This approach has the potential of revealing significant compositional variations simultaneously among several variables, such as trace element ratios or isotope systems.

Using the dataset reported in this study, as well as previously published data for basaltic lavas from the TSVZ volcanic front and back-arc, as well as the GG melt pockets (from sources listed in section 3.4), we performed two different PCAs: one for radiogenic

isotope (Sr, Nd, Hf, ^{206}Pb , ^{207}Pb , ^{208}Pb) systematics and the other for ITE (Rb, Ba, Th, U, Nb, K_2O , La, Ce) systematics. We use these particular geochemical variables in order to focus our approach on assessing the character of the mantle source, and to test whether melt pockets in metasomatized mantle xenoliths represent a compositional endmember. ITE and radiogenic isotope contents are largely unaffected by variable degrees of melting, meaning that the variations that they do exhibit likely reflect heterogeneities in the melt sources of the lava samples. We consider ITE contents as ratios with Nb as the common denominator. Use of a common denominator in all ITE ratios implies that mixing relationships in Cartesian diagrams constitute straight lines in Cartesian plots.

Following the approach outlined by Allègre et al. (1995), all data used in the PCA calculations were first normalized to the standard deviation of the data for each variable, and then weighted by a correction factor (Table 5). This correction factor of a given variable is the ratio of the total concentration range divided by the absolute analytical error (i.e., the relative analytical error values from Table 2 multiplied by the average concentration for each variable). Application of correction factors means that the ITEs or isotopes exhibiting larger concentration ranges will have a larger influence on the principal components. Among the previously published geochemical data considered for PCA, many lacked data for one or multiple ITEs or isotope ratios. Any sample that lacked values for at least one ITE was excluded from the PCA. The same criterion was applied to the PCA of isotopes.

A PCA was performed using ITE ratios from 521 TSVZ lavas and 4 GG melt pockets that have all been petrographically associated with metasomatic amphibole (Laurora et al., 2001). This PCA has >95% of the total variance explained by the first three principal components (PC1, PC2, and PC3), of which PC1 explains 90%, PC2 explains

5%, and PC3 explains 3%. Loading factors for all trace element ratios, represented by blue arrows in Figure 6, all point in the positive PC1 direction. PC1 scores for volcanic front lavas are exclusively positive, whereas melt pocket, ND area, SC area, and Miocene sample compositions have increasingly negative PC1 scores in that order. U/Nb and Th/Nb have high loading factors in the positive PC2 direction, whereas Rb/Nb, K₂O/Nb, and Ba/Nb have high loading factors in the negative PC2 direction. While volcanic front lavas compositions are dispersed in the PC2 direction, the majority of back-arc sample compositions trend from near-zero PC2 scores for GG melt pockets and Miocene and SC area samples to positive PC2 scores for ND area Payenia samples. Lastly, U/Nb has the highest loading factor in the positive PC3 direction, followed by Rb/Nb, K₂O/Nb, and Th/Nb. The remainder of the ITE ratios have similarly negative loading factors for PC3. Scores for VF sample compositions also show a dispersion in the positive and negative PC3 directions, and back-arc compositions trend from positive PC3 scores for Early Miocene samples and SC area Payenia samples to negative PC3 scores for ND area Payenia samples.

We also performed a PCA using the Sr, Nd, and Pb isotope data of 204 TSVZ samples (Figure 7, GG melt pockets have no isotope data). While 114 samples from the data compilation have measurements for Sr, Nd, Pb, and Hf isotopes, we did not consider Hf isotopes, because none of the Miocene samples had Hf isotope measurements. The isotope based PCA results also have >95% of the total variance explained by the first three principal components (PC1, PC2, and PC3), of which PC1 explains 89%, PC2 explains 6%, and PC3 explains 4%. ⁸⁷Sr/⁸⁶Sr, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb values correlate positively with both PC1 and PC2, ²⁰⁶Pb/²⁰⁴Pb correlates positively with PC1 and negatively with PC2, and ¹⁴³Nd/¹⁴⁴Nd correlates negatively with PC1 and PC2. PC1 scores for volcanic

front lavas are exclusively positive, whereas the majority of back-arc lavas are negative, of which SC area and some Miocene lavas have the most negative PC1 scores. ND area and VF samples have PC2 scores that range from ~0 to negative values. Most SC area samples have positive PC scores and exhibit a weak negative correlation with PC1.

Based on these results, increases in the PC1 direction for ITEs and isotopes clearly reflect an increase in input from slab-derived material in the mantle source. In this regard, samples from the Infiernillo area of the back-arc closely resemble mafic lavas from the volcanic front. This variation in slab-derived input may relate to the melting of the fluid-fluxed mantle wedge or to the melting of mantle lithosphere metasomatized by mantle wedge-derived melts, similar to the modeled arc-type cumulate component modeled in chapter 1. Given the use of Nb as a common denominator, variation in arc signature is expected to dominate the variations observed in ITE ratios, since Nb is depleted in arc lavas. Pb isotopes, which have the highest PC1 loading factors, show the clearest distinction between VF and back-arc samples.

Presumably, just as PC1 likely measures the arc signature in TSVZ lava compositions for isotope and ITE contents, other principal components represent other aspects of the TSVZ mantle source. The observation that some U/Nb and Th/Nb trend in the positive PC2 direction, while Rb/Nb, Ba/Nb and K₂O trends in the negative PC2 direction may offer some insight into the mineral phases controlling the ITE budget of the TSVZ mantle source. Melt-residue partitioning behavior of U, Th, Ba, Rb, and K should not vary significantly for a melt source consisting of olivine, pyroxene and garnet, since these ITEs are all highly incompatible in these mineral phases (Adam and Green, 2006; Hart and Dunn, 1993). In contrast, K is compatible in amphibole and phlogopite and Rb and Ba are compatible in phlogopite and moderately incompatible in amphibole, whereas

Th and U are highly incompatible in both phases (Dalpé, 1994; LaTourrette et al., 1995; Tiepolo et al., 2007).

Because the ITE ratios controlling variation in PC2 are consistent with the partitioning behavior of amphibole and phlogopite, decreasing scores in PC2 appear to reflect the increasing signal of melted amphibole and/or phlogopite, which we expect to represent metasomatized SCLM. Miocene and SC area Payenia samples constitute the lowest PC2 scores of back-arc lavas, suggesting that the consumption of amphibole and/or phlogopite played an important role in the petrogenesis of these lavas. Trace element patterns for SC area and Miocene lavas also display negative U-Th anomalies—an expected consequence of melting of amphibole and/or phlogopite-bearing lithologies (Foley et al., 1995; Förster et al., 2018; Pilet et al., 2008). Previous geochemical modeling indicated that SC area lavas represented melts in part from a SCLM cumulate from an EDMM-derived metasomatic agent (Chilson-Parks et al., *in prep*). These PCA results suggest that the EDMM-type cumulate signature identified in SC lavas is also associated with the compositions of Miocene back-arc lavas as well as the GG melt pockets. While the PC2 scores of the four melt pocket compositions are somewhat scattered, the three melt pockets with unexpectedly high PC2 scores have dramatically higher enrichments in Nb and Ta than the one melt pocket with PC2 $\approx$ 0. The low-PC2 melt pocket also differs from the other three in its high-Ti content, which was interpreted to represent modestly Nb-enriched, high-Ti amphiboles formed relatively deep in the SCLM during extensive metasomatism. Conversely, the highly Nb-enriched, low-Ti melt pockets represent amphiboles crystalized from shallow SCLM that was metasomatized by a smaller amount of a residual metasomatic agent (Laurora et al., 2001). We would expect alkali magma compositions to reflect the melting of the more thoroughly metasomatized base of the

SCLM, given that it would be closer to an asthenospheric heat source and would constitute a larger abundance of readily fusible, hydrous veined cumulates. Therefore, we find it reasonable to consider the one high-Ti melt pocket as a representative compositional endmember despite there being more analyses of the low-Ti melt pockets. While it explains less of the variance, PC3 for ITEs also shows that melt pocket compositions are closely associated with the compositions of SC area and Miocene lavas, with all three groups having positive PC3 scores. We require further consideration of the PC3 signal to determine why melt pockets and Miocene and SC area lavas have positive PC3 scores.

If the PC2 of the isotope PCA is also related to a SCLM source signature, it is not immediately apparent why $^{207}\text{Pb}/^{204}\text{Pb}$, which has the largest and most positive PC2 loading factor, would most strongly reflect the SCLM signature. Thoric Pb is not expected to exhibit ingrowth behavior distinct from uranic Pb in amphibole and phlogopite, since U-Th variations are not expected from partitioning between these phases and melt. The isotope ingrowth calculations reported by Chilson-Parks et al., *in prep* will need to be expanded upon to test whether isotopic ingrowth of radiogenic Pb is consistent with the results of PCA and its potential SCLM signature. We note that although Hf isotopes were not considered in this PCA, Miocene Punta del Agua sample 16-1 has the most negative $\Delta\epsilon_{\text{Hf}}$ value among TSVZ back-arc lavas, which supports the interpretation that Miocene lavas represent endmember composition

PC2 scores for the isotope PCA yield considerable scatter among Miocene lavas. This variability is likely due to Miocene lavas having both higher and lower $\Delta 7/4$ values than other back-arc lavas, whereas Miocene $\Delta 8/4$ values are consistently higher than other back-arc lavas. The small amount of Pb isotope data for Miocene lavas limits our

evaluation of this variability, which may not necessarily reflect the mantle source signal of Miocene basaltic volcanism.

This PCA approach may not be able to highlight all heterogeneities in the TSVZ mantle source. As the modeling in Chilson-Parks et al., (*in prep*) demonstrates, the cumulate signal in SC lavas is not just a cumulate signal, but rather an EDMM-type endmember of the SCLM cumulate source signal. ND area lavas exhibit an arc-type cumulate signal. Some TSVZ lavas may lack prominent Th-U depletions because the melts forming their cumulate source were enriched in Th and U by slab-derived sediments and fluids. In this case, arc-type cumulate melts would be more enriched in Th and U than SC area and some Miocene basalts because of the arc signature inherited from the asthenospheric melt that formed their SCLM cumulate source.

6.3) Other indications of the role of SCLM in TSVZ back-arc volcanism

Some of the geochemical characteristics highlighted by the ITE- and isotope-based PCAs are not definitive indicators of a SCLM cumulate signature in TSVZ lavas. Previous studies argue that SC are lavas that exhibit trace element and isotope contents akin to EM-1 ocean island basalts (Dyhr et al., 2013a; Dyhr et al., 2013b; Jacques et al., 2013; Kay and Copeland, 2006; Kay et al., 2013; S  ager and Holm, 2013; S  ager et al., 2013), and that this EM-1 source constitutes a peridotite-pyroxenite mixture of ascending asthenospheric mantle (S  ager and Holm, 2013; S  ager et al., 2015b). Gough Island OIBs, which represent an EM-1 endmember, have characteristically high $^{87}\text{Sr}/^{86}\text{Sr}$ and low $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$, as well as positive $\Delta 7/4$ and $\Delta 8/4$ at $^{206}\text{Pb}/^{204}\text{Pb}$ values similar to or lower than SC lavas (Willbold and Stracke, 2010; Zindler and Hart, 1986). Moreover, Gough basalts have similarly high Ba/Th, Nb/La, and Ce/Pb (Class and le Roex, 2008) compared to SC area lavas.

However, comparisons between these and other trace element ratios reveals that the TSVZ back-arc compositions diverge from EM-1 OIBs. TSVZ back-arc lavas do have comparable values of Ba/Th, Nb/La, Ce/Pb and Nb/Th to EM-1 basalts (Figure 8). However, TSVZ back-arc lavas trend to markedly higher U/Nb, K/La, Sr/Nd, and P/Nd than not only EM-1 basalts but also EM-2 and HIMU OIBs and South Atlantic and Pacific MORBs. These distinct trace element contents are not expected from varying degrees of melting, because each ratio pairs trace elements are expected to partition similarly during mantle melting. Additionally, neither slab-derived nor continental crust-derived inputs would cause this trend, given that TSVZ volcanic front lavas, Chile trench sediments, and continental crust xenoliths have low Ba/Th, Ce/Pb, Nb/Th, Nb/La, and P/Nd.

Alternatively, GG melt pocket compositions represent an endmember in the distinctive trends displayed by TSVZ back-arc lavas. Melt pockets, like the back-arc lavas, have high Ba/Th, K/La, Sr/Nd, Ce/Pb, and low U/Nb. In particular, the high-Ti melt pocket GG92, which was closely associated with Miocene and SC lava compositions in the PCA results, represents a high Ba/Th, Ce/Pb, K/La, Nb/La endmember of the trends formed by back-arc lavas. While P/Nd values are unavailable for GG melt pockets, we expect that the apatite likely to be present in SCLM cumulates would impart high P/Nd to the melt pockets associated with these metasomatic cumulates. Similar to these melt pockets, experimental melts generated from a clinopyroxene hornblendite (Pilet et al., 2008) exhibit high Ba/Th, Nb/La, and K/L. Therefore, the consideration of additional trace elements and alternative melt source inputs/contaminants leaves us with the same interpretations gleaned from the PCA results: melt pockets in Patagonian mantle xenoliths constitute a compositional endmember for TSVZ back-arc lava compositions and demonstrate that metasomatized SCLM played an important role in TSVZ melt generation.

The lack of melt pockets associated with hydrous phases in xenoliths from the TSVZ brings into question our ability to identify melt pockets as a “smoking gun” in TSVZ melt production. The mantle xenoliths that do occur in the TSVZ in the Agua Poca locality lack hydrous metasomatic phases; glass veins are present but too small to be measured by LA-ICP-MS. The lack of hydrous cumulates may result from a lack of modal metasomatism, or from melting to such a degree that the hydrous phases were consumed. Yaxley and Kamenetsky (1999) show evidence for the latter scenario in amphibole-free xenoliths from Australia, which contain glass patches and veins exhibiting amphibole-like trace element patterns. Moreover, the modeled melt compositions of Chilson-Parks et al., (*in prep*) indicate that amphibole is consumed during low degrees of melting ($F < \sim 7\%$), and that the modeled cumulate-derived melts that resemble Payenia basalts have no residual amphibole. Therefore, glass veins in Agua Poca xenoliths may have compositions that exhibits this hydrous cumulate signature without hydrous phases present in the xenolith.

6.4) *The unique composition of Cerro de la Laguna basanites*

Lavas from the Cerro de la Laguna locality are unique in their basanitic composition (Figure 2). The only other known occurrence of basanitic melts in the TSVZ occur as olivine-hosted melt inclusions from the ND area of Payenia (chapter 2, Brandt et al., 2017), which was attributed to the melting of SCLM metasomatized by a subduction-related agent. In contrast to these melt inclusions and to virtually all other TSVZ lavas, Cerro de la Laguna lavas have anomalously low Ba/Th, U/Nb, K/La, and high Ce/Pb (Figure 8). These trace element traits resemble OIB compositions, but their low Nb/Th and high P/Nd values and negative Ti anomalies are distinct from OIBs. Cerro de la Laguna lavas are also distinct in their Th and U enrichments and their negative K anomaly in PM-normalized trace

element patterns (Figure 9). The occurrence of a negative K anomaly has been observed in other continental intraplate lavas, and was attributed to the melting of a source with a K-rich residual phase, such as amphibole or phlogopite (Ma et al., 2011; Panter et al., 2006). Despite their differing trace element patterns, a similar process was posed as the origin of basanitic MIs from the ND area (chapter 2).

This possibility can be tested by considering the composition of melts sourced from amphibole and phlogopite-bearing cumulates, the modeling results of which are presented in Chilson-Parks et al. (*in prep*). Given that amphibole and phlogopite would need to remain in the melt residue during melting, melt fractions would have to remain low (i.e., $F < \sim 7\%$). As shown in Figure 9, the trace element pattern of Cerro de la Laguna lava resembles the 1-5% batch melt of a solid composition resembling a SCLM cumulate formed from a low-degree asthenospheric melt with EDMM composition. This cumulate, melted to this extent, still contains residual amphibole, phlogopite, and apatite, which allow for the enrichment in P and negative anomalies in K, Pb, and Ti.

The resemblance of Cerro de la Laguna basanites to modeled melts of an SCLM cumulate elicits multiple important insights. Firstly, because Cerro de la Laguna lavas are compositionally distinct from the rest of the observed TSVZ lava compositions they may be unique in representing a melt source that retained residual amphibole and phlogopite. In contrast, other TSVZ lavas that display a cumulate signature have enrichments in K and depletions in Th and U (Figure 4)—features indicative of melting of a source exhausted of amphibole and/or phlogopite.

Secondly, because SiO_2 concentrations are anomalously low, Cerro de la Laguna lavas may also be unique in representing minimal melting of and/or interaction with a peridotitic source lithology, from which SiO_2 enrichment of the melt would be expected.

Peridotite-hornblendite sandwich melting experiments demonstrate that the initial cumulate-derived melt can increase in SiO₂ by ~4-5 wt.% during interaction with peridotite (Pilet et al., 2008)—an increase similar to the difference in SiO₂ between Cerro de la Laguna lavas and other alkali lavas from the TSVZ back-arc. If Cerro de la Laguna lavas represent a low-degree melt of SCLM cumulate, then this may imply that melting occurred at relatively cool temperatures, which would limit chemical exchange with the surrounding peridotite.

Lastly, the distinct Nd, Sr, Pb and Hf isotope contents of Cerro de la Laguna Lavas (Figure 5) suggest that the origin of the SCLM cumulate melted to form these lavas differs from the SCLM cumulates that contributed to volcanism elsewhere in the TSVZ. The unique isotopic signature of Cerro de la Laguna lavas may indicate that its SCLM cumulate source underwent a different duration of ingrowth, and/or that the asthenospheric melts that precipitated the cumulate source had higher ¹⁷⁶Hf/¹⁷⁷Hf and ¹⁴³Nd/¹⁴⁴Nd and lower ⁸⁷Sr/⁸⁶Sr and ²⁰⁷Pb/²⁰⁴Pb values than the sources of other TSVZ lavas. These isotopic characteristics most closely resemble MORB values, which is consistent with Cerro de la Laguna lavas erupting far from the influence of slab inputs relative to other Quaternary lavas at 36-37°S.

6.5) Spatio-temporal distribution of TSVZ lavas

The Pleistocene age of Cerro de la Laguna lavas underscores the spatially- and temporally-widespread influence of the SCLM melt source in the TSVZ over the last 24 million years. As early as the Early Miocene, lavas from the eruptive centers of Punta del Agua, la Matancilla, and Fortunoso exhibit similar trace element patterns and radiogenic isotope contents. Furthermore, the similarity in trace elements and isotopes between Early Miocene lavas and the Plio-Quaternary SC area lavas, as demonstrated by the PCA results,

suggests that the metasomatic SCLM source that yielded Early Miocene basaltic volcanism has persisted for over 20 million years.

To demonstrate the compositional continuity of TSVZ lavas across time and space, Figure 10 compares Ar-Ar ages and sample longitude (a proxy for across-arc distance) to the trace element ratios indicative of the SCLM source component in mafic TSVZ lavas. Firstly, variations in these trace element ratios demonstrate that the EDMM-type cumulate signal exhibited by SC area and Early Miocene lavas does not decrease with increasing distance from the volcanic front. SC area and Miocene lavas as a group exhibit higher Nb/La, Nb/Th, Ce/Pb, and Ba/Th and lower U/Nb than the volcanic front and TBR lavas that erupted to the east and the ND area lavas that erupted to the west. Even though this EDMM-type cumulate signal is strongest at $\sim 69^{\circ}$ - 70° E, Punta del Agua and Auca Mahuida lavas exhibit high Nb/La, Nb/Th, and Ba/Th values, demonstrating that the cumulate signal extends into the northeastern and southeastern extents of the TSVZ back-arc. At a similar position as the SC area, electromagnetic observations have identified a region of high conductivity (Burd et al., 2014) that may be associated with the thermal anomaly heating and melting SCLM cumulates. The spatial concentration of lavas with the EDMM-type cumulate signal may be determined by the position of this potential thermal anomaly in the asthenosphere.

Age variations among back-arc lavas indicate that the EDMM-type cumulate signal is strongest in lavas erupted during two time periods: ~ 24 - 20 Ma and <3 Ma. The three Miocene lavas that erupted 18 - 7 Ma reflect the development of an arc signature in the TSVZ back-arc over this period, in that they have decreasing Ce/Pb, Nb/La, P/Nd, and Nb/Th, and increasing U/Nb, K/La, and Sr/Nd with decreasing age. Overlapping with this time period is the 13.7 - 3.8 Ma eastward expansion of calc-alkaline volcanism (Ramos et

al., 2014) that has been attributed to an episode of shallow slab subduction (Kay et al., 2006a; Kay and Copeland, 2006; Kay et al., 2006b).

Following this Late Miocene period of shallow subduction, ND and TBR lavas, which have 6.7 Ma-Prehistoric ages, exhibit stronger arc signatures than the older Miocene lavas and contemporaneous SC area lavas. As mentioned previously, the arc signature in TBR lavas represents a ne-norm Buta Ranquil melt. This melt lacks arc signature, having mixed with a melt with arc signature from the Tromen stratovolcano. It thus may not be indicative of the more primitive, ne-norm melt source in the TBR area. The spatial arc signature of the ND lavas versus the EDMM-type cumulate (i.e., non-arc) signature of SC lavas represent a chemical diversity that is observed in back-arc lavas prior to the shallow slab episode. The back-arc presence of lavas with arc signature does not imply that the melting processes that drive magma production in the volcanic front arc have remained the same during the transition to steeper slab subduction. Rather, the similarly high P/Nd and negative $\Delta\epsilon_{\text{HF}}$ values (Figure 5) shared between SC, and ND lavas indicate that ND lavas cannot be explained as lower-degree melts of volcanic front lavas, which lack high P/Nd and negative $\Delta\epsilon_{\text{HF}}$ values. These features of ND area lavas with arc signature were previously explained as the expression of mixing between an asthenospheric melt with arc signature and melt of a hydrous SCLM cumulate formed from a metasomatic agent with arc signature (Chilson-Parks et al., *in prep*). Moreover, the identification of basanitic, volatile-rich, olivine-hosted melt inclusions from the ND area is consistent with the melting of SCLM metasomatized by a subduction-related metasomatic agent (Chapter 2, Brandt, et al., 2017).

6.6) Implications for the history of melting metasomatized SCLM in the TSVZ

These spatio-temporal patterns provide constraints on when and where arc- and EDMM-type endmembers have contributed to TSVZ back-arc melt production and volcanism. Early Miocene and SC lavas demonstrate that EDMM-type cumulates have persisted as a melt source for at least 24 Ma throughout the SVZ back-arc. Because the ages of these lavas coincide with periods of slab rollback and lithospheric extension before and after Miocene shallow slab subduction (Kay et al., 2006a; Kay and Copeland, 2006), the melting associated with the EDMM-type geochemical signature is likely a result of changes in slab geometry. In this scenario, steepening of the subducting Nazca plate facilitates the asthenospheric inflow and lithospheric attenuation that leads to melting of metasomatized SCLM.

A different version of the EDMM-type cumulate signature is expressed in the basanites from Cerro de la Laguna. These trace element patterns indicate that the Cerro De la Laguna source experienced a degree of melting that did not reach amphibole-out, nor did the melt experience significant chemical interaction with the surrounding peridotite during ascent. The observation that the Cerro de la Laguna lavas are only found in one Pleistocene eruption locality on the northeastern margin of the TSVZ back-arc indicates that this the Cerro de la Laguna lava source does not influence the melt sources of other TSVZ back-arc lavas. Moreover, the peripheral location of these low-degree melts may reflect a thermal boundary in the asthenospheric mantle beyond which the SCLM is too cool to melt amphibole (~ 1050-1100°C, Holloway, 1973).

The <6.7 Ma ages of ND area lavas suggest that the arc-type cumulate signature appeared in the TSVZ back-arc more recently than the EDMM-type cumulate signature. This may be a consequence of sampling bias toward more recent volcanism, but if the arc-type cumulate signature is indeed a post shallow-slab phenomenon, this would be an

unexpected scenario. The TSVZ has experienced arc volcanism since the Mesozoic (Franzese et al., 2003; Kay et al., 2006a; Ramos and Folguera, 2005) and would likely experience metasomatism by subduction-related agents over this period. Additionally, previous calculations of Nd and Hf isotope ingrowth rates demonstrate that both EDMM- and arc-type cumulates may require 150-200 million years of isotopic ingrowth in order to develop the negative $\Delta\epsilon_{\text{Hf}}$ values characteristic of back-arc lavas. If arc-type metasomatism had taken place since this period, some mechanism or feature unique to the ND area may have preserved its arc-type cumulate signature. SCLM in the ND area may have been cooler and/or thicker than SCLM in the rest of the back-arc, which would have limited the heating and melting of metasomatic cumulates. Alternatively, isotopic ingrowth in metasomatized SCLM may not be the primary cause of negative $\Delta\epsilon_{\text{Hf}}$ values in back-arc lavas, in which case slab-derived material may have generated arc-type cumulates in the SCLM during the Miocene period of shallow slab subduction. In order to investigate these possibilities, we require additional investigation of variations in the geometry of the subducting Nazca slab as well as improved constraints on the thickness and thermal structure of the TSVZ SCLM .

7.) Conclusions

This study demonstrates that mafic volcanism from the TSVZ back-arc shows a geochemical affinity to mantle xenolith-hosted melt pockets associated with hydrous metasomatic minerals, and that this affinity dates back at least 24 million years. This affinity is strongest in the Early Miocene lavas of the Punta del Agua, Fortunoso, and La Matancilla areas and in the Plio-Quaternary lavas of the SC area of the Payenia volcanic province. These two periods of volcanism coincide with periods of a steepening subducting

slab and with lithospheric extension, which suggests that these processes are responsible for the asthenospheric upwelling that heats and melts the SCLM.

Although this affinity appears in disparate regions of the SVZ back-arc, the metasomatic cumulates contributing to TSVZ volcanism may not be homogeneous or experience the same melting conditions. The Cerro de la Laguna basanite exhibits compositional traits that have little in common with other mafic TSVZ back-arc lavas. Instead, it may reflect the low-degree melting of an EDMM-type cumulate with Sr, Nd, and Hf isotope contents that more closely resemble those found in MORBs. The anomalous nature of the Cerro de la Laguna basanite may be inherited from an SCLM cumulate source that formed separately from other SCLM cumulates in the TSVZ.

We also acknowledge that the arc-type cumulate signal previously identified in ND area lavas by Chilson-Parks et al. (*in prep*) remains poorly understood. Our study does not present a new approach to distinguishing the geochemical signature of a subduction-related SCLM cumulate from the signature of the subduction-influenced convecting mantle wedge. An important next step in characterizing SCLM melt contributions will require further investigation of the distinctive characteristics of arc-type SCLM cumulates and whether older back-arc basaltic lavas exhibit an arc-type cumulate signature similar to that of ND lavas.

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FIGURE CAPTIONS

Figure 3-1. A) Tectonic map of the Nazca-South America plates showing mid-ocean ridges (red lines), fracture zones (black lines) and subduction zones (orange lines with triangles). The black square marks the region displayed in part B. Velocity and convergence direction of the Nazca-South American plates taken from Kendrick et al. (2003). Abbreviations: CR: Chile Ridge, EPR: East Pacific Rise, MAR: Mid-Atlantic Ridge, TSVZ: Transitional Southern Volcanic Zone. B). Simplified geologic map of the TSVZ.

Figure 3-2. Total alkali-silica diagram (TAS, Le Bas et al., 1986) of TSVZ lavas from the volcanic front and back arc. Black dashed line separates the alkaline (above the line) from the subalkaline fields (MacDonald and Katsura, 1964). Data sources are listed in section 3.4. Smaller sample symbols of TSVZ lavas represent literature data.

Figure 3-3. Major element concentrations, in weight percent, of TSVZ samples. Hourglass symbols represent experimental melts of lower continental crust (Qian and Hermann, 2013) and of hornblendite, hornblende clinopyroxenite, and a peridotite-hornblendite sandwich charges (Pilet et al., 2008). Semi-transparent lines represent the fractionation trajectory expected from olivine crystallization. TSVZ data sources are listed in section 3.4. Smaller sample symbols of TSVZ lavas represent literature data.

Figure 3-4. Trace element concentrations of selected high-MgO TSVZ samples normalized to primitive mantle values from McDonough and Sun (1995).

Figure 3-5. Comparisons of radiogenic isotope contents. Chile trench sediments are from Lucassen et al. (2010) and Jacques et al. (2013). Peru-Chile trench sediments from Vervoort et al. (1999). MORB data from the Discovery and Shona segments of the southern Mid-Atlantic Ridge taken from Douglass et al. (1999) and Andres et al. (2002). Other southern MORB, and EPR MORB data from the compilation of Gale et al. (2013). Discovery seamount compositions from Schwindrofska et al. (2016). EM-1, EM-2, and HIMU OIB compositions from GEOROC (<http://georoc.mpch-mainz.gwdg.de/georoc/>). Precordillera crust xenolith compositions from (Kay et al., 1996) Grey dashed Northern Hemisphere Reference Line (NHRL) in the Pb-Pb plots and the formulation for $\Delta 7/4$ and $\Delta 8/4$ from Hart (1984). The green line representing the mantle array in the Nd-Hf isotope plot from Chauvel et al. (2008). TSVZ volcanic front and back-arc samples have MgO > 5 wt.%. Smaller sample symbols of TSVZ lavas represent literature data. Smaller sample symbols of TSVZ lavas represent literature data.

Figure 3-6. Results of the principal component analysis (PCA) of incompatible trace elements of TSVZ samples and melt pockets from SVZ mantle xenoliths. Coordinates of sample compositions in PC1 vs. PC2 and PC1 vs. PC3 space (i.e., sample scores) are shown by the same symbols as in previous figures. Smaller sample symbols of TSVZ lavas represent literature data. Unit vectors of each trace element ratio in PC1 vs. PC2 and PC1 vs. PC3 space are shown by blue arrows, beneath which all sample scores are represented by red dots. Smaller sample symbols of TSVZ lavas represent literature data.

Figure 3-7. Results of the principal component analysis (PCA) of isotope ratios of TSVZ samples. Coordinates of sample compositions in PC1 vs. PC2 and PC1 vs. PC3 space (i.e., sample scores) are shown by the same symbols as in previous figures. Unit vectors of each isotope ratio in PC1 vs. PC2 and PC1 vs. PC3 space are shown by blue arrows, beneath which all sample scores are represented by red dots. Note that melt pocket samples lack measurements of isotope contents. Smaller sample symbols of TSVZ lavas represent literature data.

Figure 3-8. Ba / Th vs U / Nb, K / La vs Nb / La, Ce/Pb vs Sr/Nd, and Nb/Th vs P/Nd. Note that melt pocket samples lack measurements of both P and Nd in the same sample. TSVZ volcanic front and back-arc samples have MgO>5 wt.%. Choiyoi crustal xenoliths from Llambías et al. (2003), and Las Matras block crustal xenoliths from Sato et al. (2000). Smaller sample symbols of TSVZ lavas represent literature data.

Figure 3-9. Primitive mantle-normalized trace element concentrations of Cerro de la Laguna sample CLA-009 and the modeled 1% and 5% melts sourced from a SCLM cumulate with residual phlogopite and amphibole. This modeled cumulate composition was formed from a metasomatic agent resembling a low-degree melt of EDMM. See modeling details in Chilson-Parks et al. (*in prep*). Normalization from McDonough and Sun (1995).

Figure 3-10. Comparison of Ar-Ar ages and sample longitude versus the trace element ratios considered in Figure 3-8 for TSVZ volcanic front and back-arc lavas. Symbols same as in previous figures.

FIGURES

Figure 3-1.

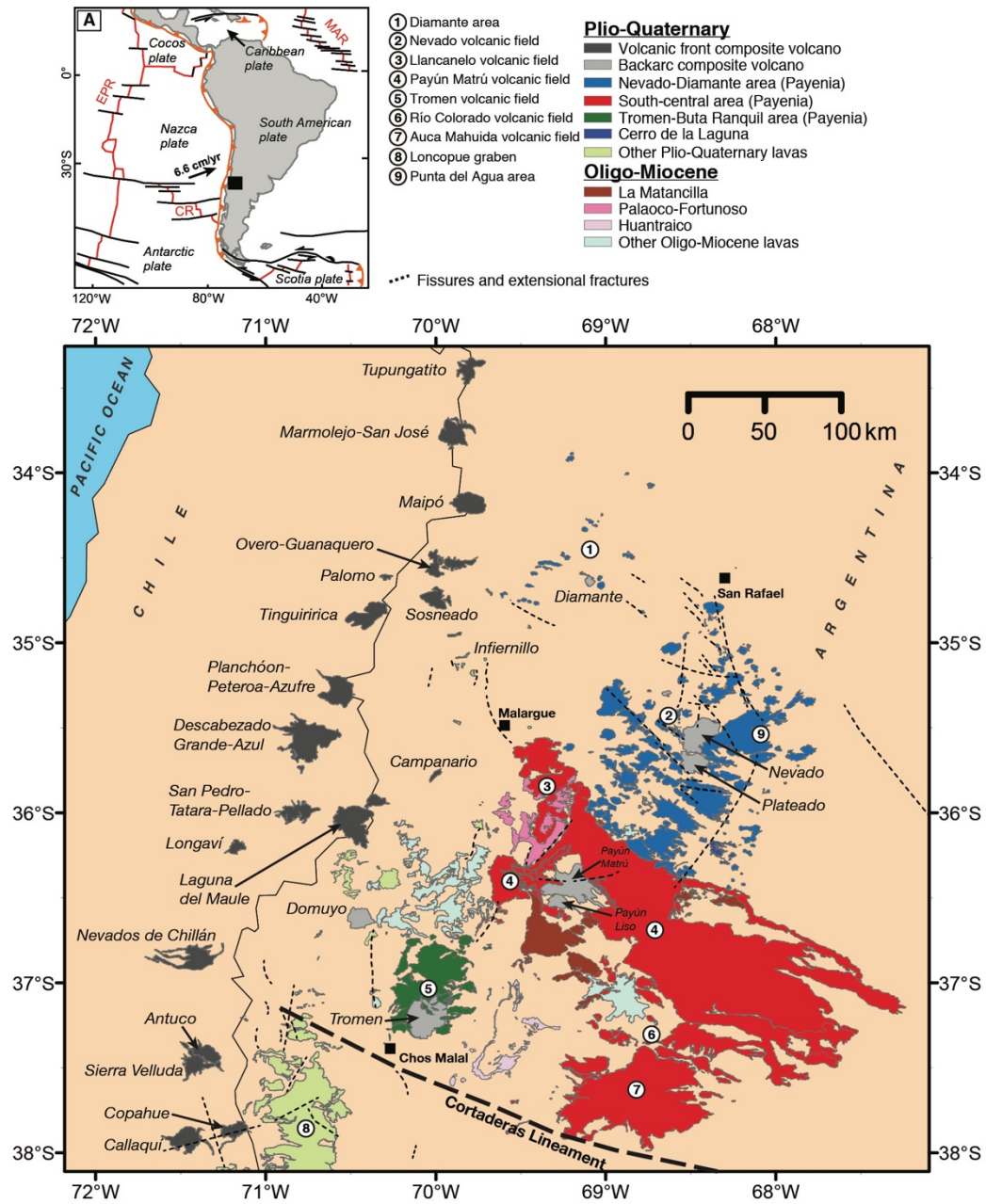


Figure 3-2.

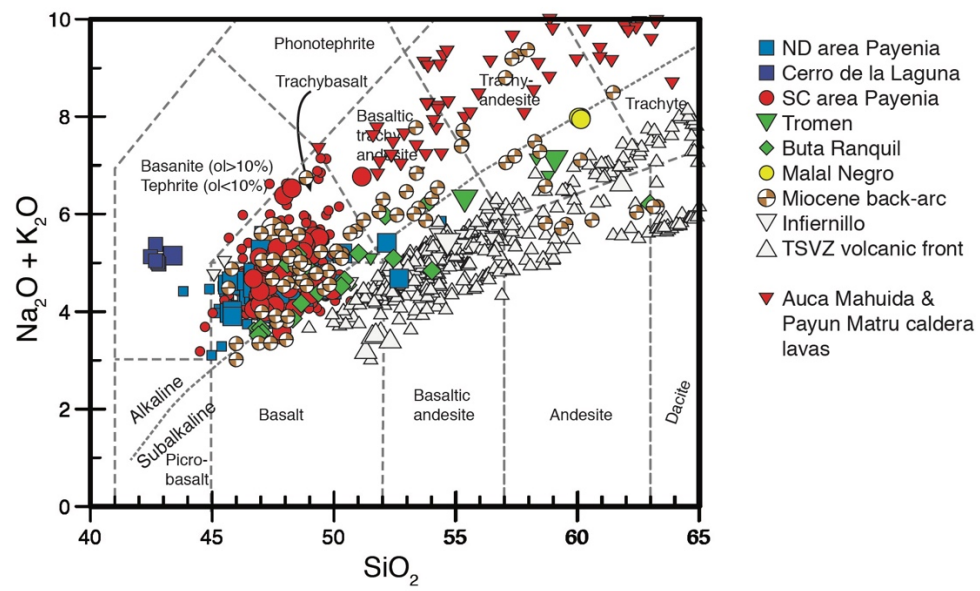


Figure 3-3.

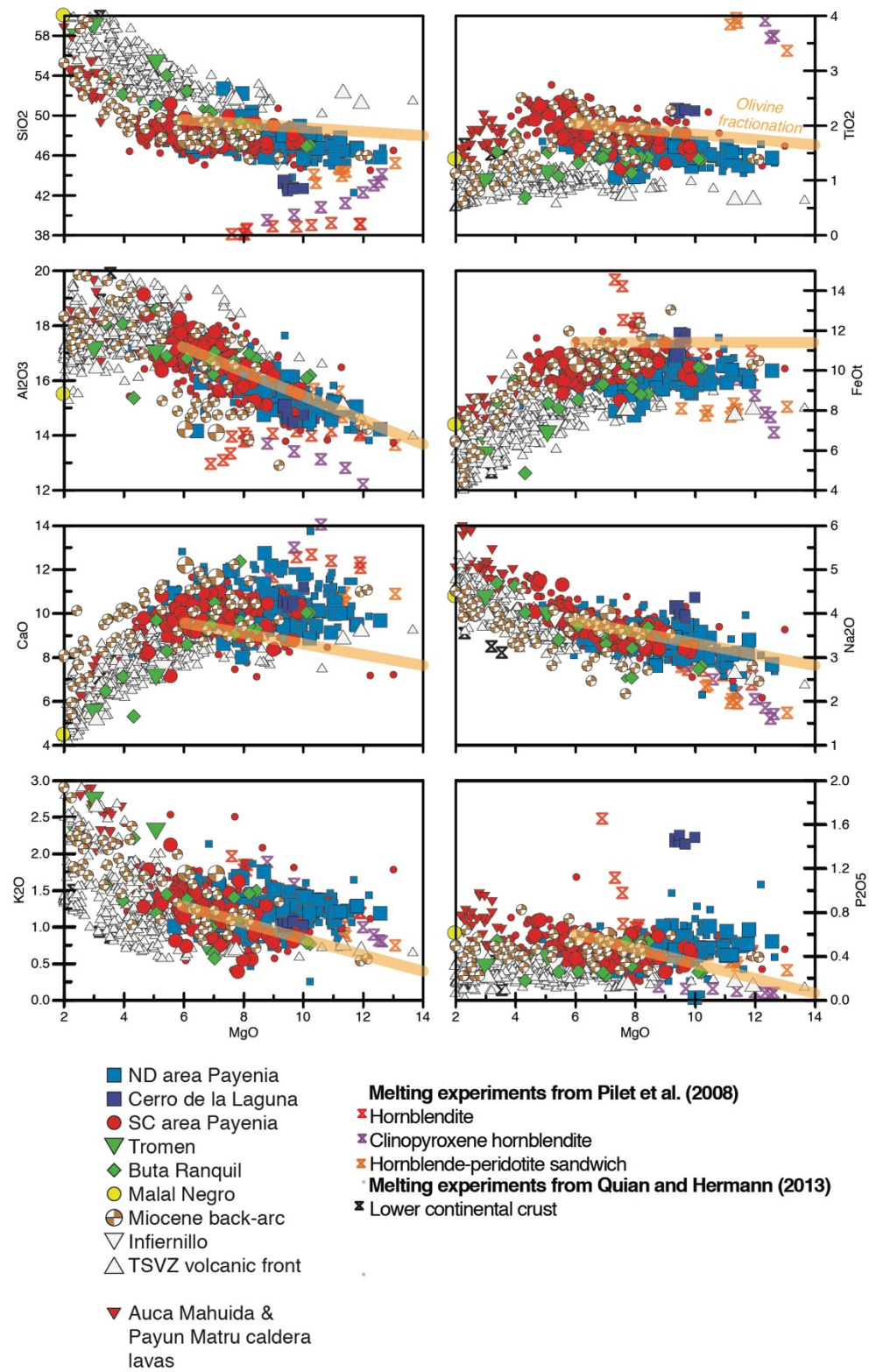


Figure 3-4.

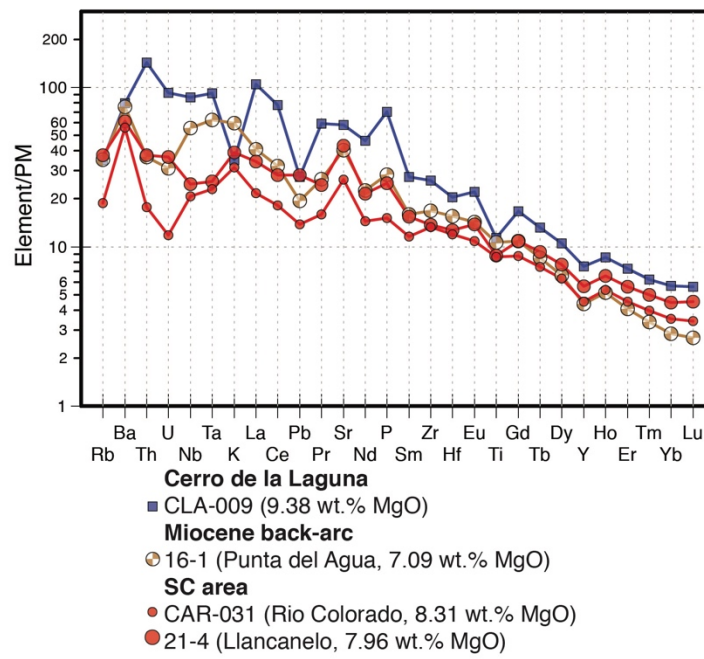


Figure 3-4 (continued).

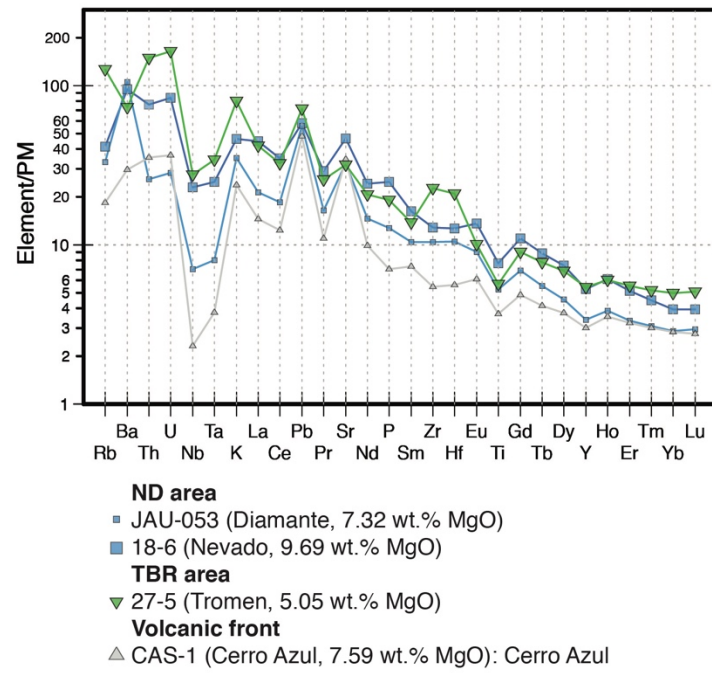


Figure 3-4 (continued).

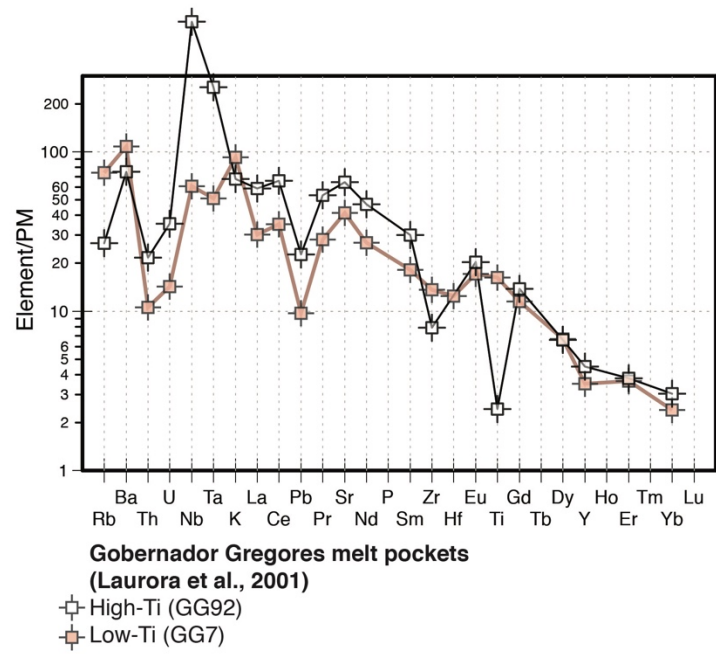


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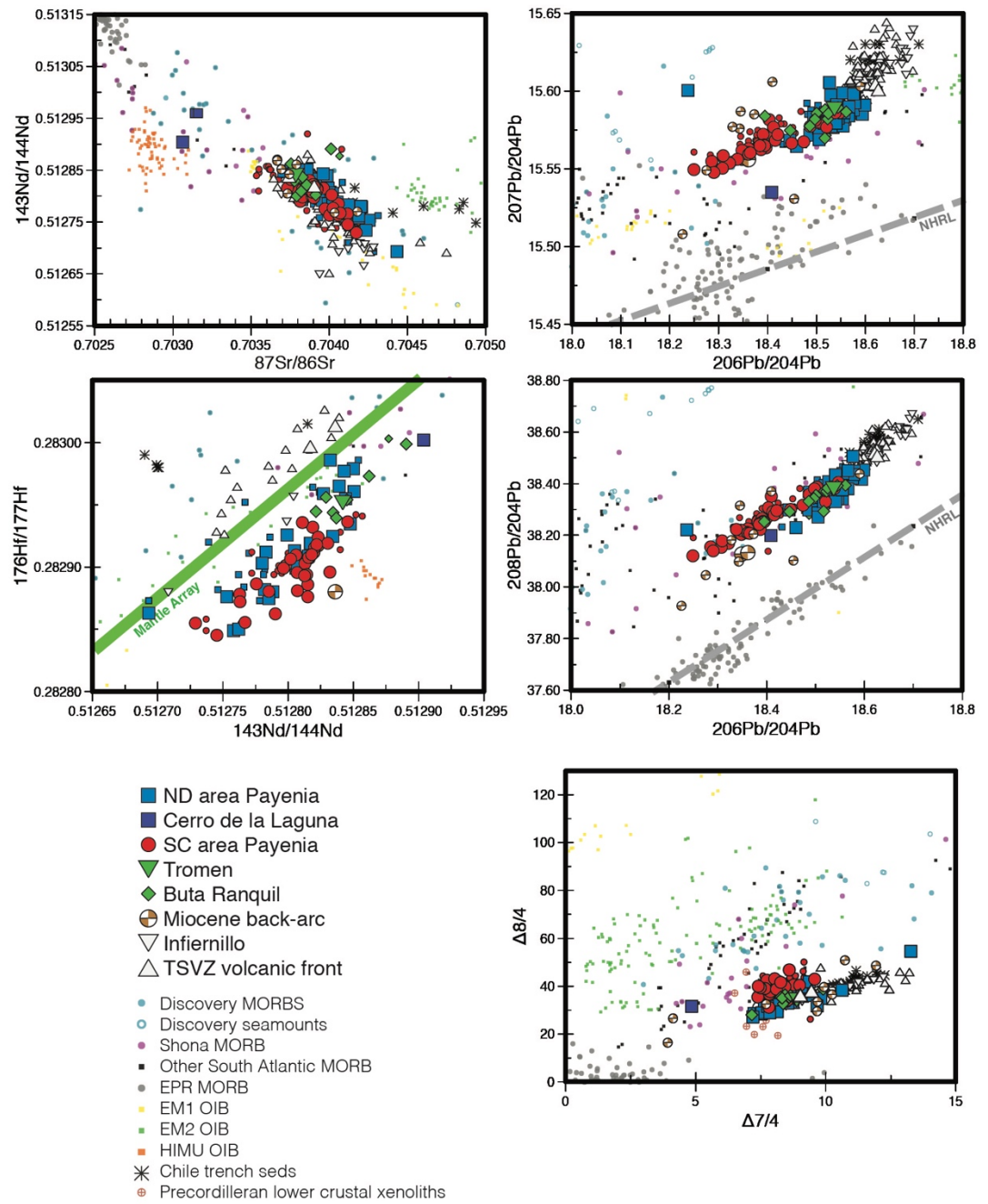


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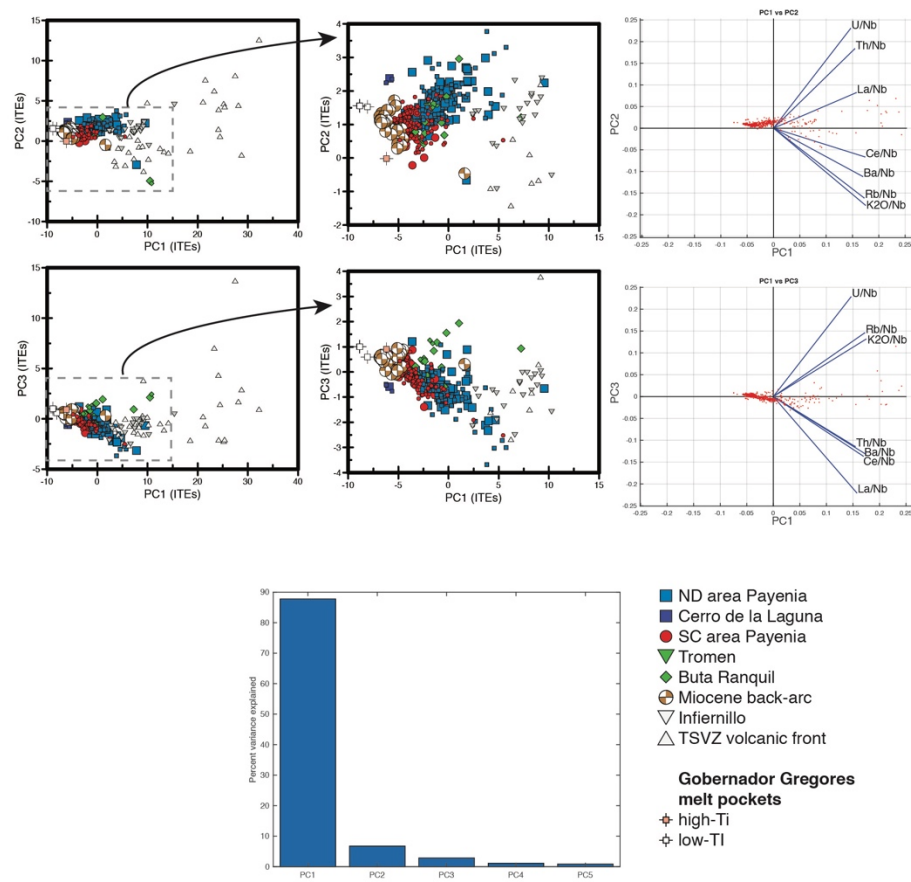


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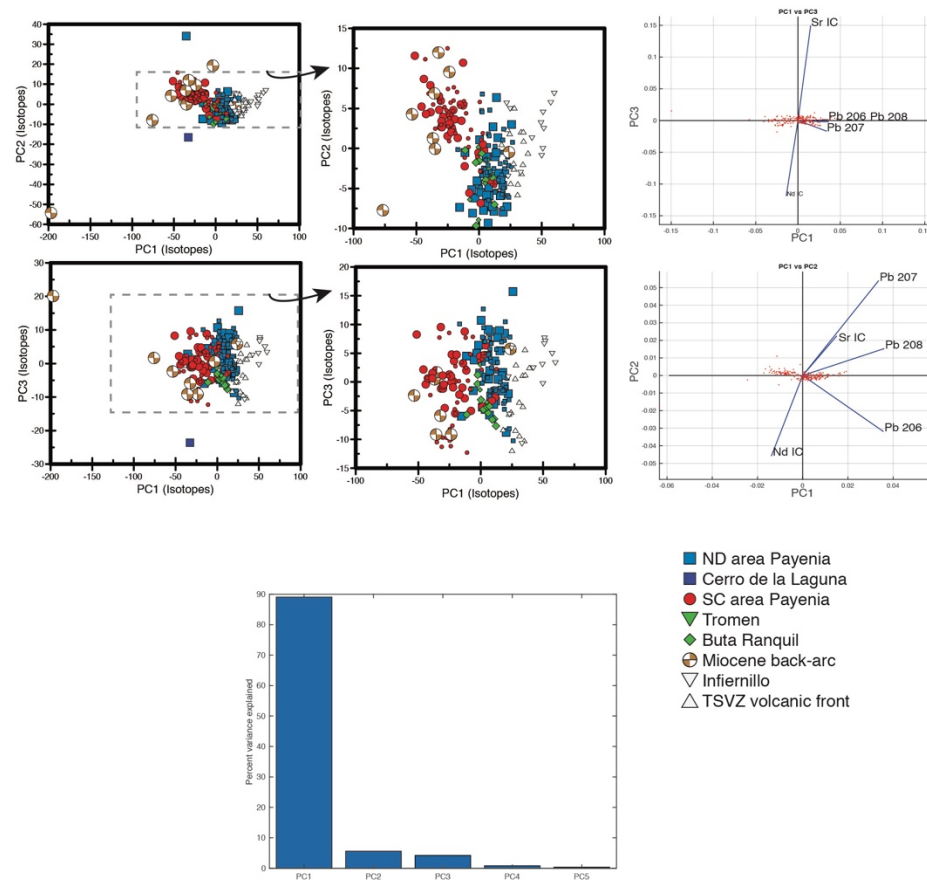


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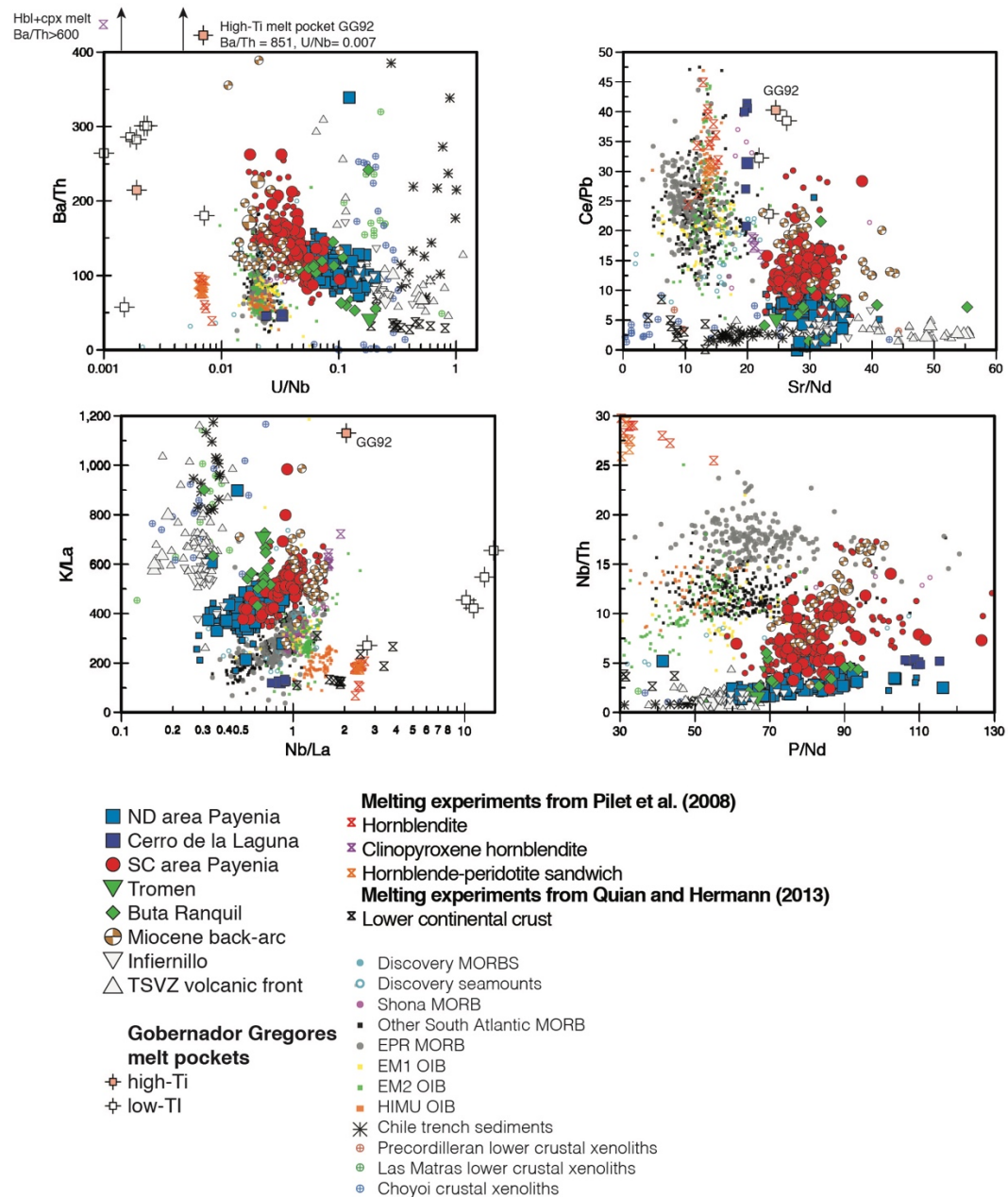


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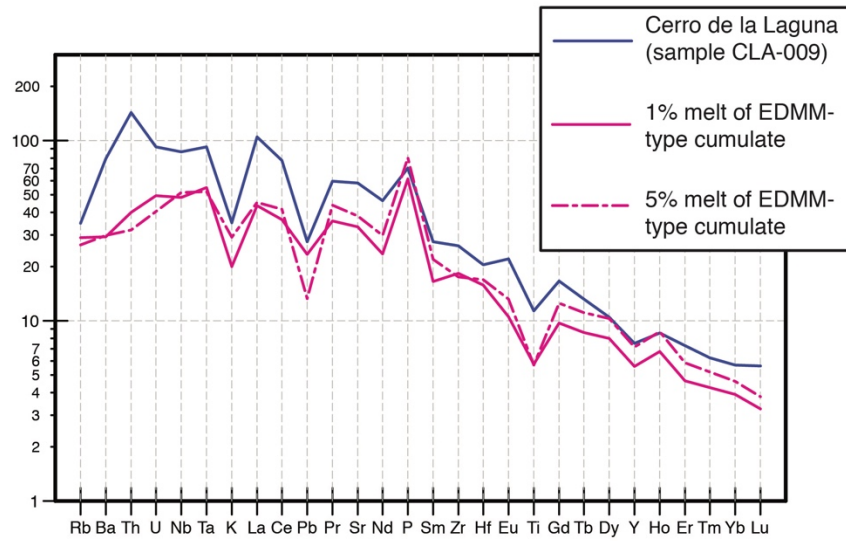


Figure 3-10.

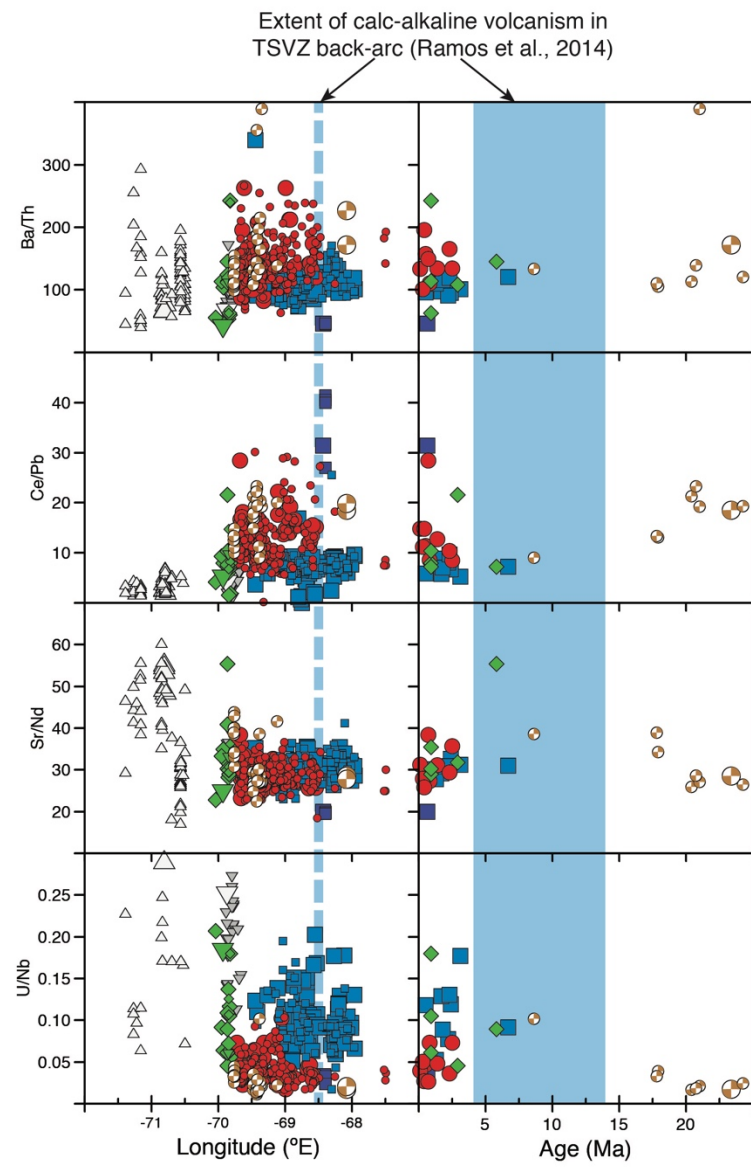


Figure 3-10 (continued).

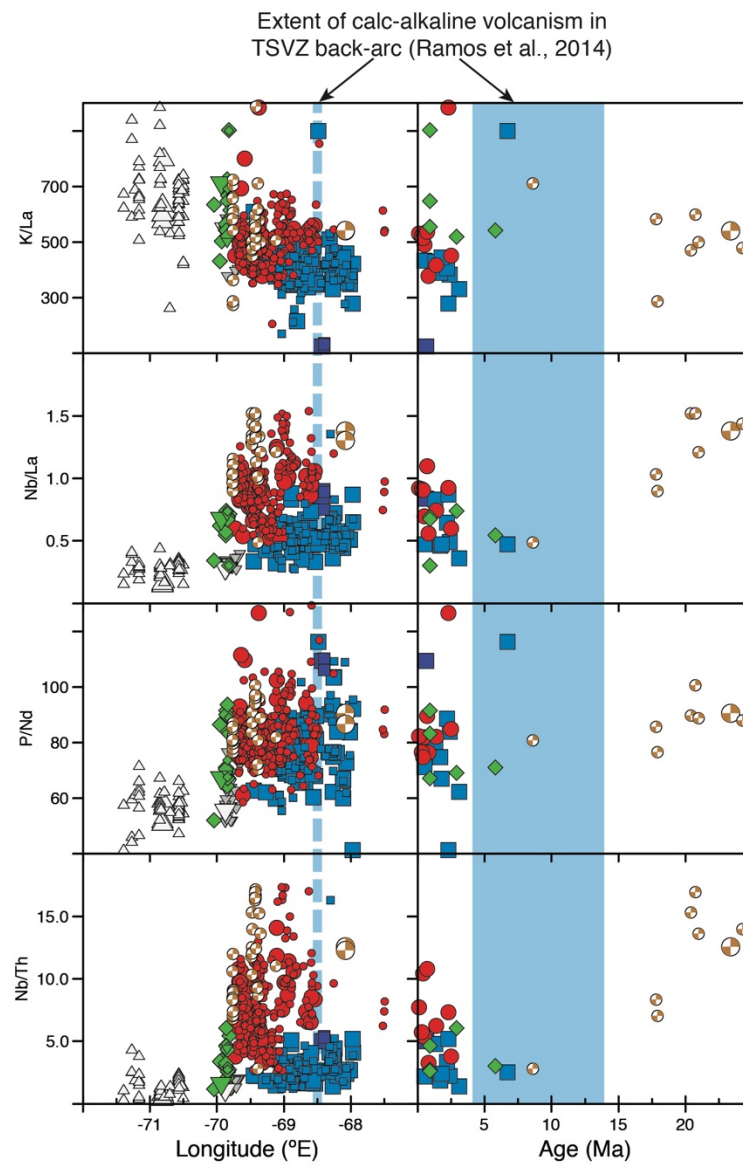


Table 3-1.

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Table 3-1 (continued).

Personal Data		Identification		Contact		Emergency		Medical		Insurance		Financial		Legal		Employment		Education		Housing		Transportation		Utilities		Healthcare		Social Security		Voting		Other	
Name	Age	Gender	DOB	SSN	Phone	Email	Address	City	State	Zip	Country	Insurance	Policy	Amount	Company	Legal	Employer	Position	Salary	Education	Level	Housing	Type	Amount	Transportation	Type	Amount	Healthcare	Plan	Amount	Other		
John Doe	35	Male	1988-05-15	123-45-6789	555-123-4567	john.doe@example.com	123 Main St	New York	NY	10001	USA	ABC Insurance	123456789	\$500,000	XYZ Corp	Software Engineer	100000	ABC Corp	Software Engineer	100000	Master's Degree	PhD	Home	1500	Car	2000	Health	Medicare	1000	Voting	Presidential	Other	
Jane Smith	28	Female	1995-03-22	987-65-4321	555-987-6543	jane.smith@example.com	456 Elm St	Los Angeles	CA	90001	USA	DEF Insurance	987654321	\$750,000	GHI Inc	Marketing Manager	80000	DEF Inc	Marketing Manager	80000	Bachelor's Degree	Master's Degree	Condo	1200	Truck	3000	Health	Private	2000	Voting	State	Other	
Michael Brown	42	Male	1981-11-08	234-56-7890	555-234-5678	michael.brown@example.com	789 Oak St	Chicago	IL	60601	USA	JKL Insurance	234567890	\$600,000	MNO Corp	Sales Representative	65000	JKL Corp	Sales Representative	65000	Bachelor's Degree	Master's Degree	House	1800	Van	1500	Health	Medicaid	500	Voting	Local	Other	
Emily White	31	Female	1992-09-01	345-67-8901	555-345-6789	emily.white@example.com	012 Pine St	San Francisco	CA	94101	USA	PQR Insurance	345678901	\$900,000	RST Corp	Data Analyst	70000	PQR Corp	Data Analyst	70000	PhD	PhD	Apartment	900	Motorcycle	1000	Health	Private	1500	Voting	State	Other	
David Green	48	Male	1975-07-19	456-78-9012	555-456-7890	david.green@example.com	321 Cedar St	Phoenix	AZ	85001	USA	UVW Insurance	456789012	\$400,000	XYZ Corp	Project Manager	55000	UVW Corp	Project Manager	55000	Bachelor's Degree	Master's Degree	House	1600	Car	2500	Health	Medicare	1200	Voting	Presidential	Other	
Sarah Black	25	Female	1998-12-03	567-89-0123	555-567-8901	sarah.black@example.com	654 Birch St	Seattle	WA	98101	USA	XYZ Insurance	567890123	\$850,000	ABC Corp	Software Engineer	85000	XYZ Corp	Software Engineer	85000	Master's Degree	PhD	Condo	1100	Truck	2000	Health	Private	1800	Voting	State	Other	
Robert Lee	55	Male	1968-04-27	678-90-1234	555-678-9012	robert.lee@example.com	987 Maple St	Portland	OR	97201	USA	ABC Insurance	678901234	\$300,000	DEF Inc	Operations Manager	45000	ABC Inc	Operations Manager	45000	Bachelor's Degree	Master's Degree	House	1400	Car	1800	Health	Medicare	800	Voting	Local	Other	
Laura King	38	Female	1985-06-10	789-01-2345	555-789-0123	laura.king@example.com	109 Elm St	San Diego	CA	92101	USA	DEF Insurance	789012345	\$700,000	GHI Inc	Marketing Manager	75000	DEF Inc	Marketing Manager	75000	PhD	PhD	Apartment	1000	Motorcycle	1200	Health	Private	2200	Voting	State	Other	
James Hall	45	Male	1978-02-28	890-12-3456	555-890-1234	james.hall@example.com	210 Oak St	Denver	CO	80201	USA	JKL Insurance	890123456	\$550,000	MNO Corp	Sales Representative	60000	JKL Corp	Sales Representative	60000	Bachelor's Degree	Master's Degree	House	1700	Van	1600	Health	Medicare	1100	Voting	Presidential	Other	
Amanda Young	33	Female	1990-10-12	901-23-4567	555-901-2345	amanda.young@example.com	321 Pine St	San Jose	CA	95101	USA	PQR Insurance	901234567	\$800,000	RST Corp	Data Analyst	78000	PQR Corp	Data Analyst	78000	Master's Degree	PhD	Condo	1200	Truck	2200	Health	Private	1900	Voting	State	Other	
Christopher King	52	Male	1971-08-05	012-34-5678	555-012-3456	christopher.king@example.com	432 Cedar St	Phoenix	AZ	85001	USA	UVW Insurance	012345678	\$450,000	XYZ Corp	Project Manager	50000	UVW Corp	Project Manager	50000	Bachelor's Degree	Master's Degree	House	1500	Car	2000	Health	Medicare	900	Voting	Local	Other	
Michelle Green	29	Female	1994-01-20	123-45-6789	555-123-4567	michelle.green@example.com	543 Birch St	Seattle	WA	98101	USA	XYZ Insurance	123456789	\$880,000	ABC Corp	Software Engineer	88000	XYZ Corp	Software Engineer	88000	Master's Degree	PhD	Apartment	1100	Motorcycle	1300	Health	Private	2100	Voting	State	Other	
Daniel White	40	Male	1983-09-14	234-56-7890	555-234-5678	daniel.white@example.com	654 Elm St	San Francisco	CA	94101	USA	PQR Insurance	234567890	\$650,000	MNO Corp	Sales Representative	68000	PQR Corp	Sales Representative	68000	Bachelor's Degree	Master's Degree	House	1600	Van	1700	Health	Medicare	1300	Voting	Presidential	Other	
Olivia Black	22	Female	2002-01-01	345-67-8901	555-345-6789	olivia.black@example.com	765 Oak St	Los Angeles	CA	90001	USA	DEF Insurance	345678901	\$950,000	GHI Inc	Marketing Manager	95000	DEF Inc	Marketing Manager	95000	PhD	PhD	Condo	1300	Truck	2500	Health	Private	2300	Voting	State	Other	
Benjamin Green	47	Male	1976-11-11	456-78-9012	555-456-7890	benjamin.green@example.com	876 Pine St	Chicago	IL	60601	USA	JKL Insurance	456789012	\$580,000	MNO Corp	Sales Representative	58000	JKL Corp	Sales Representative	58000	Bachelor's Degree	Master's Degree	House	1700	Van	1600	Health	Medicare	1100	Voting	Presidential	Other	
Isabella White	30	Female	1993-08-08	567-89-0123	555-567-8901	isabella.white@example.com	987 Cedar St	San Francisco	CA	94101	USA	PQR Insurance	567890123	\$820,000	RST Corp	Data Analyst	82000	PQR Corp	Data Analyst	82000	Master's Degree	PhD	Apartment	1200	Motorcycle	1400	Health	Private	2000	Voting	State	Other	
Ethan Brown	43	Male	1980-03-03	678-90-1234	555-678-9012	ethan.brown@example.com	098 Elm St	Phoenix	AZ	85001	USA	UVW Insurance	678901234	\$420,000	XYZ Corp	Project Manager	52000	UVW Corp	Project Manager	52000	Bachelor's Degree	Master's Degree	House	1500	Car	2100	Health	Medicare	950	Voting	Local	Other	
Ava Black	27	Female	1996-06-06	789-01-2345	555-789-0123	ava.black@example.com	109 Oak St	San Diego	CA	92101	USA	DEF Insurance	789012345	\$720,000	GHI Inc	Marketing Manager	72000	DEF Inc	Marketing Manager	72000	PhD	PhD	Apartment	1100	Motorcycle	1300	Health	Private	2100	Voting	State	Other	
Noah Green	41	Male	1982-09-09	890-12-3456	555-890-1234	noah.green@example.com	210 Pine St	Denver	CO	80201	USA	JKL Insurance	890123456	\$560,000	MNO Corp	Sales Representative	56000	JKL Corp	Sales Representative	56000	Bachelor's Degree	Master's Degree	House	1600	Van	1700	Health	Medicare	1200	Voting	Presidential	Other	
Charlotte White	32	Female	1991-12-12	901-23-4567	555-901-2345	charlotte.white@example.com	321 Cedar St	San Jose	CA	95101	USA	PQR Insurance	901234567	\$810,000	RST Corp	Data Analyst	81000	PQR Corp	Data Analyst	81000	Master's Degree	PhD	Condo	1200	Truck	2300	Health	Private	1900	Voting	State	Other	
Lucas Brown	46	Male	1977-04-04	012-34-5678	555-012-3456	lucas.brown@example.com	432 Elm St	Phoenix	AZ	85001	USA	UVW Insurance	012345678	\$470,000	XYZ Corp	Project Manager	57000	UVW Corp	Project Manager	57000	Bachelor's Degree	Master's Degree	House	1500	Car	2200	Health	Medicare	1000	Voting	Local	Other	
Hannah Black	26	Female	1997-07-07	123-45-6789	555-123-4567	hannah.black@example.com	543 Oak St	Seattle	WA	98101	USA	XYZ Insurance	123456789	\$860,000	ABC Corp	Software Engineer	86000	XYZ Corp	Software Engineer	86000	Master's Degree	PhD	Apartment	1200	Motorcycle	1400	Health	Private	2200	Voting	State	Other	
Isaac Green	44	Male	1979-10-10	234-56-7890	555-234-5678	isaac.green@example.com	654 Pine St	San Francisco	CA	94101	USA	PQR Insurance	234567890	\$630,000	MNO Corp	Sales Representative	63000	PQR Corp	Sales Representative	63000	Bachelor's Degree	Master's Degree	House	1600	Van	1800	Health	Medicare	1300	Voting	Presidential	Other	
Grace White	34	Female	1989-02-02	345-67-8901	555-345-6789	grace.white@example.com	765 Cedar St	Los Angeles	CA	90001	USA	DEF Insurance	345678901	\$920,000	GHI Inc	Marketing Manager	92000	DEF Inc	Marketing Manager	92000	PhD	PhD	Condo	1300	Truck	2600	Health	Private	2400	Voting	State	Other	
Henry Brown	49	Male	1974-05-05	456-78-9012	555-456-7890	henry.brown@example.com	876 Elm St	Chicago	IL	60601	USA	JKL Insurance	456789012	\$590,000	MNO Corp	Sales Representative	59000	JKL Corp	Sales Representative	59000	Bachelor's Degree	Master's Degree	House	1700	Van	1700	Health	Medicare	1200	Voting	Presidential	Other	
Abigail Black	24	Female	1999-08-08	567-89-0123	555-567-8901	abigail.black@example.com	987 Oak St	San Francisco	CA	94101	USA	PQR Insurance	567890123	\$890,000	RST Corp	Data Analyst	89000	PQR Corp	Data Analyst	89000	Master's Degree	PhD	Apartment	1200	Motorcycle	1500	Health	Private	2300	Voting	State	Other	
Leo Green	40	Male	1983-11-11	678-90-1234	555-678-9012	leo.green@example.com	098 Pine St	Phoenix	AZ	85001	USA	UVW Insurance	678901234	\$490,000	XYZ Corp	Project Manager	59000	UVW Corp	Project Manager	59000	Bachelor's Degree	Master's Degree	House	1500	Car	2300	Health	Medicare	1050	Voting	Local	Other	
Chloe White	36	Female	1987-03-03	789-01-2345	555-789-0123	chloe.white@example.com	210 Cedar St	San Diego	CA	92101	USA	DEF Insurance	789012345	\$780,000	GHI Inc	Marketing Manager	78000	DEF Inc	Marketing Manager	78000	PhD	PhD	Apartment	1100	Motorcycle	1400	Health	Private	2100	Voting	State	Other	
Jack Brown	45	Male	1978-06-06	890-12-3456	555-890-1234	jack.brown@example.com	321 Elm St	Denver	CO	80201	USA	JKL Insurance	890123456	\$570,000	MNO Corp	Sales Representative	57000	JKL Corp	Sales Representative	57000	Bachelor's Degree	Master's Degree	House	1600	Van	1800	Health	Medicare	1300	Voting	Presidential	Other	
Madison Black	23	Female	2001-09-09	901-23-4567	555-901-2345	madison.black@example.com	432 Oak St	San Jose	CA	95101	USA	PQR Insurance	901234567	\$840,000	RST Corp	Data Analyst	84000	PQR Corp	Data Analyst	84000	Master's Degree	PhD	Condo	1200	Truck	2400	Health	Private	2000	Voting	State	Other	
William Green	42	Male	1981-12-12	012-34-5678	555-012-3456	william.green@example.com	543 Pine St	Phoenix	AZ	85001	USA	UVW Insurance	012345678	\$460,000	XYZ Corp	Project Manager	56000	UVW Corp	Project Manager	56000	Bachelor's Degree	Master's Degree	House	1500	Car	2400	Health	Medicare	1100	Voting	Local	Other	
Evelyn White	37	Female	1986-01-01	123-45-6789	555-123-4567	evelyn.white@example.com	654 Cedar St	Los Angeles	CA	90001	USA	DEF Insurance	123456789	\$870,000	GHI Inc	Marketing Manager	87000	DEF Inc	Marketing Manager	87000	PhD	PhD	Apartment	1200	Motorcycle	1600	Health	Private	2400	Voting	State	Other	
James Brown	47	Male	1976-04-04	234-56-7890	555-234-5678	james.brown@example.com	765 Elm St	Chicago	IL	60601	USA	JKL Insurance	234567890	\$610,000	MNO Corp	Sales Representative	61000	JKL Corp	Sales Representative	61000	Bachelor's Degree	Master's Degree	House	1600	Van	1900	Health	Medicare	1400	Voting	Presidential	Other	
Olivia Black	21	Female	2003-07-07	345-67-8901	555-345-6789	olivia.black@example.com	876 Oak St	San Francisco	CA	94101	USA	PQR Insurance	345678901	\$970,000	GHI Inc	Marketing Manager	97000	DEF Inc	Marketing Manager	97000	PhD	PhD	Condo	1300	Truck	2700	Health	Private	2500	Voting	State	Other	
Benjamin Green	43	Male	1980-10-10	456-78-9012	555-456-7890	benjamin.green@example.com	987 Pine St	Phoenix	AZ	85001	USA	UVW Insurance	456789012	\$510,000	XYZ Corp	Project Manager	51000	UVW Corp	Project Manager	51000	Bachelor's Degree	Master's Degree	House	1500	Car	2500	Health	Medicare	1150	Voting	Local	Other	
Charlotte White	35	Female	1988-11-11	567-89-0123	555-567-8901	charlotte.white@example.com	098 Cedar St	San Diego	CA	92101	USA	DEF Insurance	567890123	\$910,000	GHI Inc	Marketing Manager	91000	DEF Inc	Marketing Manager	91000	Master's Degree	PhD	Apartment	1200	Motorcycle	1700	Health	Private	2600	Voting	State	Other	
Henry Brown	46	Male	1977-02-02	678-90-1234	555-678-9012	henry.brown@example.com	210 Elm St	Denver	CO	80201	USA	JKL Insurance	678901234	\$540,000	MNO Corp	Sales Representative	54000	JKL Corp	Sales Representative	54000	Bachelor's Degree	Master's Degree	House	1600	Van	2000	Health	Medicare	1500	Voting	Presidential	Other	
Abigail Black	20	Female	2004-05-05	789-01-2345	555-789-0123	abigail.black@example.com	321 Oak St	San Jose	CA	95101	USA	PQR Insurance	789012345	\$990,000	RST Corp	Data Analyst	99000	PQR Corp	Data Analyst	99000	PhD	PhD	Condo	1300	Truck	2800	Health	Private	2700	Voting	State	Other	
William Green	44	Male	1979-08-08	890-12-3456	555-890-1234	william.green@example.com	432 Pine St	Phoenix	AZ	85001	USA	UVW Insurance	890123456	\$530,000	XYZ Corp	Project Manager	53000	UVW Corp	Project Manager	53000	Bachelor's Degree	Master's Degree	House	1500	Car	2600	Health	Medicare	1250	Voting	Local	Other	
Evelyn White	38	Female	1985-11-11	901-23-4567	555-901-2345	evelyn.white@example.com	543 Cedar St	Los Angeles	CA	90001	USA	DEF Insurance	901234567	\$880,000	GHI Inc	Marketing Manager	88000	DEF Inc	Marketing Manager	88000	PhD	PhD	Apartment	1200	Motorcycle	1800	Health	Private	2700	Voting	State	Other	
James Brown	48	Male	1975-03-03	012-34-5678	555-012-3456	james.brown@example.com	654 Elm St	Chicago	IL	60601	USA	JKL Insurance	012345678	\$500,000	MNO Corp	Sales Representative	50000	JKL Corp	Sales Representative	50000	Bachelor's Degree	Master's Degree	House	1500	Car	2700	Health	Medicare	1350	Voting	Presidential	Other	
Olivia Black	19	Female	2005-06-06	123-45-6789	555-123-4567	olivia.black@example.com	765 Oak St	San Francisco	CA	94101	USA	PQR Insurance	123456789	\$1,000,000	GHI Inc	Marketing Manager	1,000,000	DEF Inc	Marketing Manager	1													

Table 3-1 (continued).

[illegible]

Table 3-1 (continued).

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Table 3-1 (continued).

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Table 3-1 (continued).

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Table 3-1 (continued).

P-02018		M09-028		A04-035		P01		P06		Toronto Blue Jays											
Roy Oswalt		Roy Oswalt		Roy Oswalt		Roy Oswalt		Roy Oswalt		Roy Oswalt											
Game ID		Game ID		Game ID		Game ID		Game ID		Game ID											
37-2803		37-2805		37-2806		37-2807		37-2808		37-2809											
66-5481		66-5289		66-5078		66-5080		66-5081		66-5082											
L (48)		L (48)		L (48)		L (48)		L (48)		L (48)											
P		P		P		P		P		P											
44.6		44.6		44.6		44.6		44.6		44.6											
10.1		10.1		10.1		10.1		10.1		10.1											
20.5		20.5		20.5		20.5		20.5		20.5											
41.3		41.3		41.3		41.3		41.3		41.3											
60.0		60.0		60.0		60.0		60.0		60.0											
16.9		16.9		16.9		16.9		16.9		16.9											
24.3		24.3		24.3		24.3		24.3		24.3											
16.9		16.9		16.9		16.9		16.9		16.9											
21.1		21.1		21.1		21.1		21.1		21.1											
2.8		2.8		2.8		2.8		2.8		2.8											
3.3		3.3		3.3		3.3		3.3		3.3											
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3.3		3.3		3.3		3.3		3.3		3.3											
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3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3.3		3.3		3.3											
3.3		3.3		3.3		3															

Table 3-1 (continued).

[illegible]

Unnormalized Major Elements (Weight %):													
Replicate r'2	SiO ₂	TO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅			
LOD (2σ)	0.9929	0.9992	0.99949	0.99948	0.99893	0.99994	0.99976	0.99891	0.99992	0.9999			
	0.58	0.017	0.16	0.2	0.002	0.076	0.064	0.045	0.031	0.005			
Normalized Major Elements (Weight %):													
Replicate r'2	SiO ₂	TO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅			
LOD (2σ)	0.99992	0.99996	0.99987	0.99965	0.99998	0.99994	0.99998	0.99989	0.99998	0.99996			
	0.012	0.082	0.18	0.002	0.073	0.043	0.036	0.015	0.003				
Trace elements (In ppm)													
Replicate r'2	Li	Cr	Sc	V	Ba	Rb	Sr	Zr	Y	Nb			
LOD (2σ)	0.99992	0.99998	0.997	0.9996	0.9997	0.9998	0.99992	0.99994	0.9987	0.99987			
	3.5	3	1.6	5	11.7	1.7	4.6	1.2	1.2				
Replicate r'2	Ga	Cu	Zn	Pb	La	Ce	Th	Nd	U				
LOD (2σ)	0.9991	0.9994	0.9966	0.9966	0.9941	0.996	0.997	0.992	0.983				
	2.7	7.4	3.3	2.6	5.7	7.9	1.6	4.3	2.7				
LOD = replicate limit of determination													

Detection limits for (ICP-MS analyses) (ppm)													
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	
0.007	0.012	0.009	0.045	0.014	0.01	0.026	0.007	0.024	0.006	0.021	0.006	0.007	
Lu	Ba	Th	Nb	Y	Hf	Ta	U	Pb	Rb	Cs	Sr	Zr	
0.007	0.258	0.009	0.018	0.015	0.032	0.014	0.014	0.204	0.057	0.014	0.115	0.055	
Realistic lower limits (thanks x 10)													
La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	
0.07	0.12	0.09	0.45	0.14	0.1	0.28	0.07	0.24	0.06	0.21	0.06	0.23	
Lu	Ba	Th	Nb	Y	Hf	Ta	U	Pb	Rb	Cs	Sr	Zr	
0.07	2.58	0.09	0.18	0.15	0.32	0.14	0.14	2.04	0.57	0.14	1.15	0.59	

Detection limits are derived from the counts on the blank plus 3 times the standard deviation of the blank calculated as an unknown.

Precision on a single sample from September 2011 to March 2012

Statistics for 54 preparations

BCR-C (N=54) run as unknown

	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm
Average	26.00	54.06	7.00	29.93	6.99	2.13	7.09	1.17	7.13	1.44	3.82	0.54	3.34
Std. Dev.	0.17	0.33	0.04	0.23	0.05	0.03	0.05	0.01	0.07	0.01	0.05	0.01	0.05
Maximum	26.30	54.44	7.08	29.75	7.15	2.17	7.16	1.19	7.25	1.45	3.90	0.55	3.39
Minimum	25.59	53.18	6.92	28.78	6.88	2.08	6.99	1.14	7.01	1.42	3.77	0.54	3.30
Coef. Var (Std Dev/Ave)	0.66	0.60	0.58	0.79	1.02	1.23	0.76	0.97	0.94	0.82	1.19	1.02	0.79
Precision on a single sample from September 2011 to March 2012													
Statistics for 33 preparations													
TED (N=33) run as unknown													
	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm
Average	3.91	10.11	1.67	8.60	2.92	1.15	3.93	0.74	4.95	1.08	3.07	0.45	2.84
Std. Dev.	0.04	0.14	0.01	0.06	0.05	0.01	0.04	0.01	0.04	0.01	0.03	0.01	0.03
Maximum	3.99	10.27	1.69	8.74	2.99	1.16	3.98	0.75	5.02	1.09	3.12	0.46	2.88
Minimum	3.86	9.71	1.65	8.52	2.87	1.12	3.79	0.72	4.88	1.07	3.01	0.44	2.79
Coef. Var (Std Dev/Ave)	0.93	1.37	0.62	0.75	1.62	1.00	0.93	1.08	0.89	0.88	1.08	1.16	0.91

Precision on a single sample from September 2011 to March 2012

Statistics for 33 preparatoinis

TED (N=33) run as unknown

Table 3-2 (continued).

Lu ppm	Ba ppm	Th ppm	Nb ppm	Y ppm	Hf ppm	Ta ppm	U ppm	Pb ppm	Rb ppm	Cs ppm	Si ppm	Sc ppm	Zr ppm
0.52	684.02	6.14	11.61	36.36	4.97	0.78	1.70	8.92	45.46	0.97	340.60	32.82	185.51
0.01	4.43	0.06	0.08	0.22	0.04	0.01	0.02	0.32	0.48	0.02	2.10	0.27	1.05
0.54	690.01	6.27	11.72	36.72	5.04	0.81	1.74	9.80	46.25	1.00	345.15	33.36	187.33
0.50	674.10	6.03	11.44	35.85	4.89	0.77	1.66	8.69	44.64	0.94	337.10	32.28	183.81
1.45	0.65	1.00	0.70	0.61	0.90	1.40	1.42	3.60	1.06	1.91	0.62	0.82	0.57
Lu ppm	Ba ppm	Th ppm	Nb ppm	Y ppm	Hf ppm	Ta ppm	U ppm	Pb ppm	Rb ppm	Cs ppm	Si ppm	Sc ppm	Zr ppm
0.46	71.02	0.44	2.38	27.30	1.84	0.15	0.14	0.82	3.52	0.10	213.51	41.97	62.83
0.01	1.22	0.01	0.02	0.23	0.02	0.00	0.00	0.02	0.09	0.01	3.34	0.56	0.49
0.47	73.56	0.45	2.42	27.49	1.87	0.16	0.15	0.84	3.72	0.11	216.65	43.25	63.94
0.45	69.64	0.43	2.34	26.75	1.81	0.15	0.14	0.79	3.42	0.10	206.23	41.30	62.29
1.56	1.71	1.77	0.99	0.84	0.99	1.90	2.40	2.19	2.50	5.75	1.56	1.34	0.78

Table 3-3.

Table 3. Sr, Nd, and Hf isotope data for TSVZ samples.

Sample ID	Volcanic field	Locality/Edifice	Lab	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\text{SE}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{SE}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2\text{SE}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm$	$^{208}\text{Pb}/^{204}\text{Pb}$
16-1	P. del Agua		Brown	0.512836	0.000008	0.703889	0.000010	18.3488	0.0006	15.5569	0.0005	38.1280
16-1 repl.			Brown	0.512835	0.000005	0.703881	0.000007	18.3516	0.0006	15.5543	0.0005	38.1244
16-2	P. del Agua		WHOI	0.512803		0.703893		18.3611		15.5559		38.1332
CLA-009	Nevado	De la Laguna	Brown	0.512904	0.000007	0.703063	0.000011	18.4084	0.0005	15.5349	0.0005	38.1988
CNE-001*	Nevado	Negro	Brown	0.512753	0.000007	0.704255	0.000012	18.4946	0.0006	15.5832	0.0005	38.3198
CCN-005	Nevado	Chanchos	Brown	0.512806	0.000008	0.703970	0.000012	18.5043	0.0006	15.5760	0.0005	38.3204
112509-7	Nevado	Chingolo	Brown	0.512805	0.000007	0.704020	0.000011	18.5779	0.0004	15.5881	0.0004	38.4279
15-3	Nevado	Grande	Brown	0.512847	0.000008	0.703710	0.000008	18.4597	0.0004	15.5645	0.0004	38.2302
15-3	Nevado	NW Ponon	Brown	0.512834	0.000006	0.703878	0.000008	18.4862	0.0004	15.5719	0.0004	38.2988
15-4	Nevado	P. Trehue	Brown	0.512799	0.000006	0.703941	0.000007	18.5342	0.0006	15.5765	0.0005	38.3435
15-5	Nevado	Chilena	MIT	0.512779		0.704208		18.5940		15.5850		38.4180
15-6	Nevado	Toldos	WHOI	0.512782		0.704108		18.5041		15.5762		38.2994
16-9	Nevado	Chanchos	WHOI	0.512776		0.704096		18.5298		15.5976		38.3787
18-2	Nevado	Yeguas	WHOI	0.512792		0.703956		18.5295		15.5850		38.3582
18-7	Nevado	Yeguas	Brown	0.512817	0.000005	0.703871	0.000008	18.5417	0.0003	15.5821	0.0003	38.3744
20-2	Nevado	Negro	Brown	0.512827	0.000005	0.703907	0.000011	18.5582	0.0005	15.5819	0.0004	38.3940
18-9	Nevado	Vacas	Brown	0.512815	0.000006	0.703993	0.000010	18.5546	0.0005	15.5774	0.0004	38.3421
18-13	Nevado	Vacas	Brown	0.512788	0.000007	0.704050	0.000010	18.5051	0.0004	15.5723	0.0004	38.2883
19-11	Nevado	Masuco	Brown	0.512806	0.000006	0.704001	0.000009	18.5754	0.0004	15.5878	0.0004	38.4214
24	Nevado	Coloradas	Brown	0.512778		0.704104		18.5287		15.6005		38.2212
19-10	Nevado	Sollario	Brown	0.512832	0.000005	0.703933	0.000008	18.5986	0.0005	15.5910	0.0004	38.4529
19-10 repl.			Brown	0.512835	0.000006	0.703924	0.000009	18.5985	0.0003	15.5915	0.0003	38.4562
2-170484	Nevado	Suiza	Brown	0.512850	0.000008	0.703756	0.000011	18.5785	0.0005	15.5989	0.0004	38.4486
2-170484 repl.			Brown			0.703757	0.000008			15.5960	0.0003	38.4390
6-110384	Nevado	Negro SW	WHOI	0.512793		0.703824		18.5661		15.5841		38.3795
83-8	Nevado	Nevado	Brown	0.512839	0.000006	0.703987	0.000009	18.5781	0.0004	15.5924	0.0004	38.4359
19-6	Nevado	Leon	Brown	0.512851	0.000006	0.703788	0.000008	18.5408	0.0003	15.5814	0.0002	38.3689
19-8	Nevado	L. Corral	Brown	0.512854	0.000005	0.703828	0.000007	18.5719	0.0003	15.5794	0.0003	38.4300
24-140384	Nevado	Borbaran	WHOI	0.512851		0.703858		18.5554		15.5834		38.3833
84-1	Nevado	Molongo	WHOI	0.512850		0.703803		18.5306		15.5773		38.3458
MJC	Nevado	M. Jarilla	WHOI	0.512783		0.704030		18.5206		15.6056		38.4084
19-7	Nevado	Borbaran	Brown	0.512785	0.000010	0.703994	0.000007	18.5053	0.0004	15.5689	0.0003	38.2711
46	Nevado	Pelado	Brown	0.512758	0.000005	0.704188	0.000008	18.5448	0.0004	15.5825	0.0004	38.3412
16-4	Nevado	Cañada Honda	Brown	0.512762	0.000005	0.704189	0.000008	18.5407	0.0004	15.5793	0.0004	38.3311
16-5	Nevado	Cañada Honda	WHOI	0.512735		0.704189		18.5418		15.5814		38.3414
16-6	Nevado	Tordillo	WHOI	0.512734		0.704235		18.5544		15.5809		38.3763
JAU-052	Diamante	La Jaula 1	Brown	0.512783	0.000007	0.704122	0.000012	18.5564	0.0005	15.5861	0.0005	38.4392
JAU-053	Diamante	La Jaula 2	Brown	0.512693	0.000006	0.704433	0.000012	18.5765	0.0007	15.5983	0.0006	38.5051
EPD-056	Diamante	Maar El Pozo	Brown	0.512788	0.000007	0.704083	0.000010	18.5123	0.0006	15.5815	0.0005	38.3909
GUA-000*	Diamante	Co. Guadalupe	Brown	0.512843	0.000009	0.703960	0.000008	18.5665	0.0004	15.5900	0.0003	38.4505
LDN-063	Diamante	Loma del Medio	Brown	0.512780	0.000007	0.704202	0.000008	18.5406	0.0004	15.5873	0.0004	38.4338
011910-192	Diamante	Diamante	Brown	0.512782	0.000009	0.704022	0.000012	18.4457	0.0006	15.5684	0.0006	38.2988
21-5	Llancanelo	El Salmo	Brown	0.512785	0.000011	0.704059	0.000006	18.4869	0.0003	15.5772	0.0004	38.3575
21-7	Llancanelo	El Morado	MIT	0.512766		0.704116		18.493		15.580		38.387
21-4	Llancanelo	El Chachao	Brown	0.512815	0.000007	0.703963	0.000011	18.4492	0.0005	15.5665	0.0004	38.2997
21-6	Llancanelo	Piedras Blancas	Brown	0.512776	0.000007	0.703972	0.000008	18.3965	0.0004	15.5635	0.0003	38.2570
21-8	Llancanelo	Piedras Blancas	Brown	0.512763	0.000006	0.704001	0.000010	18.3815	0.0004	15.5639	0.0004	38.2543
21-1	Llancanelo	Chiluido	MIT	0.512777		0.704024		18.400		15.567		38.289
TRA-050	Llancanelo	Vn Trapal	Brown	0.512763	0.000006	0.704059	0.000011	18.4977	0.0005	15.5813	0.0004	38.3807
120909-76	Llancanelo	Los Pozos	Brown	0.512816	0.000008	0.703785	0.000009	18.5206	0.0004	15.5768	0.0004	38.3303
120909-77	Llancanelo	La Portefa	Brown	0.512819	0.000008	0.703882	0.000011	18.5469	0.0004	15.5860	0.0005	38.4049
22-4	Llancanelo	Rio Grande	Brown	0.512811	0.000004	0.703853	0.000007	18.5385	0.0004	15.5859	0.0004	38.3819
24-1B	Payún Matrú	Santa Maria	Brown	0.512823	0.000005	0.703844	0.000006	18.3588	0.0007	15.5606	0.0006	38.2120
24-3	Payún Matrú	Santa Maria	WHOI	0.512799		0.703890		18.4121		15.5768		38.2914
25-1	Payún Matrú	Media Luna	Brown	0.512806	0.000005	0.703890	0.000009	18.3931	0.0003	15.5655	0.0003	38.2542
25-3	Payún Matrú	Hermia	Brown	0.512813	0.000006	0.703929	0.000007	18.4156	0.0004	15.5684	0.0003	38.2787
25-10	Payún Matrú	Vazquez	Brown	0.512814	0.000006	0.703923	0.000007	18.3866	0.0004	15.5624	0.0003	38.2230
120309-38	Payún Matrú	P. Negras	Brown	0.512823	0.000007	0.703901	0.000012	18.3855	0.0005	15.5651	0.0005	38.2462
23-1	Payún Matrú	Escorial	Brown	0.512796	0.000006	0.703903	0.000009	18.3475	0.0003	15.5619	0.0002	38.2203
24-1A	Payún Matrú	Santa Maria	Brown	0.512820	0.000006	0.703853	0.000008	18.3812	0.0011	15.5593	0.0011	38.2086
25-2	Payún Matrú	Media Luna	Brown	0.512816	0.000007	0.703861	0.000009	18.3939	0.0005	15.5650	0.0004	38.2513
22-7	Payún Matrú	Rauquillo	Brown	0.512846	0.000008	0.703758	0.000009	18.4740	0.0003	15.5675	0.0003	38.3168
23-11	Payún Matrú	Fortunoso	Brown	0.512745	0.000004	0.704117	0.000007	18.3383	0.0006	15.5562	0.0006	38.2229
25-11 repl.			Brown	0.512744	0.000006	0.704131	0.000014	18.3419	0.0003	15.5597	0.0003	38.2332
22-5	Payún Matrú	Puente	Brown	0.512802	0.000007	0.704016	0.000007	18.4205	0.0003	15.5721	0.0003	38.2955
25-4	Payún Matrú	Jarilloso	Brown	0.512820	0.000005	0.703864	0.000009	18.3647	0.0004	15.5604	0.0004	38.2075
23-14	Payún Matrú	Cortadera	Brown	0.512807	0.000006	0.703894	0.000009	18.3221	0.0006	15.5537	0.0006	38.1692
25-7	Payún Matrú	Pipeline	Brown	0.512767	0.000006	0.704070	0.000007	18.2491	0.0004	15.5496	0.0004	38.1203
25-7 repl.			Brown	0.512759	0.000006	0.704074	0.000012	18.2514	0.0004	15.5518	0.0004	38.1287
25-8	Payún Matrú	L. Colorado	Brown	0.512813	0.000008	0.703922	0.000011	18.3846	0.0004	15.5649	0.0004	38.2418
25-8	Payún Matrú	Pipeline	Brown	0.512830	0.000005	0.703873	0.000007	18.3076	0.0003	15.5504	0.0003	38.1542
26-1	Payún Matrú	P. Huicán	Brown	0.512822	0.000007	0.703898	0.000009	18.3088	0.0003	15.5584	0.0003	38.1785
26-1 repl.			Brown	0.512880	0.000005	0.703892	0.000008	18.3020	0.0007	15.5517	0.0007	38.1576
25-9	Payún Matrú	Pipeline	Brown	0.512818	0.000006	0.703903	0.000009	18.2905	0.0005	15.5477	0.0004	38.1403
VEL-041	Rio Colorado	El Jinete	Brown	0.512798	0.000006	0.703828	0.000011	18.2858	0.0005	15.5549	0.0005	38.1554
MOR-021	Rio Colorado	El Morado	Brown	0.512729	0.000009	0.704173	0.000011	18.4035	0.0005	15.5817	0.0004	38.3064
MEN-026	Rio Colorado	Mendez	Brown	0.512790	0.000008	0.703816	0.000007	18.3484	0.0005	15.5611	0.0003	38.2035
MO3-022	Rio Colorado	Morado 3	Brown	0.512807	0.000007	0.703827	0.000010	18.4092	0.0005	15.5725	0.0005	38.3514
SCN-014	Rio Colorado	Chachahuen	Brown	0.512815	0.000007	0.703734	0.000010	18.3612	0.0005	15.5631	0.0004	38.2249
AUC-035*	A. Mahuida	Aguada Lustre	Brown	0.512832	0.000007	0.703755	0.000010	18.3907	0.0004	15.5723	0.0004	38.2660
27-6	Buta Ranquil	Buta Ranquil	Brown	0.512891	0.000004	0.704011	0.000007	18.5169	0.0003	15.5698	0.0003	38.2939
BR16-81	Buta Ranquil	Buta Ranquil	WHOI			0.703765		18.3947		15.5840		38.2529
27-4	Buta Ranquil	Buta Ranquil	Brown	0.512845	0.000009	0.703765	0.000007	18.4465	0.0005	15.5749	0.0005	38.2918
27-4 repl.			Brown	0.512849	0.000006	0.703768	0.000012	18.4458	0.0005	15.5735	0.0004	38.2878
27-3	Buta Ranquil	Buta Ranquil	Brown	0.512834	0.000005	0.703814	0.000007	18.5180	0.0004	15.5881	0.0003	38.3715
27-1	Buta Ranquil	Buta Ranquil	Brown	0.512837	0.000006	0.703829	0.000009	18.5005	0.0003	1		

Table 3-3 (continued).

$\pm 2SE$	$^{176}\text{Hf}/^{177}\text{Hf}$	$\pm 2SE$
0.0014	0.282880	0.000009
0.0015	0.282864	0.000003
0.0012	0.283002	0.000005
0.0012	0.282876	0.000005
0.0014	0.282899	0.000004
0.0011	0.282913	0.000008
0.0009	0.282934	0.000006
0.0010	0.282925	0.000010
0.0013	0.282926	0.000003
0.0007	0.282919	0.000008
0.0011	0.282959	0.000005
0.0011	0.282909	0.000006
0.0009	0.282880	0.000007
0.0011	0.282903	0.000009
0.0010	0.282986	0.000005
0.0008	0.282979	0.000004
0.0011	0.282979	0.000005
0.0008	0.282974	0.000005
0.0010	0.282965	0.000005
0.0007	0.282961	0.000006
0.0007	0.282955	0.000006
0.0011	0.282875	0.000005
0.0010	0.282849	0.000008
0.0010	0.282850	0.000007
0.0014	0.282912	0.000004
0.0018	0.282863	0.000004
0.0015	0.282918	0.000006
0.0010	0.282977	0.000005
0.0010	0.282903	0.000006
0.0015	0.282882	0.000006
0.0009	0.282880	0.000003
0.0010	0.282876	0.000005
0.0009	0.282887	0.000006
0.0010	0.282878	0.000006
0.0011	0.282872	0.000005
0.0011	0.282907	0.000006
0.0014	0.282932	0.000007
0.0012	0.282936	0.000004
0.0017	0.282917	0.000003
0.0008	0.282910	0.000008
0.0008	0.282903	0.000007
0.0010	0.282894	0.000006
0.0012	0.282924	0.000006
0.0009	0.282899	0.000008
0.0027	0.282912	0.000005
0.0011	0.282908	0.000005
0.0009	0.282936	0.000005
0.0016	0.282845	0.000004
0.0008	0.282844	0.000003
0.0010	0.282907	0.000004
0.0011	0.282916	0.000009
0.0015	0.282896	0.000006
0.0009	0.282855	0.000008
0.0009	0.282851	0.000003
0.0011	0.282893	0.000006
0.0009	0.282919	0.000007
0.0009	0.282918	0.000004
0.0017	0.282916	0.000004
0.0011	0.282910	0.000005
0.0011	0.282901	0.000006
0.001	0.282855	0.000013
0.0013	0.282862	0.000003
0.0012	0.282881	0.000001
0.0011	0.282886	0.000005
0.001	0.282896	0.000006
0.0008	0.282999	0.000004
0.0012	0.282954	0.000006
0.0009	0.282947	0.000004
0.0008	0.282944	0.000007
0.0007	0.282939	0.000007
0.0009	0.282945	0.000006
0.0016	0.282973	0.000008
0.0016	0.282956	0.000006
0.0010	0.282925	0.000004
0.0008	0.282953	0.000002
0.0012	0.282772	0.000004
0.0011	0.283013	0.000005
0.0013	0.282996	0.000005

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Table 3-4 (continued).

[illegible]

Table 3-5.

Table 5a. Data normalization and parameters for the PCA of highly incompatible trace elements.

	K2O/Nb	Rb/Nb	Ba/Nb	La/Nb	Ce/Nb	Th/Nb	U/Nb
Standard deviation	0.0815	1.7495	23.9565	0.96802484	2.14194826	0.31315045	0.10521634
Range	0.7122	10.9652	148.8966	6.3610	13.8119	2.8989	1.1483
Mean	0.1001	2.0016	33.5882	1.6520	3.4980	0.3080	0.0854
Analytical Error	1.0095	1.5015	0.9202	0.9331	0.8580	1.4266	2.0193
Weighting Factor	7.0495	3.6485	4.8175	4.1268	4.6020	6.5970	6.6605
	PC1	PC2	PC3	PC4	PC5	PC6	PC7
K2O/Nb	0.1744713	-0.1778842	0.13126614	-0.0952723	-0.2192517	-0.0163582	-0.0715822
Rb/Nb	0.17193141	-0.1610241	0.1456039	-0.115017	0.42283378	0.03582632	-0.0640038
Ba/Nb	0.16939244	-0.1115202	-0.1363513	0.32534763	0.03316622	-0.1960043	-0.0498528
La/Nb	0.15704195	0.08200948	-0.2201655	0.00818295	-0.0191029	0.31599137	-0.2493559
Ce/Nb	0.17342241	-0.0662757	-0.1313078	-0.0240407	-0.0112725	0.14018992	0.38108671
Th/Nb	0.15408097	0.18325835	-0.1142585	-0.1937539	0.00947617	-0.2083466	-0.0129147
U/Nb	0.14628386	0.23018305	0.22795794	0.13820522	-0.0111801	0.05409077	0.04049691
Variance	36.519	2.80	1.17563723	0.45551654	0.34343455	0.21455029	0.09651036
Percent explained	87.784	6.72	2.82593735	1.09494763	0.82553062	0.51572513	0.23198673

Table 5b: Data normalization and parameters for the PCA of Nd, Sr, and Pb isotopes.

	143Nd/144Nd	87Sr/86Sr	206Pb/204Pb	207Pb/204Pb	208Pb/204Pb
Standard deviation	0.000043	0.000181	0.1097	0.0256	0.1405
Range	0.00031	0.00137	0.7908	0.315	1.4018
Mean	0.51279723	0.70393622	18.4890034	15.5816223	38.3510544
Analytical Error	5.8583E-05	5.3503E-05	0.0001063	0.00011623	0.00016356
Weighting Factor	10.3191424	36.3757919	402.357403	173.930542	223.470384
	PC1	PC2	PC3	PC4	PC5
143Nd/144Nd	-0.0137858	-0.0455955	-0.1181727	0.05707009	0.27823818
87Sr/86Sr	0.01491275	0.02229401	0.14891489	0.02735349	0.06202853
206Pb/204Pb	0.03552208	-0.0317423	0.00110768	0.01348411	-0.005737
207Pb/204Pb	0.03345927	0.05378994	-0.0165671	0.03798813	-0.0043557
208Pb/204Pb	0.0358699	0.01522777	-0.002122	-0.0524607	0.01413174
Variance	754.1987	47.3056764	35.7547349	6.72903459	3.09848529
Percent explained	89.0344237	5.58451458	4.22090653	0.79437384	0.36578139

SYNTHESIS

The research in this thesis constitutes a new approach to explaining the geochemical diversity observed in the mafic volcanism of the Andean TSVZ over the past 24 million years. Our interpretations integrate previous geochemical datasets with the data reported in this thesis, which constitutes new measurements of the radiometric ages and chemical and isotopic compositions of whole-rock lava samples, the oxygen isotope contents of olivine phenocrysts formed in these lavas, as well as the first dataset to include major, trace, and volatile (H₂O, CO₂, F, Cl, S) element contents for olivine-hosted melt inclusions from this region.

The investigation of these data demonstrates that metasomatic cumulates from the subcontinental lithospheric mantle of the TSVZ represent a viable source component in mafic back-arc lavas that exhibit both an intraplate signature in their trace element and isotopic contents and an arc signature in these traits. Because both signatures displayed by TSVZ back-arc lavas can be explained by melting in the SCLM, the cumulates responsible for these signatures must be heterogeneous, and would thus reflect SCLM metasomatism driven by different processes. These conclusions contrast with the previous explanations of the intraplate signature seen in mafic TSVZ volcanism, which propose that the melting of an eclogite-derived pyroxenite-peridotite asthenosphere is the source of the chemical and isotopic characteristics displayed by the Early Miocene intraplate lavas in the Fortunoso, La Matancilla and Punta del Agua areas, and the Plio-Quaternary SC area lavas in the Payenia Province (Søager and Holm, 2013; Søager et al., 2013; Søager et al., 2015).

Chapter 1 characterizes the chemical and isotopic composition of mafic lavas from the back-arc Payenia volcanic province to demonstrate that the existence of three compositional endmembers: one with low $\delta^{18}\text{O}_{\text{olivine}}$, intraplate trace element patterns,

negative $\Delta\epsilon_{\text{Hf}}$, and low Mg#; a second with intermediate $\delta^{18}\text{O}_{\text{olivine}}$, arc-like trace element patterns, $\Delta\epsilon_{\text{Hf}} \approx 0$, and high Mg#, and a third with high $\delta^{18}\text{O}_{\text{olivine}}$, arc-like trace element patterns, negative $\Delta\epsilon_{\text{Hf}}$, and low Mg#. Compositional variations between these endmembers were explained by the modeled mixture between an asthenospheric melt and melts produced by two SCLM cumulate compositions, one representing a cumulate formed from a melt of EDMM-like asthenosphere, and another representing a cumulate from a melt of the subduction-influenced mantle wedge. Nd and Hf isotope ingrowth estimates for the modeled cumulate compositions indicate that ~150-200 million years of isotopic ingrowth is required to generate the negative deviation in $\Delta\epsilon_{\text{Hf}}$ of Payenia lavas, a length of time that coincides with the Jurassic breakup of Gondwana and the development of the proto-Pacific magmatic arc (Franzese et al., 2003).

Chapter 2 presents the major, trace, and volatile element contents of olivine-hosted melt inclusions from three Plio-Quaternary TSVZ back-arc localities: Diamante in the north, Auca Mahuida in the southeast, and Loncopué in the southwest. Volatile contents in the Loncopué and Diamante melt inclusions exceed 3 wt% H_2O , ppm Cl, ppm F, and ppm S. While H_2O contents in Loncopué and Diamante inclusions reflect modification from H^+ diffusion, other volatile species in these samples correlate with arc signature-indicative trace element ratios such as Ba/Nb, which demonstrates that slab-derived inputs caused volatile enrichment. Despite having similarly enriched volatile contents, the low-silica and high Rb and Ba contents of Diamante MIs indicate that these melt inclusions originate from a different mantle source than the Loncopué melt inclusions. Comparisons between the SiO_2 , H_2O , and trace element contents of modeled arc-type cumulate-derived melts and the Fo_{90} -corrected Diamante compositions show a close resemblance, suggesting that these melt inclusions represent the melting of a SCLM cumulates formed from a subduction-

influenced metasomatic agent. Loncopué melt inclusions more closely resemble F_{90} -corrected compositions of SVZ volcanic front melt inclusions, which indicates that the Loncopué mantle source represents with minimal contribution from the SCLM. In contrast, the Auca Mahuida melt inclusions are low in H_2O (<0.7 wt.%) and do not display significant influence from slab inputs. F/Cl values for Auca Mahuida glasses trend toward higher values than arc melt inclusions or MORB glasses, consistent with an increasing melt contribution from a source that has phlogopite and/or amphibole, in which F is more compatible than Cl. These results show that the melting of heterogeneously metasomatized SCLM modifies the volatile budgets of mafic TSVZ volcanism.

Chapter 3 integrates the dataset of chapter 1 into a broader characterization of TSVZ lavas erupted since the Early Miocene. Principal component analyses of incompatible trace elements and Sr, Nd, and Pb isotopes demonstrate that the primary control on geochemical variability in mafic TSVZ volcanism is the input of slab-derived materials. Secondary variations in composition demonstrate that lavas with the strongest intraplate signature, which date to the early Miocene as well as the Pliocene and younger, most closely resemble the composition of mantle xenolith-hosted melt pockets from the Gobernador Gregores locality in Patagonia. Payenia lavas that show a melt pocket affinity were identified in chapter 1 as having a strong affinity to EDMM-type cumulates. These data demonstrate a close association between melt pockets and TSVZ lavas spanning disparate ages in proximal localities as well as disparate localities. These spatio-temporal trends indicate that the SCLM-derived melts that these melt pockets represent have been an important contributor to TSVZ volcanism throughout the back-arc over the last 24 million years.

The differences between findings of this thesis versus previous explanations of mafic volcanism in the TSVZ continues a broader effort to explain the mantle reservoirs and fluxes behind mafic volcanism in the Andean magmatic arc. Hickey et al. (1986) was one of the first studies to identify mantle source heterogeneity in the mafic volcanism of the SVZ, and to propose that these variations reflect enrichment of an ancient OIB-like asthenospheric mantle source or a more recent metasomatized lithospheric mantle source. In the years since this study, additional investigations of mafic SVZ volcanism have considered the cause for enrichment in the SVZ mantle source, reemphasizing that the enriched character of SVZ basalts comes from asthenosphere, lithosphere, and/or lithosphere that was eroded or delaminated into the asthenosphere (e.g., Hickey-Vargas et al., 2016; Kay et al., 1994; Stern et al., 1991; Stern et al., 1991). While the focus of this thesis was to demonstrate the plausibility of metasomatized SCLM as a melt source, these interpretations are not necessarily meant as a rejection of the presence of an enriched asthenospheric source. Instead, this thesis demonstrates the plausibility that the melting of metasomatized SCLM constitutes a viable explanation for the enriched intraplate signature of TSVZ lavas.

By demonstrating the plausibility of the SCLM source, new questions arise. Firstly, do the glass veins in anhydrous xenoliths from the eastern margin of the Payenia province (Bertotto et al., 2013) show any evidence that they originate from hydrous cumulates? The lack of amphibole or phlogopite in the Agua Poca xenoliths may suggest that modal metasomatism did not occur in the TSVZ SCLM. However, Yaxley and Kamenetsky (1999) demonstrate that the melting of amphibole, which would remove it from the xenolith phase assemblage, can explain the Th-U depletions and Nb-Ta enrichments of glass veins in amphibole- and phlogopite-free peridotite xenoliths from Australia.

Amphibole consumption during melt pocket formation in the Gobernador Gregores xenoliths was also identified from geochemical observations (Aliani et al., 2009). A limitation in testing this hypothesis in glass veins in Payenia xenoliths would be the thickness of the glass veins ($\sim 10\ \mu\text{m}$), which would prevent it from analysis by LA-ICP-MS. Microbeam techniques such as nanoSIMS may allow for reliable measurements at this spatial resolution.

Furthermore, analyzing the oxygen isotope contents of glasses and the coexisting mineral phases in the mantle xenoliths from the SVZ would offer a direct test of the conclusions made in the first chapter. Oxygen isotope systematics predicted by the model in this chapter suggest that the melt produced from SCLM cumulates have moderately lower $\delta^{18}\text{O}_{\text{olivine}}$ values than the asthenospheric melt that produced the cumulate. By measuring the $\delta^{18}\text{O}$ values of the melt pocket and the metasomatic minerals directly associated, we can test the validity of mineral-melt oxygen isotope fractionations modeled in this thesis. The identification of a hydrous-phase signature in the glass veins of Agua Poca xenoliths would significantly strengthen the conclusion that the melt veins, patches and pockets frozen into mantle xenoliths in the SVZ have a petrogenetic relationship with the back-arc alkali magmas in this region.

Secondly, can periods of metasomatism more recent than $\sim 150\text{-}200\ \text{Ma}$ be identified in the geochemistry of TSVZ volcanism? Nd and Hf ingrowth trends predicted by the SCLM cumulate formation model of chapter 1 indicate that if SCLM cumulates come from an asthenospheric source that presently has $\Delta\epsilon_{\text{Hf}} \sim 0$, the cumulate would have to ingrow radiogenic Hf and Nd for $\sim 150\text{-}200\ \text{Ma}$ in order to attain the negative $\Delta\epsilon_{\text{Hf}}$ values exhibited by Cenozoic lavas in the TSVZ back-arc. Modeling results from this thesis will be used to test whether a similar duration of isotopic ingrowth is required to produce the

observed trends in Pb and Sr isotopes of these lavas. This period in the region coincides with the breakup of the Gondwanan supercontinent and the development of a magmatic arc along the Proto-Pacific convergent margin. These two events would be likely cause significant volumes of asthenospheric melts, some generated from decompression melting beneath the rifting of the South American and African continents, while other melts would be formed from slab inputs released by the subducting slab. These two types of melts would both create significant volumes of metasomatic cumulates in the TSVZ SCLM with a variable degree of arc signature in their trace element contents. However, more recent events in the SVZ also may have contributed to and melted from SCLM cumulates, such as the subduction of the Chasca-Catequil and Farallon-Aluk spreading centers during the Cretaceous and Paleogene (Aragón et al., 2011; Iannelli et al., 2018; Seton et al., 2012) as well as the late Miocene episode of shallow slab subduction (Kay et al., 2006; Ramos and Folguera, 2009). A multi-episodic history of SCLM cumulate formation and melting will be considered as I refine the interpretations established in this thesis.

In addition to a temporally variable history of metasomatism, isotope ingrowth patterns may also be dependent on variability in the cumulate mineral assemblages produced by metasomatism across the depth range of the SCLM. The bulk parent-daughter ratios of SCLM cumulates are sensitive to trace element partitioning characteristics of its mineral assemblage (as is proposed by Pilet et al., 2011), such as high Lu/Hf in garnet and high Rb/Sr in phlogopite. The distribution of these minerals at variable depths in the mantle would impact the isotopic evolution of the variable mineral assemblages at these depths. For instance, if garnet-bearing anhydrous SCLM cumulates form deeper than amphibole- and phlogopite- bearing hydrous cumulates, the deep cumulates may ingrow to considerably higher $^{176}\text{Hf}/^{177}\text{Hf}$ than the shallow cumulates. Furthermore, if the garnet-rich

(dense) base of the SCLM was removed by subduction erosion or delamination, it would leave the amphibole- and phlogopite-rich layer of cumulates exposed to hot asthenosphere and would thus generate melts with isotope contents controlled by this mineral assemblage. The isotope ingrowth modeling approaches I pursue in the future will also take this possibility into account.

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**APPENDIX: GEOCHEMISTRY AND CRYSTALLOGRAPHIC-
PREFERRED ORIENTATIONS OF PERIDOTITE XENOLITHS FROM
THE WYOMING CRATON, MONTANA, USA**

Archean Wyoming Craton of the western United States endured an extended period of flat slab subduction during the Laramide orogeny in the late Mesozoic and early Cenozoic. In order to investigate the tectonic and magmatic effects of this event on the mantle keel of the Wyoming craton, I conducted a study that investigated the geochemistry and crystallographic-referred orientations (CPOs) of a suite of 23 peridotite xenoliths that were erupted along a transect that crosses the northwestern margin of the craton. With the analytical work for this research project completed, preparation of a manuscript that discusses these results will begin Spring 2019.

Below is the long abstract for the 11th Kimberlite Conference oral presentation that introduces this project and the preliminary data collected for it. Figures 1-4 are figures from the long abstract. EBSD pole figure data measured on Oxford Instruments EBSD detector at Brown University. Figures 5-11 are slide figures from the oral presentation.

Figures 12-25 presents xenolith thin section CPO measurements and phase maps, which were made on an Oxford Instruments AZtecHKL Symmetry EBSD detector at the Scripps Institution of Oceanography by Drs. Emily Chin and Yuval Boneh.

Major, trace and H₂O concentrations measured in mineral phases of the xenoliths are reported in Tables 1-6. This dataset includes measurements collected before and after the Kimberlite conference presentation. Major element concentrations were measured on the Cameca SX-100 electron microprobe at Brown University. Trace element concentrations were measured by LA-ICP-MS using a Thermo Scientific X-series-2 ICP-

MS and a Photon-Machines Analyte G2 Laser at Brown. H₂O concentrations were measured on a Cameca IMS 6F SIMS at Carnegie DTM.

Deciphering the composition and structure of Wyoming craton mantle lithosphere: insights from peridotite xenoliths

Benjamin Parks¹, Emily J. Chin², Alberto Saal¹, Greg Hirth¹, Carter Hearn³, Jean-
Louis Bodinier⁴

¹Brown University, Providence, USA, benjamin_parks@brown.edu, alberto_saal@brown.edu,
greg_hirth@brown.edu

²Scripps Institution of Oceanography, La Jolla, USA, e8chin@ucsd.edu

³USGS, Reston, USA, chearn@usgs.gov

⁴Université de Montpellier, Montpellier, France

Introduction

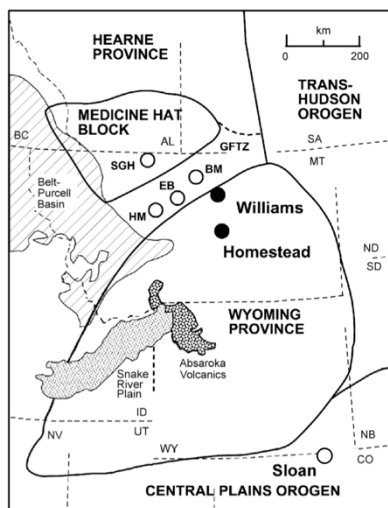


Figure 1: Tectonic map of the Homestead and Williams sample locations with respect to the Wyoming craton and other neighboring basement geologic terranes. Modified from Carlson et al. (2004).

The Wyoming craton stands out among Archean cratons as one that underwent widespread, thick-skinned deformation relatively recently, specifically during the Laramide orogeny. If this deformation occurred within the lithospheric mantle of the Wyoming craton, the thermal, compositional, and rheological effects of this tectonism should be documented by

the xenoliths subsequently transported to the surface. A large portion of the mantle xenolith-bearing magmatism occurred in the Eocene-aged Montana high-potassium igneous province at the end of the Laramide (Hearn Jr. 1989; O'Brien, et al. 1991). The xenoliths in this region span the northwestern margin of the Wyoming craton (Figure 1A). In particular, two kimberlite diatremes bear an abundance of garnet and garnet-spinel peridotites: the Homestead diatreme, located toward the the interior of the craton, and the Williams diatreme, located near the Proterozoic-aged Great Falls Tectonic Zone. To elucidate how Wyoming cratonic mantle has been modified prior to and during the Laramide, we present the first integrated investigation of mineral major and trace element compositions and deformation microstructures of peridotite xenoliths from the Homestead and Williams kimberlites.

Xenolith Suites & Petrography

Garnet and garnet-spinel peridotite xenoliths sampled from the Homestead and Williams kimberlites can be divided into three groups. The Williams xenoliths comprise one low-temperature group (group LTW) and one high-temperature group (group HTW), as previously categorized (Carlson, et al. 1999). The third group consists of the Homestead xenoliths (group HS). Among all groups, the xenoliths are predominantly harzburgites, while less than 15% of the samples are lherzolites.

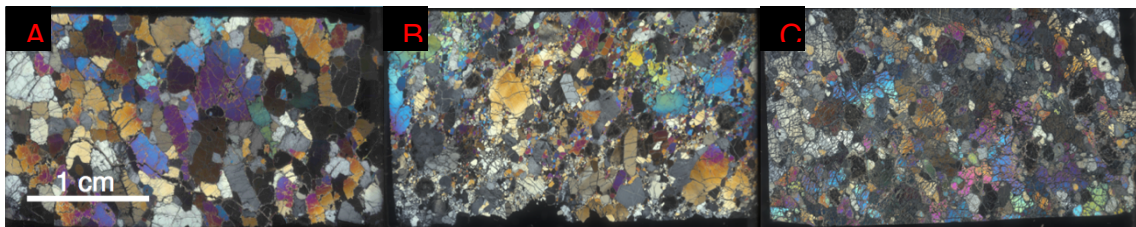


Figure 2: Photomicrographs in cross-polarized light of samples from each of the three xenolith groups: group LTW sample H68-16B (A), group HTW sample H81-26 (B), and group HS sample H00-11-16 (C).

LTW xenoliths yield inter-mineral major element equilibrium temperatures of 850-1050°C and ~3-4.2 GPa, which fall along a 38 mW/m² shield geotherm (Hearn Jr. 2004). This group exhibits a coarse tabular texture with weak foliation relative to group HTW, and predominantly isolated garnet and clinopyroxene grains (Figure 2A). Group HTW is hotter than this shield geotherm, yielding temperatures of 1100-1450°C and pressures of 4-5.5 GPa, and exhibit coarse porphyroclastic to mosaic porphyroclastic textures (Figure 2B). Olivine grains in HTW samples appear as mm-scale porphyroclasts, smaller anhedral neoblasts, and in polygonal tablets that overprint porphyroblasts and neoblasts, which suggests the occurrence of post-deformation annealing. Group HS yields similar P-T estimates to group HTW, with temperatures of 1100-1400°C and pressures of 3.6-4.8 GPa (Hearn Jr. 2004). Group HS xenoliths exhibit predominantly coarse grained to coarse-porphyroclastic textures, including a subset of samples exhibiting coarse grained textures with intimately associated garnet and clinopyroxene (Figure 2C). Re-depletion model ages of group LTW (1.77-2.55 Ga, Carlson, et al. 1999) and group HS (2.30-2.77 Ga, Carlson, et al. 2004) are significantly older than the ages of group HTW (<0.83 Ga, Carlson, et al. 1999). However, the highly variable and unreliable garnet and clinopyroxene tie-line ages given by Rb-Sr, Lu-Hf, and Sm-Nd isotopes for Williams and Homestead peridotite xenoliths (Carlson et al. 2004) suggest that significant, more recent melt-rock interaction occurred.

Mineral Chemistry

Mineral compositions of the sampled xenoliths are generally depleted with respect to major elements. Most olivine Mg# values range from 0.91 to 0.93, falling within the expected

range for cratonic peridotites (Bernstein, et al. 2007). The exceptions are two HS samples (one of which is sample H00-11-16, Figure 2C), both with olivine $Mg\# = 0.90$. In clinopyroxenes, molar Cr/Al ratios correlate positively with $Mg\#$; H00-11-16 clinopyroxenes yield the lowest Cr/Al (<0.3), which indicates relatively low depletion, while grains from LTW sample H68-16B yield the highest (~ 0.6), indicating high depletion. Among all samples, H68-16B yields the largest range in garnet Cr_2O_3 concentrations, such that rims have lower range in Cr_2O_3 (4.0-5.7 wt.%) than cores (4.2-6.4 wt.%).

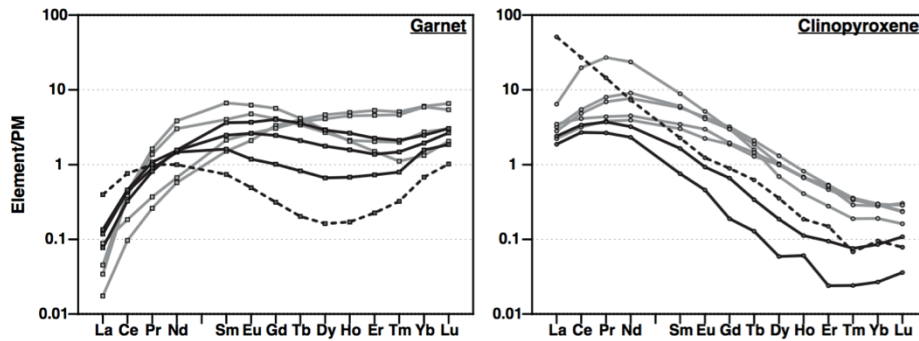


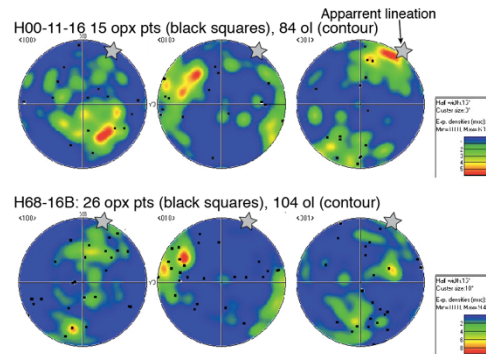
Figure 3: Primitive mantle- normalized REE concentrations in garnet (left) and clinopyroxene (right) for groups HS (solid grey lines), LTW (dashed black lines), and HTW (solid black lines). Normalizing concentrations from McDonough and Sun (1995).

Trace element compositions of garnet and clinopyroxene show significant systematic variations in enrichment, indicating varying degrees and styles of metasomatism among the analyzed sample suite (Figure 3). Primitive-mantle normalized REE patterns in clinopyroxenes range from MREE-enriched (i.e., $(La/Nd)_N < 1$) for groups HTW and HS to LREE-enriched (i.e., $(La/Nd)_N > 1$) for group LTW. For most of the observed samples, garnets have sinusoidal REE patterns. The two HS samples with low olivine $Mg\#$ and low cpx Cr/Al have monotonic garnet REE patterns. The low level of depletion in the HS

samples that have monotonic REE patterns suggests that parts of the Wyoming craton lithosphere beneath Homestead interacted with an infiltrating melt/fluid at a high melt/fluid-to-rock ratio, while the garnet, cpx and melt/fluid approach chemical equilibrium. In contrast, group LTW, represented by sample H68-16B, shows significant chemical disequilibrium, based on between- and within-grain variation in major element and REE concentrations.

Crystallographic-preferred orientations

The crystallographic-preferred orientations (CPO) of olivines, measured using EBSD, indicate that these peridotites record different fabrics. CPO patterns, shown in Figure 4 for



LTW sample H68-16B and HS sample H00-11-16. In the HS sample, opx and olivine align in the $[001]$ direction, parallel to lineation and parallel to the (100) plane, which indicates a B-type fabric. Though few were measured, opx CPOs in both samples appear aligned with olivine CPO perpendicular to foliation in the (010) plane. The significantly different CPO for H00-11-16 may signify that the deformation conditions reflected by mineral CPOs may relate to its relatively undepleted, well-equilibrated chemical composition. Such traits suggest that prior to the ascent of these xenoliths to the surface, considerable removal and (or) reworking of the base of the Wyoming craton mantle lithosphere occurred, potentially related to the Laramide orogeny.

Figure 4: Olivine and orthopyroxene CPO patterns, plotted as lower hemisphere, equal-area projections.

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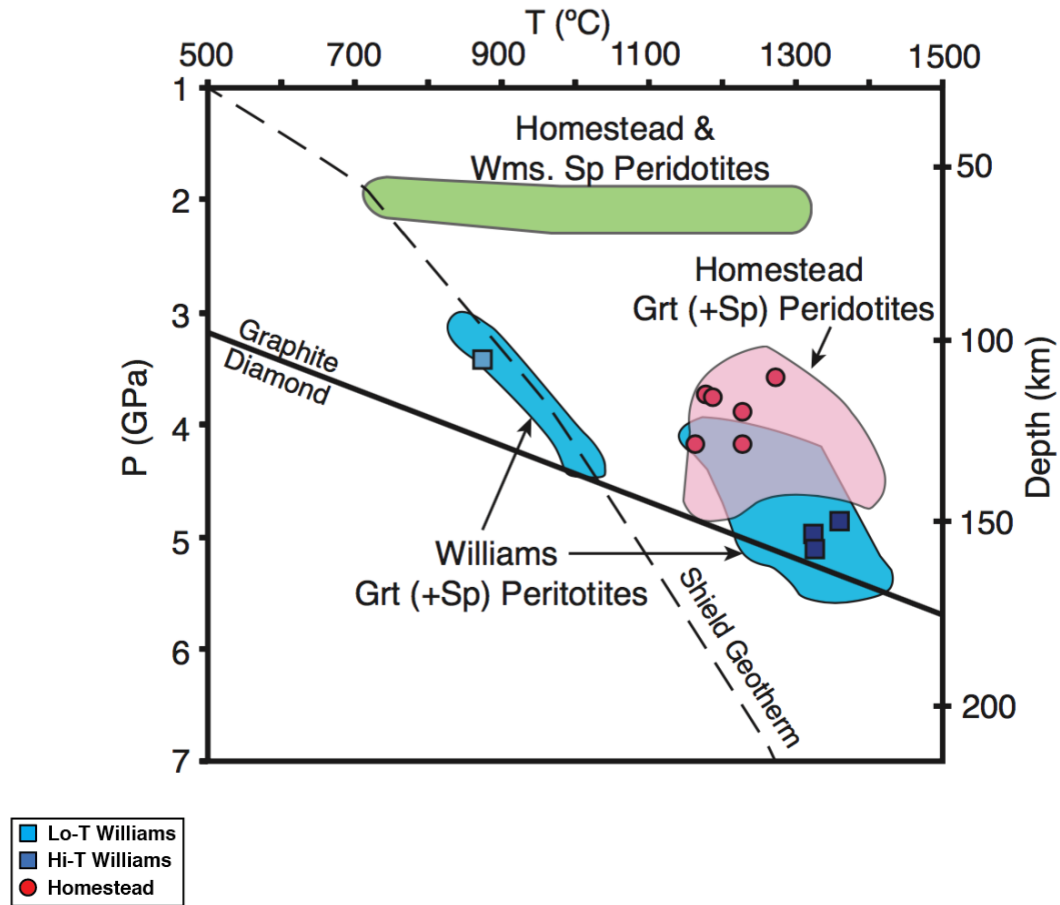


Figure 5. Calculated equilibrium pressures and temperatures for Homestead and Williams xenoliths. Thermobarometry calculations use the thermobarometer of Kohler and Brey (1990). Green, blue, and pink fields from Hearn (2004).

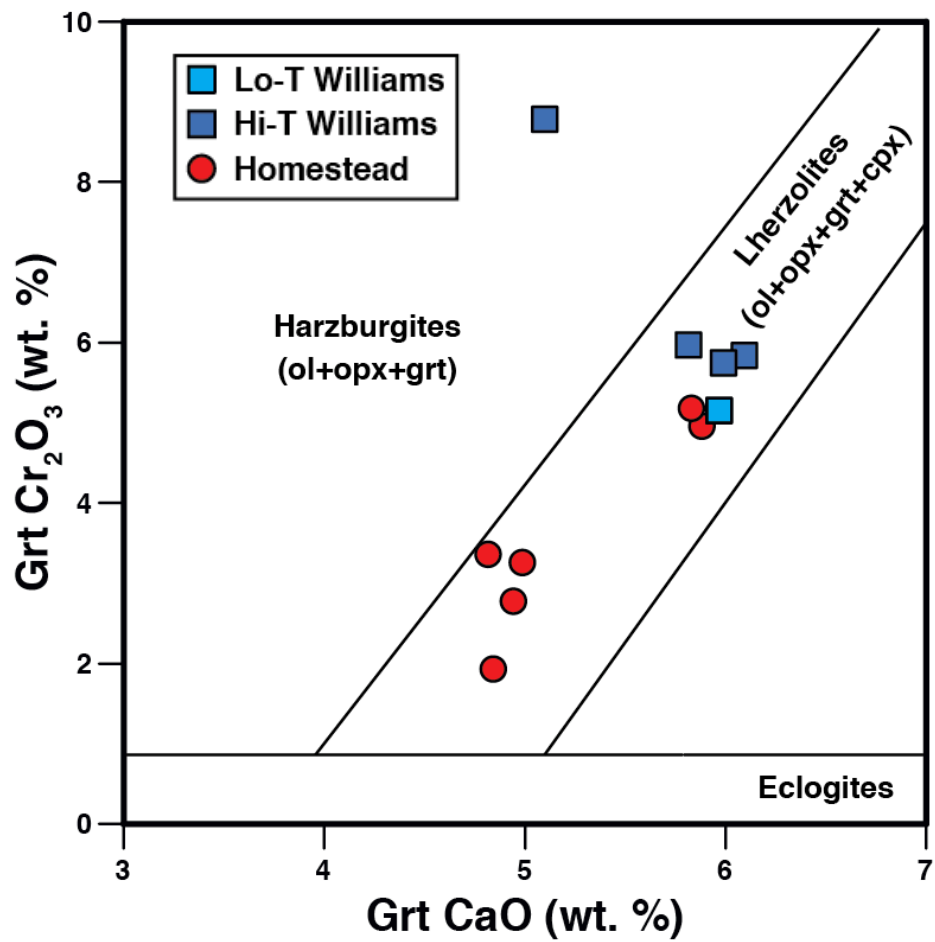


Figure 6. Average garnet Cr_2O_3 and CaO concentrations for Homestead and Williams xenoliths. Fields from Grutter et al. (2004).

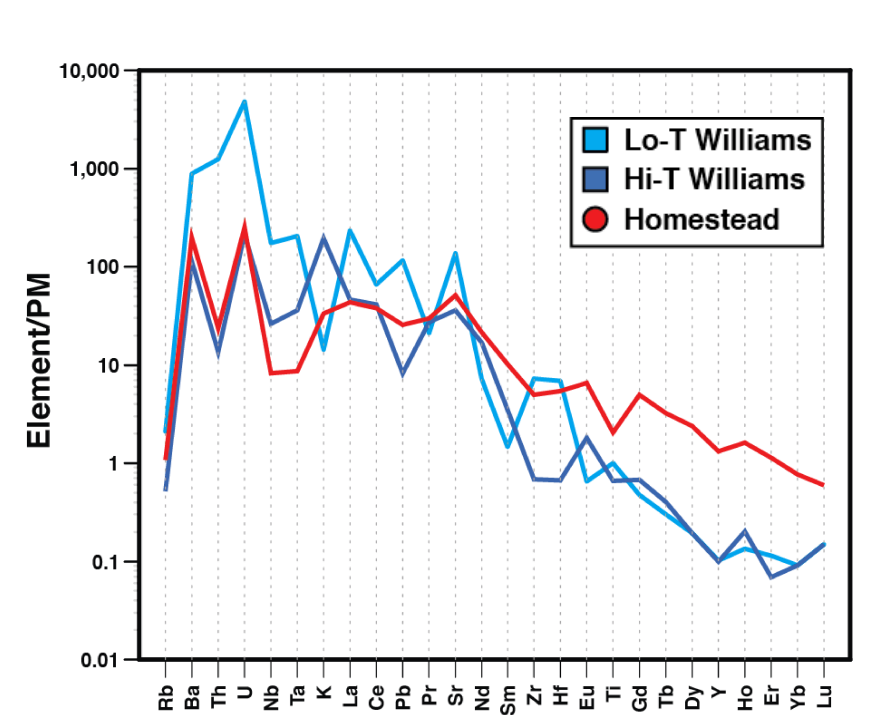


Figure 8. Primitive mantle normalized trace element diagram for melts calculated to be in equilibrium with analyzed clinopyroxene compositions. Clinopyroxene-melt partition coefficients from Hart and Dunn (1993). Primitive mantle normalization from McDonough and Sun (1995).

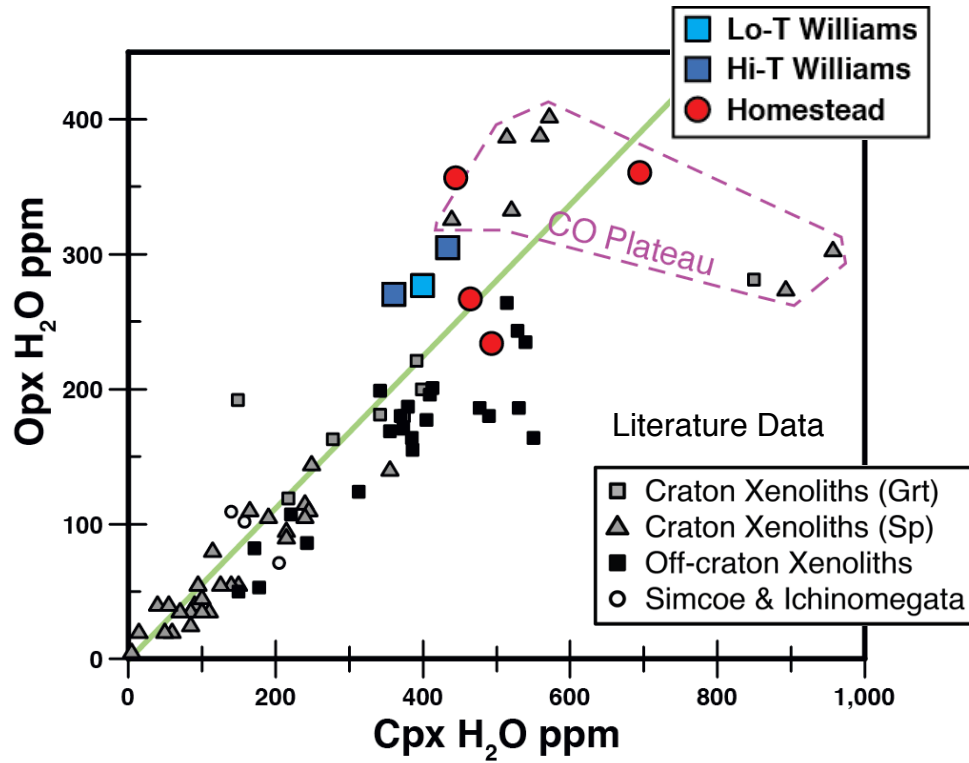


Figure 9. Orthopyroxene and clinopyroxene H₂O concentrations, averaged for each Wyoming craton xenolith sample. Green line represents experimentally determined orthopyroxene-clinopyroxene H₂O partition coefficient from Tenner et al. (2009). Black, grey and white symbols from the compilation of Peslier (2010).

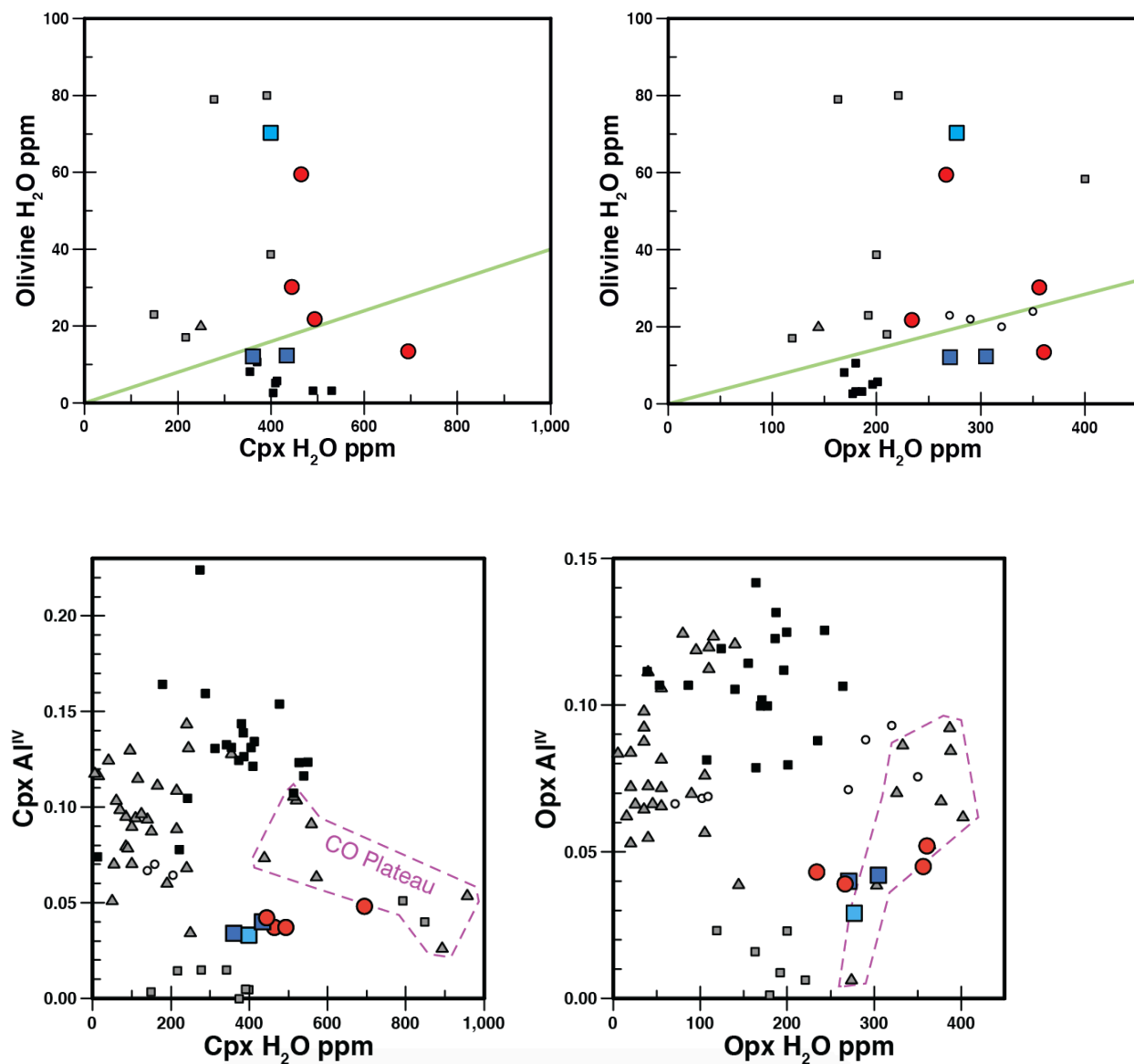


Figure 10. Clinopyroxene and orthopyroxene H₂O concentrations versus olivine H₂O concentration and the tetrahedral Al content (pfu) of each mineral. Values are averaged for each Wyoming craton xenolith sample. Black, grey and white symbols from the compilation of Peslier (2010).

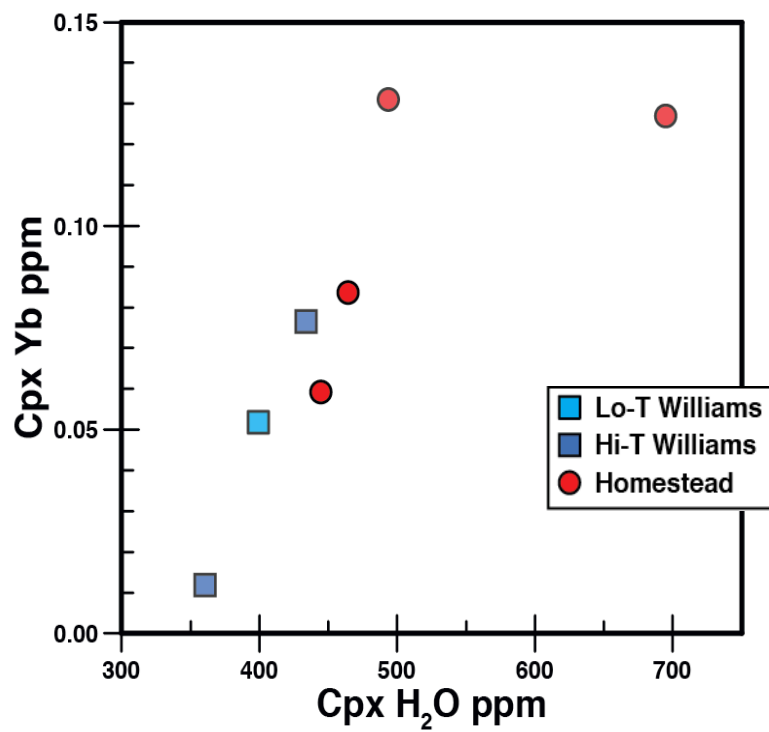


Figure 11. Clinoopyroxene H₂O concentrations versus Yb concentrations, averaged for each Wyoming craton xenolith sample.

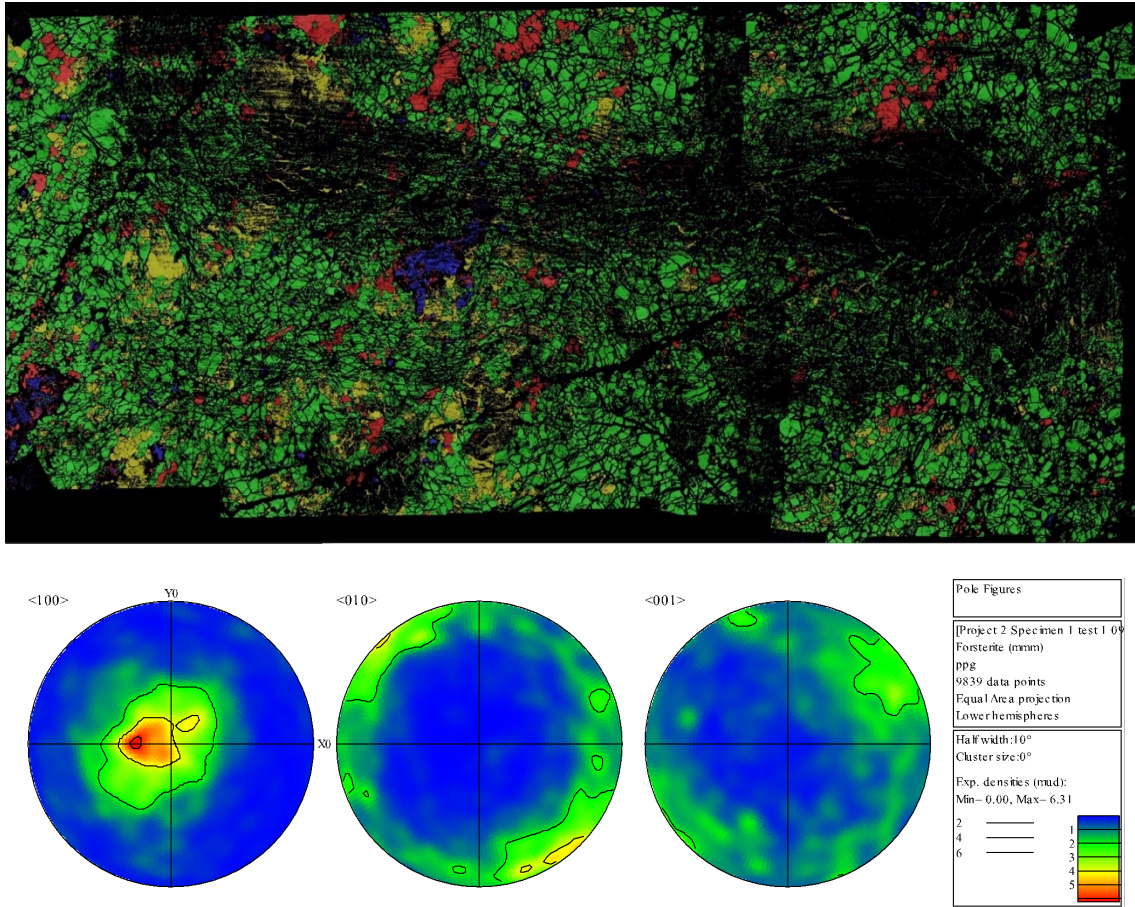


Figure 12. Mineral phase map and olivine crystallographic-preferred orientations for Bearpaw xenolith sample WC-98. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is spinel.

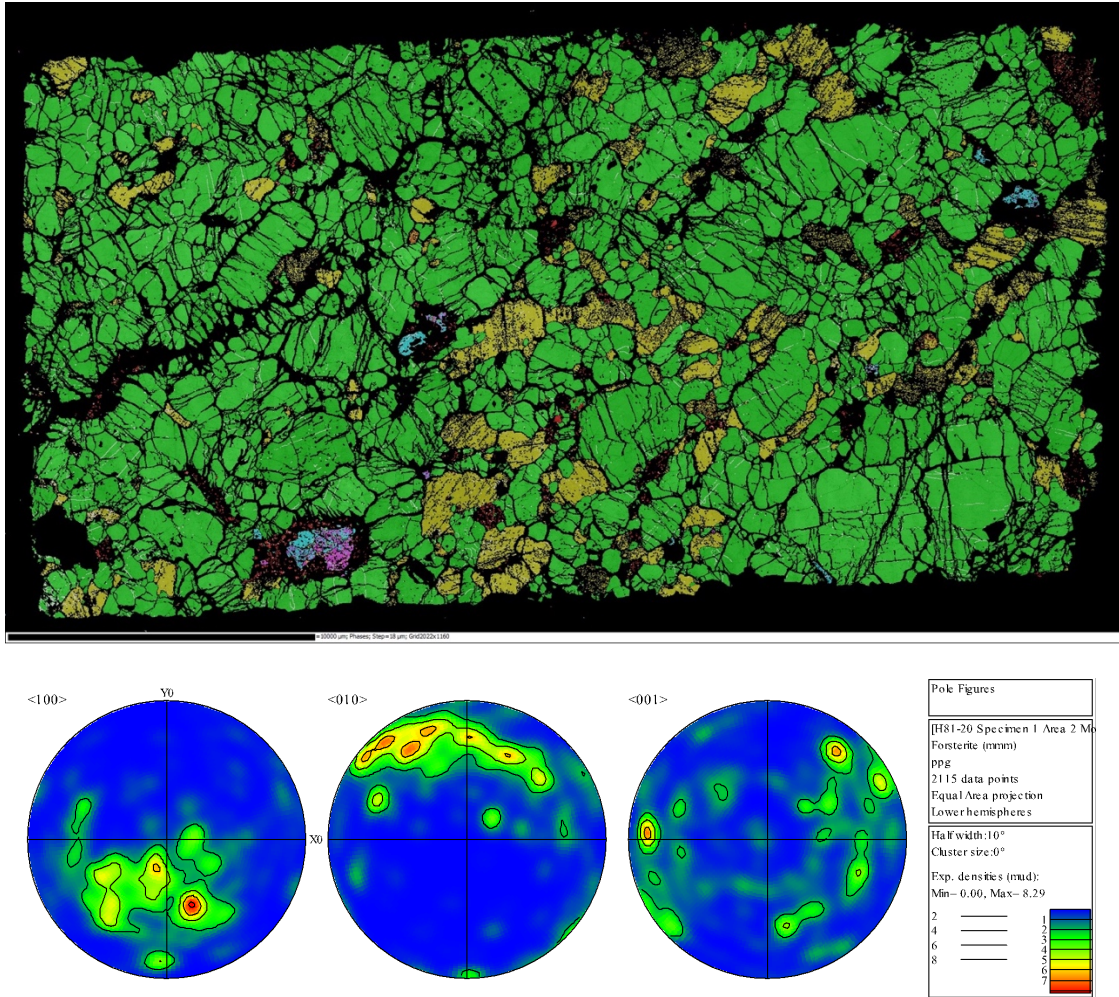


Figure 13. Mineral phase map and olivine crystallographic-preferred orientations for Williams xenolith sample H81-20. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and cyan is spinel.

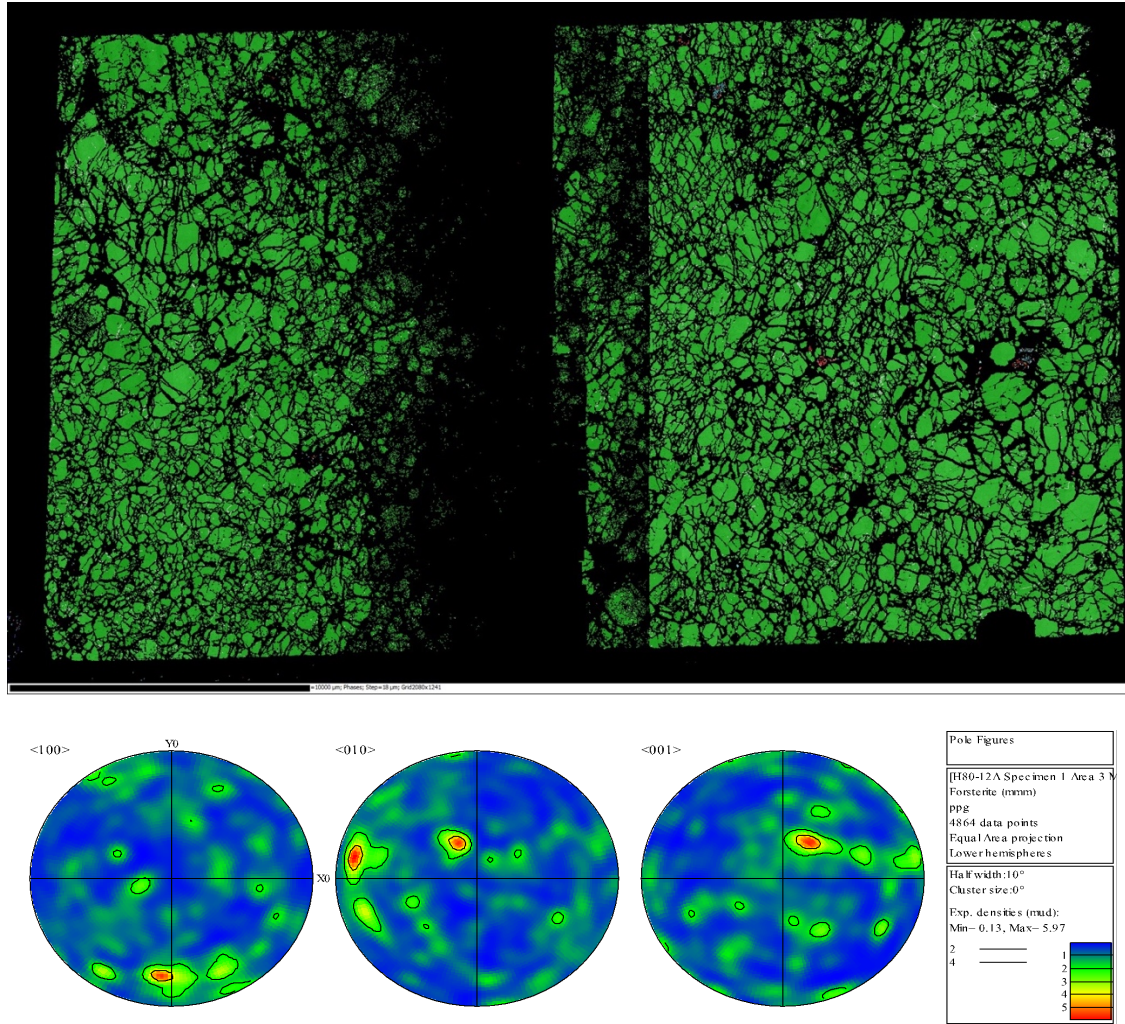


Figure 14. Mineral phase map and olivine crystallographic-preferred orientations for Williams xenolith sample H80-12A. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is spinel.

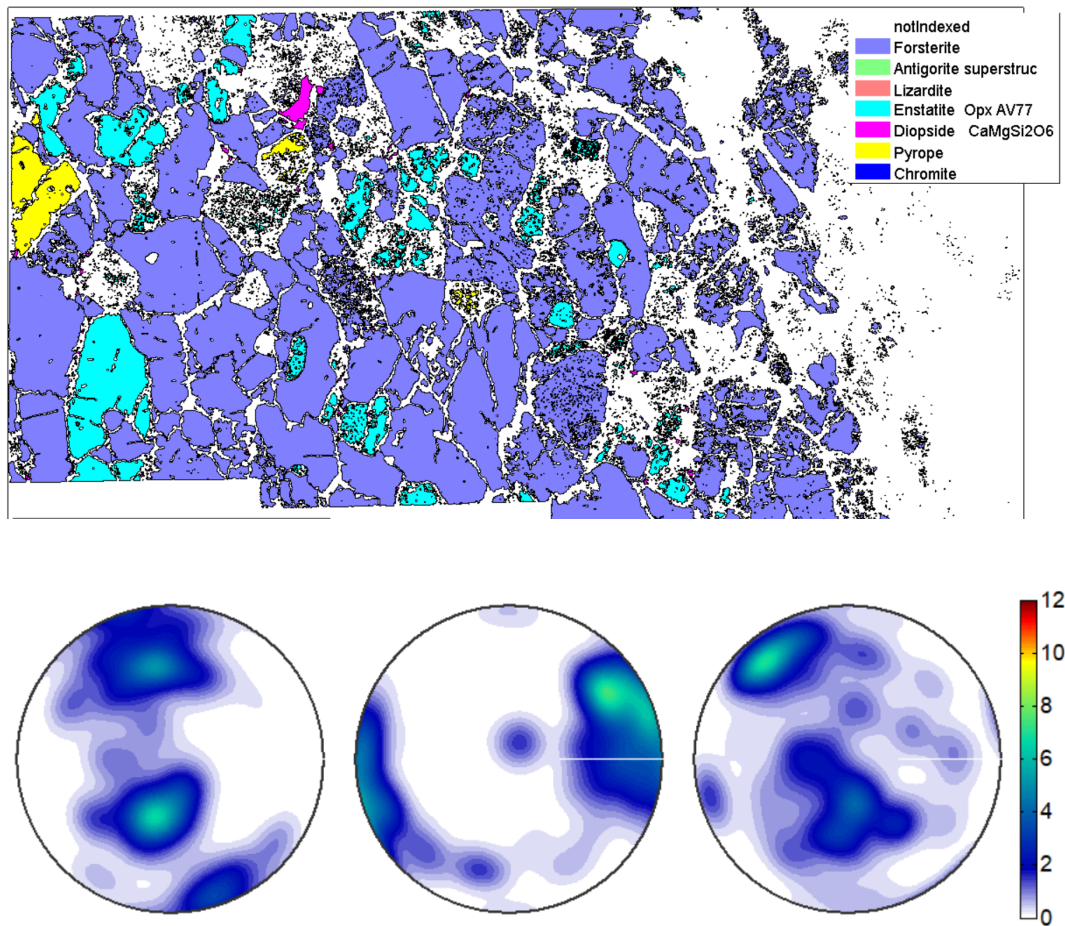


Figure 15. Mineral phase map and olivine crystallographic-preferred orientations for Williams xenolith sample H68-16B.

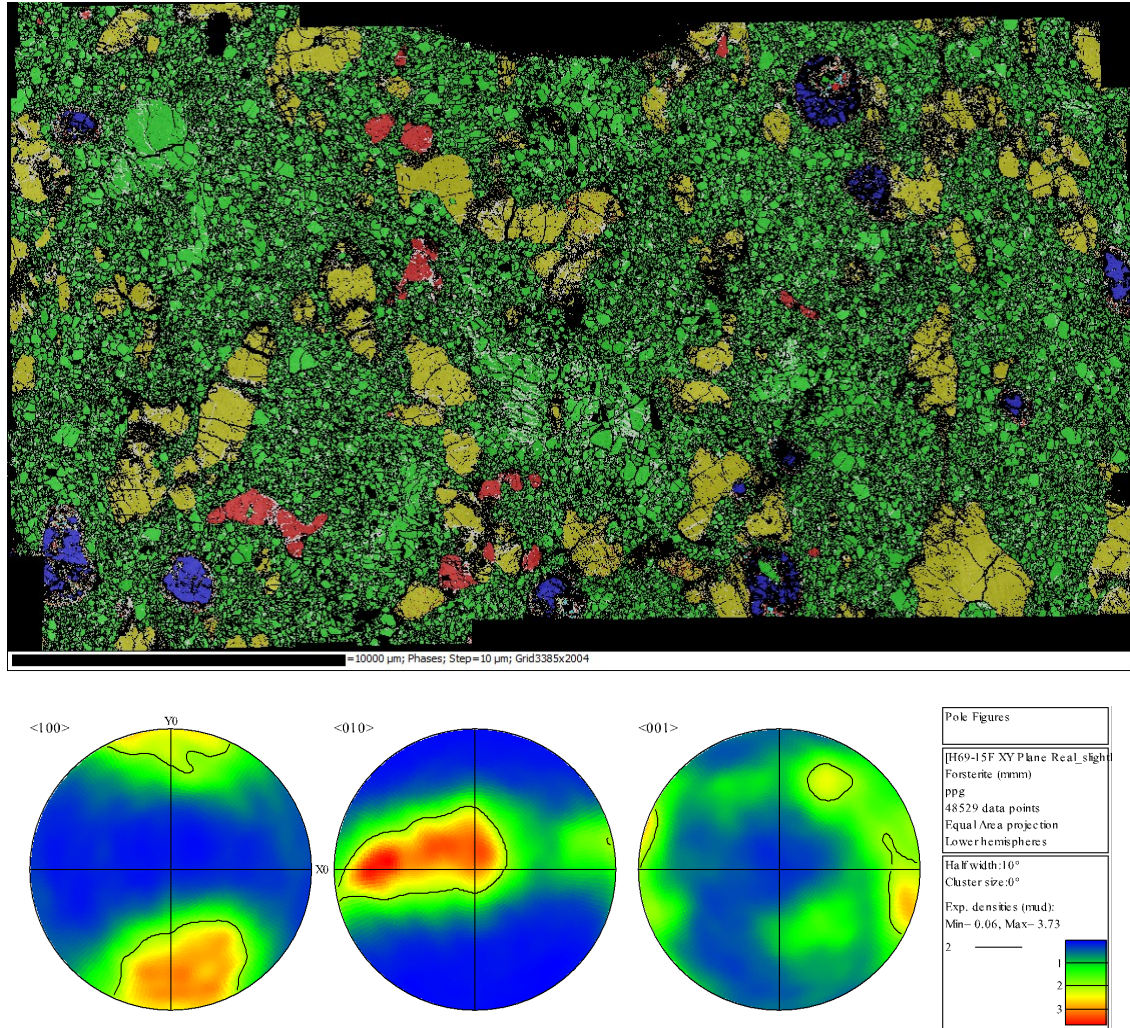


Figure 16. Mineral phase map and olivine crystallographic-preferred orientations for Williams xenolith sample H69-15F. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is garnet.

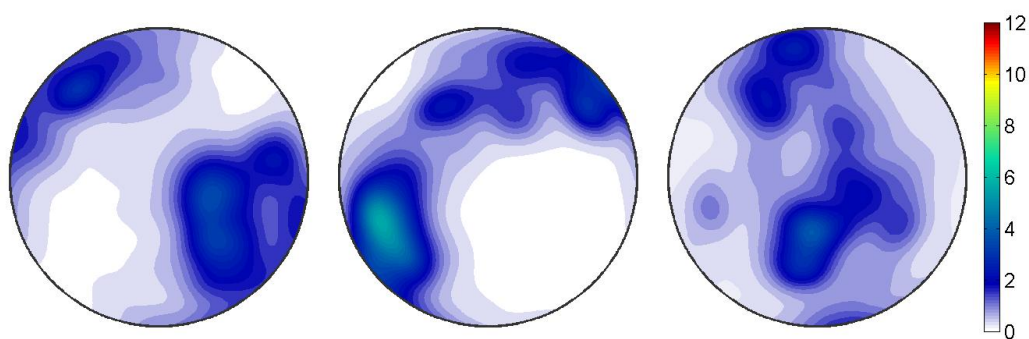


Figure 17. Olivine crystallographic-preferred orientations for Williams xenolith sample H81-26.

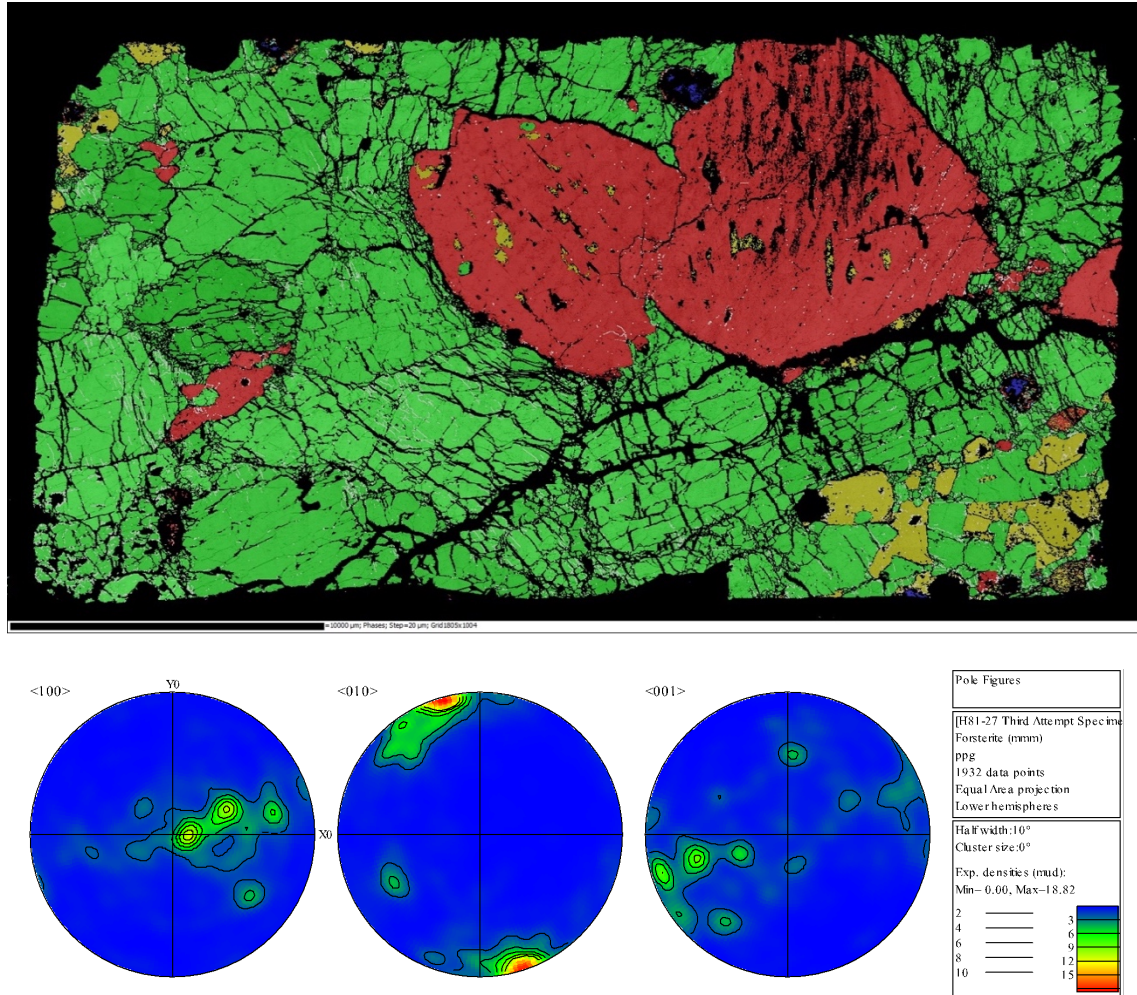


Figure 18. Mineral phase map and olivine crystallographic-preferred orientations for Williams xenolith sample H81-27. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is garnet.

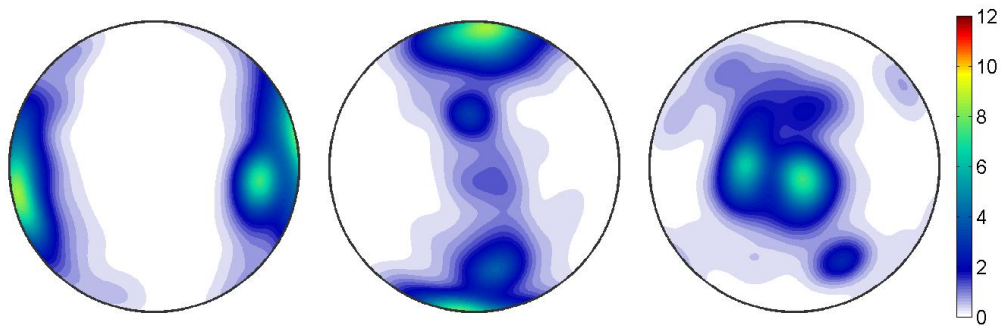
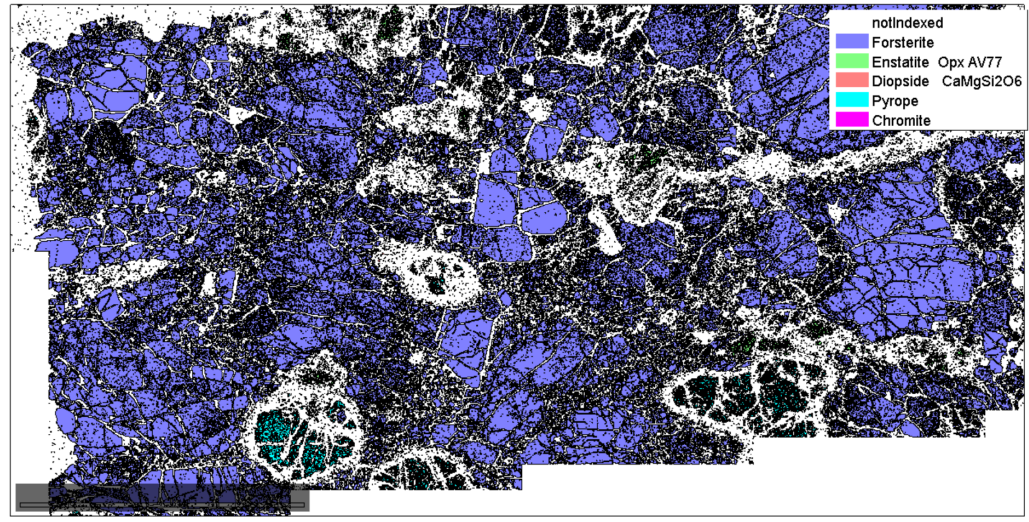


Figure 19. Mineral phase map and olivine crystallographic-preferred orientations for Williams xenolith sample H93-11B.

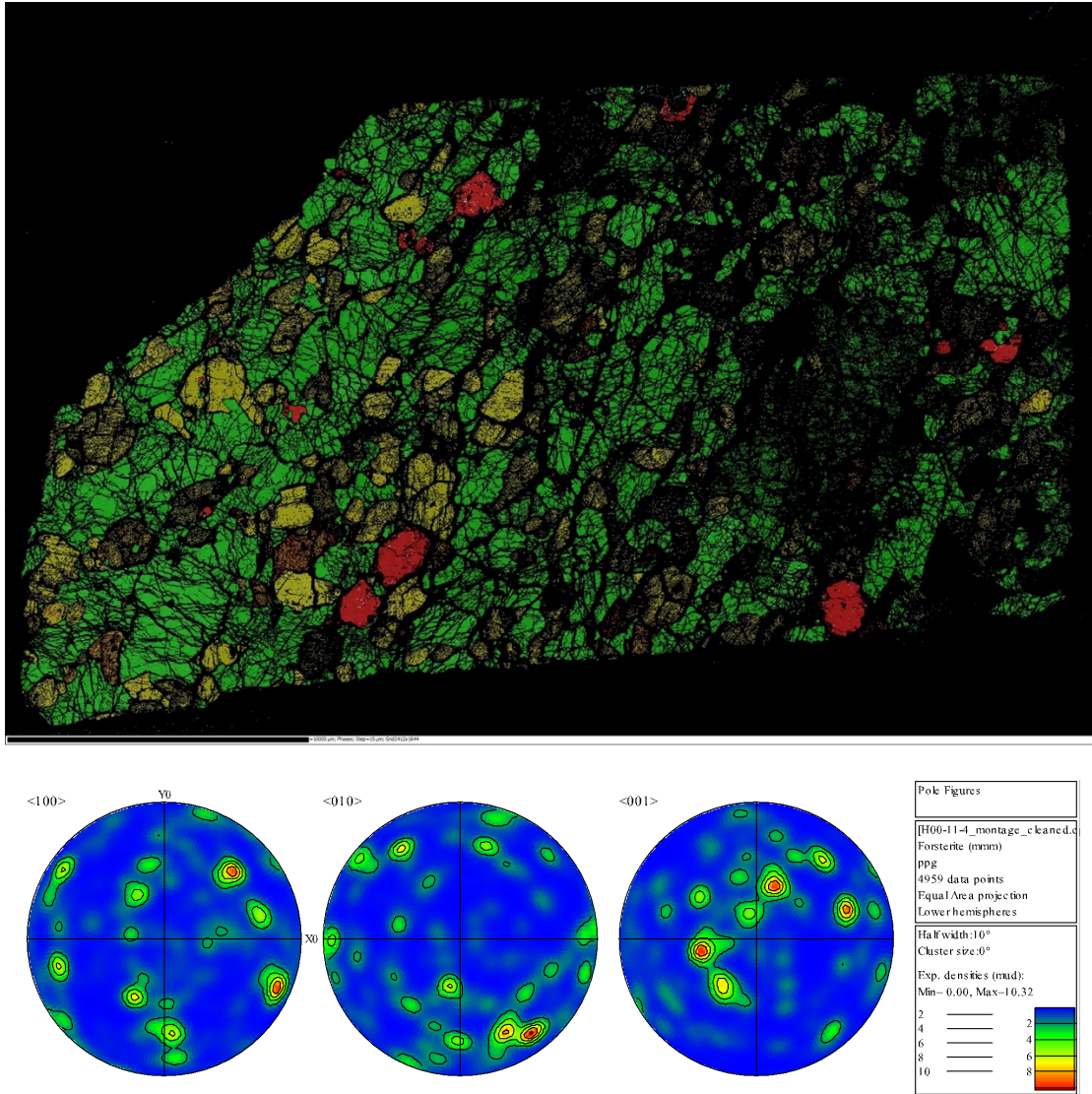


Figure 20. Mineral phase map and olivine crystallographic-preferred orientations for Homestead xenolith sample H00-11-4. In the phase map, green is olivine, yellow is orthopyroxene, and red is clinopyroxene.

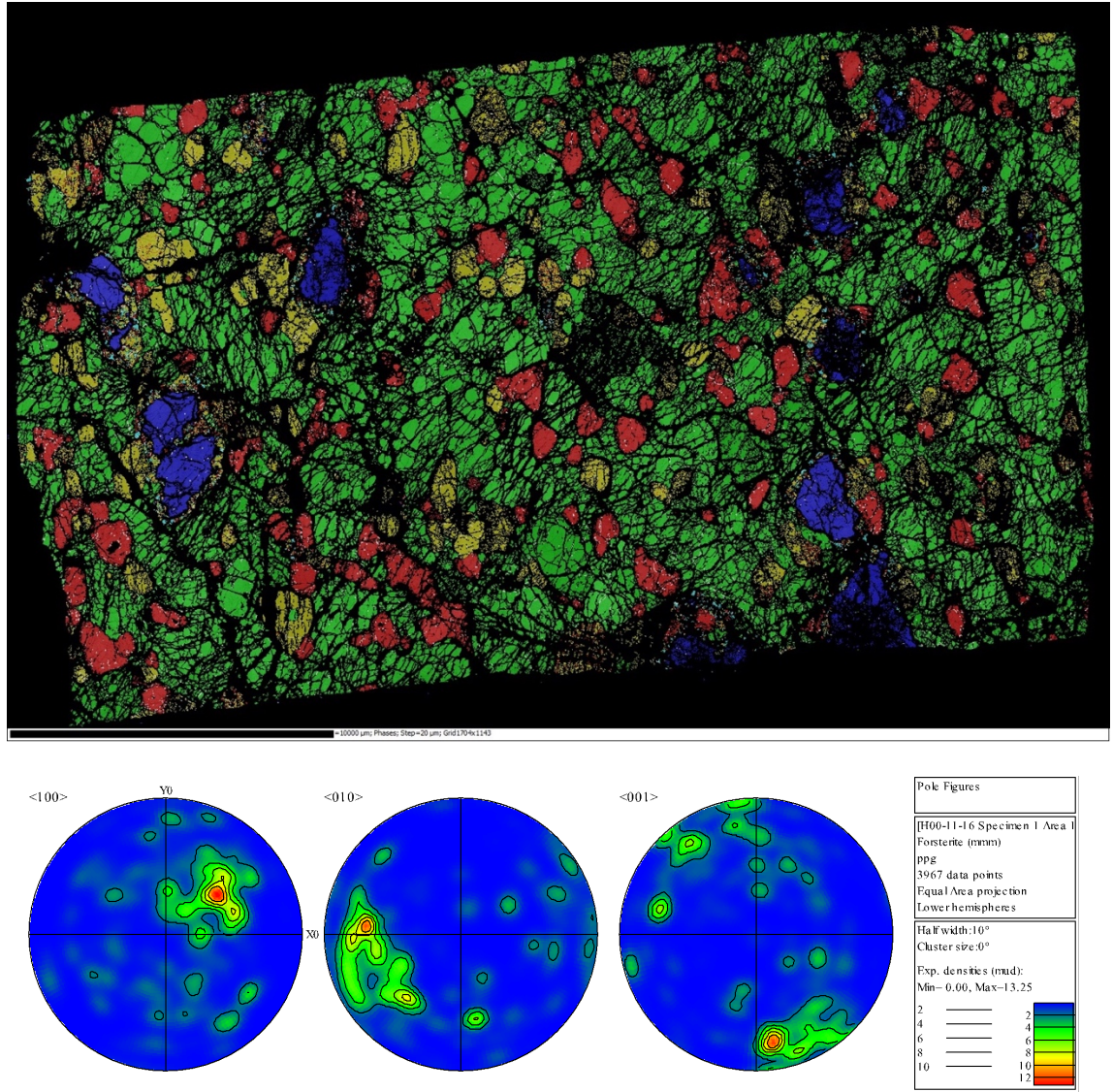


Figure 21. Mineral phase map and olivine crystallographic-preferred orientations for Homestead xenolith sample H00-11-16. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is garnet.

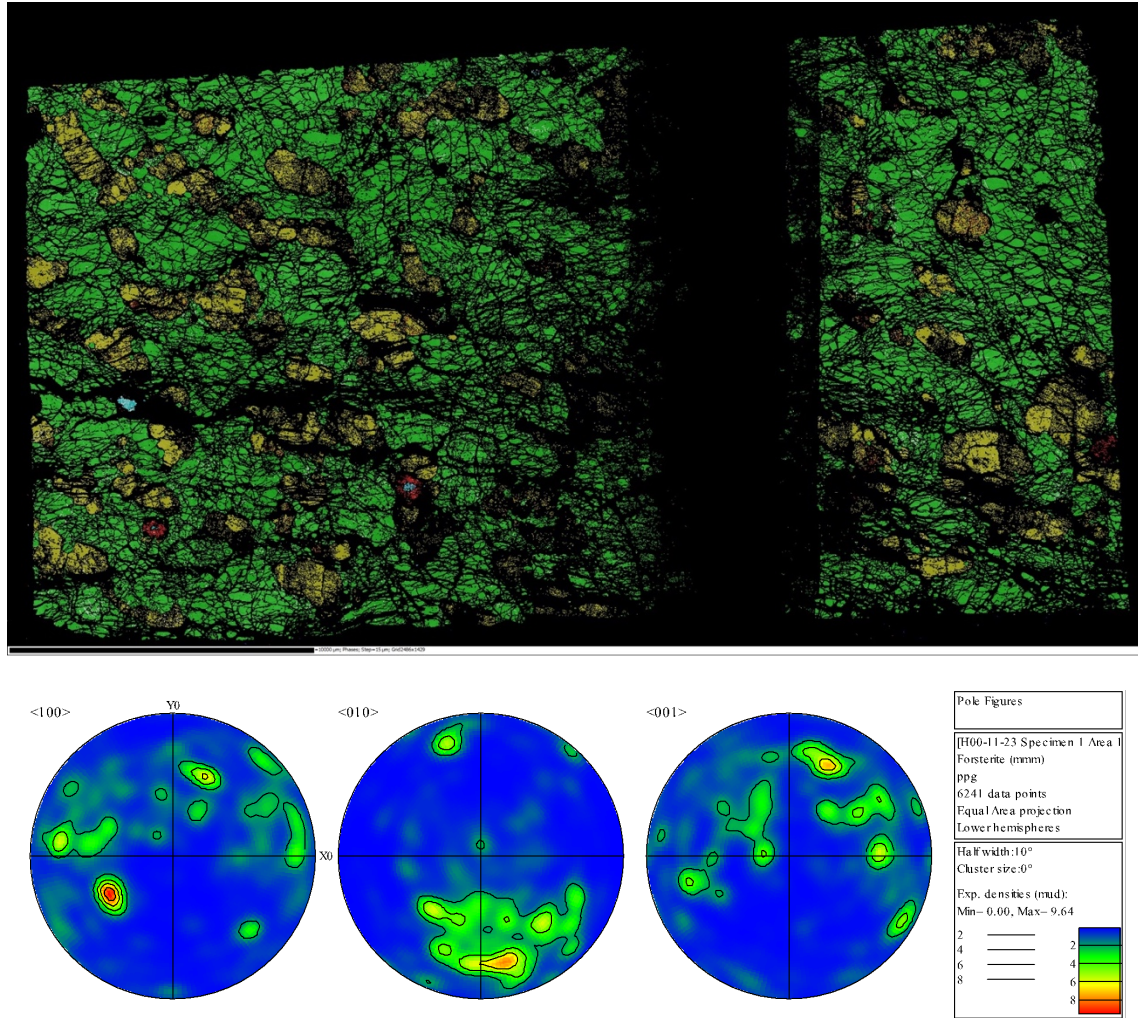


Figure 22. Mineral phase map and olivine crystallographic-preferred orientations for Homestead xenolith sample H00-11-23. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and cyan is spinel.

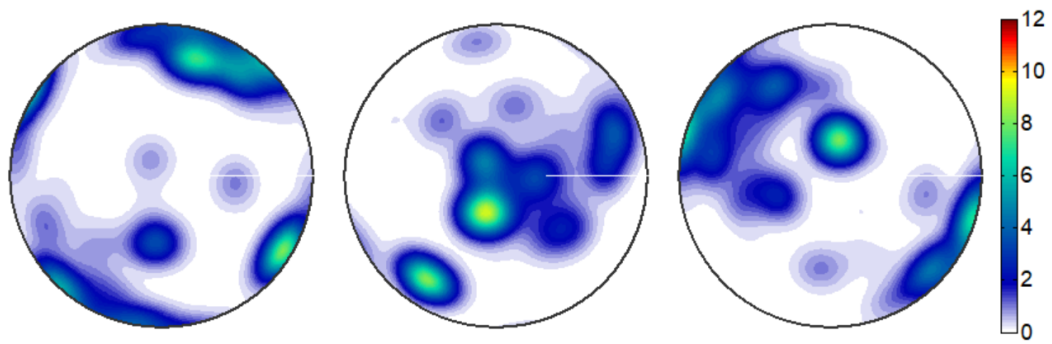
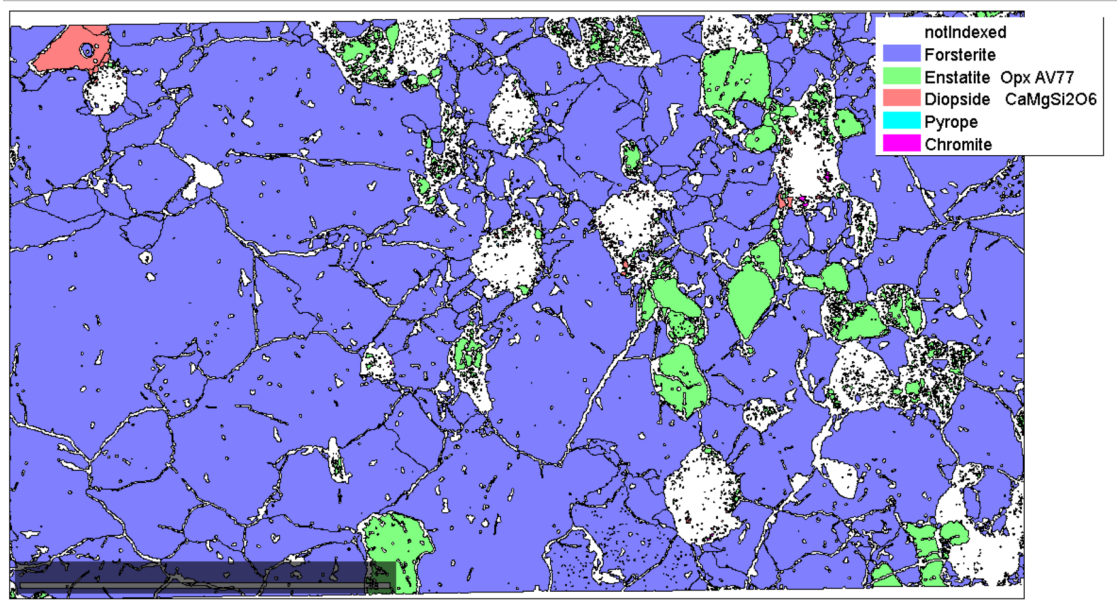


Figure 23. Mineral phase map and olivine crystallographic-preferred orientations for Homestead xenolith sample H00-12-1.

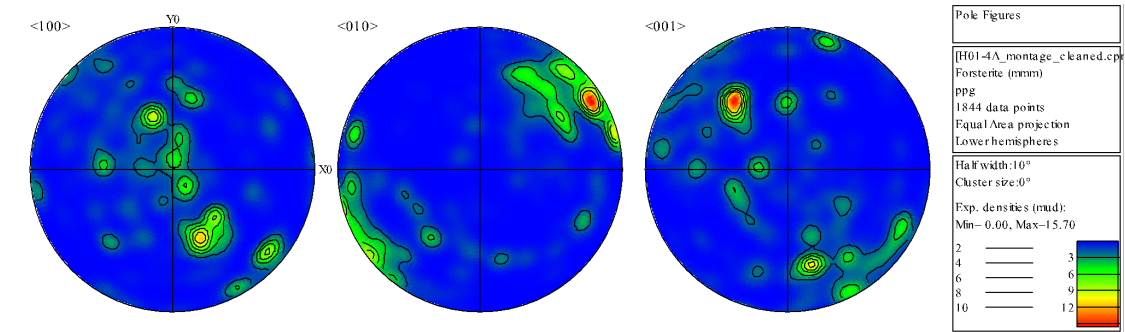
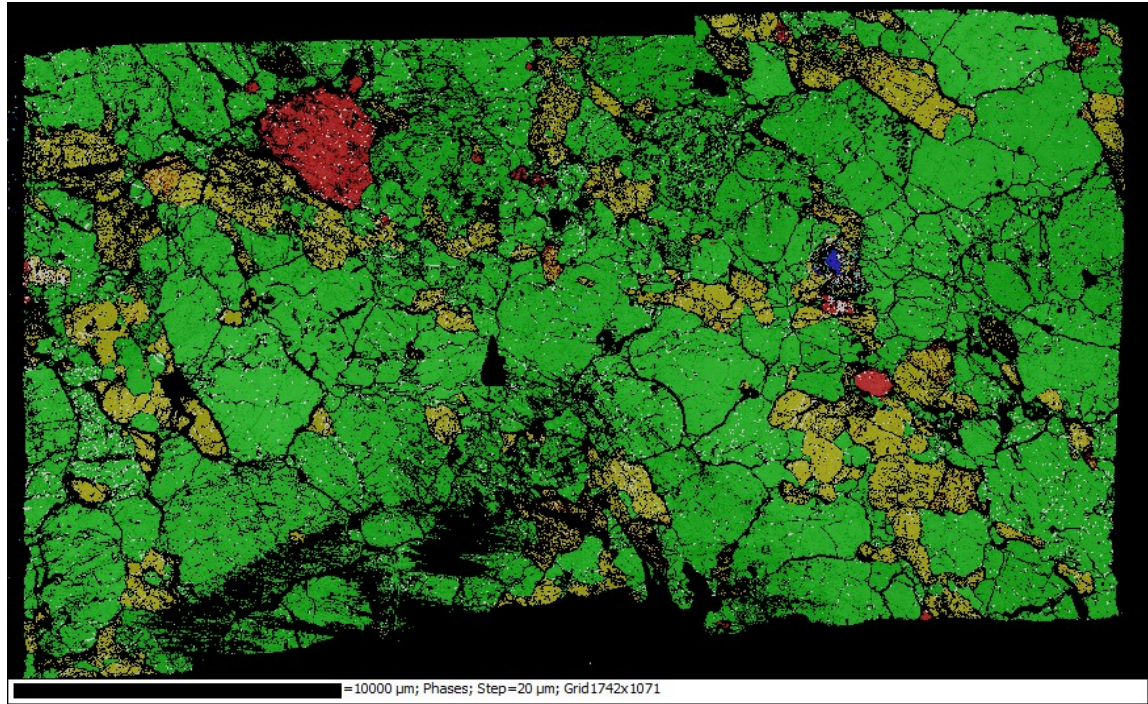


Figure 24. Mineral phase map and olivine crystallographic-preferred orientations for Homestead xenolith sample H01-4A. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is spinel.

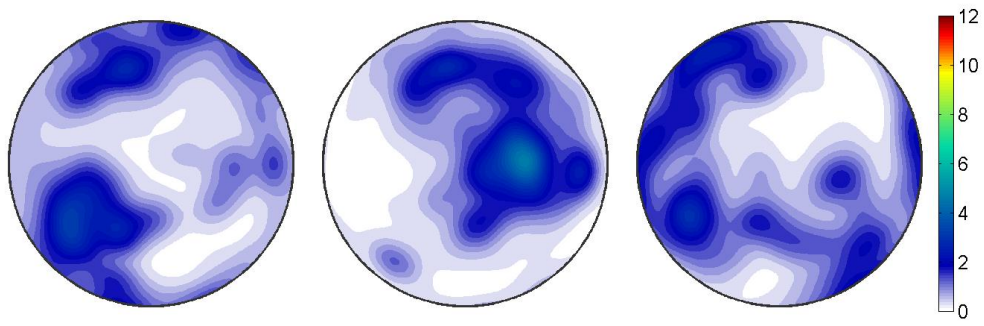


Figure 25. Olivine crystallographic-preferred orientations for xenolith sample H01-4C.

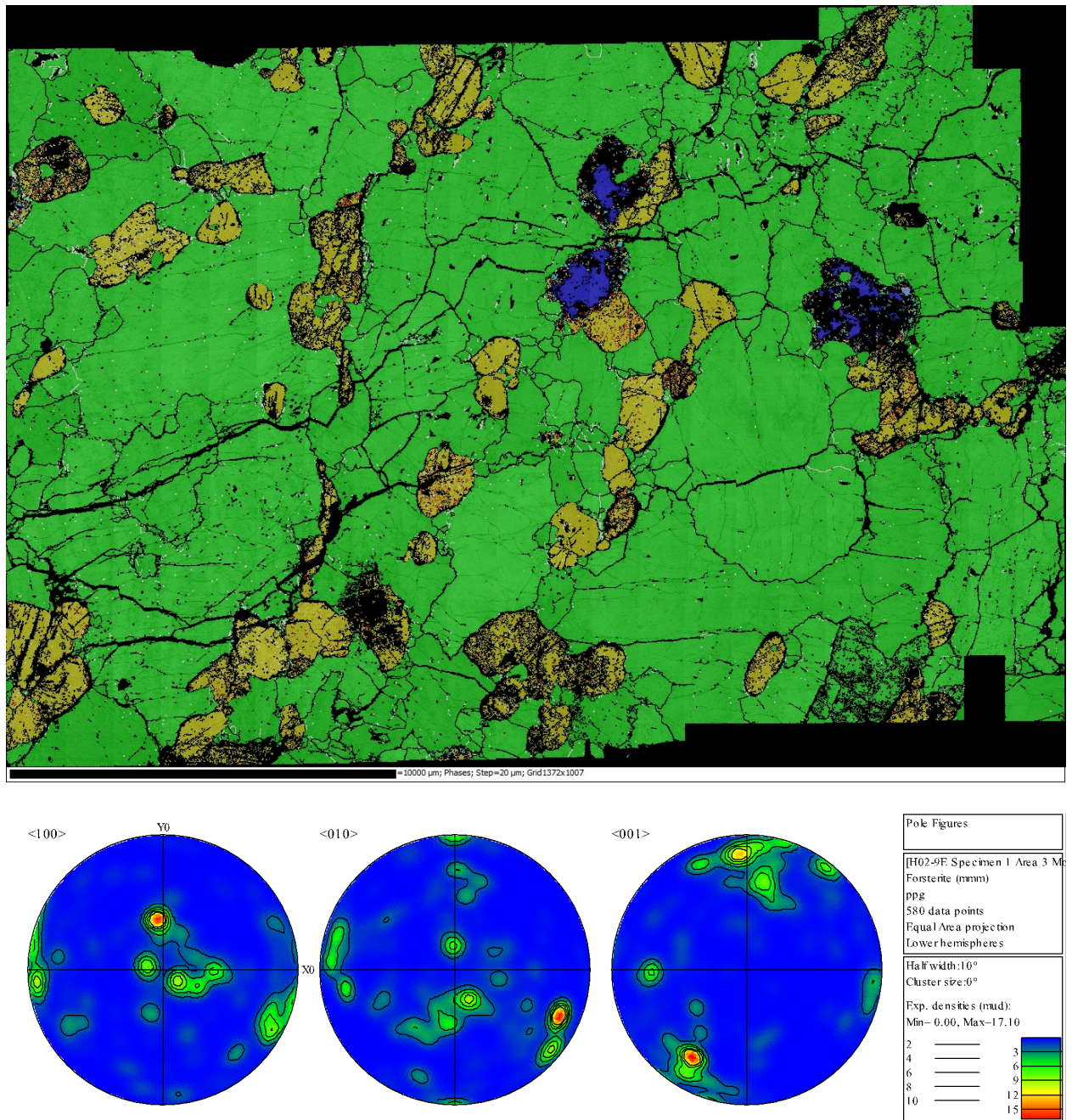


Figure 26. Mineral phase map and olivine crystallographic-preferred orientations for Homestead xenolith sample H02-9E. In the phase map, green is olivine, yellow is orthopyroxene, red is clinopyroxene, and blue is spinel.

TABLES

Table 1.

Table 1. Major and minor element composition of the studied rocks (wt%) and trace element concentrations (ppm) in the rocks.			Major and minor element composition (wt%)														Trace element concentrations (ppm)															
			SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Sum	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Sum	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Sum
Sample	Rock Type	Field	45.2	0.1	15.8	12.5	0.1	10.2	1.2	0.5	0.1	75.2	45.2	0.1	15.8	12.5	0.1	10.2	1.2	0.5	0.1	75.2	45.2	0.1	15.8	12.5	0.1	10.2	1.2	0.5	0.1	75.2
2	Basalt	Basalt	46.5	0.1	16.2	13.0	0.1	10.5	1.3	0.5	0.1	77.2	46.5	0.1	16.2	13.0	0.1	10.5	1.3	0.5	0.1	77.2	46.5	0.1	16.2	13.0	0.1	10.5	1.3	0.5	0.1	77.2
3	Basalt	Basalt	47.8	0.1	16.8	13.5	0.1	10.8	1.4	0.5	0.1	79.6	47.8	0.1	16.8	13.5	0.1	10.8	1.4	0.5	0.1	79.6	47.8	0.1	16.8	13.5	0.1	10.8	1.4	0.5	0.1	79.6
4	Basalt	Basalt	48.5	0.1	17.2	14.0	0.1	11.0	1.5	0.5	0.1	81.9	48.5	0.1	17.2	14.0	0.1	11.0	1.5	0.5	0.1	81.9	48.5	0.1	17.2	14.0	0.1	11.0	1.5	0.5	0.1	81.9
5	Basalt	Basalt	49.2	0.1	17.8	14.5	0.1	11.2	1.6	0.5	0.1	84.5	49.2	0.1	17.8	14.5	0.1	11.2	1.6	0.5	0.1	84.5	49.2	0.1	17.8	14.5	0.1	11.2	1.6	0.5	0.1	84.5
6	Basalt	Basalt	50.0	0.1	18.5	15.0	0.1	11.5	1.7	0.5	0.1	87.4	50.0	0.1	18.5	15.0	0.1	11.5	1.7	0.5	0.1	87.4	50.0	0.1	18.5	15.0	0.1	11.5	1.7	0.5	0.1	87.4
7	Basalt	Basalt	50.8	0.1	19.2	15.5	0.1	11.8	1.8	0.5	0.1	90.3	50.8	0.1	19.2	15.5	0.1	11.8	1.8	0.5	0.1	90.3	50.8	0.1	19.2	15.5	0.1	11.8	1.8	0.5	0.1	90.3
8	Basalt	Basalt	51.5	0.1	19.8	16.0	0.1	12.0	1.9	0.5	0.1	93.0	51.5	0.1	19.8	16.0	0.1	12.0	1.9	0.5	0.1	93.0	51.5	0.1	19.8	16.0	0.1	12.0	1.9	0.5	0.1	93.0
9	Basalt	Basalt	52.2	0.1	20.5	16.5	0.1	12.2	2.0	0.5	0.1	95.8	52.2	0.1	20.5	16.5	0.1	12.2	2.0	0.5	0.1	95.8	52.2	0.1	20.5	16.5	0.1	12.2	2.0	0.5	0.1	95.8
10	Basalt	Basalt	53.0	0.1	21.2	17.0	0.1	12.5	2.1	0.5	0.1	98.5	53.0	0.1	21.2	17.0	0.1	12.5	2.1	0.5	0.1	98.5	53.0	0.1	21.2	17.0	0.1	12.5	2.1	0.5	0.1	98.5
11	Basalt	Basalt	53.8	0.1	21.8	17.5	0.1	12.8	2.2	0.5	0.1	101.2	53.8	0.1	21.8	17.5	0.1	12.8	2.2	0.5	0.1	101.2	53.8	0.1	21.8	17.5	0.1	12.8	2.2	0.5	0.1	101.2
12	Basalt	Basalt	54.5	0.1	22.5	18.0	0.1	13.0	2.3	0.5	0.1	104.0	54.5	0.1	22.5	18.0	0.1	13.0	2.3	0.5	0.1	104.0	54.5	0.1	22.5	18.0	0.1	13.0	2.3	0.5	0.1	104.0
13	Basalt	Basalt	55.2	0.1	23.2	18.5	0.1	13.2	2.4	0.5	0.1	106.8	55.2	0.1	23.2	18.5	0.1	13.2	2.4	0.5	0.1	106.8	55.2	0.1	23.2	18.5	0.1	13.2	2.4	0.5	0.1	106.8
14	Basalt	Basalt	56.0	0.1	23.8	19.0	0.1	13.5	2.5	0.5	0.1	109.6	56.0	0.1	23.8	19.0	0.1	13.5	2.5	0.5	0.1	109.6	56.0	0.1	23.8	19.0	0.1	13.5	2.5	0.5	0.1	109.6
15	Basalt	Basalt	56.8	0.1	24.5	19.5	0.1	13.8	2.6	0.5	0.1	112.4	56.8	0.1	24.5	19.5	0.1	13.8	2.6	0.5	0.1	112.4	56.8	0.1	24.5	19.5	0.1	13.8	2.6	0.5	0.1	112.4
16	Basalt	Basalt	57.5	0.1	25.2	20.0	0.1	14.0	2.7	0.5	0.1	115.2	57.5	0.1	25.2	20.0	0.1	14.0	2.7	0.5	0.1	115.2	57.5	0.1	25.2	20.0	0.1	14.0	2.7	0.5	0.1	115.2
17	Basalt	Basalt	58.2	0.1	25.8	20.5	0.1	14.2	2.8	0.5	0.1	118.0	58.2	0.1	25.8	20.5	0.1	14.2	2.8	0.5	0.1	118.0	58.2	0.1	25.8	20.5	0.1	14.2	2.8	0.5	0.1	118.0
18	Basalt	Basalt	59.0	0.1	26.5	21.0	0.1	14.5	2.9	0.5	0.1	120.8	59.0	0.1	26.5	21.0	0.1	14.5	2.9	0.5	0.1	120.8	59.0	0.1	26.5	21.0	0.1	14.5	2.9	0.5	0.1	120.8
19	Basalt	Basalt	59.8	0.1	27.2	21.5	0.1	14.8	3.0	0.5	0.1	123.6	59.8	0.1	27.2	21.5	0.1	14.8	3.0	0.5	0.1	123.6	59.8	0.1	27.2	21.5	0.1	14.8	3.0	0.5	0.1	123.6
20	Basalt	Basalt	60.5	0.1	27.8	22.0	0.1	15.0	3.1	0.5	0.1	126.4	60.5	0.1	27.8	22.0	0.1	15.0	3.1	0.5	0.1	126.4	60.5	0.1	27.8	22.0	0.1	15.0	3.1	0.5	0.1	126.4
21	Basalt	Basalt	61.2	0.1	28.5	22.5	0.1	15.2	3.2	0.5	0.1	129.2	61.2	0.1	28.5	22.5	0.1	15.2	3.2	0.5	0.1	129.2	61.2	0.1	28.5	22.5	0.1	15.2	3.2	0.5	0.1	129.2
22	Basalt	Basalt	62.0	0.1	29.2	23.0	0.1	15.5	3.3	0.5	0.1	132.0	62.0	0.1	29.2	23.0	0.1	15.5	3.3	0.5	0.1	132.0	62.0	0.1	29.2	23.0	0.1	15.5	3.3	0.5	0.1	132.0
23	Basalt	Basalt	62.8	0.1	29.8	23.5	0.1	15.8	3.4	0.5	0.1	134.8	62.8	0.1	29.8	23.5	0.1	15.8	3.4	0.5	0.1	134.8	62.8	0.1	29.8	23.5	0.1	15.8	3.4	0.5	0.1	134.8
24	Basalt	Basalt	63.5	0.1	30.5	24.0	0.1	16.0	3.5	0.5	0.1	137.6	63.5	0.1	30.5	24.0	0.1	16.0	3.5	0.5	0.1	137.6	63.5	0.1	30.5	24.0	0.1	16.0	3.5	0.5	0.1	137.6
25	Basalt	Basalt	64.2	0.1	31.2	24.5	0.1	16.2	3.6	0.5	0.1	140.4	64.2	0.1	31.2	24.5	0.1	16.2	3.6	0.5	0.1	140.4	64.2	0.1	31.2	24.5	0.1	16.2	3.6	0.5	0.1	140.4
26	Basalt	Basalt	65.0	0.1	31.8	25.0	0.1	16.5	3.7	0.5	0.1	143.2	65.0	0.1	31.8	25.0	0.1	16.5	3.7	0.5	0.1	143.2	65.0	0.1	31.8	25.0	0.1	16.5	3.7	0.5	0.1	143.2
27	Basalt	Basalt	65.8	0.1	32.5	25.5	0.1	16.8	3.8	0.5	0.1	146.0	65.8	0.1	32.5	25.5	0.1	16.8	3.8	0.5	0.1	146.0	65.8	0.1	32.5	25.5	0.1	16.8	3.8	0.5	0.1	146.0
28	Basalt	Basalt	66.5	0.1	33.2	26.0	0.1	17.0	3.9	0.5	0.1	148.8	66.5	0.1	33.2	26.0	0.1	17.0	3.9	0.5	0.1	148.8	66.5	0.1	33.2	26.0	0.1	17.0	3.9	0.5	0.1	148.8
29	Basalt	Basalt	67.2	0.1	33.8	26.5	0.1	17.2	4.0	0.5	0.1	151.6	67.2	0.1	33.8	26.5	0.1	17.2	4.0	0.5	0.1	151.6	67.2	0.1	33.8	26.5	0.1	17.2	4.0	0.5	0.1	151.6
30	Basalt	Basalt	68.0	0.1	34.5	27.0	0.1	17.5	4.1	0.5	0.1	154.4	68.0	0.1	34.5	27.0	0.1	17.5	4.1	0.5	0.1	154.4	68.0	0.1	34.5	27.0	0.1	17.5	4.1	0.5	0.1	154.4
31	Basalt	Basalt	68.8	0.1	35.2	27.5	0.1	17.8	4.2	0.5	0.1	157.2	68.8	0.1	35.2	27.5	0.1	17.8	4.2	0.5	0.1	157.2	68.8	0.1	35.2	27.5	0.1	17.8	4.2	0.5	0.1	157.2
32	Basalt	Basalt	69.5	0.1	35.8	28.0	0.1	18.0	4.3	0.5	0.1	160.0	69.5	0.1	35.8	28.0	0.1	18.0	4.3	0.5	0.1	160.0	69.5	0.1	35.8	28.0	0.1	18.0	4.3	0.5	0.1	160.0
33	Basalt	Basalt	70.2	0.1	36.5	28.5	0.1	18.2	4.4	0.5	0.1	162.8	70.2	0.1	36.5	28.5	0.1	18.2	4.4	0.5	0.1	162.8	70.2	0.1	36.5	28.5	0.1	18.2	4.4	0.5	0.1	162.8
34	Basalt	Basalt	71.0	0.1	37.2	29.0	0.1	18.5	4.5	0.5	0.1	165.6	71.0	0.1	37.2	29.0	0.1	18.5	4.5	0.5	0.1	165.6	71.0	0.1	37.2	29.0	0.1	18.5	4.5	0.5	0.1	165.6
35	Basalt	Basalt	71.8	0.1	37.8	29.5	0.1	18.8	4.6	0.5	0.1	168.4	71.8	0.1	37.8	29.5	0.1	18.8	4.6	0.5	0.1	168.4	71.8	0.1	37.8	29.5	0.1	18.8	4.6	0.5	0.1	168.4
36	Basalt	Basalt	72.5	0.1	38.5	30.0	0.1	19.0	4.7	0.5	0.1	171.2	72.5	0.1	38.5	30.0	0.1	19.0	4.7	0.5	0.1	171.2	72.5	0.1	38.5	30.0	0.1	19.0	4.7	0.5	0.1	171.2
37	Basalt	Basalt	73.2	0.1	39.2	30.5	0.1	19.2	4.8	0.5	0.1	174.0	73.2	0.1	39.2	30.5	0.1	19.2	4.8	0.5	0.1	174.0	73.2	0.1	39.2	30.5	0.1	19.2	4.8	0.5	0.1	174.0
38	Basalt	Basalt	74.0	0.1	39.8	31.0	0.1	19.5	4.9	0.5	0.1	176.8	74.0	0.1	39.8	31.0	0.1	19.5	4.9	0.5	0.1	176.8	74.0	0.1	39.8	31.0	0.1	19.5	4.9	0.5	0.1	176.8
39	Basalt	Basalt	74.8	0.1	40.5	31.5	0.1	19.8	5.0	0.5	0.1	179.6	74.8	0.1	40.5	31.5																

Table 1 (continued).

[illegible]

Table 2.

Project Overview		Phase 1: Planning & Design										Phase 2: Development & Testing										Phase 3: Deployment & Monitoring										Phase 4: Review & Feedback																											
Task ID	Task Name	Start Date	End Date	Duration (Days)	Priority	Assignee	Status	Progress (%)	Completion Date	Start Date	End Date	Duration (Days)	Priority	Assignee	Status	Progress (%)	Completion Date	Start Date	End Date	Duration (Days)	Priority	Assignee	Status	Progress (%)	Completion Date	Start Date	End Date	Duration (Days)	Priority	Assignee	Status	Progress (%)	Completion Date	Start Date	End Date	Duration (Days)	Priority	Assignee	Status	Progress (%)	Completion Date																		
P1-001	Project Kick-off Meeting	2023-01-01	2023-01-05	5	High	John Doe	Completed	100	2023-01-05	P1-002	Requirement Gathering	2023-01-06	2023-01-15	10	High	Jane Smith	In Progress	75	2023-01-15	P1-003	System Architecture Design	2023-01-16	2023-01-25	10	High	John Doe	Not Started	0	2023-01-25	P1-004	Database Schema Design	2023-01-26	2023-02-05	10	High	Jane Smith	In Progress	60	2023-02-05	P1-005	UI/UX Design	2023-02-06	2023-02-15	10	Medium	John Doe	Not Started	0	2023-02-15	P1-006	Backend API Design	2023-02-16	2023-02-25	10	High	Jane Smith	In Progress	50	2023-02-25
P1-007	Frontend Development	2023-02-26	2023-03-15	20	High	John Doe	In Progress	80	2023-03-15	P1-008	Backend Development	2023-03-16	2023-03-25	10	High	Jane Smith	In Progress	70	2023-03-25	P1-009	Integration Testing	2023-03-26	2023-04-05	10	High	John Doe	Not Started	0	2023-04-05	P1-010	User Acceptance Testing	2023-04-06	2023-04-15	10	High	Jane Smith	In Progress	40	2023-04-15	P1-011	Performance Testing	2023-04-16	2023-04-25	10	Medium	John Doe	Not Started	0	2023-04-25	P1-012	Security Testing	2023-04-26	2023-05-05	10	High	Jane Smith	In Progress	30	2023-05-05
P1-013	Deployment Planning	2023-05-06	2023-05-15	10	High	John Doe	Not Started	0	2023-05-15	P1-014	Go-Live	2023-05-16	2023-05-20	5	High	Jane Smith	Not Started	0	2023-05-20	P1-015	Post-Launch Monitoring	2023-05-21	2023-06-05	15	Medium	John Doe	In Progress	20	2023-06-05	P1-016	Feedback Collection	2023-06-06	2023-06-15	10	Medium	Jane Smith	Not Started	0	2023-06-15	P1-017	Project Review	2023-06-16	2023-06-20	5	High	John Doe	Not Started	0	2023-06-20	P1-018	Final Report	2023-06-21	2023-06-25	5	High	Jane Smith	Not Started	0	2023-06-25

Table 2 (continued).

[illegible]

Table 3 (continued).

[illegible]

Table 4.

[illegible]

Table 4 (continued).

[illegible]

Table 5.

Table 5. Major element, H₂O, and F concentrations for indium-mounted xenolith mineral separates.

Sample	Location	Mineral	ID	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	NiO	Total	H ₂ O ppm	F ppm
H01-4A	Homestead	cpk	H01-4Acp1@34.ais	53.77	0.14	3.08	2.56	2.35	0.09	15.73	19.32	2.45	0.06	99.54	400.721	116.405
H01-4A	Homestead	cpk	H01-4Acp1@35.ais	53.93	0.13	3.12	2.56	2.32	0.06	15.56	19.27	2.39	0	99.34	476.017	113.688
H01-4A	Homestead	cpk	H01-4Acp3@36.ais	53.66	0.14	2.92	2.52	2.38	0.07	16.21	18.89	2.34	0.03	99.06	572.310	123.610
H01-4A	Homestead	cpk	H01-4Acp4@37.ais	53.72	0.13	3.04	2.55	2.45	0.09	16.2	19.05	2.25	0.07	99.35	406.321	123.866
H01-4A	Homestead	cpk	H01-4Acp5@38.ais	53.7	0.12	2.94	2.53	2.6	0.07	16.19	18.81	2.33	0.17	99.46	488.270	124.332
H01-4A	Homestead	cpk	H01-4Acp7@39.ais	53.98	0.14	2.92	2.59	2.46	0.07	16.28	19.25	2.28	0.07	100.04	474.085	124.321
H01-4A	Homestead	cpk	H01-4Acp8@40.ais	53.87	0.13	2.97	2.61	2.3	0.07	16.06	19.13	2.33	0.03	99.6	521.352	122.477
H01-4A	Homestead	cpk	H01-4Acp11@44.ais	53.89	0.14	3.08	2.5	2.49	0.08	16.21	18.36	2.45	0	99.2	504.41	124.871
H01-4A	Homestead	cpk	H01-4Acp12@45.ais	53.79	0.14	2.91	2.39	2.55	0.06	16.24	19.18	2.2	0.07	99.53	453.789	124.982
H01-4A	Homestead	cpk	H01-4Acp13@46.ais	53.72	0.14	2.83	2.53	2.42	0.12	16.26	19.13	2.21	0.07	99.43	439.497	125.566
H01-4A	Homestead	cpk	H01-4Acp14@47.ais	53.73	0.12	2.97	2.57	2.48	0.09	16.26	19.22	2.32	0	99.76	504.894	126.749
H01-4A	Homestead	cpk	H01-4Acp15@48.ais	53.77	0.14	3.08	2.61	2.34	0.09	15.69	19.17	2.45	0.05	99.39	449.225	122.621
H01-4A	Homestead	cpk	H01-4Acp16@76.ais	53.85	0.12	3.14	2.38	2.32	0.06	15.76	19.43	2.51	0.03	99.6	444.508	125.466
H01-4A	Homestead	cpk	H01-4Acp17@77.ais	53.87	0.13	3.11	2.52	2.45	0.07	15.81	19.25	2.49	0.08	99.78	388.576	115.827
H01-4A	Homestead	cpk	H01-4Acp18@78.ais	53.92	0.12	2.9	2.53	2.37	0.05	16.1	19.24	2.23	0.08	99.54	465.898	117.132
H01-4A	Homestead	cpk	H01-4Acp19@16.ais	54.02	0.13	2.9	2.34	2.65	0.09	16.4	18.9	2.13	0	99.56	370.008	124.800
H01-4A	Homestead	cpk	H01-4Acp3@17.ais	53.99	0.11	2.89	2.3	2.55	0.07	16.5	18.73	2.32	0	99.46	543.585	137.506
H01-4A	Homestead	cpk	H01-4Acp12@8.ais	53.7	0.11	2.91	2.48	2.37	0.11	16.14	19.1	2.22	0.11	99.25	503.339	128.054
H01-4A	Homestead	cpk	H01-4Acp5@9.ais	53.68	0.13	2.94	2.49	2.49	0.07	16.05	19.04	2.23	0.04	99.16	400.510	128.053
H01-4A	Homestead	cpk	H01-4Acp1@19.ais	57.22	0.06	1.2	0.4	1.48	0.1	35.13	0.61	0.19	0.11	100.5	269.426	53.148
H01-4A	Homestead	cpk	H01-4Acp3@20.ais	57.29	0.07	0.98	0.33	1.48	0.12	35.36	0.49	0.17	0.08	100.37	262.341	49.930
H01-4A	Homestead	cpk	H01-4Acp3@24.ais	57.44	0.06	0.89	0.33	1.24	0.11	35.51	0.34	0.11	0.04	100.07	1432.132	86.132
H01-4A	Homestead	cpk	H01-4Acp4@25.ais	57.57	0.06	0.98	0.32	1.19	0.12	35.41	0.56	0.15	0.07	100.43	265.745	47.996
H01-4A	Homestead	cpk	H01-4Acp5@26.ais	57.02	0.06	1.2	0.52	1.16	0.11	35.34	0.49	0.14	0.1	100.14	304.595	52.323
H01-4A	Homestead	cpk	H01-4Acp1c1@30.ais	57.11	0.05	1.16	0.35	1.37	0.14	35.24	0.6	0.17	0.08	100.27	215.391	51.803
H01-4A	Homestead	cpk	H01-4Acp1@11.ais	57.16	0.07	1.07	0.38	1.26	0.1	35.26	0.56	0.12	0.13	100.11	240.137	45.542
H01-4A	Homestead	cpk	H01-4Acp1@12.ais	57.51	0.04	0.82	0.34	1.25	0.1	35.66	0.24	0.11	0.09	100.21	220.206	38.482
H01-4A	Homestead	cpk	H01-4Acp3@13.ais	57.5	0.04	0.9	0.35	1.25	0.1	35.38	0.37	0.11	0.08	100.08	217.327	39.173
H01-4A	Homestead	cpk	H01-4Acp5@14.ais	57.23	0.06	1.18	0.43	1.06	0.11	35.35	0.46	0.17	0.1	100.15	636.351	56.407
H01-4A	Homestead	cpk	H01-4Acp5@15.ais	57.3	0.06	1.15	0.41	1.05	0.12	35.24	0.42	0.17	0.1	100.15	531.476	45.313
H01-4A	Homestead	cpk	H01-4Acp1c2@7.ais	57.12	0.06	1.14	0.37	1.41	0.07	35.5	0.43	0.15	0.06	100.31	258.248	55.042
H01-4A	Homestead	oil	H01-4Acl1@8.ais	40.87	0.01	0.01	0.03	8.46	0.1	50.13	0.04	0	0.19	99.84	67.974	55.264
H01-4A	Homestead	oil	H01-4Acl2@8.ais	41.16	0.01	0	0	8.27	0.01	50.36	0.04	0	0.37	100.32	146.73	53.887
H01-4A	Homestead	oil	H01-4Acl3@6.ais	41.27	0.01	0	0	8.06	0.11	50.42	0.04	0	0.39	100.93	58.404	53.311
H01-4A	Homestead	oil	H01-4Acl4@7.ais	41.24	0	0.03	0.05	8.64	0.08	50.29	0.05	0.04	0.51	100.35	42.284	52.237
H01-4A	Homestead	oil	H01-4Acl5@8.ais	41.08	0.01	0	0	8.4	0.07	50.43	0.04	0.02	0.49	100.58	58.409	54.633
H01-4A	Homestead	oil	H01-4Acl6@9.ais	41.17	0.01	0	0.02	8.25	0.15	50.33	0.03	0	0.42	100.38	41.857	51.176
H01-4A	Homestead	oil	H01-4Acl7@10.ais	41.19	0.02	0.01	0.04	8.42	0.12	50.42	0.04	0	0.38	100.64	45.608	51.812
H01-4A	Homestead	oil	H01-4Acl8@11.ais	41.16	0.02	0	0	8.52	0.08	50.36	0.04	0	0.36	100.36	43.618	51.033
H01-4A	Homestead	oil	H01-4Acl9@12.ais	41.22	0.01	0	0.05	8.62	0.09	50.36	0.04	0	0.45	100.84	36.470	51.879
H01-4A	Homestead	oil	H01-4Acl10@13.ais	41.15	0.01	0	0.01	8.44	0.13	50.4	0.04	0.02	0.45	100.68	168.429	54.428
H01-4A	Homestead	oil	H01-4Acl11@14.ais	41.2	0.01	0	0.05	8.47	0.1	50.46	0.04	0.01	0.35	100.71	50.779	55.399
H01-4A	Homestead	oil	H01-4Acl12@15.ais	41.25	0	0.01	0.02	8.5	0.08	50.41	0.04	0.02	0.49	100.82	39.047	53.904
H01-4A	Homestead	oil	H01-4Acl13@16.ais	41.28	0.01	0	0.02	8.5	0.1	50.35	0.02	0.01	0.41	100.71	60.621	55.617
H01-4A	Homestead	oil	H01-4Acl14@17.ais	41.13	0.01	0	0.04	8.19	0.13	50.16	0.04	0.01	0.39	100.1	54.967	54.855
H01-4A	Homestead	oil	H01-4Acl15@18.ais	41.1	0.02	0	0.04	8.38	0.09	50.28	0.03	0	0.37	100.31	55.039	53.146
H01-4A	Homestead	oil	H01-4Acl16@19.ais	41.05	0.01	0	0.03	8.62	0.1	50.3	0.04	0.01	0.43	100.43	49.361	55.232
H01-4A	Homestead	oil	H01-4Acl18@16.ais	41.16	0.01	0	0.05	8.57	0.11	50.29	0.04	0	0.51	100.74	61.746	48.669
H01-4A	Homestead	oil	H01-4Acl19@17.ais	41.35	0	0.01	0.03	8.63	0.08	50.61	0.03	0.02	0.43	101.19	53.953	47.432
H01-4A	Homestead	oil	H01-4Acl20@18.ais	41.15	0.02	0	0.01	8.53	0.1	50.42	0.03	0.01	0.39	100.71	59.236	79.796
H01-4A	Homestead	oil	H01-4Acl21@19.ais	41.01	0.01	0.02	0.03	8.34	0.1	50.31	0.04	0.05	0.46	100.59	43.968	47.710
H01-4A	Homestead	oil	H01-4Acl22@20.ais	41.21	0.01	0.01	0.05	8.28	0.09	50.24	0.05	0.03	0.37	100.34	40.919	58.762
H01-4A	Homestead	oil	H01-4Acl23@21.ais	41.04	0.01	0.04	0.04	8.73	0.09	50.4	0.04	0.01	0.41	100.41	73.814	58.528
H01-4A	Homestead	oil	H01-4Acl1@27.ais	47.18	0.12	21.05	4.15	7.71	0.43	20.11	5.07	0.01	0	100.43	8.855	8.640
H01-4A	Homestead	grt	H01-4Agt1@28.ais	41.97	0.08	21.64	3.16	7.69	0.43	20.45	4.66	0	0	100.08	9.613	9.058
H01-4A	Homestead	grt	H01-4Agt1@29.ais	41.83	0.09	21.73	3.4	8	0.47	20.48	4.64	0	0	100.54	409.633	12.187
H01-4A	Homestead	grt	H01-4Agt1@30.ais	41.91	0.09	21.42	3.37	8.02	0.46	20.49	4.74	0.06	0	100.56	12.583	8.973
H01-4A	Homestead	grt	H01-4Agt1@31.ais	41.81	0.09	21.33	3.56	7.94	0.45	20.41	4.8	0.09	0.03	100.51	8.538	8.892
H01-4A	Homestead	grt	H01-4Agt1@32.ais	41.79	0.07	21.51	3.4	7.88	0.46	20.48	4.64	0.09	0.03	100.42	13.029	8.851
H01-4A	Homestead	grt	H01-4Agt1@33.ais	41.97	0.1	21.67	3.36	7.63	0.42	20.7	4.72	0.01	0.03	100.61	9.800	8.857
Sample	Location	Mineral	ID	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	NiO	Total	H ₂ O ppm	F ppm
H00-11-4	Homestead	cpk	H00-11-4cp1@24.ais	54.25	0.19	2.75	1.68	2.66	0.07	17.33	18.7	2.01	0.11	99.75	533.583	161.629
H00-11-4	Homestead	cpk	H00-11-4cp2@25.ais	54.42	0.17	2.18	1.67	2.69	0.09	17.68	19.59	1.63	0	100.12	452.216	142.961
H00-11-4	Homestead	cpk	H00-11-4cp2@26.ais	54.01	0.22	3.49	2.29	2.62	0.07	16.91	17.98	2.42	0.09	99.78	429.730	174.603
H00-11-4	Homestead	cpk	H00-11-4cp2@27.ais	54.62	0.08	0.58	3.2	3.06	0.12	19.18	17.2	1.58	0.09	99.71	974.083	552.290
H00-11-4	Homestead	cpk	H00-11-4cp3@28.ais	53.82	0.22	3.5	2.33	2.58	0.11	16.84	17.33	2.41	0.12	99.86	1552.186	197.878
H00-11-4	Homestead	cpk	H00-11-4cp4@29.ais	57.04	0.09	1.63	0.64	4.96	0.12	34.93	0.75	0.21	0.17	100.54	424.034	78.180
H00-11-4	Homestead	cpk	H00-11-4cp2@6.ais	57.48	0.09	1.28	0.46	5.1	0.13	35.3	0.64	0.15	0.13	100.76	130.171	141.731
H00-11-4	Homestead	cpk	H00-11-4cp3@7.ais	57.34	0.08	1.11	0.38	5.02	0.13	35.47	0.47	0.11	0.05	100.18	156.067	71.601
H00-11-4	Homestead	cpk	H00-11-4cp4@8.ais	56.74	0.1	1.73	0.68	5.21	0.11	34.84	0.74	0.19	0.13	100.47	275.614	98.609
H00-11-4	Homestead	cpk	H00-11-4cp5@9.ais	57.26	0.09	1.38	0.51									

Table 5 (continued).

H00-11-16	Homestead	oil	H001116o8@97.ais	41.14	0	0.04	0.02	9.65	0.19	52.28	0.06	0.02	0.48	103.88	12.591	22.041
H00-11-16	Homestead	oil	H001116o9@98.ais	40.64	0.01	0.01	0.01	9.71	0.11	48.56	0.06	0	0.49	99.64	13.565	22.451
H00-11-16	Homestead	oil	H001116o9@99.ais	40.85	0.01	0.01	0.01	9.81	0.09	48.98	0.06	0.01	0.42	100.27	14.308	20.820
H00-11-16	Homestead	oil	H001116o10@100.ais	40.38	0.01	0.01	0.02	9.6	0.13	48.4	0.05	0	0.39	99.01	11.949	21.594
H00-11-16	Homestead	oil	H001116o11@101.ais	40.53	0.01	0	0.04	9.77	0.11	49.07	0.07	0.01	0.35	99.96	15.191	21.245
H00-11-16	Homestead	grt	H001116grt1@78.ais	41.65	0.26	22.15	1.72	7.53	0.29	21.1	4.65	0.03	0	99.38	6.407	5.303
H00-11-16	Homestead	grt	H001116grt5@79.ais	42.13	0.27	22.33	2.06	7.67	0.28	21.09	4.93	0.04	0	100.8	7.628	5.161
H00-11-16	Homestead	grt	H001116grt4@80.ais												39.466	0.316
H00-11-16	Homestead	grt	H001116grt5@84.ais	42.09	0.26	22	2.02	7.37	0.3	20.99	4.84	0.04	0	99.91	5.845	5.410
H00-11-16	Homestead	grt	H001116grt11@86.ais	42.13	0.25	22.13	2.07	7.5	0.31	21.13	4.77	0.02	0	100.31	22.188	12.747
H00-11-16	Homestead	grt	H001116grt12@87.ais	42.18	0.26	22.27	2.1	7.47	0.29	21.27	4.87	0.02	0	100.73	705.814	14.148
Sample	Location	Mineral	ID	SiO2	TiO2	Al2O3	C2O3	FeO	MnO	MgO	CaO	Na2O	H2O	Total	H2O ppm	F ppm
H02-9E	Homestead	opx	H02-9Eopx2@25.ais	56.91	0.03	1.69	0.7	4.56	0.13	34.95	0.81	0.21	0.06	100.08	258.70	84.767
H02-9E	Homestead	opx	H02-9Eopx3@26.ais	57.05	0.02	1.77	0.68	4.29	0.13	35.09	0.83	0.26	0.06	100.18	349.742	80.392
H02-9E	Homestead	opx	H02-9Eopx5@28.ais	57.37	0.02	1.52	0.55	4.31	0.08	35.52	0.74	0.2	0.13	100.44	646.833	78.111
H02-9E	Homestead	opx	H02-9Eopx6@29.ais	57.04	0.02	1.62	0.64	4.42	0.11	35.18	0.78	0.21	0.06	100.1	535.346	82.121
H02-9E	Homestead	opx	H02-9Eopx7@30.ais	56.96	0.02	1.76	0.72	4.71	0.11	35.2	0.84	0.25	0.13	100.7	332.157	90.582
H02-9E	Homestead	opx	H02-9Eopx8@31.ais	56.89	0.02	1.77	0.67	4.35	0.12	35.24	0.85	0.21	0.09	100.21	1631.846	102.632
H02-9E	Homestead	opx	H02-9Eopx9@32.ais	57.19	0.02	1.69	0.62	4.32	0.08	35.37	0.8	0.18	0.09	100.36	331.963	77.891
H02-9E	Homestead	opx	H02-9Eopx10@33.ais	56.91	0.02	1.84	0.71	4.45	0.09	35.26	0.85	0.21	0.09	100.43	304.865	86.362
H02-9E	Homestead	opx	H02-9Eopx11@34.ais	56.77	0.01	1.82	0.73	4.19	0.11	35.06	0.83	0.2	0.1	99.82	353.385	83.340
H02-9E	Homestead	opx	H02-9Eopx12@35.ais	57.12	0.01	1.77	0.7	4.63	0.12	35.27	0.81	0.26	0.07	100.76	282.542	77.313
H02-9E	Homestead	opx	H02-9Eopx2@36.ais	56.92	0.03	1.79	0.71	4.35	0.1	35.1	0.82	0.25	0.12	100.19	297.003	95.769
H02-9E	Homestead	opx	H02-9Eopx1@37.ais	57.6	0.02	1.48	0.51	4.5	0.12	35.6	0.74	0.16	0.14	100.87	380.912	69.593
H02-9E	Homestead	opx	H02-9Eopx1@38.ais	57.24	0.02	1.4	0.53	4.27	0.14	35.31	0.74	0.18	0.11	99.94	405.862	73.928
H02-9E	Homestead	opx	H02-9Eopx1@39.ais	57	0.02	1.65	0.66	4.44	0.1	35.2	0.78	0.2	0.1	100.15	341.947	76.141
H02-9E	Homestead	opx	H02-9Eopx1@40.ais	57.12	0.01	1.64	0.61	4.45	0.12	34.99	0.76	0.23	0.07	100	358.825	77.202
H02-9E	Homestead	opx	H02-9Eopx1@41.ais	56.89	0.02	1.88	0.73	4.57	0.12	35.08	0.83	0.25	0.07	100.44	920.077	102.353
H02-9E	Homestead	oil	H02-9Eoil@5.ais	39.32	0	0.01	0.06	7.26	0.07	50.75	0.04	0.04	0.29	97.84	36.437	51.509
H02-9E	Homestead	oil	H02-9Eoil2@6.ais	41.18	0.01	0	0.05	7.29	0.11	51.12	0.04	0	0.34	100.15	84.650	52.060
H02-9E	Homestead	oil	H02-9Eoil7@7.ais	41.32	0.01	0.01	0.03	7.35	0.09	51.51	0.06	0.01	0.42	100.8	38.638	49.471
H02-9E	Homestead	oil	H02-9Eoil4@8.ais	41.5	0	0.01	0.08	7.19	0.1	52.01	0.04	0.01	0.33	101.27	38.144	48.958
H02-9E	Homestead	oil	H02-9Eoil5@9.ais	41.25	0.01	0	0.05	7.05	0.12	51.22	0.04	0.01	0.39	100.58	52.022	49.254
H02-9E	Homestead	oil	H02-9Eoil6@10.ais	41.17	0	0	0.06	7.07	0.1	51.36	0.04	0	0.36	100.16	30.247	50.618
H02-9E	Homestead	oil	H02-9Eoil7@11.ais	41.52	0.01	0.01	0.06	7.02	0.08	52.03	0.05	0.02	0.38	101.18	25.226	51.781
H02-9E	Homestead	oil	H02-9Eoil12@12.ais	41.34	0	0	0.05	7.17	0.13	51.85	0.02	0	0.45	100.93	33.386	48.785
H02-9E	Homestead	oil	H02-9Eoil9@13.ais	41.17	0.01	0.03	0.06	7.12	0.09	51.39	0.05	0	0.32	100.24	49.990	53.384
H02-9E	Homestead	oil	H02-9Eoil10@14.ais	41.18	0	0.02	0.05	7.06	0.09	51.99	0.04	0.02	0.41	101.06	48.480	50.778
H02-9E	Homestead	oil	H02-9Eoil11@15.ais	41.37	0.01	0.01	0.07	6.98	0.07	51.6	0.04	0.01	0.41	100.57	16.139	49.491
H02-9E	Homestead	oil	H02-9Eoil11c1@16.ais	41.18	0.01	0.01	0.07	7.23	0.1	51.2	0.06	0.02	0.24	100.12	29.529	49.528
H02-9E	Homestead	oil	H02-9Eoil11r@17.ais	39.41	0.01	0.01	0.06	7	0.06	52.35	0.05	0.01	0.46	99.42	22.096	48.468
H02-9E	Homestead	oil	H02-9Eoil6c1@18.ais	41.31	0	0	0.06	7.32	0.14	51.47	0.05	0	0.42	100.77	37.497	50.958
H02-9E	Homestead	oil	H02-9Eoil6@19.ais	41.22	0	0	0.05	7.11	0.12	50.58	0.05	0.03	0.35	99.51	26.216	51.551
H02-9E	Homestead	oil	H02-9Eoil7c1@20.ais	41.38	0	0.01	0.06	7.58	0.08	51.56	0.05	0.01	0.27	101	30.350	52.056
H02-9E	Homestead	oil	H02-9Eoil7@21.ais	41.53	0.01	0	0.04	7.12	0.11	51.69	0.04	0	0.36	100.8	20.346	50.137
H02-9E	Homestead	oil	H02-9Eoil12@47.ais	41.44	0	0.02	0.04	6.93	0.11	51.21	0.05	0.03	0.31	100.14	9.571	52.578
H02-9E	Homestead	oil	H02-9Eoil13@50.ais	41.28	0.01	0.03	0.07	7.13	0.11	51.45	0.06	0.01	0.39	100.54	8.526	48.904
H02-9E	Homestead	grt	H02-9Egrt1@44.ais	41.92	0.03	20.61	1.35	6.03	0.32	21.68	6.18	0.03	0	101.35	12.398	8.782
H02-9E	Homestead	grt	H02-9Egrt4@45.ais	42	0.07	20.52	5.26	5.95	0.29	21.67	5.31	0.02	0.02	101.11	7.775	8.256
H02-9E	Homestead	grt	H02-9Egrt5@46.ais	41.55	0.03	20.42	5.1	5.91	0.33	20.92	6.08	0.03	0.03	100.4	9.305	8.802
H02-9E	Homestead	grt	H02-9Egrt6@48.ais	41.99	0.08	20.5	5.08	5.74	0.29	21.79	5.29	0.05	0	100.85	5.808	8.215
Sample	Location	Mineral	ID	SiO2	TiO2	Al2O3	C2O3	FeO	MnO	MgO	CaO	Na2O	H2O	Total	H2O ppm	F ppm
H69-16B	Williams	cpz	H68-16Bcpz1@49.ais	54.66	0	1.72	1.55	1.65	0.05	17.2	21.92	1.46	0.09	100.3	497.128	80.121
H69-16B	Williams	cpz	H68-16Bcpz2@50.ais	54.34	0.01	1.85	1.65	1.58	0.05	17.13	21.65	1.36	0.05	99.69	488.807	21.776
H69-16B	Williams	cpz	H68-16Bcpz3@51.ais	54.45	0.01	1.74	1.58	1.59	0.09	17.09	21.37	1.37	0.09	99.9	395.519	29.767
H69-16B	Williams	cpz	H68-16Bcpz4@52.ais	54.5	0.01	1.73	1.6	1.73	0.08	17.09	21.83	1.33	0	99.9	376.578	17.901
H69-16B	Williams	cpz	H68-16Bcpz5@53.ais	54.59	0	1.73	1.59	1.58	0.09	17.2	22.04	1.34	0.13	100.29	405.978	20.790
H69-16B	Williams	cpz	H68-16Bcpz6@54.ais	54.46	0.03	1.74	1.61	1.63	0.08	18.12	21.87	1.33	0.04	100.44	394.479	16.329
H69-16B	Williams	cpz	H68-16Bcpz1c1@23.ais	54.61	0.01	1.81	1.59	1.73	0.07	17.17	21.59	1.37	0	99.95	701.076	45.258
H69-16B	Williams	cpz	H68-16Bcpz1@25.ais	41.14	0.02	0.01	0.03	8.4	0.12	50.76	0.06	0.02	0.34	100.9	47.743	14.581
H69-16B	Williams	cpz	H68-16Bcpz1@25.ais	54.49	0.01	1.69	1.49	1.68	0.12	21.9	24.61	1.51	0.04	100.54	325.961	19.617
H69-16B	Williams	cpz	H68-16Bcpz4@26.ais	54.62	0	1.73	1.63	1.61	0.07	17.05	21.93	1.44	0.03	100.11	696.175	102.184
H69-16B	Williams	cpz	H68-16Bcpz1@27.ais	54.21	0.02	1.62	1.58	1.63	0.07	16.24	21.88	1.33	0.08	98.66	519.416	35.182
H69-16B	Williams	cpz	H68-16Bcpz5@28.ais	54.18	0.25	2.39	1.8	1.8	0.14	18.16	21.34	1.86	0.15	1181.728	68.466	6.466
H69-16B	Williams	cpz	H68-16Bcpz2@21.ais	54.61	0.02	1.72	1.66	1.47	0.07	17.2	21.95	1.46	0.05	100.21	10939.729	115.614
H69-16B	Williams	cpz	H68-16Bcpz2@16.ais	54.18	0.26	1.73	1.66	2.38	0.1	17.38	21	1.37	0	100.06	2263.071	61.542
H69-16B	Williams	cpz	H68-16Bcpz3@20.ais	54.59	0.02	1.72	1.62	1.66	0.07	17.22	21.84	1.3	0	100.14	628.101	31.415
H69-16B	Williams	cpz	H68-16Bopz1@59.ais	57.81	0	0.78	0.29	4.74	0.11	36.35	0.3	0.08	0.13	100.59	283.316	8.290
H69-16B	Williams	cpz	H68-16Bopz2@60.ais	57.94	0	0.8	0.33	4.93	0.12	36.44	0.31	0.04	0.16	101.07	289.454	12.162
H69-16B	Williams	cpz	H68-16Bopz3@61.ais	57.83	0	0.79	0.35	4.61	0.13	36.37	0.3	0.02	0.16	100.56	310.489	11.885
H69-16B	Williams	cpz	H68-16Bopz4@62.ais	57.82	0	0.78	0.32	4.73	0.11	36.53	0.3	0.07	0.16	100.82	300.066	14.001
H69-16B	Williams	cpz	H68-16Bopz5@63.ais	57.98	0	0.77	0.31	4.61	0.11	36.4	0.3	0.1	0.09	100.67	280.192	14.511
H69-16B	Williams	cpz	H68-16Bopz1@63.ais	57.89	0	0.78	0.33	4.82	0.14	36.36	0.29	0.05	0.12	100.78	233.177	6.930

Table 5 (continued).

H69-15F	Williams	opx	H69-15F opx7@44.ais	56.85	0.08	1.43	0.66	5.35	0.13	34.36	1.35	0.21	0.12	100.54	343.627	52.556
H69-15F	Williams	opx	H69-15F opx8@45.ais	56.94	0.09	1.44	0.65	5.27	0.11	34.36	1.36	0.18	0.14	100.54	309.315	45.204
H69-15F	Williams	opx	H69-15F opx9@46.ais	57	0.09	1.48	0.66	5.38	0.13	34.17	1.38	0.21	0.16	100.66	302.938	46.189
H69-15F	Williams	ol	H69-15F ol1@47.ais	40.93	0	0.01	0.08	8.76	0.14	50.14	0.09	0.01	0.47	100.63	17.795	9.194
H69-15F	Williams	ol	H69-15F ol3@48.ais	41	0.01	0.01	0.07	8.81	0.13	50.05	0.09	0.01	0.43	100.61	21.668	10.515
H69-15F	Williams	ol	H69-15F ol4@49.ais	41	0.01	0.01	0.08	8.9	0.11	50.08	0.08	0.05	0.55	100.89	8.938	10.465
H69-15F	Williams	ol	H69-15F ol5@50.ais	40.91	0.01	0.01	0.1	8.92	0.14	50.04	0.11	0.02	0.41	100.69	7.918	10.865
H69-15F	Williams	ol	H69-15F ol6@51.ais	56.78	0.09	1.45	0.61	5.32	0.15	34.29	1.36	0.21	0.15	100.4	172.997	29.142
H69-15F	Williams	ol	H69-15F ol7@52.ais	40.86	0.01	0.02	0.09	8.92	0.13	50.11	0.09	0.02	0.33	100.58	8.702	11.516
H69-15F	Williams	ol	H69-15F ol8@53.ais	41	0.02	0.02	0.1	8.8	0.11	50.08	0.11	0.01	0.39	100.64	9.104	11.191
H69-15F	Williams	grt	H69-15F grt1@65.ais	41.89	0.42	19.15	6.14	6.62	0.27	20.6	5.81	0.01	0	100.91	5.761	4.890
H69-15F	Williams	grt	H69-15F grt3@66.ais	41.78	0.44	19.01	6.11	6.55	0.33	20.61	5.85	0.04	0.04	100.76	12.091	5.006
Sample	Location	Mineral	ID	SiO2	TiO2	Al2O3	Cr2O3	FeO	MnO	MgO	CaO	Na2O	NiO	Total	H2O ppm	F ppm
H81-26	Williams	cpz	H81-26cpz1@82.ais	54.05	0.06	1.56	0.99	3.11	0.11	19.92	18.55	0.61	0.13	99.09	323.865	55.951
H81-26	Williams	cpz	H81-26cpz3@83.ais	54.24	0.06	1.59	0.97	2.99	0.11	20.16	18.69	0.7	0.08	99.59	346.890	54.783
H81-26	Williams	cpz	H81-26cpz4@84.ais	54.2	0.05	1.61	1	3.13	0.12	20.3	18.35	0.68	0.15	99.59	475.970	56.905
H81-26	Williams	cpz	H81-26cpz5@85.ais	54.3	0.09	1.67	0.96	3.05	0.12	21.5	18.38	0.68	0.02	100.77	316.308	53.634
H81-26	Williams	cpz	H81-26cpz6@86.ais	54.22	0.07	1.56	0.98	3.06	0.09	20.1	18.55	0.61	0.03	99.29	321.823	54.894
H81-26	Williams	cpz	H81-26cpz7@87.ais	54.44	0.05	1.57	1.02	3.03	0.12	20.16	18.62	0.69	0.09	99.79	1586.856	63.665
H81-26	Williams	cpz	H81-26cpz8@88.ais	54.53	0.07	1.6	0.95	3.24	0.13	20.4	18.56	0.73	0.13	100.34	342.785	60.147
H81-26	Williams	opx	H81-26opx1@67.ais	56.86	0.04	1.35	0.51	5.23	0.12	34.49	1.38	0.08	0.11	100.17	313.136	41.730
H81-26	Williams	opx	H81-26opx2@68.ais	56.61	0.06	1.32	0.52	5.22	0.12	34.49	1.37	0.08	0.19	99.98	270.823	42.731
H81-26	Williams	opx	H81-26opx3@69.ais	56.95	0.05	1.32	0.5	5.24	0.11	34.23	1.4	0.11	0.09	100	270.714	43.163
H81-26	Williams	opx	H81-26opx4@70.ais	57.06	0.04	1.36	0.49	5.2	0.12	34.35	1.38	0.08	0.13	100.21	267.066	40.047
H81-26	Williams	opx	H81-26opx5@71.ais	56.88	0.05	1.33	0.51	5.19	0.12	34.48	1.39	0.07	0.15	100.18	276.062	37.504
H81-26	Williams	opx	H81-26opx6@72.ais	57.1	0.04	1.36	0.52	5.5	0.13	34.67	1.39	0.07	0.14	100.92	267.814	38.236
H81-26	Williams	ol	H81-26ol1@73.ais	40.86	0	0.02	0.05	8.41	0.12	49.67	0.1	0.02	0.38	99.63	12.725	7.650
H81-26	Williams	ol	H81-26ol2@74.ais	40.81	0.01	0.04	0.09	8.88	0.15	50.47	0.09	0	0.4	100.96	38.348	7.519
H81-26	Williams	ol	H81-26ol3@75.ais	40.76	0.01	0.03	0.07	8.66	0.13	49.86	0.1	0.03	0.35	100	10.073	7.369
H81-26	Williams	ol	H81-26ol4@76.ais	40.58	0.01	0.03	0.05	8.72	0.12	49.97	0.1	0.01	0.36	99.97	7.835	7.084
H81-26	Williams	ol	H81-26ol5@77.ais	40.97	0.01	0.03	0.08	8.83	0.11	50.41	0.11	0.03	0.3	100.88	34.849	7.310
H81-26	Williams	ol	H81-26ol6@78.ais	40.84	0.01	0.03	0.08	8.92	0.13	49.89	0.09	0.01	0.36	100.36	8.894	7.046
H81-26	Williams	grt	H81-26grt3@89.ais	41.62	0.25	19.43	5.97	6.67	0.28	20.77	6.09	0	0.01	101.09	4.022	3.789
H81-26	Williams	grt	H81-26grt4@90.ais	41.61	0.23	19.35	5.75	6.25	0.31	20.41	6.12	0	0	100.03	3.655	3.781

Table 6.

Table 6. H₂O and F concentrations for indium-mounted xenolith mineral separates.

Sample	Locality	Mineral	ID	H2O	F ppm	Sample	Locality	Mineral	ID	H2O ppm	F ppm	Sample	Locality	Mineral	ID	H2O ppm	F ppm
H01-48	Hornstead	oil	H01-48a02t54.ais	52.600	60.037	H01-27	Williams	oil	H01-27a01c18t5.ais	275.143	28.792	USC-247	Bearyear	oil	USC247a01c18t64.ais	226.897	33.421
H01-48	Hornstead	oil	H01-48a02t55.ais	29.512	60.632	H01-27	Williams	oil	H01-27a01c18t6.ais	264.003	30.008	USC-249	Bearyear	oil	USC249a01c18t65.ais	27.959	27.990
H01-48	Hornstead	oil	H01-48a01c18t57.ais	49.040	66.234	H01-27	Williams	oil	H01-27a01c18t7.ais	282.877	29.957	USC-250	Bearyear	oil	USC247a01c18t66.ais	44.429	28.740
H01-48	Hornstead	oil	H01-48a01c18t58.ais	49.391	65.424	H01-27	Williams	oil	H01-27a01c18t8.ais	291.448	31.518	USC-251	Bearyear	oil	USC247a01c18t67.ais	39.430	27.722
H01-48	Hornstead	oil	H01-48a02c18t59.ais	44.895	60.040	H01-27	Williams	oil	H01-27a01c18t9.ais	266.521	31.483	USC-252	Bearyear	oil	USC247a01c18t68.ais	42.024	28.301
H01-48	Hornstead	oil	H01-48a02c18t60.ais	378.861	64.483	H01-27	Williams	oil	H01-27a01c18t10.ais	266.521	30.151	USC-253	Bearyear	oil	USC247a01c18t69.ais	48.785	28.322
H01-48	Hornstead	oil	H01-48a01c18t61.ais	310.578	96.889	H01-27	Williams	oil	H01-27a01c18t12.ais	276.575	29.978	USC-254	Bearyear	oil	USC247a01c18t70.ais	46.686	29.022
H01-48	Hornstead	oil	H01-48a02c18t62.ais	278.390	73.619	H01-27	Williams	oil	H01-27a01c18t14.ais	273.071	27.859	USC-255	Bearyear	oil	USC247a01c18t71.ais	46.222	28.611
H01-48	Hornstead	oil	H01-48a02c18t63.ais	27.842	103.652	H01-27	Williams	oil	H01-27a01c18t15.ais	274.198	28.072	USC-256	Bearyear	oil	USC247a01c18t72.ais	47.739	27.603
H01-48	Hornstead	grt	H01-48a01c18t70.ais	25.587	10.832	H01-27	Williams	oil	H01-27a01c18t16.ais	276.760	29.448	USC-257	Bearyear	oil	USC247a01c18t73.ais	41.856	27.601
						H01-27	Williams	oil	H01-27a01c18t17.ais	26.820	5.792	USC-258	Bearyear	oil	USC247a01c18t74.ais	44.379	28.290
						H01-27	Williams	oil	H01-27a01c18t18.ais	95.774	12.549	USC-259	Bearyear	oil	USC247a01c18t75.ais	42.009	27.633
						H01-27	Williams	oil	H01-27a01c18t22.ais	16.761	5.386	USC-260	Bearyear	oil	USC247a01c18t76.ais	44.203	28.800
						H01-27	Williams	oil	H01-27a01c18t26.ais	59.370	3.476						
H01-11-9	Hornstead	oil	H01-11a01c18t31.ais	16.782	8.338	H01-27	Williams	oil	H01-27a01c18t27.ais	20.711	4.869	WC-98	Bearyear	oil	WC98a01c18t31.ais	12.124	31.022
H01-11-11	Hornstead	oil	H01-11a01c18t35.ais	435.766	105.945	H01-27	Williams	oil	H01-27a01c18t28.ais	21.971	5.795	WC-98	Bearyear	oil	WC98a01c18t32.ais	85.828	10.800
H01-11-13	Hornstead	oil	H01-11a01c18t36.ais	352.888	99.884	H01-27	Williams	oil	H01-27a01c18t29.ais	22.068	5.626	WC-98	Bearyear	oil	WC98a01c18t33.ais	47.139	37.900
H01-11-15	Hornstead	oil	H01-11a01c18t39.ais	369.646	90.860	H01-27	Williams	oil	H01-27a01c18t30.ais	19.084	5.464	WC-98	Bearyear	oil	WC98a01c18t34.ais	11.328	1.811
H01-11-16	Hornstead	oil	H01-11a01c18t41.ais	385.792	105.156	H01-27	Williams	oil	H01-27a01c18t31.ais	22.068	5.464	WC-98	Bearyear	oil	WC98a01c18t35.ais	11.328	1.811
H01-11-19	Hornstead	oil	H01-11a01c18t43.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t33.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t37.ais	26.108	12.000
H01-11-20	Hornstead	oil	H01-11a01c18t45.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t34.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t38.ais	26.108	12.000
H01-11-21	Hornstead	oil	H01-11a01c18t47.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t35.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t39.ais	26.108	12.000
H01-11-22	Hornstead	oil	H01-11a01c18t49.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t36.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t40.ais	26.108	12.000
H01-11-23	Hornstead	oil	H01-11a01c18t51.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t37.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t41.ais	26.108	12.000
H01-11-24	Hornstead	oil	H01-11a01c18t53.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t38.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t42.ais	26.108	12.000
H01-11-25	Hornstead	oil	H01-11a01c18t55.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t39.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t43.ais	26.108	12.000
H01-11-26	Hornstead	oil	H01-11a01c18t57.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t40.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t44.ais	26.108	12.000
H01-11-27	Hornstead	oil	H01-11a01c18t59.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t41.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t45.ais	26.108	12.000
H01-11-28	Hornstead	oil	H01-11a01c18t61.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t42.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t46.ais	26.108	12.000
H01-11-29	Hornstead	oil	H01-11a01c18t63.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t43.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t47.ais	26.108	12.000
H01-11-30	Hornstead	oil	H01-11a01c18t65.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t44.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t48.ais	26.108	12.000
H01-11-31	Hornstead	oil	H01-11a01c18t67.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t45.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t49.ais	26.108	12.000
H01-11-32	Hornstead	oil	H01-11a01c18t69.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t46.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t50.ais	26.108	12.000
H01-11-33	Hornstead	oil	H01-11a01c18t71.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t47.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t51.ais	26.108	12.000
H01-11-34	Hornstead	oil	H01-11a01c18t73.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t48.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t52.ais	26.108	12.000
H01-11-35	Hornstead	oil	H01-11a01c18t75.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t49.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t53.ais	26.108	12.000
H01-11-36	Hornstead	oil	H01-11a01c18t77.ais	279.647	102.873	H01-27	Williams	oil	H01-27a01c18t50.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t54.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t51.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t55.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t52.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t56.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t53.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t57.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t54.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t58.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t55.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t59.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t56.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t60.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t57.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t61.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t58.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t62.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t59.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t63.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t60.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t64.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t61.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t65.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t62.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t66.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t63.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t67.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t64.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t68.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t65.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t69.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t66.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t70.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t67.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t71.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t68.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t72.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t69.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t73.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t70.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t74.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t71.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t75.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t72.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t76.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t73.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t77.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t74.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t78.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t75.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t79.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t76.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t80.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t77.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t81.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t78.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t82.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t79.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t83.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t80.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t84.ais	26.108	12.000
						H01-27	Williams	oil	H01-27a01c18t81.ais	284.638	40.551	WC-98	Bearyear	oil	WC98a01c18t85.ais	26.108	12.000
						H01-27											