**Geochemistry of basalts from small eruptive centers near Villarrica stratovolcano,
Chile: Evidence for lithospheric mantle components in continental arc magmas**

R. Hickey-Vargas ^{a,*}, M. Sun ^a, S. Holbik ^a

^a *Department of Earth and Environment, Florida International University, Miami, FL
33199, USA*

* Corresponding Author. Address: Department of Earth and Environment, AHC5-394,
Florida International University, Miami, FL 33199, USA

E-mail address: hickey@fiu.edu (R. Hickey-Vargas)

Version 2, March 14, 2016

1 ABSTRACT

2 In the Central Southern Volcanic Zone (CSVZ) of the Andes, the location of
3 stratovolcanoes and monogenetic small eruptive centers (SEC) is controlled by the
4 Liquiñe-Ofqui Fault Zone (LOFZ), a trench-parallel strike-slip feature of over 1000 km
5 length. The geochemistry of basalts from SEC is different from those of stratovolcanoes,
6 and are termed Type 2 and Type 1 basalts, respectively. In the region of Villarrica
7 stratovolcano, contemporaneous SEC are more MgO-rich, and have greater light rare
8 earth element (LREE) enrichment, lower $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, and lower ratios of
9 large ion lithophile elements (LILE) to LREE and high field strength elements (HFSE). A
10 unique finding in this region is that basalts from one SEC, San Jorge, has Type 1
11 character, similar to basalts from Villarrica stratovolcano. Type 1 basalts from Villarrica
12 and San Jorge SEC have strong signals from time-sensitive tracers of subduction input,
13 such as high $^{10}\text{Be}/^9\text{Be}$ and high ($^{238}\text{U}/^{230}\text{Th}$), while Type 2 SEC have low $^{10}\text{Be}/^9\text{Be}$ and
14 ($^{238}\text{U}/^{230}\text{Th}$) near secular equilibrium. Based on new trace element, radiogenic isotope
15 and mineral analyses, we propose that Type 1 basaltic magma erupted at San Jorge SEC
16 and Villarrica stratovolcano forms by melting of the ambient actively subduction-
17 modified asthenosphere, while Type 2 SEC incorporate melts of pyroxenite residing in
18 the supra-subduction zone mantle lithosphere. This scenario is consistent with the close
19 proximity of the volcanic features and their inferred depths of magma separation. The
20 pyroxenite forms from arc magma produced during earlier episodes of subduction
21 modification and magmatism, which extend back >300 Ma along this segment of the
22 western South American margin. Type 2 basaltic magmas may reach the surface during
23 LOFZ-related decompression events, and they may also be a normal but episodic part of
24 the magma supply to large stratovolcanoes, resulting in cryptic geochemical variations
25 over time. The presence and mobilization of stored and aged subduction-related
26 pyroxenite in the mantle lithosphere complicates the identification of subducted, mantle
27 and crustal inputs to magma erupted in continental arcs.

*Keywords: Subduction zone magmatism, basaltic magma origin, Andean Southern
Volcanic zone, small eruptive centers, stratovolcanoes, pyroxenite*

1. INTRODUCTION

Understanding the origin and evolution of basaltic magma in continental subduction zones is a challenging problem, complicated by the large number of potential influences on magma chemistry. By focusing on young oceanic island arcs, studies of arc magma generation can discern inputs from the subducting lithosphere by minimizing the influence of overriding mantle lithosphere and crust. Similarly, studies of plume-related magmatism can discern interactions of deep-seated magma with mantle lithosphere and crust. In continental arcs, the variation of subduction inputs, variations in the sub-arc asthenospheric melting regime, and the interaction of magma with mantle lithosphere and continental crust play superimposed roles in influencing the composition of resulting subduction-related magmas.

The Southern Volcanic Zone (SVZ) of the Andes, extending from 33°S to 46°S along the west coast of South America (Figure 1), is a well-recognized location for study of the complex parameters influencing the composition of continental arc magmas. This chain of late Pleistocene-active stratovolcanoes and small volcanic centers is sited on South American plate crust and mantle lithosphere of varying age (0 to > 300Ma), composition and thickness, and overlies 0-40 Ma subducting Nazca plate lithosphere. Geochemical studies of temporal changes within individual stratovolcanoes, across-strike and along-strike comparisons have addressed and hypothesized which geochemical patterns are produced by crust, mantle, and subduction inputs (Lopez-Escobar et al., 1977; Deruelle et al., 1983; Hickey et al., 1986; Hildreth and Moorbath, 1988; Davidson et al., 1988; Hickey-Vargas et al., 1989; Sigmarsson et al., 1990; Morris et al., 1990; Tormey et al., 1991; Lopez-Escobar et al., 1995a; Dungan et al., 2001; Lara et al. 2004;

Reubi et al., 2011; Watt et al., 2013; Jacques et al., 2013; 2014; Turner and Langmuir, 2015).

A major impediment to understanding mantle processes in continental arcs is the relatively rare occurrence of primitive or mafic lavas, those with Mg/Fe ratios indicating equilibrium with mantle peridotite, which are most likely to retain compositional features of sub-crustal processes. In the SVZ, rare MgO-rich basalts ($>6\% \text{MgO}$, $<52\% \text{SiO}_2$) are found at a few stratovolcanoes in the Central SVZ (CSVZ, Figure 1) and more commonly at small monogenetic basaltic cones. In the CSVZ, the locations of both stratovolcanoes and small eruptive centers (SEC) are controlled by the Liquiñe-Ofqui fault zone (LOFZ; Cembrano and Lara, 2009), a regional scale strike-slip fault extending from 38° to 46°S (Figure 1). Both their high MgO composition and the observed fault control suggest these mafic magmas are potential windows into mantle processes beneath the SVZ. Interestingly, regional comparisons of mafic stratovolcano and SEC basalts (Hickey-Vargas et al., 1989; Lopez-Escobar et al. 1995a and b) demonstrate that they are typically compositionally different, which presents an additional puzzle in the interpretation of their origin. In this paper, we compare most-mafic basalts from Holocene-recent Villarrica stratovolcano at 39.4°S in the CSVZ to basalts from five nearby contemporaneous mafic small eruptive centers with the goal of interpreting the source of their compositional differences. This work builds on the results of prior studies (Hickey-Vargas et al., 1989; Lopez-Escobar et al. 1995a and 1995b; Hickey-Vargas et al., 2002) and incorporates new petrologic, long-lived radiogenic isotope and ICP-MS trace element data for samples collected from the Villarrica region SEC in 1994 and 2004.

2. BACKGROUND

75 **2.1 Geological background**

76 The Southern Volcanic Zone of the Andes (33°-46°S; Figure 1) is formed by the
77 subduction of the oceanic Nazca plate beneath the western South American plate margin.
78 The northern and southern boundaries of the SVZ correspond with subducting Nazca
79 plate features – the inactive, plume-related Juan Fernandez Ridge in the north and the
80 actively spreading Chile Rise in the south. The dip of the slab shallows to about 25° at
81 the northern and southern boundaries, and the Nazca plate lithosphere ages from about 40
82 Ma in the north to 0 Ma in the south (Stern et al., 2007). The subduction angle is slightly
83 oblique, and the subduction rate changes from north to south (Cembrano et al., 2007).
84 Based on the age and character of coastal and basement rocks, subduction processes have
85 shaped this margin for at least 350Ma (Parada et al., 2007; Herve et al., 2007). The
86 continental crust thins from about 55 km at 33°S to about 30 km south of 37.5° S (Tassara
87 et al., 2006; Tassara and Echaurren, 2012). Broad changes in the composition and
88 petrographic features of volcanic products along the SVZ led to its subdivision into
89 Northern, Transitional, Central and Southern segments (Tormey et al., 1991; Lopez-
90 Escobar et al., 1995a). Stratovolcanoes of the Northern SVZ (33°-34.5°S) are dominated
91 by hornblende-bearing andesite, with minor more mafic and silicic lithologies. The
92 Transitional SVZ (34.5°-37°S), where crustal thickness changes, is characterized by
93 stratovolcanoes with dominant basaltic andesite ranging to more silicic products, with
94 significant variations between centers. In the Central and Southern SVZ (37°-46°S),
95 many active stratovolcanoes erupt basalt to basaltic andesite with minor dacite/rhyolite,
96 although highly silicic and dominantly andesitic volcanoes are also present.

97 The volcanic front of the CSVZ is defined by active

stratovolcanoes aligned from north to south: Antuco, Callaqui, Lonquimay, Llaima, Villarrica, Mocho-Choshuenco, Puyehue, Casablanca, Osorno and Calbuco. Within the CSVZ the volcanic front is roughly linear and shifts westward at Osorno and Calbuco. Many stratovolcanoes lie on the trace of the Liquiñe - Ofqui Fault Zone (LOFZ), or are aligned with cross-faults. The LOFZ is dextral strike-slip feature interpreted to accommodate oblique subduction of the Nazca plate (Cembrano et al., 2000; Cembrano and Lara, 2009). Fields of small eruptive centers (SEC) are found throughout the CSVZ, located north, east and west (trenchward) of the volcanic front.

Cembrano and Lara (2009) analyzed the relationship between tectonics and the location of active volcanic features in the SVZ. They concluded that the NW-SE trending chain of stratovolcanoes Villarrica, Quetrupillan and Lanin (Figure 1) overlies an ancient left lateral basement fault uncoupled to the current right lateral transpressive crustal stress state. SW-NE trending flank vents on Vn Villarrica and some monogenetic centers are controlled by the present crustal stress state, whereas others directly overlie the N-S trending LOFZ master fault

In the Villarrica region, small eruptive centers typically have volumes of less than a tenth of a cubic km and their ages are estimated to be between 4 and 16.5 thousand years, based on tephrochronology. SEC are capped by pyroclastic flow deposits erupted from Villarrica stratovolcano at 3,740 a (Pucon ignimbrite), but not those erupted at 16,500 a (the Lican ignimbrite) (Moreno et al., 1994; Fontijn et al., 2014). Villarrica Volcano (39°25'S, 71°57'W) has an active summit cone reaching 2,847 m a.s.l (Figure 2). Volcanic products are Pleistocene (Villarrica I) to recent in age (Moreno et al., 1994; Clavero and Moreno, 2004). Villarrica II comprises volcanic material emitted beginning with the Lican ignimbrite and culminating with the Pucon ignimbrite. Villarrica Unit III

comprises the currently growing active cone, including historic eruptions in 1948, 1964, 1971, 1984 and 1994 and 2014. The basement of this region contains Cretaceous / Miocene plutonic rocks, Triassic / Cretaceous / Miocene sedimentary rocks and volcanogenic series and Plio – Pleistocene volcanic series (Parada et al., 2007).

Figure 2 shows the location the SEC described in this work, and the inferred location of faults related to the LOFZ. SEC Caburgua and La Barda are located to the north of Villarrica stratovolcano, and SEC Huelemolle (consisting of three cones) is south of La Barda. San Jorge is located east of Huelemolle, and SEC Cerro Redondo is to the northeast. The SECs rise to about 500 – 1,500m a.s.l

2.2 Geophysical background

The lithospheric structure of a section of the SVZ from 39° to 40° S, including the area of Villarrica Vn. and the slip surface of the 1960 9.5 Mw Valdivia earthquake, was explored using a seismic network in place from 2008 to 2009 (Dzierma et al. 2012; Thorwart et al., 2015). Results were reported for four subregions of the subduction zone, from west to east: the Coastal Range, the Central Valley, the Volcanic Arc and the Back-arc Region in Argentina. Receiver function studies show the Moho located at 30 km beneath Vn. Volcano, consistent with prior regional studies (Dzierma et al., 2012), with the crust thinning slightly beneath, the Central Valley to the west. Tomographic and surface wave dispersion studies show that S-wave velocities decrease and V_p/V_s increase under the volcanic arc compared to adjacent regions, which is consistent with the presence of fluid, such as melt or aqueous fluids released by slab dehydration (Thorwart et al., 2014). They note that a low resistivity zone, also consistent with the presence of fluid, was identified between 25 and 50 km beneath the volcanic arc at 39°S in the magnetotelluric study of Brasse and Soyer (2001). The seismic studies did not resolve the depth of the mantle

lithosphere – asthenosphere boundary (LAB) beneath the volcanic arc, although an inverted S-wave velocity profile was found in the back arc in Argentina at about 55 km depth (Thorwart et al., 2015). In the gravity model of Tassara et al. (2006) and Tassara and Echaurren (2012), the Moho is located at about 35 km beneath Vn. Villarica, the LAB at about 65 km and the slab surface at about 90 km.

2.3 Geochemical background

Lopez-Escobar et al. (1995a) presented a regional geochemical study of basalts from the SVZ and noted that most SEC are geochemically different from basalts erupted from frontal arc stratovolcanoes such as Villarica, Llaima, Osorno and Puyehue. They classified basalts in the CSVZ as either Type 1, typical of the stratovolcanoes, and Type 2, typical of behind the front volcanoes and small eruptive centers. Key trace element differences are greater light rare earth element (LREE) enrichment relative to heavy REE (HREE) in SEC basalts, and lower abundances of alkali elements (K, Rb and Cs) and Ba compared with REEs and high field strength elements (HFSEs) such as Nb, Ta, Hf and Zr. In studying cross-arc and along-arc trends in CSVZ basalt geochemistry, both Hickey-Vargas et al. (1989) and Lopez-Escobar et al. (1995a) proposed that the overall geochemical patterns of Type 1 and Type 2 basalts were consistent with a model in which a larger contribution of subduction derived hydrous fluid (enriched with LILEs) was incorporated into the mantle sources of Type 1 magmas. As a result, a greater degree of partial melting is induced in the source, producing the lower LREE/HREE ratios of the Type 1 magmas. This hypothesis makes geologic sense where there are Type 1 basalts in the volcanic front and Type 2 basalts behind the front (e.g., Lara et al., 2004; Watt et al., 2013a; Jacques et al., 2013) so that progressive subduction would influence the extent of slab dehydration. The same reasoning is difficult to reconcile with the small distances and

scattered location of the SEC relative to adjacent stratovolcanoes in the Villarrica region and elsewhere. Hickey-Vargas et al., (2002) analyzed time-sensitive tracers of subduction inputs, $^{10}\text{Be}/^9\text{Be}$ and $^{238}\text{U}/^{230}\text{Th}$, in Villarrica region SEC and found that they were positively correlated with high alkali element/LREE ratios and low LREE/HREE. They also found that one SEC, San Jorge, located within 10 km of several Type 2 SEC, had Type 1 characteristics like Villarrica stratovolcano. Therefore, a key issue that we address in this paper is the origin of the geochemical differences among the SEC's and Villarrica stratovolcano in the context of their temporal and spatial arrangement.

3. SAMPLE COLLECTION AND ANALYTICAL TECHNIQUES

Samples having new geochemical data reported in this work were collected from the small eruptive centers east and north of Villarrica Stratovolcano: Caburgua, LaBarda, Huelemolle, San Jorge and Cerro Redondo in 1994 by Leopoldo Lopez Escobar. Additional samples were collected from SEC Caburgua and San Jorge by R. Hickey-Vargas in 2004. Samples included both pyroclastic material (bombs and scoria) and lava when present. Petrography and mineral compositions are discussed for these samples together with samples described in Hickey-Vargas et al. (1989).

Mineral analyses were performed with the JEOL 8900 EPMA, Florida Center for Analytical Electron Microscopy, in the Department of Earth and Environment at Florida International University, using methods reported in Holbik (2014). Major and select trace elements (Ni, Cr, Co, V, Sc, Cu, Zn) were analyzed using the Jobin Yvon 70 ICP-OES in the FIU Department of Earth and Environment, using methods reported in Hickey-Vargas (1998). Additional trace elements for 1994 samples were measured by ICP-MS at the University of Kansas and Boston University, using techniques reported in

Johnson and Plank (1999). Samples were dissolved at FIU, following recommended procedures, and sent for analysis as solutions. Li-Be-B measurements for select samples were completed using the ARL Spectra Span 7 DCP at the University of South Florida, Tampa, using methods described in Ryan et al. (1996). Additional trace elements for 2004 samples were measured by ICP-MS at the GeoAnalytical Laboratory, Washington State University, Pullman, using methods described on the GeoAnalytical Laboratory website, Technical Notes.

Analyses of radiogenic isotopes were performed at the Department of Terrestrial Magnetism (DTM), Carnegie Institution of Washington or in the Geochemistry Laboratory at the National High Magnetic Field Laboratory (NHMFL) at Florida State University. At DTM, Sr, Nd and Pb isotopes were analyzed using the VG 354 TIMS using methods described in Walker et al. (1989) and Carlson and Irving (1994). Isotopic values are corrected for fractionation using $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.7219$ and the Todt et al. (1996) values for the NBS-981 Pb isotopic standard. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to 0.71025 for NBS 987 and to 0.511860 for the La Jolla Nd standard, respectively. Typical errors for the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are ± 0.000015 , and $\pm 0.05\%$ per amu or better for Pb isotopes. At the NHMFL, samples were analyzed with the Finnegan MAT 251 TIMS. Isotopic values are corrected for fractionation by using $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$, $^{143}\text{Nd}/^{144}\text{Nd} = 0.7219$ and the Todt et al. (1996) values for the NBS-981 Pb isotopic standard. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios were normalized to 0.708000 for the E&A Sr standard and 0.511860 for the La Jolla Nd standard, respectively. Typical errors for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are ± 0.000010 and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios is ± 0.000010 , and 0.05% per amu or better for Pb-isotope ratios.

4. PETROGRAPHY and MINERAL CHEMISTRY

Basaltic rocks from Villarrica stratovolcano are broadly similar to those of other predominantly mafic Holocene CSVZ stratovolcanoes, such as Llaima and Osorno (Reubi et al., 2011; Lopez-Escobar et al., 1992). Rocks with $\text{SiO}_2 < 53\%$ are porphyritic with abundant plagioclase and rare olivine phenocrysts in a fine-grained intersertal groundmass. Villarrica stratovolcano basalts ($< 53\% \text{ SiO}_2$) have a larger proportion of phenocrysts (up to 20% of sample volume) than most of the SEC basalts (Cabargua, Cerro Redondo, Huelemolle, La Barda), which contain less than 6% phenocrysts. Except for SEC San Jorge, SEC samples are composed of a fine-grained plagioclase-rich intersertal groundmass. Phenocryst phases are olivine or olivine and plagioclase, with less common clinopyroxene. Basalts from San Jorge are unusually mafic ($\text{SiO}_2 < 50.5\%$ and $\text{MgO} > 9.1\%$), and phenocrysts are predominantly olivine with rare plagioclase. Olivines are generally euhedral, but some grains are broken or rounded and contain minute spinel/chromite crystals which could indicate that they are cumulate antecrysts.

Olivine phenocryst compositions, highlighting some differences between Villarrica stratovolcano and the SEC, are shown in Figure 3. Olivine core compositions for basaltic rocks ($< 53\% \text{ SiO}_2$) from Villarrica stratovolcano range from Fo 74-79, in contrast to values of Fo 79-90 for basaltic rocks from Cabargua (82-88), Huelemolle (79-82), La Barda (87-89) and S. Jorge (85-90). Plagioclase phenocryst cores from Villarrica basaltic rocks range from An 58 to An 85, peaking at An 63. Rare plagioclase phenocrysts from SEC Cabargua and Huelemolle basalts have more uniform and higher core An contents of 77-87.

5. GEOCHEMICAL RESULTS

5.1 Major elements

Major and trace element data for SEC are listed in Table 1, and new ICP-MS trace element data for Villarrica stratovolcano are listed in Table 2. Major element differences between Villarrica stratovolcano and SEC volcanic rocks are illustrated in Figure 4. Compared with the SEC, Villarrica stratovolcano samples exhibit a larger range of SiO₂ content, 51-56 wt%, and are shifted to higher SiO₂ for a given MgO, CaO, Al₂O₃ and Fe₂O₃ content. Most SEC samples are true basalts (<52% SiO₂), even at low MgO contents of 4-5% and low Mg#, whereas only a few lavas from the stratovolcano, all with MgO >6.5%, are true basalts. Basalts from San Jorge SEC have unusually high MgO and Mg# (9.0-14.5 wt%), with highest MgO (13-14.5) in scoria samples. Basalts from SEC Caburgua, Huelemolle, La Barda and Cerro Redondo have slightly higher K₂O and Na₂O than basalts from Villarrica, whereas basalts from San Jorge lie along the trend formed by Villarrica basalt through andesite, at lower SiO₂ (Figure 4).

5.2 Trace elements

5.2.1 Compatible trace elements:

Trace elements Ni, Cr, Sc and Sr are likely to be compatible (bulk D >1) during melting of mantle peridotite or during magma crystallization involving the assemblage olivine + spinel +/- clinopyroxene +/- plagioclase. Variations of these elements versus MgO are shown in Fig. 5. The basalt to andesite suite from Vn. Villarrica exhibits decreasing Ni and Cr, increasing then decreasing Sr and constant then decreasing Sc with decreasing MgO. Compared with Vn. Villarrica basaltic rocks, the SEC Caburgua, La Barda, Huelemolle and Cerro Redondo basalts have systematically higher abundances of Sr and lower Sc for a given MgO. Stratovolcano and SEC basaltic rocks plot along similar

trends for Ni and Cr versus MgO, although Cr contents are slightly higher in the SEC at high MgO. SEC San Jorge basalts, with high MgO, plot at exceptionally high Ni and Cr contents, especially in samples with 12-14.5% MgO. In contrast, Sc and Sr in San Jorge samples plot at concentrations similar to those for basaltic rocks from Villarrica stratovolcano.

5.2.2 Incompatible trace elements:

Figure 6 shows normalized trace element diagrams for basaltic rocks from Vn. Villarrica and the SEC, and Figure 7 shows the details of REE patterns. Normalized elemental patterns for all rocks exhibit the typical characteristics of subduction magmas: high abundances of LILE Ba, Sr, Rb and low abundances of HFSE Nb and Ta compared with LREE. Comparing basaltic rocks from the SEC and Villarrica stratovolcano, overall patterns noted originally by Hickey-Vargas et al. (1989), and Lopez-Escobar et al. (1995a) are confirmed in this work, with the exception of SEC San Jorge. SEC Cabargua, La Barda, Huelemolle and Cerro Redondo have higher LREE/HREE ratios (Figure 7), and higher concentrations of LREE and HFSE Nb, Ta, Zr and Hf (Figure 6), whilst HREE abundances are similar (Figure 6 and 7). Compared with basaltic rocks from Vn. Villarrica, abundances of elements Ba, U and Th are higher in SEC basalts, and abundances of Rb and Cs are similar or lower (Tables 1 and 2), and ratios of all of these elements to LREE are lower (Figure 8). These characteristics are consistent with their being Type 2 in the system of Lopez-Escobar (1995a). Basalts from SEC San Jorge have lowest overall incompatible element abundances, with normalized multi-element (Figure 6) and REE patterns (Figure 7) roughly parallel to those for rocks from Vn. Villarrica, and are therefore Type 1. These results confirm the finding of Hickey-Vargas et al. (2002), that SEC San Jorge is geochemically unlike other Villarrica region SEC but

similar to Vn. Villarrica. More mafic Type 1 and 2 basalts do not exhibit Eu anomalies, but slight negative Eu anomalies appear in more silicic endmembers, basaltic andesite in the cases of Villarrica stratovolcano and SEC Huelemolle (Figure 7).

5.3 Radiogenic isotopes

Sr, Nd and Pb isotope data from this work are listed in Table 3. On a plot of $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ (Figure 9), ratios for samples from Villarrica stratovolcano are typical of basaltic rocks from CSVZ stratovolcanoes. Both Sr- and Nd- isotope ratios for basalts from SEC Caburgua, Cerro Redondo, Huelemolle and La Barda are notable in being lower than those of basaltic rocks from Vn. Villarrica and thus more “mantle-like”. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary from 0.70374 to 0.70397 and $^{143}\text{Nd}/^{144}\text{Nd}$ varies from 0.51278 to 0.51291. SEC basalts group into two clusters, one having lowest $^{87}\text{Sr}/^{86}\text{Sr}$ (Cerro Redondo, La Barda and Caburgua) with Huelemolle basalts shifted toward slightly higher $^{87}\text{Sr}/^{86}\text{Sr}$. Sr and Nd isotope ratios for basalts from San Jorge overlap completely with those for Vn. Villarrica, confirming their Type 1 character (Hickey-Vargas et al., (2002).

Pb isotopic ratios of SEC basalts range from 18.52 to 18.62 ($^{206}\text{Pb}/^{204}\text{Pb}$), 15.58 - 15.63 ($^{207}\text{Pb}/^{204}\text{Pb}$) and 38.40 - 38.56 ($^{208}\text{Pb}/^{204}\text{Pb}$) (Table 3). This range overlaps entirely with that for basalts from Villarrica stratovolcano (Hickey-Vargas et al., 1989), and the total variation does not exceed 4 to 5 times analytical error. These and other CSVZ volcanic rocks have Pb isotopic compositions that overlap with Nazca and Pacific plate sediments (Hickey-Vargas et al., 1989, Figure 12)

5.5 Other results:

Hickey-Vargas et al. (2002) reported $^{10}\text{Be}/^9\text{Be}$, ($^{238}\text{U}/^{232}\text{Th}$), ($^{230}\text{Th}/^{232}\text{Th}$) and ($^{210}\text{Po}/^{230}\text{Th}$) results for a subset of samples with analyses reported in this paper, marked

with asterisks in Tables 1, 2 and 3. Overall results of that work were that $^{10}\text{Be}/^9\text{Be}$ ratios in basalt from Vn. Villarrica and SEC San Jorge were similar and high (4.0 and 4.6×10^{-11} respectively) relative to basalts from Caburgua, La Barda and Huelemolle (1.6 - 1.9×10^{-11}). Vn. Villarrica and San Jorge basalts also had high ($^{210}\text{Po}/^{230}\text{Th}$), (a proxy for ($^{226}\text{Ra}/^{230}\text{Th}$)) and high ($^{238}\text{U}/^{232}\text{Th}$), clearly out of secular equilibrium, whereas basalts from Caburgua, La Barda, Huelemolle and Cerro Redondo have ($^{238}\text{U}/^{230}\text{Th}$) close to but slightly less than equilibrium values. ($^{230}\text{Th}/^{232}\text{Th}$) are 0.87 - 0.92 for the Type 2 SEC, and 0.76 - 0.77 for San Jorge and Vn. Villarrica.

6. DISCUSSION

6.1 Magmatic differentiation

The location of the SEC, along the LOFZ and nearby faults, as well as their high MgO character, support the idea that SEC basalts could be derived from mantle melting processes with little interaction with the crust. The SEC have characteristics even more primitive than high-MgO stratovolcano basalts: low SiO_2 and a limited range of major element variation. The latter mitigates against their influence by extended magma chamber processes, which would operate at Villarrica stratovolcano, such as magmatic differentiation to produce intermediate and/or felsic derivatives, magma mixing, heating of crust by repeated magmatic intrusion and crustal assimilation. Nonetheless, aspects of their magmatic evolution from primary mantle melts could have a significant impact on major, trace element and isotopic compositions. In this section we examine evidence for the pathways from mantle melts to the erupted products for the SEC.

6.1.1 Possible liquid lines of descent and parental magmas

In Figure 10, the composition of basaltic rocks from San Jorge and Villarrica stratovolcano (Figure 10a) and SEC Caburgua, La Barda, Huelemolle and Cerro Redondo (Figure 10b) are plotted as recalculated mineral components projected from PLAG onto a CPX-OL-QTZ pseudoternary diagram, together with experimentally determined phase boundaries from Grove et al., (1982; 1983). All samples contain olivine and plagioclase and plot in the field of olivine plus plagioclase. Rocks from Villarrica form an “L-shaped” array, from most MgO-rich basaltic rocks which are displaced toward OL from the 1 atm olivine-plagioclase-augite multiple saturation curve, to more andesitic samples which plot along the 1 atm curve. The basaltic rocks plot near an experimentally determined saturation curve for water saturated melts at 2 kbar and follow an olivine control trend toward the andesitic rocks. A probable interpretation is that hydrous Villarrica basaltic magma evolved by crystallization of olivine at depth, and reached augite and plagioclase saturation during differentiation and ascent to the surface. Basalts from San Jorge plot in two groups displaced toward the olivine apex from most mafic Villarrica basalts. Given the trace element and isotopic similarities between San Jorge and Villarrica basalts, these could be related either by olivine crystallization or by olivine accumulation.

Basaltic rocks from the Type 2 SEC also plot toward the olivine apex compared with the 1 atm multiple saturation curve. More evolved ($\text{MgO} < 5.5\%$) rocks from Huelemolle and Cerro Redondo form linear trends toward QTZ component, parallel to the hydrous high pressure saturation curves, and may have undergone olivine + augite +/- plagioclase crystallization at depth in the crust. One group of basalts from Cerro Redondo is also displaced in this direction. However, the most MgO-rich basalts from Caburgua, Huelemolle and La Barda, bearing sparse olivine and plagioclase phenocrysts, plot in a

tight cluster at lower QTZ component than these and MgO-rich San Jorge basalts. We interpret these compositions as parental magmas for Type 2 SEC.

6.1.2 Equilibrium with olivine phenocrysts

In Figure 3, the Mg-numbers of olivine phenocryst cores from SEC and Vn. Villarrica rocks are plotted versus whole rock Mg-numbers together with an envelope centered on the experimentally determined Fe/Mg exchange coefficient of 0.3 for olivine/liquid. Olivines from Villarrica stratovolcano rocks extend from the equilibrium curve toward lower Fo in the olivine, suggesting differentiation and magma mixing has taken place. In contrast, many SEC olivines plot within the envelope, including Caburgua, Huelemolle and San Jorge. Some olivines from Caburgua, Huelemolle and La Barda plot above the curves; these may have crystallized from more mafic precursor magmas. Olivines from San Jorge have maximum Fo contents in the range 88-89, which is consistent with basalt with Mg-number 66-68, which have MgO = 9-10% (Table 1). We interpret this group of San Jorge basalts as probable liquids, and the higher MgO group (12-14 % MgO) on Figures 3 and 11 as olivine cumulates.

6.1.3 Compatible element trends

Decreasing Ni and Cr with MgO in basaltic rocks (Figure 5) is consistent with olivine plus spinel crystallization and/or accumulation affecting all samples.. The pseudoternary diagrams suggest that multiple olivine, plagioclase and clinopyroxene saturation occurred in certain samples, mostly those having MgO <5.5. Abundances of Sc ($K_d > 1$ for clinopyroxene) and Sr ($K_d > 1$ for plagioclase) show little systematic variation in SEC rocks over their small range of MgO. In basalt through andesite from Vn. Villarrica, Sc decreases very slightly and Sr increases then decreases, consistent with plagioclase and augite crystallization. Relationships between Sc, Sr and MgO contents for San Jorge

parental basalts and Villarrica stratovolcano basalts are consistent with crystallization of olivine. However, these observed variations with MgO content are minor compared with the systematic differences between Sc and Sr for Type 1 and Type 2 parental basalts (Figure 5), which suggests that plagioclase and clinopyroxene crystallization is not responsible. Similarly, the position of Type 2 parental compositions on the pseudoternary diagram and on major element plots are not consistent with the evolution of Type 2 SEC basaltic magma from Type 1 basaltic magma by high pressure crystallization which would involve a higher proportion of clinopyroxene relative to olivine and plagioclase (Grove and Baker, 1984; Sisson and Grove, 1993). Therefore, we conclude that the systematic differences in Sr and Sc abundances between SEC San Jorge and Type 2 SEC probably arise from processes related to source composition or to interaction with lower crust or mantle. High Sr abundances may be related to the overall incompatible element enrichment of Type 2 magmas. In subsequent discussion, we will focus on basalts that have been identified as likely parental compositions.

6.1.4 Primary magmas

With evidence that identified parental SEC basalts compositions formed mainly by olivine + spinel fractionation, we calculated primary magma compositions by olivine addition using approach of Lee et al. (2009). An important unknown for the SECs is the primary water content. We calculated primary magma compositions over a range of water contents and $\text{Fe}^{3+}/\text{Fe}^{2+}$ typically reported for SVZ and subduction related magma (Tormey et al., 1991; Johnson et al., 1994; Leeman et al., 2005; Wacaster et al., 2008; Watt et al., 2013a) and list examples for each SEC at a magma water content of 4% H_2O in Table 4, with the amounts of olivine added. The model estimates the temperature and pressure of magma extraction from mantle rock containing olivine, orthopyroxene and

clinopyroxene, including both peridotite and olivine bearing pyroxenite (Lee et al., 2009), and these values are also listed in Table 4. Primary magma compositions calculated for the SEC are similar to those estimated for subduction magma, (e.g. Plank and Langmuir; 1988), although CaO contents are lower and most similar to those for basaltic magma produced by 10% partial melting.

6.2 Origin of incompatible trace element and isotopic differences among the SEC

6.2.1 Assimilation of felsic to intermediate crust

Hickey-Vargas et al. (1989; 2002), and Lopez-Escobar et al. (1995a) noted that the trace element and isotopic characteristics of Type 2 SEC are contrary to assessments of the influence of sialic crust on magma compositions, at least as compared with basalts from stratovolcanoes such as Villarrica. Because of this, the discovery of a mafic, Type 1 SEC assists in interpreting that relationship because its geologic setting and magma ascent history is presumably similar to the Type 2 SEC. A near universal indicator of crustal assimilation is increasing SiO₂, together with trace element and isotopic parameters such as increasing alkali element (K, Rb, Cs) enrichment, increasing ⁸⁷Sr/⁸⁶Sr and increasing δ¹⁸O for old upper continental crust. None of these are observed in the contrast between Type 1 and Type 2 SEC. In areas of the SVZ underlain by young plutonic rocks, researchers have noted that crustal assimilation would not necessarily affect ⁸⁷Sr/⁸⁶Sr ratios (Davidson et al., 1988; Dungan and Davidson, 2004). However, trace element effects are still evident in these cases. For example, for nearby Llaima stratovolcano, Reubi et al. (2011) document increasing Rb/SiO₂, increasing Th/La, decreasing Ba/Th and diminishing U-series disequilibrium in basalt through basaltic andesite, as evidence of increasing assimilation of Tertiary granitic to dioritic plutonic basement. As shown in

Figure 8, SEC basalts have varying Th/La, from 0.11 to 0.14 in basalts from San Jorge, and from 0.10 to 0.22 in Type 2 SEC. Type 2 SEC do not exhibit U-series disequilibrium (Hickey-Vargas et al., 2002), but have significantly lower Rb/SiO₂, K/La, Rb/La and Cs/La than Type 1 basalts, contrary to a model in which Type 2 basaltic magma assimilates plutonic rocks. Our conclusion is that although assimilation of sialic crust could account for Th/La and U-series trends among Type 1 basalts and basaltic andesites (e.g., at Llaima), it is not the source of trace element and isotopic differences between Type 1 and Type 2 basalts.

6.2.2 Variation in subduction inputs

Both Type 1 and Type 2 basalts have trace element and isotopic signatures shared by many subduction related basalts worldwide, indicating incorporation of fluids derived from subducted sediment and altered basalt in the source regions for mantle melts: LILE enrichment compared with MORB, depletion in Ta and Nb relative to LREE, lower than MORB-like ¹⁴³Nd/¹⁴⁴Nd and Pb-isotope ratios within the field for sediments (Figures 6, 8, 9; Table 3; Hickey-Vargas et al., 1989). One of the most compelling arguments against variations in subduction inputs as the source of distinct Type 1 and Type 2 SEC, is their spatial proximity within 10 km of each other (Figure 2). Based on models of regional lithospheric structure for the CSVZ (Tassara et al., 2006; Tassara and Echaurren, 2012), and for the Villarrica region (Thorwart et al., 2015), slab-derived components would transit from the subducted Nazca plate surface at 100 km through the mantle to arrive in asthenosphere hot enough to melt (Figure 12). Magma would then rise through the mantle lithosphere, located regionally at about 60 km, to the Moho at about 30 km, then through lower and upper crust to the surface. That individual subduction components would do so without mixing or homogenization over a surface distance of

less than 20 km² is unlikely, particularly given the likelihood of homogenization at the level of melt generation in the asthenosphere (Figure 12). Temporal differences in slab inputs could permit such an explanation, thus the fact that Villarrica stratovolcano erupted Type 1 basalts over the lifetime of the Type 2 SECs is important. That Type 1 basaltic magmas are most voluminous, based on their occurrence at the stratovolcano, and have strong time-dependent subduction signals like ¹⁰Be activity and ²³⁸U enrichment, suggests that they represent the magma type actively generated in the asthenosphere of the current subduction system beneath the Villarrica region.

Type 2 SEC have small but detectable ¹⁰Be/⁹Be signals that differentiate them from mantle rocks like MORBs and OIBs (Morris et al., 1990), therefore some subduction input is needed in their evolution. The small signal could result from dilution by a large proportion of non-subduction related melt or by aging of the source. Based on the assumption that Type 2 mantle sources had the same initial ¹⁰Be/⁹Be as sources for Type 1 SEC, Hickey-Vargas et al. (2002) suggested that aging alone placed a minimum age of about 3 Ma on sources for Type 2 magma. An alternative hypothesis is that the Type 2 SEC contain melts from ancient enriched subcontinental or OIB-like mantle. This was proposed by Hickey et al. (1986) and Hickey-Vargas et al. (1989) for behind the front SVZ volcanoes. Similar models for enriched behind the front volcanos in the SVZ have been proposed by Lara et al. (2004; Lanin); by Watt et al. (2013) in the southern SVZ, and Jacques et al. (2013) for across arc variations in the TSVZ. Unlike these behind the arc rocks, the Villarrica region magmas show little or no correlation between LREE-enrichment and trace element parameters connected with subduction. For example, negative anomalies, such as high La/Nb and La/Ta are not correlated with LREE/HREE, and enrichments such as U/La, Th/La, Rb/La and Cs/La are scattered, as

shown in Figure 8, which is inconsistent with mixing with an OIB-like source with low La/Nb and Ba/La. For this reason, we suggest that the source of incompatible element enrichment for Type 2 SEC is itself subduction-related, most likely pyroxenite or eclogite formed in the mantle lithosphere from older subduction-related basaltic magmas. Such mantle rocks could form by reaction of ascending subduction-related basaltic magma with peridotite or by crystallization during ascent due to cooling and volatile loss. It is a plausible conclusion that such modification of the mantle lithosphere has taken place given the long interval of subduction related magmatism that has affected the western margin of South America (>300 Ma; Munizaga et al., 1988; Lucassen et al., 2004; Parada et al., 2007). Tertiary magmatism and plutonism, for example, occurred along roughly the same locus as the current Pleistocene-recent arc (Lucassen et al., 2004; Parada et al., 2007).

6.2.3 Mantle melting, peridotite and pyroxenite

One of the long-standing puzzles of the Type 1 and 2 basalts is how the differing REE patterns could be generated by mantle melting processes (Lopez Escobar et al. 1977; Lopez-Escobar et al., 1995a). Figure 11 shows REE ratios and REE abundances produced by melting of different potential source rocks for Type 1 and 2 SEC. In these calculations we match primary basalt REE abundances calculated by adding olivine in the amounts shown in Table 4. Using a mantle peridotite source (60% olivine, 20% orthopyroxene, 15% clinopyroxene and 5% spinel, Figure 11a) with E-MORB trace element abundances to approximate a mantle slightly LREE-enriched by subduction inputs, approximately 25% partial melting matches the field for Type 1 primary magmas from San Jorge. However, using the same initial source composition and peridotite mineralogy, it is impossible to match La/Yb ratios and La and Yb abundances of Type 2

basaltic magmas at any melt fraction. A larger modal abundance of clinopyroxene or clinopyroxene plus garnet is needed to produce the high La/Yb but low Yb concentrations of these magmas. As shown in Figure 11a, an olivine-bearing, garnet-free pyroxenite lithology (20 olivine: 40 orthopyroxene: 30 clinopyroxene: 10 spinel), closely matches that of Type 2 SEC primary magmas at melt fractions of 5 to 10%.

The model calculation shown in Figure 11a presumes the same slightly enriched mantle source for Type 1 and Type 2 SEC basalts. However, if enrichment of Type 2 sources results from reaction with or crystallization of ascending subduction basalt melt, we would expect such sources to be more enriched in incompatible trace elements.

In Figure 11b, we estimate melt compositions produced from a pyroxenite lithology having the trace element content of an arc basalt rather than a mantle basalt source. In this case, La/Yb ratios and La and Yb abundances can be matched only if garnet is a residual mineral. For example, using Type 1 San Jorge primary basalt as a proxy for aged subduction basalt in the mantle lithosphere, Type 2 SEC primary magmas are matched by 25% to 45% partial melting of garnet pyroxenite (10% olivine, 30% orthopyroxene, 50-55% clinopyroxene and 5-10% garnet). Thus, variations in La/Yb ratios and La and Yb abundances of the Type 2 SEC can be explained by melting of enriched mantle with a pyroxenite lithology, or melting of basalt with a garnet pyroxenite lithology. A third possible scenario implicit in Figure 11 would be partial melting of enriched mantle peridotite to form Type 1 magmas, followed by assimilation of or mixing with melts of subduction basalt having garnet pyroxenite lithology.

A pyroxenite source for the Type 2 SEC magmas is supported by the REE modeling calculations. It is also consistent with lower Sc contents of the Type 2 SEC basalts (Figure 3) because K_d for Sc both clinopyroxene and garnet is higher than for

olivine and orthopyroxene (Hart and Dunn, 1993; Hauri et al., 1994). The possible presence of garnet in melting residues may constrain the depth of melting. In the SVZ, interaction with garnet in the lower crust is commonly proposed to produce steep or variable REE patterns in parts of TSVZ and especially the NSVZ where crust is thick (Lopez-Escobar et al., 1985; Tormey, et al; 1991; 1995; Ferguson et al., 1992). In the CSVZ, with relatively thin crust, garnet is unlikely to be stable in mafic lower crustal lithologies, nor is it stable in peridotite until sub-lithospheric depths are reached. Therefore, if garnet is an essential residual phase, the source of the Type 2 melts is likely to be pyroxenite within the mantle lithosphere (30-60 km).

Since major element compositions of Type 1 and Type 2 SEC basalts are similar, these models depend on the likelihood that melting of peridotite and pyroxenite will lead to similar bulk compositions. In a recent review of experimental results seeking to define indicators of pyroxenite melting in oceanic basalts, Lambart et al. (2013), point out that in many cases, melts of the two lithologies are indistinguishable. This is especially true when the extent of melting of pyroxenite is high, as in the model of Figure 11b. Alternatively, the similar major element compositions of Type 1 and 2 basaltic magmas may indicate that Type 2 melts form by assimilation of pyroxenite by Type 1 melts rather than being generated separately.

6.2.4 Pyroxenite from prior subduction zone magmatism

An interesting feature of the Type 2 SEC is that they have lower $^{143}\text{Nd}/^{144}\text{Nd}$ and lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared with those for San Jorge, Villarrica and other volcanic front stratovolcanoes in the Central SVZ (Figure 9). Using global mantle reservoirs to explain this difference, one could propose that the sources for the SEC were more “mantle-like”, possibly having an OIB-type signature, or that they incorporate a lesser subduction input

from altered oceanic crust having high $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. It could also indicate a different proportion of Sr from subducted sediment versus slab-derived fluid in the two magma types. These are all possible variations that could occur over time in generating subduction magmas. Therefore, one simple explanation for the isotope characteristics of the Type 2 SEC is that they reflect temporal permutations of the long-lived subduction system, i.e., the stored pyroxenite component was generated in a slightly different subduction setting from the present one. In order to test this idea, we looked at data for Tertiary and Late Mesozoic plutonic rocks from the basement of the CSVZ (Lucassen et al., 2004) and for Miocene basalts from the Chilean Central Valley (Vergara et al., 1999; 2004). As shown in Figure 9, some of the Miocene basalts have relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ similar to the Type 2 SEC. Isotopic compositions of Tertiary plutonic rocks, have $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ which overlap with Villarrica stratovolcano and San Jorge SEC. Further study of older rocks, especially basalts, in the SVZ is needed to test both models for crustal assimilation and models for subduction basalt/pyroxenite stored in the mantle lithosphere.

6.3. Magma ascent and interaction in the CSVZ

6.3.1 Magma extraction depths and temperatures

We hypothesize that the Type 2 SEC form either by melting of pyroxenite or by mixing of pyroxenite melt with ascending ambient subduction zone magma produced the in asthenospheric mantle (Type 1). Using primary magma compositions (Table 4), we used the thermobarometric model of Lee et al. (2009) to estimate temperatures, depths and pressures at which SEC primary magmas last equilibrated with their mantle sources. According to Lee et al. (2009), this model is valid for assemblages of orthopyroxene,

clinopyroxene and olivine which includes both peridotite and olivine-bearing pyroxenite as used in our trace element model.. Depths calculated for the SEC are: 43 km for San Jorge, 52 km (Caburgua and La Barda) and 56 km (Huelemolle), with errors of +/-5 km. These depths are all sub-crustal, based on the 30 km Moho location of Dzierma et al., (2012) for the Villarrica region. They are also all shallower than the 60 km deep regional mantle lithosphere/asthenosphere boundary modelled by Tassara et al (2006); Tassara and Echaurren (2012). This indicates that depths of SEC melt extraction occurred within the mantle lithosphere, or that the LAB was locally more shallow. These depths are consistent with the findings of Dzierma et al., (2012) and Thorwart et al. (2015) that the sub-crustal mantle in the Villarrica region contains melt, as indicated by low V_s and V_s/V_p .

Figure 12 is a schematic picture of the conditions of melt formation and extraction for Villarrica stratovolcano and SEC in the Villarrica region. Type 1 magmas (Vn. Villarrica and SEC San Jorge) form from melting of peridotite in the asthenospheric mantle, which shallows beneath the volcanic front where melt production is enhanced by the input of slab-derived aqueous fluids. Pyroxenite bodies in the surrounding mantle lithosphere are heated either by thermal conduction from the upwelling asthenosphere or by entrainment in rising Type 1 magmas, and melt. Given a conduit to the surface such as the LOFZ or associated faults, Type 2 SEC melts rise to the surface and form the monogenetic SEC. Type 2 melts may also be incorporated in magma that forms stratovolcano, greatly diluted by Type 1.

Because Type 2 SEC are restricted to the LOFZ, it is probable that their magma volumes are small and that the fault system is essential for transport to the surface. In the Villarrica region, the timing of SEC volcanism seems to be a short episode, concurrent

with Vn. Villarrica Stage II. It is possible that SEC magmatism was triggered by stresses related to the fault, such as decompression related to uplift or transpressional motion along the LOFZ. Given the age of the SEC between 16,500-3,740 a, decompression could also be related to lithospheric uplift following the last glacial maximum (Watt et al., 2013b). Considering the calculated extraction depths in detail (Table 4), the depth for Type 1 SEC San Jorge is slightly closer to the Moho than Type 2 SEC. This could indicate that this unique Type 1 SEC formed at a time when Type 1 magma production increased overall, invading the lithosphere to reach shallower depths. Better temporal constraints on the eruption of each of the SEC is needed to evaluate such possibilities.

6.3.2 Relationship between basalts of SEC San Jorge and Vn. Villarrica

San Jorge SEC is located about 15 km NE of Villarrica stratovolcano. On the basis of major and compatible element trends, relationships on mineral component projections, radiogenic isotope compositions, in addition to U-series and $^{10}\text{Be}/^9\text{Be}$ ratios, these Type 1 basalts appear to be genetically related to the stratovolcano basalts. Compared with liquid evolution curves on Figure 10, they appear to be potential parental magmas for the stratovolcano. The basalts also have similar ratios of some incompatible elements, such as La/Yb, Ba/La and La/Nb, but ratios of other highly incompatible elements, such as Th/La, U/La, Rb/La and Cs/La (Figure 8) are lower in San Jorge basalts. Several explanations could account for this. First, since these elements are all notably enriched in subduction fluids or sediment melts (Elliot et al., 1997; Plank and Langmuir, 1993; 1998), it could be that their subduction-produced parental magmas are in fact different, or that these ratios are variable in Type 1 magmas and the minor San Jorge eruption sampled only one part of that range of variation. Alternatively, it is well established that these ratios increase in stratovolcano magmas as they evolve from basalt to dacite or

rhyolite. For example, rhyolite at Villarrica and rhyolites at Puyehue volcano have significantly higher Th/La, U/La, Rb/La and Cs/La than associated basalts (Hickey-Vargas et al., 1989; Gerlach et al., 1988). Thus, the higher ratios in Villarrica basalts could reflect the continuous incorporation of small amounts of evolved melt over the lifetime of its magma chamber and supply system. It is also possible that the elevated ratios reflect assimilation of melts of plutonic basement rocks, as proposed by Dungan and Davidson (2004) and Reubi et al. (2011), or a combination of the latter two processes. The higher SiO₂ for a given MgO in the stratovolcano basalts could reflect either internal magma mixing or assimilation of felsic basement rocks. Further study of the San Jorge basaltic magmas and their relationship to Villarrica stratovolcano would be a useful approach to understanding the evolution of mafic magma in the CSVZ generally.

6.4 Implications for the SVZ and other continental arcs

The hypothesis that subduction components stored and aged in the subarc lithosphere contribute to the formation of subduction magma in active systems has been proposed in studies of the Cascades (Leeman et al., 2005) and Central America (Heydolph et al., 2012). A shared issue of these studies and the present one is distinguishing material from mantle lithosphere and the lower continental crust. In the SVZ, assimilation of the lower crust has been widely implicated for geochemical variation in mafic and evolved magma (Hildreth and Moorbath, 1988; Dungan and Davidson (2004); Reubi et al. (2011). The signature of melting pyroxenite versus plagioclase rich-lower crust, with impacts on the extent of LREE-enrichment, Eu-depletion and Sr and Sc systematics, are lines of evidence that can be used to place melting in the mantle lithosphere. In the SVZ, mafic magmas at many stratovolcanoes display cryptic geochemical variation, particularly in REE element abundances (Ferguson et al. 1992; Tormey et al., 1995), which could be

attributed to random and episodic inputs of Type 2 magmas into the magmatic supply system. Gradual assimilation of aged subduction-related pyroxenite in the mantle lithosphere may be a normal part of magma evolution at stratovolcanoes in long-lived subduction settings, as is assimilation of crustal material. An important implication of this conclusion is that studies which seek to distinguish and quantify subducted, mantle wedge and crustal contributions to arc magma, and to quantify rates of transfer of these materials from one reservoir to another, must consider the impact of stored subduction-related pyroxenite in the mantle lithosphere, including its volume and age.

7. CONCLUSIONS

Based on the geochemical studies of Hickey-Vargas et al. (1989; 2002), Lopez-Escobar et al. (1995a) and new petrologic, trace element and radiogenic isotope data reported in this work we conclude that the unusually mafic, fault controlled, small eruptive centers in the region of Vn. Villarrica in the CSVZ erupt two kinds of basaltic magma: 1) the ambient, voluminous, subduction-related magma generated by active inputs from the subducted Nazca plate and asthenospheric melting (Type 1); and 2) magmas produced in small volumes by partial melting of aged, subduction-related pyroxenite in the mantle lithosphere (Type 2).

Geochemical characteristics of Type 2 basalts are greater LREE/HREE enrichment, lower abundances of alkali elements and Ba compared with REE and HFSE, lower abundances of time-sensitive subduction tracers $^{10}\text{Be}/^9\text{Be}$ and $^{238}\text{U}/^{230}\text{Th}$ and lower $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ than Type 1 basalts. REE modeling indicates that melting in the presence of a clinopyroxene-rich or clinopyroxene and garnet-bearing residue is required to generate the Type 2 magmas, thus supporting the role of pyroxenite.

Calculated depths of magma separation for SEC primary magmas are 43-56 km, deeper than the Moho and shallower than the regional lithosphere-asthenosphere boundary.

In the CSVZ, Type 1 magma is normally erupted at stratovolcanoes, like Vn. Villarrica, but our data confirm that one SEC in the Villarrica region erupted Type 1 magma. Based on the association of SEC with the Liquiñe-Ofqui Fault Zone (LOFZ), we conclude that Type 2 magmas only reach the surface when ascent is facilitated by faults. However, the extent of their pyroxenite sources within the mantle lithosphere is unknown. Therefore, Type 2 magmas could also be an episodic, low-volume component in the normal magma recharge system of Type 1 stratovolcanoes.

We hypothesize that the pyroxenite originates from the interaction of basaltic magma formed during the >300Ma history of subduction magmatism along the western margin South American continent, with sub-arc mantle peridotite. Improved knowledge of the geochemical characteristics of older CSVZ basement rocks is needed to test this concept. The potential for storage of subduction-related pyroxenite in the mantle lithosphere of long-lived continental arcs, and its later mobilization, complicates the identification of subducted, mantle and crustal contributions to arc magma.

ACKNOWLEDGEMENTS:

R. Hickey-Vargas gratefully acknowledges support from the US National Science Foundation, grant EAR 0337483, to conduct this work, which supported the doctoral research of M. Sun. We gratefully acknowledge the late Leopoldo Lopez Escobar for providing samples as well as sharing his expertise and insights into SVZ magmatism. L. Lopez Escobar and H. Moreno Roa facilitated re-sampling of the San Jorge SEC by RH-V in 2004. We thank Thomas Beasley for support with the FIU EPMA, and Vincent

696 Salters for hosting M. Sun at the NHMFL Isotope lab at FSU to perform isotopic
697 analyses. David Pyle and an anonymous reviewer are thanked for their thoughtful
698 reviews which led to numerous improvements of the manuscript. Ultimate thanks go to
699 Frederick A. Frey, for sharing his interest and insights into the geochemistry of the
700 Chilean SVZ and its volcanoes, and for continuing mentorship.

702 **REFERENCES**

- 703 Baker D.R. and Eggler D.H. (1987) compositions of anhydrous and hydrous melts
704 coexisting with plagioclase, augite, and olivine or low – Ca pyroxene from 1 atm to 8
705 kbar: application to the Aleutian volcanic center of Atka. *Am. Mineral.* 72, 12 – 28.
- 706 Brasse, H. and Soyer, W. (2001) A magnetotelluric study in the Southern Chilean Andes.
707 *Geophys. Res. Lett.* 28, 3757–3760.
- 708 Carlson R. W. and Irving, A.J. (1994) Depletion and enrichment history of
709 subcontinental lithospheric mantle: An Os, Sr, Nd and Pb isotopic study of
710 ultramafic xenoliths from the northwestern Wyoming craton. *Earth Planet. Sci. Lett.*
711 26, 457-472
- 712 Cembrano, J. and Lara, L. (2009) The link between volcanism and tectonics in the
713 southern volcanic zone of the Chilean Andes: a review. *Tectonophys.* 471, 96-113.
- 714 Cembrano, J., Schermer, E., Lavenue, A. and Sanheuzza, A. (2000) Contrasting nature of
715 deformation along an intra-arc shear zone, the Liquiñe–Ofqui fault zone, southern
716 Chilean Andes. *Tectonophys.* 319, 129-149.
- 717 Cembrano, J., Lavenue, A., Yanez, G., Riquileme, R., Garcia, M., Gonzalez, G. and
718 Herail, G. (2008) Neotectonics. in *The Geology of Chile*, (Teresa Moreno and Wes
719 Gibbon, Eds.), Geological Society of London, pp. 231-262..

720 Clavero, R.J. and Moreno – Roa, H. (1994) Ignimbritas Lican y Pucon: Evidencias de
 721 erupciones explosivas andesítico – basálticas postglaciales del volcán Villarrica,
 722 Andes del sur, 39°25'S. 7° Congreso Geológico Chileno 1994, *Actas* Vol. I, pp. 250-
 723 254
 724 Clavero, R.J. and Moreno, H. (2004) Evolution of Volcán Villarrica, in *Villarrica*
 725 *Volcano (39.5°S) Southern Andes, Chile*, (Luis Lara and Jorge Clavero, Eds.),
 726 SERNAGEOMIN Bulletin No. 61, pp. 17-27.
 727 Davidson, J.P., Ferguson, K.M., Colucci, M.T. and Dungan, M.A. (1988) The origin and
 728 evolution of magmas from the San Pedro-Pellado volcanic complex, S. Chile:
 729 multicomponent sources and open system evolution. *Contrib. Mineral. Petrol.* 100,
 730 429–445.
 731 Deruelle B., Harmon R.S. and Moorbath S. (1983) Combined Sr – O isotope relationships
 732 and petrogenesis of Andean Volcanics of South America. *Nature* 302, 814 - 816
 733 Dungan, M.A., Wulff, A., Thompson, R. (2001) Eruptive stratigraphy of the Tatara–San
 734 Pedro Complex, 36°S, Southern Volcanic Zone, Chilean Andes: reconstruction
 735 method and implications for magma evolution at long-lived arc volcanic centers. *J.*
 736 *Petrol.* 42, 555–626.
 737 Dungan, M. A. and Davidson, J. (2004) Partial assimilative recycling of the mafic
 738 plutonic roots of arc volcanoes: An example from the Chilean Andes. *Geology* 32,
 739 773-776.
 740 Dzierma, Y., Thorwart, M., and Rabbel, W. (2012) Moho topography and subducting
 741 oceanic slab of the Chilean continental margin in the maximum slip segment of the
 742 1960 Mw 9.5 Valdivia (Chile) earthquake from P-receiver functions. *Tectonophys.* 530-
 743 531, 180-192.

744 Elliott T., Plank T, Zindler A and White W. (1997) Element transport from slab to
 745 volcanic front at the Mariana arc. *J. Geophys. Res.* 102 (B7) 14991-15019
 746 Ferguson, K M; Dungan, M A; Davidson, J P; Colucci, M T. (1992) The Tatara-San
 747 Pedro Volcano, 36 degrees S, Chile; a chemically variable, dominantly mafic
 748 magmatic system, *J. Petrol.* 33, 1-43.
 749 Fontijn, K., Lachowycz, S. M., Rawson, H., Pyle, D. M., Mather, T. A., Naranjo, J. A.,
 750 and Moreno-Roa, H. (2014). Late quaternary tephrostratigraphy of southern chile and
 751 argentina. *Quat.. Sci. Rev.* 89, 70-84.
 752 Gerlach D.C., Frey F.A., Moreno H. and Lopez – Escobar L. (1988) Recent volcanism in
 753 the Puyehue – Cordon Caulle region, Southern Andes, Chile (40.5oS): Petrogenesis
 754 of evolved lavas. *J. Petrol.* 29, 333 - 382
 755 Grove T.L. and Baker M.B. (1984) Phase equilibrium controls on the tholeiitic versus
 756 calc-alkaline differentiation trends. *J. Geophys. Res.* 89 (B5) 3253-327
 757 Grove T.L., Gerlach D.C. and Sando, T.W. (1982) Origin of calc-alkaline series lavas at
 758 medicine lake volcano by fractionation, assimilation and mixing. *Contrib. Mineral*
 759 *Petrol.* 80, 160-182
 760 Grove, T.L., Gerlach, D.C., Sando, T.W. and Baker, M.B. (1983) Origin of Calc-Alkaline
 761 Series Lavas at Medicine Lake Volcano by Fractionation, Assimilation and Mixing:
 762 Corrections and Clarifications. *Contrib. Mineral. Petrol.* 82, 407-408.
 763 Hart, S.R. and Dunn, T. (1993). Experimental cpx/melt partitioning of 24 trace elements.
 764 *Contrib. Mineral. Petrol.* 113: 1-8.
 765 Hauri, E.H., Wagner, T.P. and Grove, T.L. (1994). Experimental and natural partitioning
 766 of Th, U, Pb and other trace elements between garnet, clinopyroxene and basaltic
 767 melts. *Chem. Geol.* 117: 149-166..

768 Herve, F., Faundez, V., Calderon, M., massonne, H.-J. and Willner, A.P. (2008)
 769 Metamorphic and plutonic basement complexes. in *The Geology of Chile*, (Teresa
 770 Moreno and Wes Gibbon, Eds.), Geological Society of London, pp. 5-20.
 771 Heydolph, K., Hoernle, K., Hauff, F., van den Bogaard, P., Portnyagin, M., Bindeman, I.
 772 and Garbe-Schonberg, D. (2012) Along and across arc geochemical variations in NW
 773 Central America: Evidence for involvement of lithospheric pyroxenite. *Geochim.*
 774 *Cosmochim. Acta* 84, 459-491.
 775 Hickey - Vargas R., Moreno H., Lopez-Escobar L., Frey F.A. (1989) Geochemical
 776 variations in Andean basaltic and silicic lavas from the Villarrica-Lanin volcanic
 777 chain (39.5°S): an evaluation of source heterogeneity, fractional crystallization and
 778 crustal assimilation. *Contrib. Mineral. Petrol.* 103, 361-386
 779 Hickey R.L., Frey F.A., Gerlach D.C., Lopez-Escobar L. (1986) Multiple sources for
 780 basaltic arc rocks from the Southern Volcanic Zone of the Andes (34-42°S): Trace
 781 element and isotopic evidence for contributions from subducted oceanic crust, mantle
 782 and continental crust. *J. Geophys. Res.* 91, 5963-5983
 783 Hickey-Vargas R., Sun M., Lopez-Escobar L., Moreno-Roa H., Reagan M.K., Morris
 784 J.D. (2002) Multiple subduction components in the mantle wedge; evidence from
 785 eruptive centers in the central Southern volcanic zone, Chile. *Geology* 30, 199-202.
 786 Hickey-Vargas, R. (1998) Geochemical characteristics of oceanic island basalts from the
 787 Philippine Sea Plate: Implications for the sources of East Asian Plate margin and
 788 intraplate basalts, In: Flower, M.F.J., Chung, S-L., Lee, T-Y. (Eds.), *Mantle*
 789 *Dynamics and Plate Interactions in East Asia*, AGU Geodynamics. Monograph. 27,
 790 AGU, pp. 365-384.
 791 Hildreth, W. and Moorbath, S. (1988) Crustal contributions to arc magmatism in the

792 Andes of central Chile. *Contrib. Mineral. Petrol.* 98, 455–489.
 793 Holbik, S. (2014) Arc crust-magma interaction in the Andean Southern Volcanic Zone
 794 from thermobarometry, mineral composition, radiogenic isotope and rare earth
 795 element systematics of the Azufre-Planchon-Peteroa Volcanic Complex, Chile [Ph.D.
 796 thesis]: FIU Electronic Theses and Dissertations.
 797 Jacques, G., Hoernle, K., Gill, J., Hauff, F., Wehrmann, H., Garbe-Schönberg, D., van
 798 den Bogaard, P., Bindeman, I., Lara, L.E. (2013) Across-arc geochemical variations
 799 in the Southern Volcanic Zone, Chile (34.5–38.0°S): Constraints on mantle wedge
 800 and slab input compositions. *Geochim. Cosmochim. Acta* 123, 218–243.
 801 Jacques, G., K. Hoernle, J. Gill, H. Wehrmann, I. Bindeman, Lara, L.E. (2014)
 802 Geochemical variations in the Central Southern Volcanic Zone, Chile (38–43°S): The
 803 role of fluids in generating arc magmas. *Chem. Geol.* 371, 27–45.
 804 Johnson M.C. and Plank T. (1999) Dehydration and melting experiments constrain the
 805 fate of subducted sediments. *Geochemistry, Geophysics, Geosystems* 1, doi:
 806 10.1029/1999GC000014.
 807 Johnson, K.T.M. (1994). Experimental cpx/ and garnet/melt partitioning of REE and
 808 other trace elements at high pressures; petrogenetic implications. *Mineral. Magazine*
 809 58, 454-455.
 810 Johnson, K.T.M. (1998). Experimental determination of partition coefficients for rare
 811 earth and high-field-strength elements between clinopyroxene, garnet, and basaltic
 812 melt at high pressures. *Contrib. Mineral. Petrol.* 133, 60-68.
 813 Lambart, S., Laport, D. and Schiano, P. (2013) Markers of the pyroxenite contribution in
 814 the major element compositions of oceanic basalts: Review of experimental
 815 constraints. *Lithos* 160-161, 14-36.

816 Lee, C.-T.A., Luffi, P., Plank, T., Dalton, H., Leeman, W.P. (2009) Constraints on the
817 depths and temperatures of basaltic magma generation on Earth and other terrestrial
818 planets using new thermobarometers for mafic magmas. *Earth Planet. Sci. Lett.* 279,
819 20–33.

820 Leeman, W.P., Lewis, J.F., Evarts, R.C., Conrey, R.M. and Streck., M.J. (2005)
821 Petrologic constraints on the thermal structure of the cascades arc. *Journ. Volcan.*
822 *Geotherm. Res.* 140, 67–105.

823 Lopez – Escobar L., Frey F.A. and Vergara, M. (1977) Andesites and high alumina-
824 basalts from the Central-South Chile high Andes: Geochemical evidence bearing on
825 the their petrogenesis. *Contrib. Mineral Petrol.* 63, 199-228.

826 Lopez-Escobar, L. Moreno, H., Tagiri, M. Notsu, K. and Onuma, N. (1985)
827 Geochemistry of lavas from the San Jose Volcano, southern Andes (33°45'S).
828 *Geochemical Journ.* 19, 209-222.

829 Lopez-Escobar L., Parada M.A., Moreno H., Frey F.A., Hickey – Vargas R.L. (1992) A
830 contribution to the petrogenesis of Osorno and Calbuco volcanoes, Southern Andes
831 (41 degrees 00'-41 degrees 30'S); a comparative study. *Revista Geologica de Chile*
832 19, 211-226

833 López-Escobar, L., Cembrano, J. and Moreno, H. (1995) Geochemistry and tectonics of
834 the Southern Andes basaltic Quaternary volcanism associated with the Liquiñe-Ofqui
835 Fault Zone, (37°-46°S). *Revista Geológica de Chile* 22, 219–234.

836 López-Escobar, L., Parada, M., Hickey-Vargas, R., Frey, F., Kempton, P., Moreno, H.
837 (1995b). Calbuco Volcano and minor eruptive centers distributed along the Liquiñe-
838 Ofqui Fault Zone, Chile (41°-42° S): contrasting origin of andesitic and basaltic

839 magma in the Southern Volcanic Zone of the Andes. *Contrib. Mineral. Petrol.* 119,
840 345-361.

841 Lucassen, F., Trumbull, R., Franz, G., Creixell, C., Vasquez, P., Romer, R.L. and
842 Figueroa, O. (2004) Distinguishing crustal recycling and juvenile additions at active
843 continental margins: the Paleozoic to recent compositional evolution of the Chilean
844 Pacific margin (36°–41°S). *Journ. S. Amer. Earth Sci.* 17, 103-119.

845 Moreno, H., Clavero, J. and Lara, L. (1994) Actividad explosiva postglacial del Volcan
846 Villarrica, Andes del Sur (39°25'S). 7° Congreso Geológico Chileno, *Actas* Vol. 1,
847 329-333.

848 Morris J.D., Leeman W.P. and Tera F. (1990) The subducted component in island arc
849 lavas: constraints from Be isotopes and B-Be systematics. *Nature* 344, 31-36

850 Parada, M.A., Lopez-Escobar, L., Oliveros, V., Fuentes, F., Morata, D., Calderon, M.,
851 Aguirre, L., Feraud, G., Espinosa, F., Moreno, H., Figueroa, O., Munoz Bravo, J.,
852 Troncoso Vasquez, R. and Stern, C.R. (2008) Andean Magmatism, in *The Geology of*
853 *Chile*, (Teresa Moreno and Wes Gibbon, Eds.), Geological Society of London, pp.
854 115-146.

855 Plank T. and Langmuir C.H. (1988) An evaluation of the global variations in the major
856 element chemistry of arc basalts. *Earth Planet. Sci. Lett.* 90, 349-370

857 Plank T. and Langmuir C.H. (1993) Tracing trace elements from sediment input to
858 volcanic output at subduction zones. *Nature* 362, 739-742

859 Plank T. and Langmuir C.H. (1998) The chemical composition of subducting sediment
860 and its consequences for the crust and mantle. *Chem. Geol.* 145, 325-394.

861 Reubi, O., B. Bourdon, M. A. Dungan, J. M. Koornneef, D. Sellés, C. H. Langmuir, and
862 S. Aciego (2011) Assimilation of the plutonic roots of the Andean arc controls

863 variations in u-series disequilibria at Volcan Llaima, Chile. *Earth Planet. Sci.*
 864 *Lett.* 303, 37–47.
 865 Roeder, P.L. and Emslie, R.F. (1970) Olivine-liquid equilibrium. *Contrib. Mineral.*
 866 *Petrol.* 29, 275–289.
 867 Ryan, J.G., Leeman, W.P., Morris, J.D. and Langmuir, C.H. (1996) The boron
 868 systematics of intraplate lavas: implications for crust and mantle evolution. *Geochim.*
 869 *Cosmochim. Acta* 60, 415-422.
 870 Sanchez, P., Pérez-Flores, P., Arancibia, A., Cembrano, J. and Reich, M. (2013) Crustal
 871 deformation effects on the chemical evolution of geothermal systems: the intra-arc
 872 Lliquiñe-Ofqui fault system, Southern Andes, *Int. Geol. Review* 55, 1384-1400.
 873 Sigmarsson O., Condomines M., Morris J.D. and Harmon R.S. (1990) Uranium and ¹⁰Be
 874 enrichments by fluids in Andean arc magmas. *Nature* 346, 163-165.
 875 Sisson T.W. and Grove T.L. (1993) Experimental investigations of the role of H₂O in
 876 calc-alkaline differentiation and subduction zone magmatism. *Contrib. Mineral*
 877 *Petrol.* 113, 143-166
 878 Stern, C.R., Moreno, H., Lopez-Escobar, L., Clavero, J.E., Lara, L.E., Naranjo, J.A.,
 879 Parada, M.A. and Skewes, M.A. (2008) Chilean volcanoes, in *The Geology of Chile*,
 880 (Teresa Moreno and Wes Gibbon, Eds.), Geological Society of London, pp. 147-178.
 881 Sun S.S. and McDonough W.F. (1989) Chemical and isotopic systematics of oceanic
 882 basalts: implications for mantle composition and processes, in *Magmatism in the*
 883 *Ocean Basins*, A.D. Saunders, and M.J. Norry (eds), Geological Society Special
 884 Publication No.42, 313-345
 885 Tassara, A.; Gotze, H-J., Schmidt, S. and Hackney, R. (2006) Three-dimensional density
 886 model of the Nazca plate and the Andean continental margin. *Journ. Geophys. Res.*

887 *Solid Earth*, 111, B909404.

888

889 Tassara, A. and Echaurren, A. (2012) [Anatomy of the Andean subduction zone; three-](#)
890 [dimensional density model upgraded and compared against global-scale models.](#)
891 *Geophys. Journ. Int.* 189, 161-168.

892 Thorwart M., Dzierma Y., Lieser K., Buhs H., and Rabbel W. (2015) Shear-wave
893 velocity structure of the Chilean subduction zone (39-40 degrees S) based on
894 Rayleigh wave dispersion; evidence of fluid release and melts in the mantle beneath
895 the Villarrica Volcano, *The Role of Volatiles in the Genesis, Evolution and Eruption*
896 *of Arc Magmas* (G.F. Zellmer, M. Edmonds, & S.M. Straub, eds.) Geological
897 Society, London, Special Publications, 410, 59–70.

898 Todt, W., Cliff, R.A., Hanser, A., Hofmann, A.W. (1996) Evaluation of a ^{202}Pb - ^{205}Pb
899 double spike for high precision lead isotope analyses. In: Basu, A., Hart, S. (Eds.),
900 *Reading the Isotopic Code*, AGU Geophysical Monograph 95. AGU, pp. 429-437.

901 Tormey, D.R., Frey, F.A., Lopez-Escobar, L. (1995) Geochemistry of the Active
902 Azufre—Planchon—Petroa volcanic complex, Chile (35°15'S): Evidence for
903 multiple sources and processes in a cordilleran arc magmatic system. *J. Petrol.* 36,
904 265–298.

905 Tormey, D.R., Hickey-Vargas, R., Frey, F.A., López-Escobar, L. (1991) Recent lavas
906 from the Andean volcanic front (33 to 42°S); Interpretations of along-arc
907 compositional variations. *Geol. Soc. Amer. Special Paper* 265, 57–78.

908 Turner, S.J., Langmuir, C.H., 2015. The global chemical systematics of arc front
909 stratovolcanoes; evaluating the role of crustal processes. *Earth Planet. Sci. Lett.* 422,
910 182-193.

911

912 Vergara, M., Morata, D., Hickey-Vargas, R., Lopez-Escobar, L. and Beccar, I. (1999)

913 Geochemistry of the Tertiary volcanic rocks from the Colbún area Linares

914 Precordillera, Central Chile (35° 35' - 35° 60'S). *Revista Geologica de Chile* 26, 23-

915 41.

916 Vergara, M., L. López-Escobar, J.L. Palma, R. Hickey-Vargas and C. Roeschmann

917 (2004) Late tertiary volcanic episodes in the area of the city of Santiago de Chile:

918 new geochronological and geochemical data, *Journ. S. Amer. Earth Sci.* 17, 227-238.

919 Wacaster, S., Hickey-Vargas, R., Wallace, P. (2008) Volatiles in olivine hosted melt

920 inclusions from small eruptive centers, Central Southern Volcanic Zone (CSVZ),

921 Chile. *EOS, Amer. Geophys. Union*, Fall Meeting, abstract #V21A-0284.

922 Walker, R.W. Carlson, S.B. Shirey, F.R. Boyd (1989) Os, Sr, Nd and Pb isotope

923 systematics of southern African peridotite xenoliths: Implications for the chemical

924 evolution of subcontinental mantle. *Geochim. Cosmochim. Acta* 53, 1583-1595.

925 Watt, S. F. L., Pyle, D.M., Mather, T.A. and Naranjo, J. A. (2013a) Arc magma

926 compositions controlled by linked thermal and chemical gradients above the

927 subducting slab. *Geophys. Res. Lett.* 40, 2550–2556.

928 Watt, S.F.L., Pyle, D.M. and Mather, T.A. (2013b) The volcanic response to

929 deglaciation; evidence from glaciated arcs and a reassessment of global eruption

930 records. *Earth-Science Reviews* 122, 77-102.

931

Figure Captions

Figure 1: Map of the northern part of the Andean Southern Volcanic Zone showing the boundaries of the Northern (NSVZ), Transitional (TSVZ) and Central (CSVZ) segments, the location of stratovolcanoes and the Liquiñe-Ofqui Fault zone (Cembrano and Lara, 2009).

Figure 2: Google Earth image of Villarrica stratovolcano and SEC from this study located to the north and east. The trace of the Liquiñe-Ofqui Fault Zone (LOFZ) is shown in white (Cembrano and Lara, 2009). The trace of other faults inferred from geology and the location of geothermal systems in the Villarrica region are shown by blue dashed lines (Sanchez et al., 2013).

Figure 3: Mg-number (molar $\text{Mg}/(\text{Mg}+\Sigma\text{Fe})$) of olivine phenocryst cores plotted versus Mg-number of whole rocks containing them. Olivine core compositions are averages of multiple analyses from thin sections taken from the same rock. A curve showing Fe/Mg equilibrium compositions for olivine-melt pairs is shown for comparison with dashed error envelope of 0.30 ± 0.03 (Roeder and Emslie, 1970; Baker and Eggler, 1987).

Figure 4: Major element oxides versus SiO_2 for SEC and Villarrica stratovolcano. Data for Villarrica stratovolcano are from Hickey-Vargas et al. (1989)

Figure 5: Compatible trace elements versus MgO for SEC and Villarrica stratovolcano. Data for Villarrica stratovolcano are from Hickey-Vargas et al. (1989) and Table 2.

Figure 6: Incompatible trace element abundances for Type 1 and Type 2 SEC normalized to primitive mantle compositions of Sun and McDonough (1989).

Figure 7: Normalized REE abundances in basalts from: a) Type 1 SEC San Jorge compared with Villarrica stratovolcano; b) Type 1 SEC San Jorge compared with Type 2 SEC.

Figure 8: Th/La, U/La, Rb/La, Cs/La, Ba/La and La/Nb versus La/Yb, showing basalts from Type 1 and 2 SEC, and a field for Villarrica stratovolcano. Dashed lines are ratios for E-MORB (Sun and McDonough, 1989) plotted for comparison, as a mantle-derived, non-subduction related basalt type.

Figure 9: $^{143}\text{Nd}/^{144}\text{Nd}$ versus $^{87}\text{Sr}/^{86}\text{Sr}$ showing data for SEC and fields for basaltic rocks from active SVZ stratovolcanoes, Villarrica stratovolcano, and Tertiary and Mesozoic basement rocks. The field for Villarrica stratovolcano is from Hickey-Vargas et al. (1989). Data for Miocene basalts from the Central Valley are from Vergara et al. (1999; 2004). Data for intrusive rocks from the CSVZ arc basement (Tertiary plutons from 37°-39°S and Late Mesozoic plutons from 38.5°-39.5°S) are from Lucassen et al. (2004). The field for SVZ stratovolcano basalts and basaltic andesites is constructed from data in the literature,

Figure 10: Pseudoternary diagrams showing compositions of rocks from San Jorge SEC and Villarrica stratovolcano (top) and Type 2 SEC (bottom) as mineral components clinopyroxene (CPX), olivine (OL) and quartz (QTZ) projected from plagioclase using the component formulae and projection scheme of Grove et al. (1982; 1983). The 1 atmosphere cotectic is from Grove and Baker (1984) and the 2 Kbar H_2O saturated cotectic is from Sisson and Grove (1994).

Figure 11: Variation of La and Yb abundances and La/Yb ratios with partial melting of peridotite and pyroxenite. In Figure 11a, partial melting of peridotite and pyroxenite lithologies with an EMORB source composition (Sun and McDonough, 1989) are compared as the origin of Type 1 and Type 2 SEC. Peridotite is modelled with proportions: 60% olivine, 20% orthopyroxene, 15% clinopyroxene and 5% spinel. Olivine pyroxenite is modeled with 20% olivine, 40% orthopyroxene, 30% clinopyroxene

and 10% spinel. In Figure 11b, partial melting of pyroxenite with an arc basalt composition (San Jorge, this study) is compared with Type 2 SEC. Two garnet pyroxenites are shown: 10% olivine, 30% orthopyroxene, 50% clinopyroxene and 10% garnet (left) or 10% olivine, 30% orthopyroxene, 55% clinopyroxene and 5% garnet (right). Partition coefficients used are from Hart and Dunn (1993); Hauri et al. (1994); and Johnson (1993;1998):

Kds	Olivine	Orthopyroxene	Clinopyroxene	Spinel	Garnet
La	0.0001	0.0008	0.0536	0.01	0.0016
Yb	0.01	0.22	0.432	0.01	6.6

Figure 12: Schematic sections of the crust and mantle near Vn. Villarrica, illustrating the origin of Type 1 and Type 2 magma at small eruptive centers (SEC). Figure 12a shows a west-east transect at 39.5°S. The surface elevation, depth to the Moho and to the surface of the subducting Nazca plate are from Thorwart et al. (2015). The location of the regional lithosphere-asthenosphere boundary (LAB) is from Tassara et al., (2006) and Tassara and Echaurren (2012). Based on our calculated magma equilibration depths, we infer that the LAB is shallower beneath the volcanic arc. The location of Vn. Villarrica and SEC and their magmatic systems are projected on the W-E section. Figure 12b shows a N-S section along the arc front coincident with the LOFZ, with the projected locations of the SEC, Vn. Villarrica and their magmatic systems. Black arrows show magma rising from the asthenosphere. Type 1 magmas (blue) rise directly from the asthenosphere. Type 2 magmas (green) form by melting of olivine-pyroxenite in the mantle lithosphere. The possible shape and distribution of pyroxenite in the mantle lithosphere is not addressed in the diagram. See text for further discussion. Vi=Vn. Villarrica, SJ=SEC San Jorge, Hu=SEC Huelemolle, CR=SEC Cerro Redondo, LB=SEC La Barda, Ca=SEC Caburgua.

Table 1: Major oxides (in weight %) and trace elements (in ppm) for basalts from small eruptive centers north and northeast of Villarrica Volcano

	Huelemolle			Caburgua				
	1	2	3	4	5	6	1	2
	110194-1	110194-2	110194-3 ^a	120194-1	120194-2	150194-7	150104-4	120194-4A
SiO ₂	52.28	52.10	50.98	50.48	50.69	52.24	51.53	51.51
TiO ₂	1.28	1.17	1.18	1.07	1.10	1.15	1.12	1.13
Al ₂ O ₃	18.26	18.19	17.76	18.53	18.65	18.72	18.03	18.25
Fe ₂ O ₃	9.50	9.84	9.42	9.56	9.76	9.33	9.64	9.39
MnO	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.15
MgO	4.60	4.26	5.74	5.67	5.99	4.67	5.84	6.15
CaO	8.90	9.35	8.95	9.57	9.44	9.22	9.29	9.16
Na ₂ O	3.40	2.79	3.46	3.37	3.26	3.65	2.63	3.57
K ₂ O	1.12	0.82	1.07	0.82	0.84	0.96	0.74	0.83
P ₂ O ₅	0.55	0.42	0.41	0.38	0.41	0.42	0.33	0.31
Total	100.06	99.10	99.13	99.61	100.30	100.52	99.31	100.45
Mg# ^b	49.0	46.2	54.7	54.0	54.9	49.8	54.5	56.5
Ni	24.1	38.5	75.1	50.1	50.8	36.5	85.6	83.2
Cr	99.16	142	213	191	161	127	266	281
Sc	25.18	26.0	27.0	26.2	26.8	25.9	25.4	24.6
V	215	206	211	198	200	196	203	186
Cu	73.23	81.6	81.7	76.8	86.5	77.6	77.4	79.9
Zn	87.6	88.2	98.0	78.7	95.1	76.8	72.0	65.7
Sr	680*	773	621	616	628	651	770	803
Ba	461	346	382	295	329	325	283	280
Y	29.02	22.1	27.0	24.3	26.0	25.5	22.3	21.6
Nb	9.71	7.21	7.57	6.55	6.72	7.17	6.2	3.76
Zr	191.69	151.5	165.9	146.1	160.5	154.4	106.7	96.3
Rb	21.8	15.0	22.3	13.5	13.9	16.1		13.2
Cs	0.879	0.736	0.951	0.675	0.707	0.712		0.646
La	28.9	21.3	22.3	19.2	20.8	20.6	17.1	14.4
Ce	63.1	46.4	49.1	42.1	46.4	45.0		32.8
Pr	8.14	6.14	6.36	5.52	5.94	5.91		4.56
Nd	33.5	25.5	26.4	23.0	24.9	24.6		19.9
Sm	6.73	5.35	5.57	4.86	5.13	5.15		4.41
Eu	1.89	1.57	1.62	1.42	1.52	1.50		1.34
Gd	6.25	4.99	5.36	4.82	4.96	4.75		4.13
Tb	0.913	0.754	0.786	0.705	0.733	0.734		0.625
Dy	5.21	4.34	4.52	4.11	4.31	4.35		3.74
Ho	1.039	0.879	0.906	0.828	0.877	0.863		0.74
Er	2.77	2.36	2.41	2.26	2.36	2.32		1.99
Yb	2.63	2.28	2.34	2.22	2.24	2.29		1.97
Lu	0.414	0.357	0.366	0.348	0.355	0.356		0.307
Hf	4.25	3.42	3.50	3.05	3.28	3.44		2.54
Ta	0.516	0.384	0.401	0.352	0.373	0.385		0.211
Pb	11.49	10.08	9.45	8.33	8.89	9.13		7.56
Th	3.18	2.19	3.01	1.79	2.01	1.99		2.72
U	0.89	0.646	0.814	0.544	0.619	0.602		0.736
B		24	3.1		11			
Be		1.08	1.06		1.04			
Li		23	14		14			

^a Samples with asterisks have U-series isotope and ¹⁰Be data published in Hickey-Vargas et al. (2002)

^b Mg# is molar MgO/(MgO + ΣFeO)

Table 1: Major oxides (in weight %) and trace elements (in ppm)

SEC	Caburgua							
	3	4	5	6	7	8	9	10
	120194-4B	120194-4C	120194-5	150104-1*	150194-2	150194-3	CB Sc 1208A	CB Sc 1208B
SiO ₂	51.54	51.59	51.38	50.91	51.42	51.28	51.56	52.34
TiO ₂	1.13	1.10	1.10	1.10	1.10	1.10	1.22	1.15
Al ₂ O ₃	18.25	17.93	18.10	18.15	18.97	17.92	17.81	17.41
Fe ₂ O ₃	9.41	9.56	9.33	9.30	9.56	9.61	9.20	9.02
MnO	0.15	0.15	0.15	0.15	0.16	0.16	0.17	0.16
MgO	5.99	6.68	6.54	6.45	4.90	6.32	7.04	7.07
CaO	9.16	9.16	9.19	9.18	9.80	9.36	8.49	8.61
Na ₂ O	3.54	3.55	3.42	3.48	2.79	2.69	3.38	3.21
K ₂ O	0.80	0.80	0.77	0.71	0.69	0.71	0.77	0.73
P ₂ O ₅	0.32	0.31	0.30	0.31	0.31	0.30	0.35	0.31
Total	100.29	100.83	100.28	99.74	99.70	99.45	100.00	100.00
Mg#	55.8	58.1	58.1	57.9	50.4	56.6	60.3	60.8
Ni	67.1	82.7	114.7	70.1	31.1	120.9	70.5	90.9
Cr	313	364	308	293	151	384		
Sc	24.8	25.2	25.2	25.8	27.3	25.0	26.0	25.8
V	198	196	190	207	215	206		
Cu	78.2	82.3	78.5	85.2	77.3	86.0		
Zn	67.7	70.5	68.4	66.2	80.9	213.3		
Sr	806	800	807	837	629	781	799	792
Ba	269	257	276	288	253	295	251	250
Y	21.7	20.9	20.9	21.6	26.5	21.4	22.01	21.53
Nb	4.3	3.23	3.29	3.20	3.32	3.42	3.174	3.142
Zr	99.7	90.8	89.2	97.4	95.4	101.6	95.4	96.0
Rb		11.0	11.2	9.81	10.2	10.5	11.0	9.9
Cs		0.557	0.612	0.537	0.521	0.575	0.54	0.54
La	14.4	13.3	13.9	13.2	13.2	14.3	12.80	12.64
Ce		30.2	31.8	30.9	29.8	33.1	29.31	29.06
Pr		4.24	4.52	4.33	4.16	4.56	4.11	4.06
Nd		18.8	20.2	19.4	18.3	20.3	18.14	18.02
Sm		4.16	4.44	4.30	4.11	4.42	4.24	4.18
Eu		1.30	1.39	1.35	1.27	1.38	1.38	1.34
Gd		4.17	4.26	4.19	3.94	4.24	3.89	3.81
Tb		0.606	0.626	0.612	0.607	0.624	0.61	0.61
Dy		3.51	3.56	3.59	3.64	3.61	3.65	3.65
Ho		0.714	0.743	0.72	0.734	0.744	0.74	0.74
Er		1.95	1.97	1.90	2.00	2.01	1.96	1.99
Yb		1.91	1.90	1.84	1.99	1.90	1.78	1.77
Lu		0.303	0.302	0.285	0.311	0.301	0.28	0.28
Hf		2.33	2.42	2.38	2.42	2.43	2.20	2.25
Ta		0.185	0.182	0.175	0.18	0.189	0.20	0.19
Pb		7.36	7.73	7.46	7.44	7.74	6.60	6.57
Th		2.51	2.74	2.73	1.99	2.70	2.53	2.53
U		0.68	0.735	0.743	0.565	0.741	0.70	0.70
B			6.0	4.2		5.6		
Be			0.70	0.75		0.70		
Li			13	13		14		

Table 1: Major oxides (in weight %) and trace elements (in ppm)

SEC	Caburgua	Cerro Redondo			La Barda		
	11	1	2	3	1	2	3
	CB La 1208C	140194-9*	140194-10	140194-11	150194-5B	150194-5A	150194-6
SiO ₂	51.62	51.55	51.56	50.97	50.77	50.65	50.35
TiO ₂	1.16	1.01	1.00	1.11	1.05	1.06	1.06
Al ₂ O ₃	18.03	17.96	17.93	19.33	17.34	17.37	17.82
Fe ₂ O ₃	9.51	9.37	9.53	9.65	9.56	9.70	9.59
MnO	0.16	0.15	0.15	0.16	0.16	0.16	0.16
MgO	6.81	6.49	6.10	4.57	7.33	7.32	7.62
CaO	8.93	8.83	9.13	9.56	9.26	9.32	9.60
Na ₂ O	3.63	3.32	2.48	2.76	3.23	3.25	3.21
K ₂ O	0.72	0.84	0.77	0.84	0.75	0.73	0.67
P ₂ O ₅	0.34	0.31	0.30	0.28	0.30	0.29	0.30
Total	100.00	99.83	98.95	99.23	99.75	99.85	100.38
Mg#	58.7	57.8	55.9	48.4	59.9	60.3	61.1
Ni	56.6	144.0	119.4	168.1	222.3	210.1	93.7
Cr		434	373	115	447	572	348
Sc	27.2	23.9	24.1	24.8	26.5	26.9	27.2
V		186	187	228	208	205	208
Cu		74.2	76.8	49.7	75.3	77.6	91.7
Zn		75.9	95.0	82.8	163.5	75.2	70.7
Sr	814	598	623	924	690	694	709
Ba	258	327	305	329	281	253	273
Y	22.10	21.5	22.1	22.9	20.7	21.0	21.0
Nb	3.204	5.59	5.68	4.39	4.11	4.13	3.85
Zr	97.6	128.4	134.2	111.9	97.7	99.3	99.6
Rb	9.6	16.1	16.7	9.71	12.2	11.7	9.64
Cs	0.53	0.712	0.675	0.249	0.628	0.554	0.524
La	13.04	17.4	17.1	16.6	14.9	13.8	13.9
Ce	30.02	38.4	37.1	37.7	33.6	31.2	32.1
Pr	4.21	4.93	4.85	5.06	4.63	4.31	4.32
Nd	18.47	20.8	20.0	22.0	20.3	18.9	19.1
Sm	4.34	4.40	4.27	4.67	4.44	4.16	4.17
Eu	1.43	1.35	1.30	1.46	1.37	1.27	1.29
Gd	4.01	4.25	4.06	4.43	4.31	4.19	4.09
Tb	0.64	0.632	0.622	0.654	0.645	0.601	0.6
Dy	3.75	3.69	3.68	3.84	3.76	3.61	3.55
Ho	0.77	0.747	0.732	0.77	0.745	0.729	0.725
Er	2.09	2.02	1.99	2.07	2.00	1.98	1.94
Yb	1.82	1.92	1.96	1.97	1.96	1.93	1.84
Lu	0.28	0.302	0.305	0.305	0.302	0.309	0.293
Hf	2.27	2.99	3.02	2.68	2.58	2.47	2.46
Ta	0.18	0.32	0.314	0.236	0.232	0.225	0.219
Pb	6.80	8.12	8.30	6.13	7.90	7.02	8.11
Th	2.66	1.98	1.88	3.67	2.37	2.13	2.17
U	0.73	0.593	0.562	0.825	0.663	0.595	0.617
B		8.9		2.2	5.0		11
Be		0.93		0.88	0.72		0.77
Li		12		9.3	11		11

Table 1: Major oxides (in weight %) and trace elements (in ppm)

SEC	San Jorge							
	1	2	3	4	5	6	7	8
	140194-1*	140194-2	140194-3	140194-4	140194-5A	140194-5B	140194-7a	140194-7b
SiO ₂	50.39	50.77	50.68	50.39	50.63	50.70	50.74	50.95
TiO ₂	0.75	0.77	0.78	0.80	0.77	0.77	0.78	0.77
Al ₂ O ₃	15.70	16.02	15.99	16.23	16.16	16.19	16.20	16.07
Fe ₂ O ₃	9.46	9.57	9.48	9.45	9.66	9.68	9.50	9.69
MnO	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
MgO	10.40	10.30	9.89	9.25	9.19	9.17	9.83	9.28
CaO	10.00	9.64	9.71	9.72	10.02	10.02	9.73	10.06
Na ₂ O	2.54	2.55	2.55	2.63	1.95	1.91	2.53	1.93
K ₂ O	0.42	0.41	0.40	0.42	0.42	0.41	0.40	0.45
P ₂ O ₅	0.12	0.11	0.11	0.13	0.10	0.11	0.12	0.10
Total	99.94	100.31	99.76	99.19	99.06	99.13	100.00	99.46
Mg#	68.5	68.1	67.4	66.0	65.3	65.2	67.2	65.5
Ni	257.4	221.9	175.5	168.5	204.2	205.8	183.9	368.8
Cr	905	831	786	752	799	810	816	868
Sc	32.8	31.7	32.0	32.1	32.7	32.8	32.2	32.2
V	206	207	209	218	206	212	212	213
Cu	88.6	85.0	89.1	93.1	85.4	53.5	87.2	86.1
Zn	67.6	64.6	74.3	64.1	84.1	73.2	83.3	66.9
Sr	379	377	377	391	401	390	388	388
Ba	139	125	124	146	132	131	149	137
Y	17.0	16.8	16.8	17.6	16.8	17.2	17.2	17.1
Nb	1.42	1.39	2.2	1.56	1.50	1.45	1.52	1.56
Zr	58.3	54.3	56.2	64.1	60.9	60	63.9	64.7
Rb	8.61	8.25		8.17	8.29	7.86	8.32	9.44
Cs	0.658	0.640		0.673	0.642	0.571	0.668	0.700
La	4.90	4.88	5.1	5.62	5.23	5.25	5.30	5.43
Ce	11.9	11.7		13.6	12.5	12.5	12.8	12.9
Pr	1.79	1.71		2.00	1.83	1.82	1.94	1.88
Nd	8.4	8.1		9.4	8.7	8.5	9.1	8.9
Sm	2.27	2.19		2.45	2.31	2.29	2.47	2.36
Eu	0.80	0.76		0.86	0.80	0.79	0.86	0.82
Gd	2.69	2.63		2.89	2.78	2.58	2.91	2.84
Tb	0.429	0.415		0.459	0.436	0.426	0.46	0.441
Dy	2.69	2.60		2.84	2.75	2.71	2.88	2.77
Ho	0.571	0.551		0.618	0.582	0.573	0.614	0.597
Er	1.53	1.51		1.66	1.58	1.56	1.65	1.63
Yb	1.52	1.48		1.63	1.62	1.57	1.60	1.66
Lu	0.235	0.233		0.262	0.25	0.246	0.248	0.257
Hf	1.51	1.46		1.58	1.47	1.5	1.60	1.56
Ta	0.085	0.083		0.097	0.095	0.087	0.093	0.103
Pb	4.70	4.31		4.90	4.55	4.31	5.19	5.51
Th	0.70	0.64		0.66	0.62	0.61	0.72	0.74
U	0.268	0.236		0.254	0.227	0.229	0.265	0.264
B	6.8			6.3			7.7	
Be	0.39			0.41			0.36	
Li	8.9			8.4			8.6	

SEC	San Jorge						1027
	9	10	11	12	13	14	1028
	120194-3	SJ Sc 1104 A	SJ Sc 1104 B	SJ Sc 1104 C	SJ Sc 1104 E	SJ La 1104H	1029
SiO ₂	50.77	49.37	48.84	51.26	49.57	50.92	
TiO ₂	0.77	0.76	0.77	0.82	0.72	0.81	
Al ₂ O ₃	15.93	14.58	14.73	15.65	13.71	15.35	
Fe ₂ O ₃	9.52	9.90	10.22	9.61	9.95	9.34	
MnO	0.16	0.18	0.19	0.17	0.18	0.17	
MgO	10.36	13.91	14.20	10.09	14.98	10.95	
CaO	9.65	8.63	8.46	9.37	8.26	9.41	
Na ₂ O	2.49	2.15	2.10	2.47	2.12	2.49	
K ₂ O	0.42	0.29	0.28	0.35	0.29	0.37	
P ₂ O ₅	0.12	0.23	0.22	0.20	0.21	0.20	
Total	100.20	100.00	100.00	100.00	100.00	100.00	
Mg#	68.3	73.6	73.4	67.5	74.9	69.9	
Ni	192.1	345.4	337.2	194.9	443.0	209.4	
Cr	792						
Sc	32.3	32.0	30.9	30.3	28.8	30.003	
V	198						
Cu	87.8						
Zn	69.9						
Sr	380	315.421	358.655	317.655	313.574	355.913	
Ba	137	107	136	109	111	131	
Y	16.6	16.73	17.06	16.26	15.27	16.907	
Nb	1.42	1.248	1.337	1.233	1.144	1.341	
Zr	55.3	54.8	58.1	53.5	50.5	55.7	
Rb	8.29	6.050	7.327	6.052	6.400	7.162	
Cs	0.691	0.51	0.66	0.53	0.56	0.61	
La	5.08	4.70	4.96	4.58	4.34	4.91	
Ce	12.3	11.00	11.84	11.09	10.42	11.76	
Pr	1.82	1.64	1.73	1.62	1.55	1.72	
Nd	8.6	7.65	8.05	7.55	7.16	8.07	
Sm	2.29	2.15	2.29	2.14	2.04	2.28	
Eu	0.81	0.80	0.84	0.78	0.75	0.84	
Gd	2.69	2.42	2.53	2.40	2.32	2.55	
Tb	0.428	0.42	0.44	0.42	0.40	0.44	
Dy	2.69	2.71	2.82	2.65	2.55	2.84	
Ho	0.583	0.57	0.59	0.57	0.54	0.59	
Er	1.59	1.58	1.64	1.52	1.47	1.63	
Yb	1.55	1.45	1.47	1.40	1.35	1.47	
Lu	0.244	0.22	0.24	0.22	0.21	0.23	
Hf	1.50	1.36	1.45	1.35	1.27	1.41	
Ta	0.086	0.082	0.081	0.079	0.076	0.083	
Pb	5.52	3.98	4.18	3.98	3.81	3.97	
Th	0.67	0.63	0.66	0.61	0.57	0.60	
U	0.248	0.25	0.25	0.23	0.22	0.23	
B	8.5						
Be	0.49						
Li	11						

Table 2: Trace elements (in ppm) determined by ICP-MS for selected rocks from Villarrica Volcano. . .

	1	2	3	4	5
	280976-1	210281-1** ^a	151282-2	191284-1	151282-3
<i>SiO₂</i> ^b	51.79	52.6	55.56	52.23	55.0
<i>TiO₂</i>	1.11	1.11	0.94	1.13	1.33
<i>MgO</i>	6.63	6.05	4.53	5.85	4.20
<i>Mg#</i> ^c	56.7	55.1	53.7	51.6	45.3
Ni	91.1	71.1	21.4	65.3	17.5
Cr	236	185	84.4	152	34.5
Sc	32.8	32.7	30.2	31.9	32.4
V	278	279	207	284	333
Cu	133	134	71.1	155	138
Co	36.0	33.4	25.0	32.8	27.2
Sr	420	426	451	463	425
Ba	192	198	274	202	260
Y	24.2	24.6	24.3	24.2	26.9
Nb	2.16	2.19	3.19	2.19	3.08
Zr	92.5	95.7	114	93.9	114
Rb	15.1	15.9	19.2	15.5	20.8
Cs	1.50	1.60	1.52	1.66	1.76
La	7.86	7.90	10.5	7.92	10.32
Ce	19.3	19.4	24.3	19.5	24.6
Pr	2.84	2.88	3.42	2.92	3.52
Nd	13.4	13.6	15.4	13.9	16.12
Sm	3.51	3.58	3.76	3.65	4.05
Eu	1.10	1.10	1.16	1.12	1.26
Gd	3.99	4.08	4.11	4.14	4.54
Tb	0.633	0.643	0.646	0.651	0.712
Dy	3.93	4.02	4.00	4.04	4.43
Ho	0.855	0.869	0.857	0.870	0.951
Er	2.35	2.41	2.42	2.40	2.62
Yb	2.26	2.33	2.37	2.29	2.53
Lu	0.348	0.357	0.368	0.354	0.394
Hf	2.48	2.56	2.93	2.57	2.96
Ta	0.137	0.140	0.195	0.233	0.23
Pb	7.08	7.33	8.48	10.9	8.54
Th	1.27	1.32	2.20	1.29	1.88
U	0.446	0.458	0.683	0.450	0.571
B					
Be	0.60	0.64	0.81	0.75	0.72
Li	14	15	14	16	16

^a Samples with asterisks have U-series isotope and ¹⁰Be data published in Hickey-Vargas et al. (2002)

^b SiO₂, MgO and Mg# from Hickey-Vargas et al. (1989) are provided for reference.

^c Mg# is molar MgO/(MgO + ΣFeO)

Table 3: New radiogenic isotope data for basalts from the small eruptive centers

SEC		$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
Huelemolle	<i>110194-2^a</i>	0.70390	0.512829	18.561	15.607	38.467
	110194-1	0.70393	0.512848	18.569	15.613	38.499
	<i>110194-3^{b*}</i>	0.70393	0.512784	18.549	15.591	38.429
	120194-1	0.70391	0.512820	18.557	15.602	38.453
	120194-2	0.70388	0.512827	18.567	15.605	38.477
Caburgua	<i>150194-3</i>	0.70376	0.512832	18.594	15.615	38.513
	150194-1*	0.70374	0.512852	18.590	15.595	38.456
Cerro Redondo	<i>140194-9*</i>	0.70388	0.512835	18.553	15.603	38.452
La Barda	<i>150194-6*</i>	0.70373	0.512839	18.528	15.610	38.440
	<i>150194-5B</i>	0.70374	0.512824	18.560	15.596	38.436
San Jorge	140194-1*	0.70396	0.512909	18.567	15.626	38.522
	140194-4	0.70395	0.512910	18.594	15.629	38.560
	140194-7	0.70397	0.512888	18.576	15.608	38.488

^a Samples in non-italic type were analyzed at the Department of Terrestrial Magnetism of the Carnegie Institution of Washington. Samples in italics were analyzed at the National High Magnetic Field Laboratory at Florida State University.

^b Samples with asterisks have U-series isotopes and ¹⁰Be analyses reported in Hickey-Vargas et al. (2002).

Table 4: Examples of calculated primary magma compositions for select SEC basalts

Center	San Jorge	Caburgua	La Borda	Huellemolle	Mantle Primary Magmas (dry)^c	
Sample	140194-04	120194-04A	150194-5A	120194-01	25% melting	10% melting
SiO ₂	48.48	48.05	47.86	47.38	49.80	50.30
TiO ₂	0.71	0.89	0.87	0.83	0.65	1.15
Al ₂ O ₃	14.43	14.38	14.19	14.31	13.30	17.10
FeO	7.81	8.35	8.36	8.72	9.40	9.40
MnO	0.14	0.12	0.13	0.12		
MgO	12.59	13.53	13.58	14.12	13.60	10.60
CaO	8.64	7.22	7.61	7.39	12.00	8.40
Na ₂ O	2.34	2.81	2.66	2.60	1.30	3.00
K ₂ O	0.38	0.65	0.60	0.63		
H ₂ O ^a	3.63	3.26	3.36	3.16		
Wt. Fraction Olivine Added	1.10	1.23	1.19	1.26		
T° C^b	1274	1305	1305	1324	1277	1268
GPa	1.32	1.59	1.60	1.74	1.13	1.38

^a Calculated for 4% H₂O in basalt and $\text{Fe}^3/\Sigma\text{Fe}=0.1$, and mantle olivine with Fo 90.

^b Temperature and pressure calculated with model of Lee et al. (2009).

^c Calculated primary mantle melts for subduction zones from Plank and Langmuir (1988). T and P are calculated with the same parameters as the SEC.

Figure 1

Figure 2