



# Across-arc geochemical variations in the Southern Volcanic Zone, Chile (34.5–38.0°S): Constraints on mantle wedge and slab input compositions

G. Jacques<sup>a,\*</sup>, K. Hoernle<sup>a,b</sup>, J. Gill<sup>c</sup>, F. Hauff<sup>b</sup>, H. Wehrmann<sup>a</sup>,  
D. Garbe-Schönberg<sup>d</sup>, P. van den Bogaard<sup>a,b</sup>, I. Bindeman<sup>e</sup>, L.E. Lara<sup>f</sup>

<sup>a</sup> Collaborative Research Center (SFB574), University of Kiel and GEOMAR, 24148 Kiel, Germany

<sup>b</sup> GEOMAR Helmholtz Centre for Ocean Research Kiel, 24148 Kiel, Germany

<sup>c</sup> University of California, Santa Cruz, CA 95064, USA

<sup>d</sup> Institute of Geosciences of the University of Kiel, 24118 Kiel, Germany

<sup>e</sup> University of Oregon, Eugene, OR 97403, USA

<sup>f</sup> Servicio Nacional de Geología y Minería, Santiago, Chile

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## Abstract

Crustal assimilation (e.g. Hildreth and Moorbath, 1988) and/or subduction erosion (e.g. Stern, 1991; Kay et al., 2005) are believed to control the geochemical variations along the northern portion of the Chilean Southern Volcanic Zone. In order to evaluate these hypotheses, we present a comprehensive geochemical data set (major and trace elements and O–Sr–Nd–Hf–Pb isotopes) from Holocene primarily olivine-bearing volcanic rocks across the arc between 34.5°S and 38.0°S, including volcanic front centers from Tinguiririca to Callaqui, the rear arc centers of Infernillo Volcanic Field, Laguna del Maule and Copahue, and extending 300 km into the backarc. We also present an equivalent data set for Chile trench sediments outboard of this profile. The volcanic arc (including volcanic front and rear arc) samples primarily range from basalt to andesite/trachyandesite, whereas the backarc rocks are low-silica alkali basalts and trachybasalts. All samples show some characteristic subduction zone trace element enrichments and depletions, but the backarc samples show the least. Backarc basalts have higher Ce/Pb, Nb/U, Nb/Zr, and Ta/Hf, and lower Ba/Nb and Ba/La, consistent with less of a slab-derived component in the backarc and, consequently, lower degrees of mantle melting. The mantle-like  $\delta^{18}\text{O}$  in olivine and plagioclase phenocrysts (volcanic arc = 4.9–5.6‰ and backarc = 5.0–5.4‰) and lack of correlation between  $\delta^{18}\text{O}$  and indices of differentiation and other isotope ratios, argue against significant crustal assimilation. Volcanic arc and backarc samples almost completely overlap in Sr and Nd isotopic composition. High precision (double-spike) Pb isotope ratios are tightly correlated, precluding significant assimilation of older sialic crust but indicating mixing between a South Atlantic Mid Ocean-Ridge Basalt (MORB) source and a slab component derived from subducted sediments and altered oceanic crust. Hf–Nd isotope ratios define separate linear arrays for the volcanic arc and backarc, neither of which trend toward subducting sediment, possibly reflecting a primarily asthenospheric mantle array for the volcanic arc and involvement of enriched Proterozoic lithospheric mantle in the backarc. We propose a quantitative mixing model between a mixed-source, slab-derived melt and a heterogeneous mantle beneath the volcanic arc. The model is consistent with local geodynamic parameters, assuming water-saturated conditions within the slab. © 2013 Elsevier Ltd. All rights reserved.

\* Corresponding author. Address: GEOMAR Helmholtz Center for Ocean Research Kiel, Wischhofstraße 1-3, 24148 Kiel, Germany.  
E-mail address: [gjacques@geomar.de](mailto:gjacques@geomar.de) (G. Jacques).

## 1. INTRODUCTION

The Chilean Southern Volcanic Zone (SVZ) extends from 33°S, just south of where the Juan Fernandez ridge is subducting and the crust of the overriding plate is ~60 km thick, to 46°S where the Chile Ridge is subducting and the crust is ~30 km thick. About 70% of the Chilean population live close to some of the most active volcanoes in the Andes along the SVZ (Stern, 2004). In this paper we report data for an across-arc profile between 34.5°S and 38.0°S that overlaps and extends slightly further south than the Transitional Southern Volcanic Zone (TSVZ), 34.5–37.0°S, of Tormey et al. (1991). We also report data for trench sediments being subducted outboard of this region. The 1932 eruption at Quizapu volcano, one of the largest Plinian eruptions of an Andean volcano in historical time and older highly explosive silicic ignimbrite-forming eruptions that formed giant calderas, such as the Diamante caldera, took place in this part of the SVZ.

There are several potential sources for arc magmas in continental margin subduction zones: the subducting slab (including pelagic and continentally-derived trench sediments, seawater-altered upper oceanic crust, lower oceanic crust and possibly serpentinites in the subducting lithospheric mantle), the overlying mantle wedge, and the overriding lithosphere (including both continental crust and lithospheric mantle). In order to evaluate the relative role of these potential sources in generating the volcanism in the TSVZ, we present a new and comprehensive geochemical data set, including major and trace elements and Sr, Nd, Hf, O and high resolution Pb double spike isotope ratios, for primarily olivine-bearing Holocene and Late Pleistocene lavas and trench sediments from the region. Our igneous samples are from both the volcanic arc (VA), which includes the volcanic front in Chile and the rear arc up to 70 km behind the volcanic front in Chile/Argentina, and backarc (BA) volcanic centers in Argentina that are 100–300 km behind the volcanic front.

## 2. GEOLOGICAL SETTING

Andean volcanism results from the subduction of the Nazca (7–9 cm/year towards the northeast) and Antarctic plates (2 cm/year) beneath the South American Plate (Norbabuena et al., 1998; Angermann et al., 1999). The Andean cordillera is more than 7500 km long, extending from Colombia to southern Chile. There are four active segments divided by volcanic gaps. They have been termed the Northern Volcanic Zone (NVZ; 5°N–2°S) in Colombia and Ecuador, the Central Volcanic Zone (CVZ; 14–27°S) in Peru and northern Chile, the Southern Volcanic Zone (SVZ, 33–46°S) in central Chile, and the Austral Volcanic Zone (AVZ; 49–55°S) in southern Chile. Volcanism occurs when the slab dip angle is steep (>25°), whereas volcanic gaps occur where subduction dip angles are shallow (<10°) (Stern, 2004).

The SVZ consists of over 60 Quaternary volcanoes in Chile and Argentina, three silicic caldera systems and numerous minor eruptive centers (Stern, 2004). The SVZ has been divided into the Northern Southern Volcanic Zone

(NSVZ; 33–34.5°S; e.g. Hildreth and Moor bath, 1988), the Transitional Southern Volcanic Zone (TSVZ; 34.5–37°S; e.g. Tormey et al., 1991), the Central Southern Volcanic Zone (CSVZ; 37.0–41.5°S; e.g. Hickey et al., 1984, 1986; Hickey-Vargas et al., 1989) and the Southern Southern Volcanic Zone (SSVZ; 41.5–46°S; e.g. Naranjo and Stern, 2004), based on the geochemical characteristics of the erupted rocks (see also López-Escobar et al., 1995) (Fig. 1a). Other authors have divided the SVZ differently (e.g. Dungan et al., 2001): the Tupungato-Maipo Segment (TMS, 33–34.2°S), located entirely on thick crust; the Palomo-Tatara Segment (PTS, 34.7–36°S), where the frontal arc centers lie west of the continental divide; and the Longaví-Osorno Segment (LOS, 36.2–42°S), where the southernmost chain lies near the topographic front of the Cordillera (see also Sellés et al., 2004 for further discussion of SVZ segmentation).

The TSVZ and related backarc centers, which provide information on the mantle wedge composition, are the focus of this study (Fig. 1b). Our volcanic arc (VA) samples are from nine Quaternary centers at the volcanic front that are denoted by blue circles in Fig. 1b for centers north of 36°S (Tinguiririca, Planchón–Peteroa, and the Los Hornitos and the Resolana cones in the area of Cerro Azul), referred to as the northern volcanic arc, and blue diamonds for centers south of 36°S (San Pedro and its nearby cones, Nevado del Longaví, Chillán and its nearby cones, Antuco and Callaqui), referred to as the southern volcanic arc. It also includes three areas in the rear arc, located up to 70 km behind the front. From north to south they are the Infernillo Volcanic Field (Folguera et al., 2009; Gudnason et al., 2012), the Laguna del Maule volcanic complex (Hildreth et al., 2010), and the Copahue stratovolcano. They are grouped together as rear arc volcanism in the tables but included in the appropriate VA group in the figures.

The backarc (BA) domain, from 100 to 300 km behind the volcanic front is known as the Payenia volcanic field (Munoz and Stern, 1988; Stern, 1989) and volcanic centers are denoted by open symbols in Fig. 1b. Some authors include the Payenia field in the larger Patagonian mafic volcanic province (Kay et al., 2004; Bertotto et al., 2009), while others keep it separate for geological and tectonic reasons (Ramos and Folguera, 2011). The Payenia volcanic field covers more than 40,000 km<sup>2</sup> between 34°S and 38°S with an estimated volume of 8400 km<sup>3</sup> erupted from more than 800 centers in the last 2 Ma. The K–Ar ages of the volcanic centers between 34.5° and 35.5° range from 1.8 to <0.01 Ma (Folguera et al., 2009; Ramos and Folguera, 2011 and references therein). Eruptions were episodic with distinct spatial and temporal patterns. Eruptions near San Rafael in the north took place between 1.8 and 0.7 Ma, whereas those near Malargüe were younger, 0.1–0.01 Ma. The Pampas Negras volcanic field erupted from 320 ka to recent, and the Auca Mahuida field (including Auca Mahuida Volcano and cinder cones to the north along the Rio Colorado) erupted between 2.1 and 0.34 Ma (Gudnason et al., 2012). We have divided the Payenia volcanic field into three segments: northern, central and southern. Our samples from the northern BA segment (NBA between 34.5°S and 35.5°S; open circles in the figures), behind the northern vol-

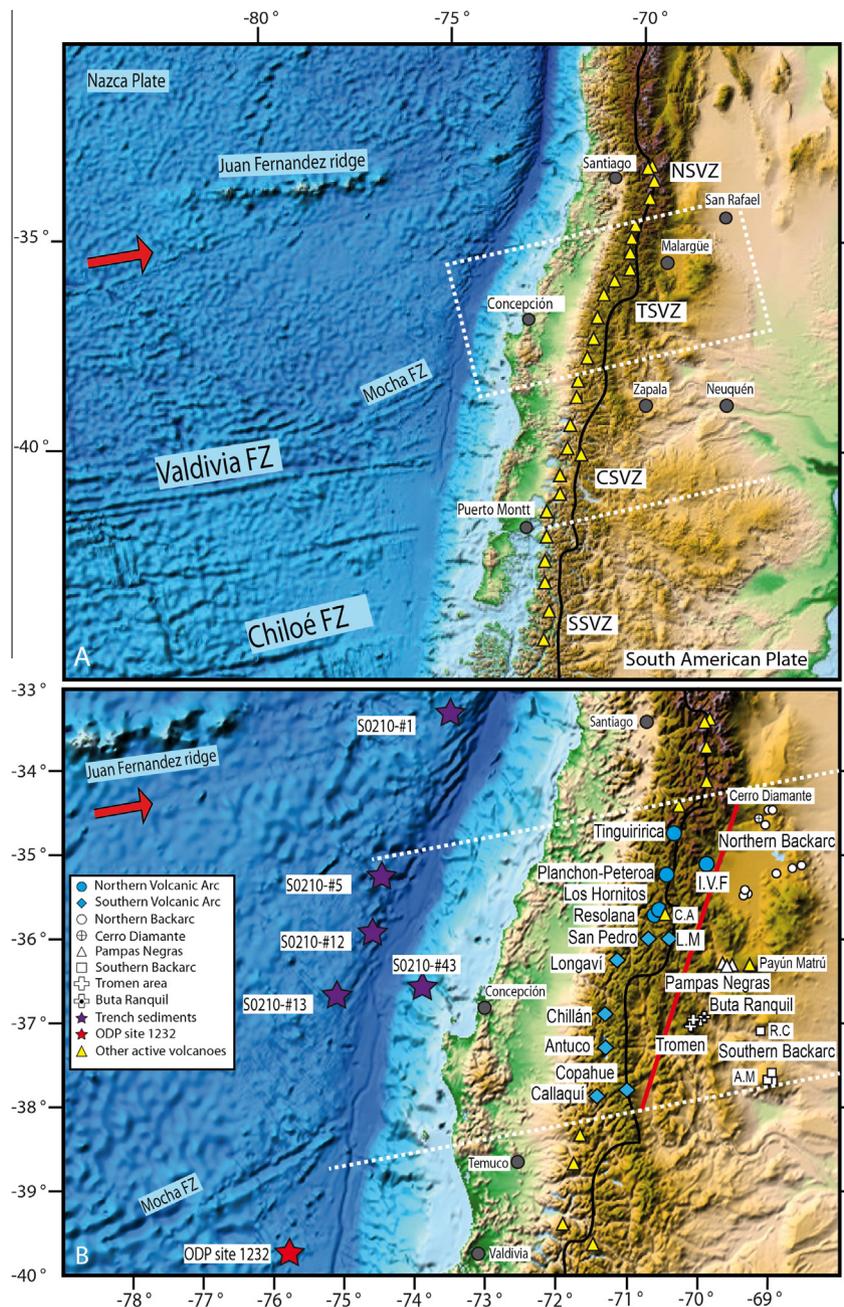


Fig. 1. (a) Map of the Southern Volcanic Zone (SVZ) in Chile and Argentina between 30°S and 45°S. Yellow triangles = Quaternary active volcanic front volcanoes. (b) Map of the Transitional Southern Volcanic Zone (TSVZ) between 34.5°S and 38°S. Red line = separates the Volcanic Arc (VA) and rear arc centers from the Backarc (BA). Blue circles and diamonds = northern and southern VA centers, respectively. Open circles = cinder cones from the Northern Backarc (NBA). Open circle with a cross = the Cerro Diamante stratovolcano that was an active arc center in the Miocene. Open triangles = central BA Pampas Negras volcanic field. Open = Southern Backarc (SBA; Auca Mahuida and Rio Colorado volcanic fields). Open crosses = Tromen stratovolcano area. Open cross with a dot = Buta Ranquil monogenetic center at the foot of Tromen. Yellow triangles = other Quaternary active VA volcanoes. Grey filled circles = major cities. Purple stars = the location of the SO210 cruise sediments. Red star = location of ODP site 1232. The white dashed lines bracket the TSVZ transect. The thick black line represents the border between Chile and Argentina. C.A. = Cerro Azul, L.M. = Laguna del Maule, I.V.F. = Infernillo Volcanic Field, R.C. = Rio Colorado, A.M. = Auca Mahuida. The ETOPO1 map source is from NOAA, modified (Amante and Eakins, 2009).

canic front, are from the monogenetic cones near San Rafael and Malargüe, and the Cerro Diamante stratovolcano and nearby cones. Samples from the Cerro Diamante stratovolcano are denoted with a circle enclosing a cross, be-

cause it may be affected by processes related to the Miocene volcanic front (Kay et al., 2004, 2005, 2006a,b; Kay and Copeland, 2006 and references therein). The central segment samples are from the Late Pleistocene to Holo-

cene Pampas Negras cones (36.0–36.5°S; open triangles in the figures) at the western end of a rift system extending from the Payún Matrú caldera. The southern BA segment (SBA between 37.0°S and 38.0°S; open squares in the figures) includes the Auca Mahuida shield volcano that is farthest from the VA, the Rio Colorado volcanic field, and the Tromen stratovolcano (open crosses). The Buta Ranquil sample (open cross with a dot inside) is from a monogenetic cone at the foot of Tromen. The Tromen samples may have been affected by the same processes as at Cerro Diamante. Most samples are Late Pleistocene to Holocene in age (Electronic Annex: Table 1).

The subducted Nazca Plate formed at the East Pacific Rise north of the Valdivia Fracture Zone (40°S) and at the Chilean Rise further south (Herron et al., 1981; Tebbens and Cande, 1997; Tebbens et al., 1997). Its age increases towards the north, from ~30 Ma at 38°S to ~35 Ma at 34.5°S. Only one fracture zone appears to be subducting beneath the TSVZ – an extension of the Mocha Fracture Zone at 38°S that might project beneath the area near Longaví (Sellés et al., 2004; Contreras-Reyes et al., 2008). This fracture zone, however, is not nearly as prominent as the Valdivia and other fracture zones further south (Fig. 1a).

The trench contains up to 2.2 km of sediments (Contreras-Reyes et al., 2008). Chilean trench sediments are mostly continentally-derived turbidites eroded from the Andean arc (Völker et al., 2008). Their trace element and Sr–Nd–Pb isotope compositions are similar to those of the Cretaceous to Holocene magmatic arc (Lucassen et al., 2010). ODP site 1232 is located at 39.9°S, 75.9°W in the Chile basin on the Nazca Plate ~50 km outboard of the trench (Fig. 1b). Its sediments are mostly continentally-derived turbidites (Mix et al., 2003; Lucassen et al., 2010).

The crust beneath the VA, especially from San Pedro to Tinguiririca where the volcanic front steps eastward onto the Cordillera, is believed to be relatively thick based on interpretations of regional gravity data (~35–45 km, Hildreth and Moor bath, 1988; Völker et al., 2011), but thinner than in the NSVZ where it reaches a maximum thickness of 60 km. The exposed basement of the volcanic arc consists primarily of Mesozoic and Cenozoic volcanic and sedimentary rocks intruded by Miocene to Pliocene plutons. Near the coast, metamorphic meta-sedimentary rocks are intruded by Carboniferous to Permian batholiths (e.g. Stern, 2004; Lucassen et al., 2004; Cembrano and Lara, 2009). In the backarc, the San Rafael block consists of Paleozoic rocks that were uplifted during the late Miocene. There is evidence of extensional deformation in the areas where crustal attenuation occurred (Gilbert et al., 2006; Yuan et al., 2006). The depth of the slab beneath the TSVZ volcanic front is relatively uniform in this part of Chile and lies between 120 and 140 km (Tassara et al., 2006). Due to relatively uniform crustal thicknesses and depths to the slab, the thickness of the intervening asthenospheric wedge beneath the VA is also relatively uniform and ranges from 60 to 80 km (Tassara et al., 2006; Völker et al., 2011). Magnetotelluric data indicate the presence of a low resistivity plume-like zone beneath the Payenia volcanic field, presently concentrated under the Payún Matrú caldera. This re-

gion of low resistivity is rooted deeper than 200 km, just above the projected Nazca Plate (Burd et al., 2008; Ramos and Folguera, 2011).

### 3. SAMPLE COLLECTION, PREPARATION, AND ANALYTICAL METHODS

The youngest and freshest, mostly olivine-bearing volcanic rocks (lava and tephra) were collected from each volcanic area along the volcanic front from Tinguiririca to Callaqui volcanoes and in the adjacent BA from 34.5°S to 38°S. During fieldwork, units containing xenolithic or xenocrystic material were avoided or only sampled where there was no obvious foreign material present, in an attempt to minimize crustal contamination. Their GPS-based locations, the presence or absence of olivine phenocrysts, and age estimates are presented in Table 1 (Electronic Annex). We also collected sediment samples during the October 2010 RV SONNE SO210 cruise. They come from gravity cores taken from the incoming Nazca Plate (12 m length) and from the Biobio Canyon in the trench (6 m length) (33.20–36.63°S, Fig. 1b). Descriptions of the cores are available in the SO210 cruise report (Linke et al., 2011, [www.dfg-ozean.de/fileadmin/DFG/Berichte\\_METEOR/Fahrtbericht\\_Sonne\\_210.pdf](http://www.dfg-ozean.de/fileadmin/DFG/Berichte_METEOR/Fahrtbericht_Sonne_210.pdf)). The cores were relatively homogeneous, consisting mostly of clay, silt, and sand derived mostly from the volcanic arc (Lucassen et al., 2010). We avoided ash layers in order to minimize the direct input of arc products. Two representative samples per core were analyzed.

Hardrock samples were crushed, sieved, and washed in distilled water in an ultrasonic bath. In order to minimize the effects of alteration and crustal contamination, 5–10 g of 1–2 mm size chips were carefully handpicked under a binocular microscope to ensure selection of the freshest part of the rock and to avoid xenocrystic and xenolithic material and tephra or lava pieces with vesicle fill. Handpicked chips were powdered in an agate mill to obtain homogenous powders for XRF and ICPMS analysis. Chips were used for isotope analysis. Fresh olivine and plagioclase phenocrysts were carefully selected for oxygen isotope analysis to avoid inclusions and attached matrix.

Major element compositions were obtained at GEOMAR and at the Institute of Geosciences at the University of Kiel, both on a Phillips X'Unique PW 1480 XRF. Several reference materials (JB-2, JB-3, JA-2, BHVO-2, HTB-1, OU) were also analyzed, and yielded deviations of <5% from the published reference values (Govindaraju, 1994; Potts and Kane, 2005; Webb et al., 2009). The sediments were analysed at the University of Hamburg on a MagixPro PW 2540 XRF.

Matrix glass compositions of Planchón–Petroa, Los Hornitos and Antuco samples were determined by electron microprobe with a Jeol JXA 8200 at GEOMAR, using polished glass shard mounts and petrographic thin sections. An accelerating voltage of 15 kV and current of 10 mA was applied; the beam was set to 10 µm in diameter with a count time of 20 s per major element. Na was analyzed first to minimize element loss. The instrument was calibrated and monitored using natural reference materials

VG-2 (USNM 111240/52), VGA-99 (USNM113498), ALV-981 (R23-5), and CFA-47. The reported composition is an average of 20–50 measurements.

Thirty-seven trace elements (Li, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Sn, Cs, Ba, rare earth elements (REE), Hf, Ta, Pb, Th, U) were determined by ICP-MS using an Agilent 7500cs at the University of Kiel. Analytical procedures are described by Garbe-Schönberg (1993). The sediments were digested using PARR bombs in an oven in order to maximize zircon dissolution. Accuracy of analytical results was assessed with rock reference materials BHVO-2 and JA-2 analyzed as unknowns (Electronic Annex: Table 1). Average accuracy of the results (in% deviation from GeoReM's recommended values) was better than 4% for all elements except Sc, Cr and Th in BHVO-2, and Cr, Zr, Nb and Hf in JA-2, being better than 10% for these elements. The average instrumental precision of the measurements as estimated from multiple analyses distributed over 5–6 h is typically better than 1% for almost all elements. The average reproducibility of the digest procedure was monitored by duplicate preparation of at least every tenth sample and found to be better than 1%.

Sr, Nd and Pb isotope ratios were determined on ThermoFinnigan TRITON (Sr, Nd) and Finnigan MAT 262-RPQ2+(Pb) thermal ionization mass spectrometers at GEOMAR. Pb analyses were carried out using a double spike method. A detailed description of the chemical and TIMS analytical procedures can be found in Hoernle et al. (2008, 2011). 100–150 mg of 0.5–2 mm sized, fresh rock chips were first leached in 2 N HCl at 70 °C for 1–2 h and then triple-rinsed with ELGA water to remove possible surface contamination. Sr and Nd isotope ratios were mass-bias corrected within run to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  and all errors are reported at the  $2\sigma$  confidence level. NBS987 and our in-house Nd SPEX reference material were measured every 4th to 5th sample to obtain a normalization value for each turret relative to our preferred values of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250$  for NBS987 and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511715$  for SPEX (corresponding to  $^{143}\text{Nd}/^{144}\text{Nd} = 0.511850$  for La Jolla, Krolukowska-Ciaglo et al., 2005). The normalization value was then applied to the sample data for each turret. This procedure compensates for machine drift over the course of the project (2009–2012) and therefore allows maximum data comparability. External  $2\sigma$  uncertainties are  $\pm 0.000011$  ( $n = 25$ ) for NBS987 and  $\pm 0.000005$  for SPEX. Long term machine drift for  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  between 2008 and 2012 is within 0.000030. The double spike corrected NBS981 values measured along with the samples are  $^{206}\text{Pb}/^{204}\text{Pb} = 16.9413 \pm 21$ ,  $^{207}\text{Pb}/^{204}\text{Pb} = 15.4994 \pm 20$ ,  $^{208}\text{Pb}/^{204}\text{Pb} = 36.7241 \pm 56$ ,  $^{207}\text{Pb}/^{206}\text{Pb} = 0.914889 \pm 37$ ,  $^{208}\text{Pb}/^{206}\text{Pb} = 2.16773 \pm 13$  ( $n = 38$ ), and compare well with published double and triple spike data for NBS981 (see Hoernle et al., 2011). Total Pb chemistry blanks were determined for each sample batch and were below 25 pg, with the exception of a single Pb blank of 200 pg. Sr–Nd chemistry blanks are typically below 100 and 50 pg, respectively. These blank levels are negligible even relative to the amount loaded on the filaments (60–80 ng Pb and 500–

1000 ng Sr and Nd). Replicate analyses by means of separate digestions are within the external  $2\sigma$  reproducibility of the Sr–Nd–Pb reference materials stated above.

Hf isotopes were determined on a NU Plasma HR MC-ICPMS at GEOMAR. 200–500 mg of 0.5–2 mm sized fresh rock chips were digested for 60 h at 130 °C in a HF–HNO<sub>3</sub> mixture. Details of the chemical separation procedures are reported in Blichert-Toft and Albarède (1997) and Geldmacher and Hoernle (2006). Prior to analysis, samples were diluted to 80–100 ppb Hf to obtain a total Hf beam of 12–14 V. Hf isotope ratios were measured using static multi-collection and were mass-bias corrected to  $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$  assuming exponential mass fractionation. Our in-house Hf reference material solution SPEX was measured every 3–5 samples to obtain a normalization value for each sample sequence. Over the course of the project (2010–2012), our in-house SPEX reference material solution had  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282170 \pm 6$  ( $2\sigma$ ,  $n = 45$ ), which corresponds to  $^{176}\text{Hf}/^{177}\text{Hf} = 0.282163$  for JMC-475 (Blichert-Toft and Albarède, 1997).

Oxygen isotope analyses were performed at the University of Oregon using CO<sub>2</sub>-laser fluorination (e.g. Bindeman, 2008) and a Newwave 35W CO<sub>2</sub> laser. Single and bulk phenocryst grains, ranging in weight from 0.6 to 2 mg, were reacted in the presence of BrF<sub>5</sub> to liberate oxygen gas (protocol #1 in Electronic Annex: Table 2). The gas generated in the laser chamber was purified through a series of cryogenic traps held at liquid nitrogen temperature, and a mercury diffusion pump was used to remove traces of fluorine gas. Oxygen was converted to CO<sub>2</sub> gas in a small platinum graphite converter, the yield was measured, and then CO<sub>2</sub> gas was analyzed on a MAT 253 mass spectrometer. Four to seven aliquots of internal garnet reference material (UOG1,  $\delta^{18}\text{O} = 6.56\text{‰}$ , calibrated against the Gore Mt. Garnet ( $\delta^{18}\text{O}_{\text{olivine}} = 5.8\text{‰}$  VSMOW, Valley et al., 1995)), as well as aliquots of reference materials (mantle olivine from San Carlos with  $\delta^{18}\text{O}_{\text{olivine}} = 5.25\text{‰}$ , Bindeman, 2008) were analyzed together with the unknowns during each analytical session. Between-run variability of the measured  $\delta^{18}\text{O}_{\text{olivine}}$  values of the reference materials ranged from 0.1‰ to 0.25‰ less than their accepted value, and samples values were adjusted to correct for this small day-to-day variability. The average precision of reference materials and duplicates of single grains and bulk analyses was in the range  $\pm 0.02\text{‰}$  to  $\pm 0.08\text{‰}$  ( $1\sigma$ ).

For oxygen isotope analysis of bulk sediment, powdered sediments were heated at 150 °C in a vacuum oven overnight to remove any loosely absorbed environmental water. Then one of two protocols was used: (1) minimal BrF<sub>5</sub> pretreatment of multiple samples hard-pressed into holes in a holder in a laser fluorination chamber (protocol #2 in Electronic Annex: Table 2); or (2) one-by-one analysis in a regular chamber or an air-lock sample chamber (protocol #3). As demonstrated with other clay-rich sediments, there is systematic  $\sim 1\text{‰}$  difference between these two methods because of rapid BrF<sub>5</sub> stripping of loosely-bound H<sub>2</sub>O in clays. Although it remains unclear which protocol is more appropriate for subducted sediment, we favor results from protocol #2.

#### 4. RESULTS

Sixty volcanic samples were analyzed for major elements, trace elements and Sr, Nd and Pb isotope compositions, 28 for Hf isotopes, and nineteen for O isotopes. Ten sediment samples were analyzed for major and trace elements, five for Sr–Nd–Hf–Pb isotopes, and seven for O isotopes. The data are presented in Table 1 (Electronic Annex) (major and trace elements) and in Table 2 (Electronic Annex) (Sr–Nd–Hf–Pb–O isotopes).

VA samples consist primarily of basalts to andesites/trachyandesites with  $\text{SiO}_2 = 51\text{--}61$  wt.% and  $\text{MgO} = 2.8\text{--}8.5$  wt.%, with the exception of one sample that plots on the andesite/dacite boundary (Fig. 2). About half of our VA samples have  $\text{MgO} > 5\%$  and  $\text{SiO}_2 < 54\%$ . They are mostly calc-alkalic (they lack Fe-enrichment). Three from Tinguiririca, one from San Pedro and one from Copahue plot in the high-K field of Gill (1981) (not shown). In MgO versus major element oxide diagrams (Fig. 3), the VA samples have positive correlations of MgO versus FeOt (total iron as FeO) and CaO (Fig. 3a and b), and negative correlations of MgO versus  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  (Fig. 3c and d),  $\text{SiO}_2$ , and  $\text{K}_2\text{O}$  (not shown).

BA samples are more mafic alkali basalts and trachybasalts with  $\text{SiO}_2 = 45\text{--}50$  wt.% and  $\text{MgO} = 4\text{--}11$  wt.%, except for three trachyandesite (Figs. 2 and 3). Most Pampas Negras samples are evolved with  $\text{MgO} = 4\text{--}6$  wt.%. BA samples have similar correlations between MgO and the other oxides as observed for the VA samples. Relative to the VA, the BA trend is shifted to lower  $\text{SiO}_2$  (Fig. 2) but higher FeOt,  $\text{Na}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$  (Fig. 3a, d–f),  $\text{K}_2\text{O}$  and MnO contents (not shown) and lower concentrations of most incompatible trace elements (e.g. Zr, Hf, Nb, Ta, REE and Ba). There is little or no overlap between VA (including rear arc) and BA samples for Ti, Na, and P, and the change occurs between 70 and 100 km behind the volcanic front.

All VA samples show typical subduction zone incompatible element signatures, characterized by enrichment in fluid-mobile Large Ion Lithophile Elements (LILE), such

as Cs, Rb, Ba, U, K and Pb, and depletion in the High Field Strength Elements (HFSE) Nb and Ta, relative to light REE (Fig. 4a). Differentiated VA samples show relative enrichment in Zr and Hf, and depletion in Ti. BA samples have similar patterns but overall greater enrichment in highly incompatible elements, steeper heavy REE patterns ( $\text{Sm}/\text{Yb}$  in VA = 1.48–2.25, in BA = 2.26–4.32), and less pronounced negative Nb and Ta troughs (Fig. 4b). Consequently, the VA samples have higher fluid-mobile (e.g. LILE) to fluid-immobile (e.g. HFSE and REE) element ratios (e.g. higher Ba/La, Ba/Nb and Th/Nb and lower Ce/Pb, Nd/Pb, Nb/U), and lower ratios of more to less incompatible HFSE and REE ratios (e.g. lower Nb/Zr, Nb/Y, Ta/Hf, Zr/Hf, Nb/Yb, Ta/Yb, Gd/Yb, Tb/Yb,  $\text{TiO}_2/\text{Yb}$ ) than the BA samples. In general, some NBA and Tromen samples show a more pronounced subduction zone signature than other BA groups. Sample CL 472 from Buta Ranquil near Tromen shows the most pronounced subduction zone signature in the BA.

Our  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope data are similar to those of previous studies for the TSVZ (Harmon et al., 1984; Hickey et al., 1986; Davidson et al., 1987, 1988; Hildreth and Moorbath, 1988; Sigmarsson et al., 1990; Tormey et al., 1995) and the BA (Kay and Copeland, 2006; Kay et al., 2006a,b; Varekamp et al., 2010).  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$  isotopes are negatively correlated for both VA and BA samples, the VA and BA data almost completely overlap, and both lie within the South Atlantic Mid-Ocean Ridge Basalt (MORB) field (Fig. 5). The Buta Ranquil sample is displaced to higher Nd and/or Sr isotope ratios and has the highest Nd isotope ratio of the samples we analyzed, while the other Tromen samples plot together with the other BA samples. The trench sediments largely overlap the volcanic rocks in Nd, but extend to higher Sr isotope ratios. Most of the sediments that we analysed lie at the enriched end of the Chilean trench sediment field in Fig. 5 defined by data from Lucassen et al. (2010).

The Pb isotope data for VA and BA samples have the same tight positive correlations on uraniumogenic Pb

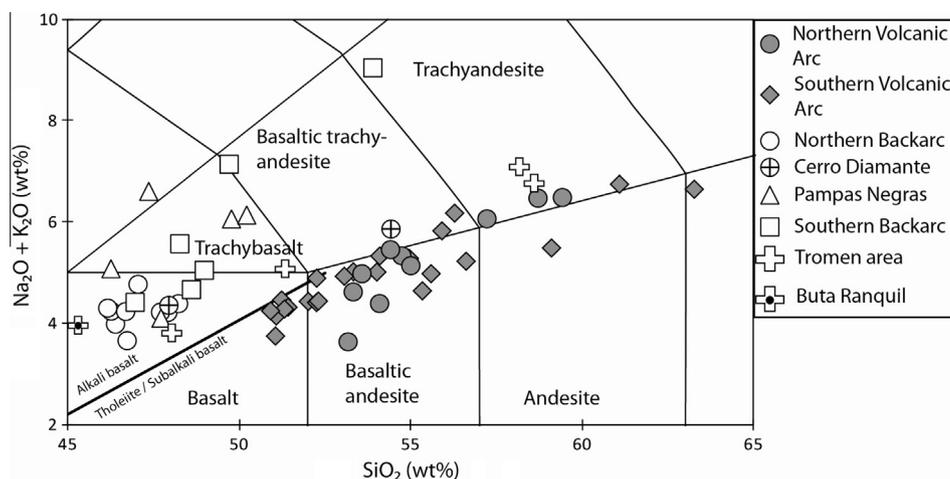


Fig. 2. Total Alkali versus Silica [TAS] after Le Maitre et al. (1989). VA samples range from basalt to trachyandesite, BA samples are mostly alkali basalts and trachybasalts. BA samples are lower in silica than the VA samples except for one sample from Cerro Diamante stratovolcano.

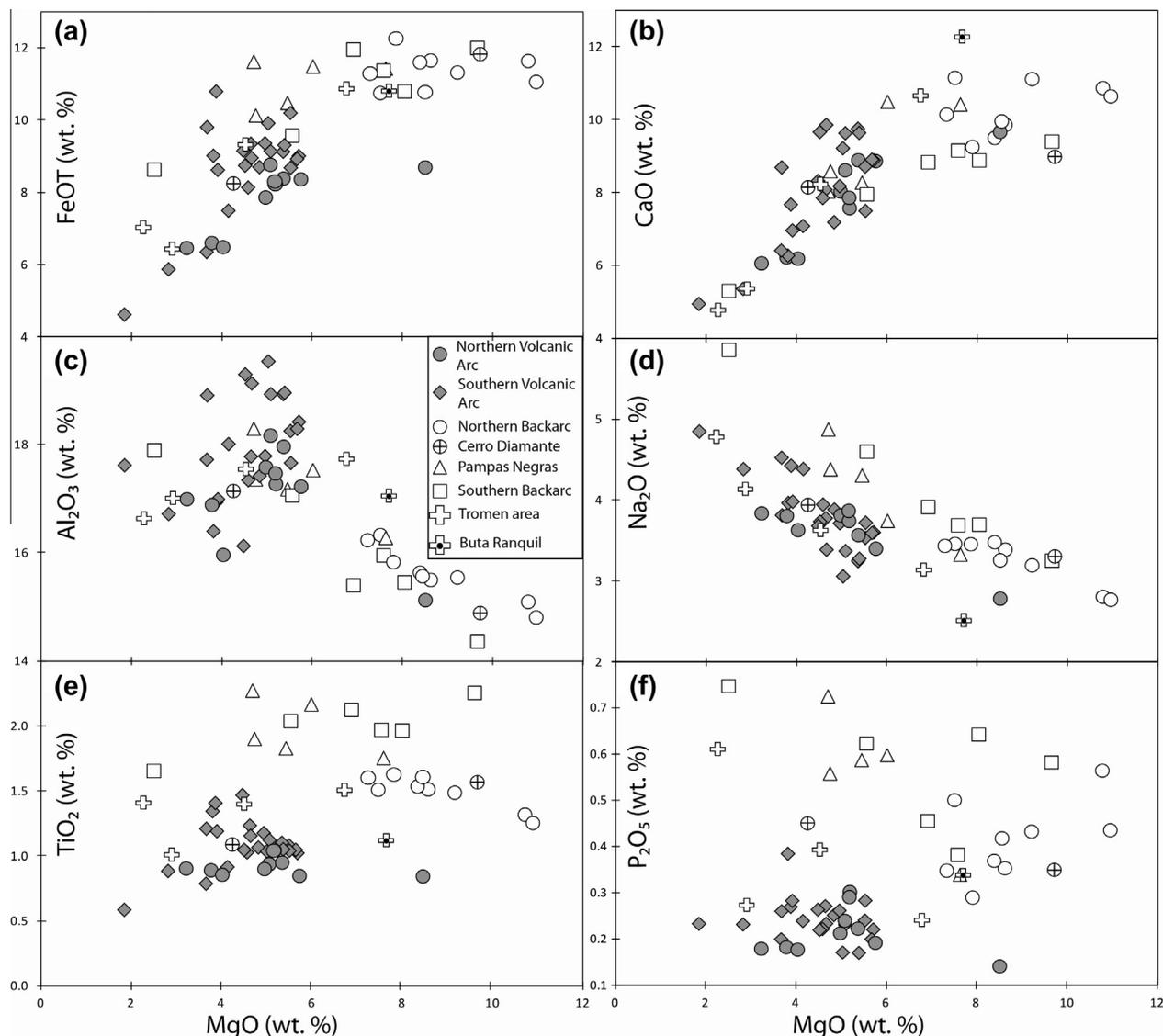


Fig. 3. MgO versus (a) FeO, (b) CaO (c) Al<sub>2</sub>O<sub>3</sub>, (d) Na<sub>2</sub>O, (e) TiO<sub>2</sub> and (f) P<sub>2</sub>O<sub>5</sub>. The VA and the BA generally form two different petrogenetic trends, reflecting different magma formation and evolution processes.

( $r^2 = 0.92$  or  $0.94$  excluding the Buta Ranquil sample) and thorogenic Pb ( $r^2 = 0.96$  or  $0.97$ ) isotope diagrams (Fig. 6a and b). This is a much tighter array than for older unspiked data (e.g. Davidson et al., 1987, 1988; Hildreth and Moor bath, 1988; Tormey et al., 1995, not shown). The VA samples (with  $^{206}\text{Pb}/^{204}\text{Pb} = 18.56\text{--}18.65$ ) fall almost completely within the field for the Chilean trench sediments and cover nearly the full range in  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios of the sediments, whereas the backarc samples (with  $^{206}\text{Pb}/^{204}\text{Pb} = 18.30\text{--}18.61$ ) extend to significantly less radiogenic ratios. The southern and central part of the BA have the least radiogenic Pb isotopic compositions, whereas the NBA, Tromen and Buta Ranquil have Pb isotope ratios intermediate between the VA and the southern BA and are shifted to slightly lower  $^{207}\text{Pb}/^{204}\text{Pb}$  at a given  $^{206}\text{Pb}/^{204}\text{Pb}$  isotope ratio (towards a Pacific MORB component). Pb isotope ratios (e.g.  $^{206}\text{Pb}/^{204}\text{Pb}$ ) correlate well

with Nb/Zr ( $r^2 = 0.70$ ), Nb/U ( $r^2 = 0.84$ ), Ce/Pb ( $r^2 = 0.81$ ) (Fig. 7), if the BA samples from Buta Ranquil and the Cerro Diamante stratovolcano are excluded. The correlations within individual volcanic centers are slightly more scattered, especially for the VA samples which overlap the Chilean trench sediment field on these diagrams.

The samples form two subparallel positive arrays on a plot of Nd versus Hf isotope ratios with the VA samples ( $r^2 = 0.86$ ) having higher  $\epsilon\text{Hf}$  for a given  $\epsilon\text{Nd}$  than the BA samples ( $r^2 = 0.47$ ) (Fig. 8). We know of no other arc like this (cf. Pearce et al., 1999; Woodhead et al., 2001; Tollstrup and Gill, 2005; Yododzinski et al., 2010; Woodhead et al., 2012). The Chilean trench sediment outboard of the TSVZ is displaced above the VA field, which we attribute to the presence of a pelagic component, while sediments from the Peru/Chile trench >2000 km farther north have lower  $\epsilon\text{Nd}$  than any of the TSVZ volcanic rocks (Vervoort

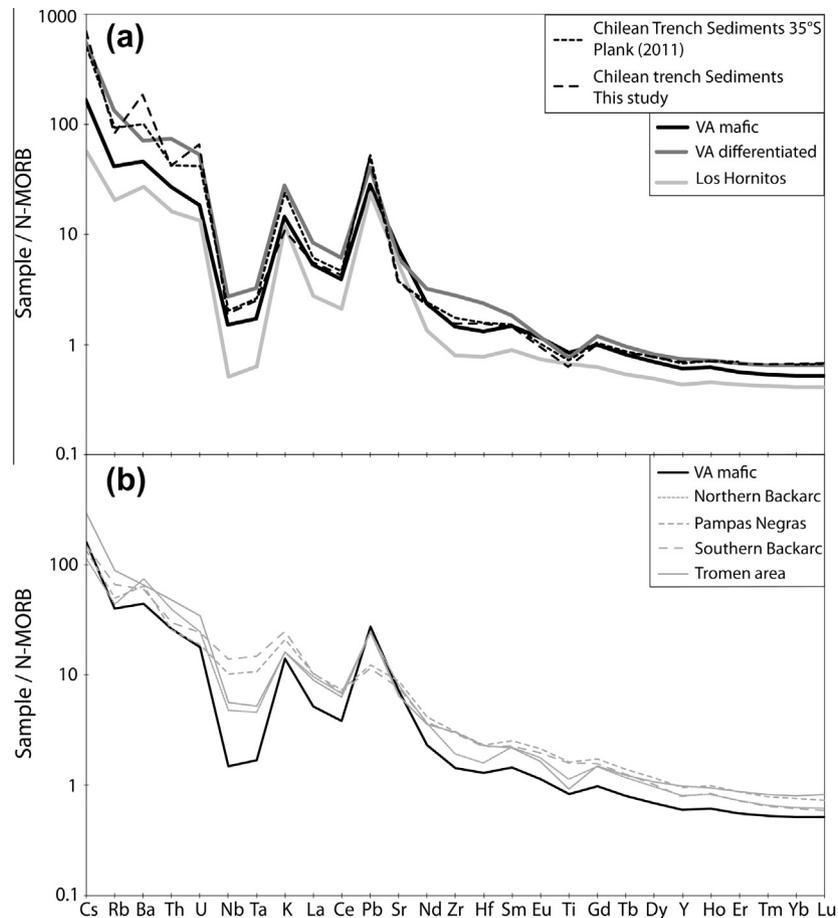


Fig. 4. Multi-element diagram normalized to N-MORB after Sun and McDonough (1989), showing (a) the VA and trench sediments and (b) the BA. VA samples show typical subduction zone trace element signatures highlighted by Pb and K peaks and Nb and Ta troughs. More differentiated VA samples (with MgO < 5 wt.% and SiO<sub>2</sub> > 54 wt.%) show greater enrichment in Cs, Rb, Zr, and Hf, and depletion in Ti. BA samples from Pampas Negras and SBA show less pronounced peaks at Pb and K, and troughs at Nb and Ta, while NBA and Tromen samples have an intermediate subduction zone signature. Trench sediments from this study and Plank (2011) overlap the VA pattern.

et al., 1999, 2011). The most radiogenic Peru trench sediment with  $\epsilon_{\text{Hf}} = +4$ –5 slightly overlaps the least radiogenic TSVZ VA samples in  $\epsilon_{\text{Hf}}$ . The sediment from the canyon on the continental slope has similar Hf–Nd isotopes to the VA.

Oxygen isotope analyses of olivine (and two plagioclase samples normalized to olivine) define narrow ranges for both the VA (4.88–5.62‰ or 5.52‰ if the plagioclase value from CL 726, the most evolved sample measured for oxygen isotopes, is excluded) and BA (5.02–5.42‰) (Fig. 6c). The VA samples spread around canonical mantle olivine values (5.0–5.4‰; Matthey et al., 1994) and extend to both slightly lighter and heavier compositions. Excluding CL726,  $\delta^{18}\text{O}$  for the other samples show no correlation with parameters of differentiation, such as SiO<sub>2</sub> (Fig. 9a) or MgO content (not shown), or with incompatible elements or Sr, Nd, or Pb isotope ratios (e.g. Fig. 6c).

The compositions of the SO210 trench sediments (major and trace elements and Sr–Nd–Pb isotopes) are comparable to those reported previously (Lucassen et al., 2010) and summarized by Plank (2011), except that our samples have higher Ba concentrations. Since our results for reference materials are close to expected values and the Ba data are

reproducible, we exclude an analytical problem with our data. Our trench sediments are quite uniform in isotopic composition apart from the one from a canyon on the continental slope where the sediments are similar to Quaternary volcanic rocks and are likely to reflect eroded volcanic arc rocks. Our “typical” trench sediment composition in Table 3 is similar to that of Plank (2011) for 35°S and 40°S except for Ba. In order to use actual samples for representative values, we used our sample SO210-#5-B for trace elements and sample 75KD(1) from Lucassen et al. (2010) for isotopes. Sample 75KD(1) comes from a bit further south of the studied area but is similar to our sediment data (Electronic Annex: Tables 1 and 2) and is the single best mixing end member to explain TSVZ VA volcanic rocks. Isotopically, our new sediment data and sample 75KD(1) enclose the values chosen by Plank (2011), although her values are more radiogenic than most of our samples. In general, the trench sediments and volcanic rocks are similar in composition, which is not unexpected because the trench sediments at 35–40°S are dominated by turbidites from the Cenozoic magmatic arc delivered through canyons in the continental slope and also contain ash from the volcanic arc. The chief isotopic

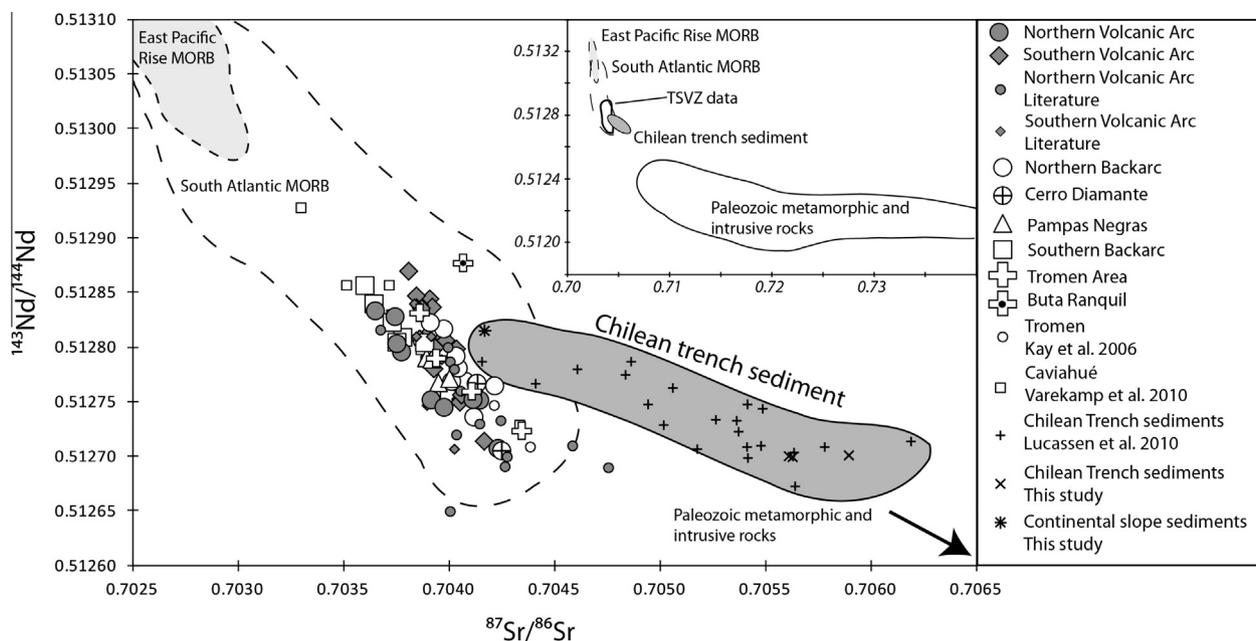


Fig. 5.  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$ . VA and BA samples form two similar negative arrays which overlap almost completely. All samples from this study lie within the South Atlantic MORB field. The BA samples from the three segments (north, central = Pampas Negras, and south = SBA, Trome) have distinct compositions (also see Fig. 12). Trench sediments have similar Nd isotopes ratios as the volcanic rocks but more radiogenic Sr isotopes. The inset shows the TSVZ data (VA and BA) in a larger scale, including the Paleozoic metamorphic and intrusive basement in Chile and Argentina. VA literature data are from Hildreth and Moorbath (1988), Tormey et al. (1995), Davidson et al. (1987, 1988), Hickey et al. (1986), Harmon et al. (1984), and Sigmarsson et al. (1990). BA literature data are from Kay et al. (2006a,b), Kay and Copeland (2006) and Varekamp et al. (2010). Trench sediment data are from this study and Lucassen et al. (2010). Basement data are from Lucassen et al. (2004). East Pacific Rise (20–34°S) MORB data are from Fontignie and Schilling (1991), Haase (2002), Hamelin et al. (1984), Hanan and Schilling (1989), Ito et al. (1980), Ito et al. (1987), Kingsley et al. (2007), MacDougall and Lugmair (1986), Mahoney et al. (1994), Newsom et al. (1986) and White et al. (1987). South Atlantic (30–50°S) MORB data are from Andres et al. (2002), Douglass et al. (1999), Fontignie and Schilling (1996), Hanan et al. (1986) and Roy-Barman et al. (1998).

differences are that the sediments have considerably higher  $\delta^{18}\text{O}$ , ranging from 7.8‰ to 14.1‰, and higher  $^{87}\text{Sr}/^{86}\text{Sr}$  relative to  $^{143}\text{Nd}/^{144}\text{Nd}$ .

## 5. DISCUSSION

Based on the major element data, two distinct magmatic series can be recognized in the TSVZ. The VA is subalkaline (calc-alkaline/medium-Fe) whereas the BA is alkaline with higher Ti, Na, and P (Figs. 2 and 3). Compared to the BA samples, the VA samples have higher fluid mobile (LILE) and lower fluid immobile element (HFSE and heavy REE) contents, and lower ratios of more to less incompatible HFSE and REE (e.g. Nb/Zr, Nb/Y, Nb/Yb, Ta/Yb, Gd/Yb, Tb/Yb) (e.g. Fig. 7c, not all ratios shown). Due to differences in bulk distribution coefficients, these ratios can be fractionated by differing degrees of mantle melting (e.g. Green et al., 2000). In contrast, some elements that cannot be easily fractionated by mantle melting can instead be fractionated by fluids or hydrous melts from the subducted slab. Ratios of fluid-mobile (e.g. LILE) to fluid-immobile (e.g. HFSE and REE) elements (e.g. Ba/Nb, U/Nb, Pb/Ce and Pb/Nd ratios) (e.g. Fig. 7a and b, not all ratios shown) are higher in VA lavas. The variations in these ratios are consistent with a higher fluid flux beneath the VA than the BA, resulting in higher degrees of melting

beneath the VA (e.g. Marianas arc, Elliot et al., 1997; Kelley et al., 2006) to produce the larger volume stratovolcanoes of the VA relative to the isolated fields of cinder cones in the BA, including those on older shield and stratovolcanoes. Although the VA and BA almost completely overlap in Sr, Nd and O isotopic composition, the VA samples have more radiogenic Pb isotopic compositions which overlap the field for Chilean trench sediments, whereas the BA samples have less radiogenic Pb, projecting into the field for South Atlantic MORB. On the Nd versus Hf isotope diagram, the VA and BA form distinct positive linear arrays with the VA samples shifted towards more radiogenic Hf at a given Nd isotopic composition.

We will next discuss possible reasons for the differences between the VA and the BA: assimilation of the continental crust, heterogeneity of the mantle wedge, and the nature of the slab-derived component.

### 5.1. Crustal assimilation

Because the TSVZ overlies 35–45 km thick crust, crustal assimilation is a distinct possibility during magma ascent. In particular, Hildreth and Moorbath (1988) and Tormey et al. (1991) noted an increase in trace element concentrations and Sr–Nd isotopic enrichment of evolved rocks erupted north versus south of 37°S, correlating with an

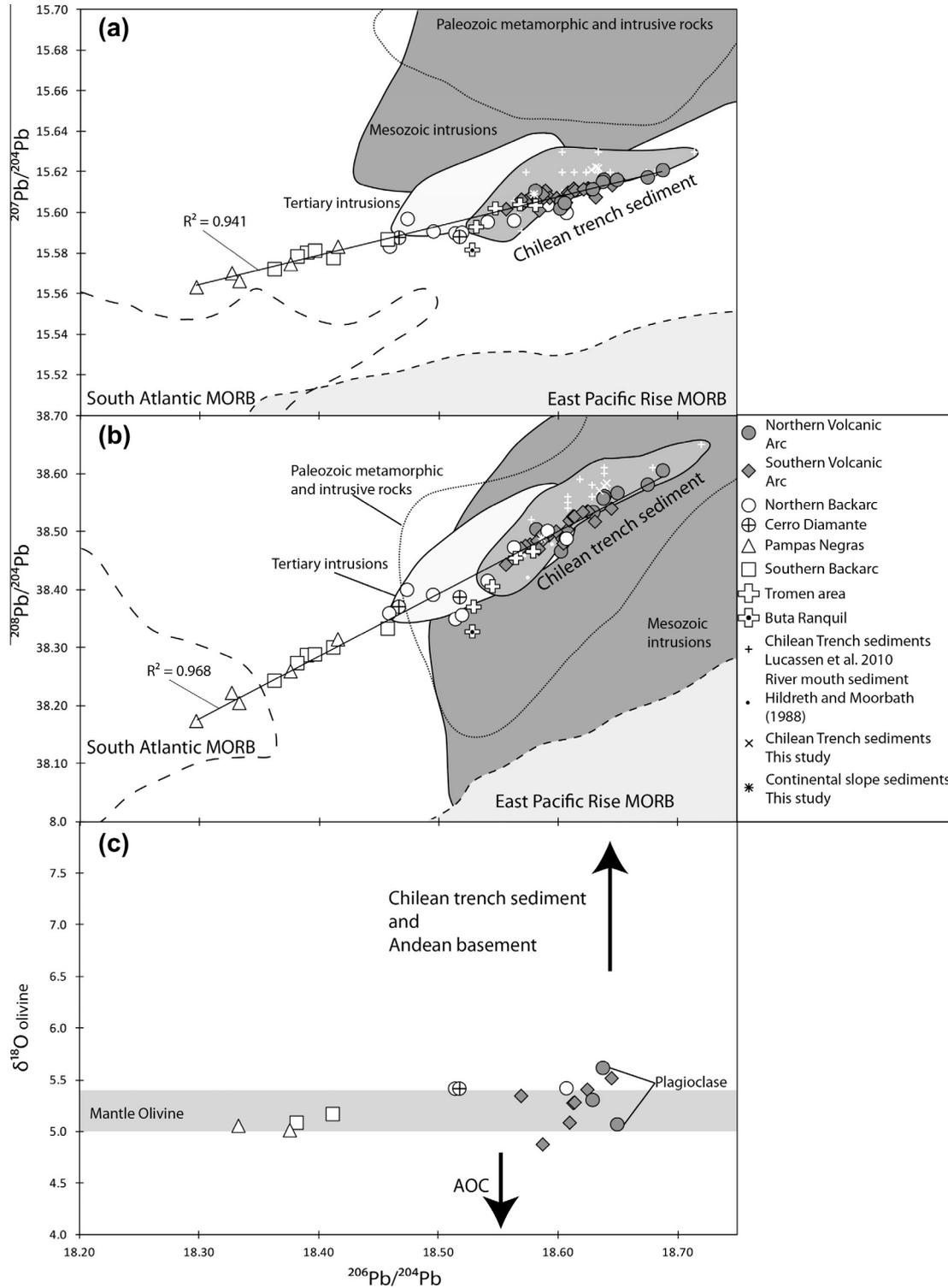


Fig. 6.  $^{206}\text{Pb}/^{204}\text{Pb}$  versus (a)  $^{207}\text{Pb}/^{204}\text{Pb}$ , (b)  $^{208}\text{Pb}/^{204}\text{Pb}$  and (c)  $\delta^{18}\text{O}_{\text{olivine}}$ . The samples form positive arrays from the BA to the VA with good correlations represented by the thin black lines ( $r^2 = 0.941$  and  $0.968$  if the Buta Ranquil sample is excluded). An extrapolation of the arrays intersects the South Atlantic MORB but not the East Pacific Rise MORB field. The trench sediments fall at the radiogenic end of the BA–VA arrays. The Cretaceous to Paleozoic basement fields overlap the data on the thorogenic Pb isotope diagram but have higher  $^{207}\text{Pb}/^{204}\text{Pb}$  on the uraniumogenic Pb isotope diagram. The NBA samples are shifted to lower  $^{207}\text{Pb}/^{204}\text{Pb}$  or more Pacific MORB-like compositions compared to the VA samples. There is no correlation between O isotopes and Pb isotopes. Data sources are the same as in Fig. 5. Trench sediment field includes river mouth sediments from Hildreth and Moorbath (1988).

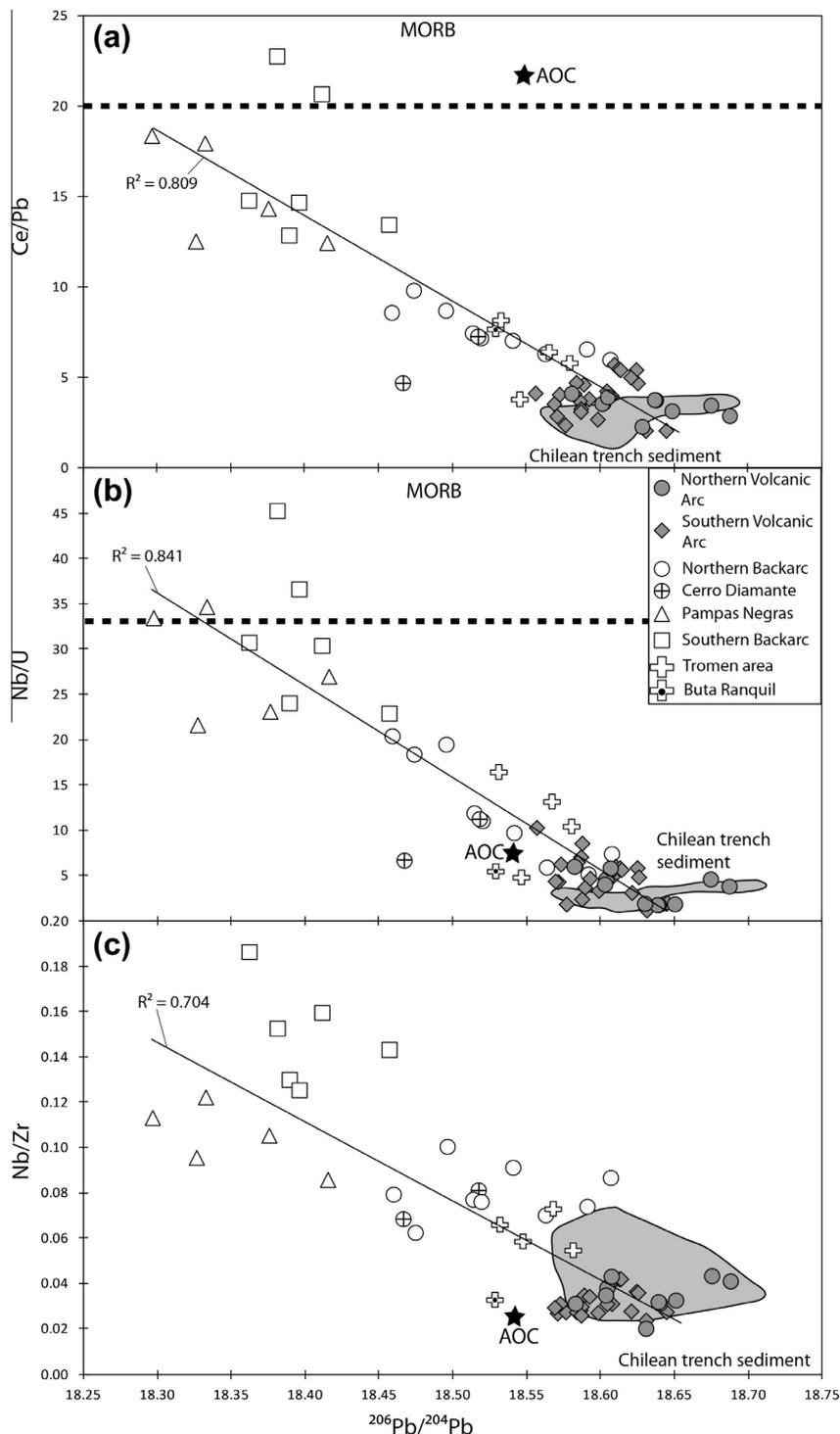


Fig. 7.  $^{206}\text{Pb}/^{204}\text{Pb}$  (a) versus  $\text{Ce}/\text{Pb}$ , (b)  $\text{Nb}/\text{U}$ , and (c)  $\text{Nb}/\text{Zr}$ . The data form good negative correlations for the BA to the VA data ( $r^2 = 0.809, 0.841$  and  $0.704$ , respectively). Two-component mixing must form a straight line when the denominator is the same on both axis as in (a). The VA samples overlap the trench sediment field. The SBA samples extend to higher  $\text{Ce}/\text{Pb}$ ,  $\text{Nb}/\text{U}$  and  $\text{Nb}/\text{Zr}$  than the Pampas Negras basalts which have similar Pb isotope ratios, which we believe reflects source heterogeneity. MORB field is represented by the dashed line box (range in average values for MORB and OIB from Hofmann et al., 1986). Trench sediments are from this study and Lucassen et al. (2010). AOC is from Tollstrup et al. (2010).

increase in crustal thickness to the north, and interpreted this to result from greater degrees of crustal assimilation in the north where the crust is thicker. Studies of single vol-

canoes north of  $37^\circ\text{S}$  also demonstrate that crustal contamination is possible in the more evolved magmas. Tormey et al. (1995) proposed that crustal assimilation played a role

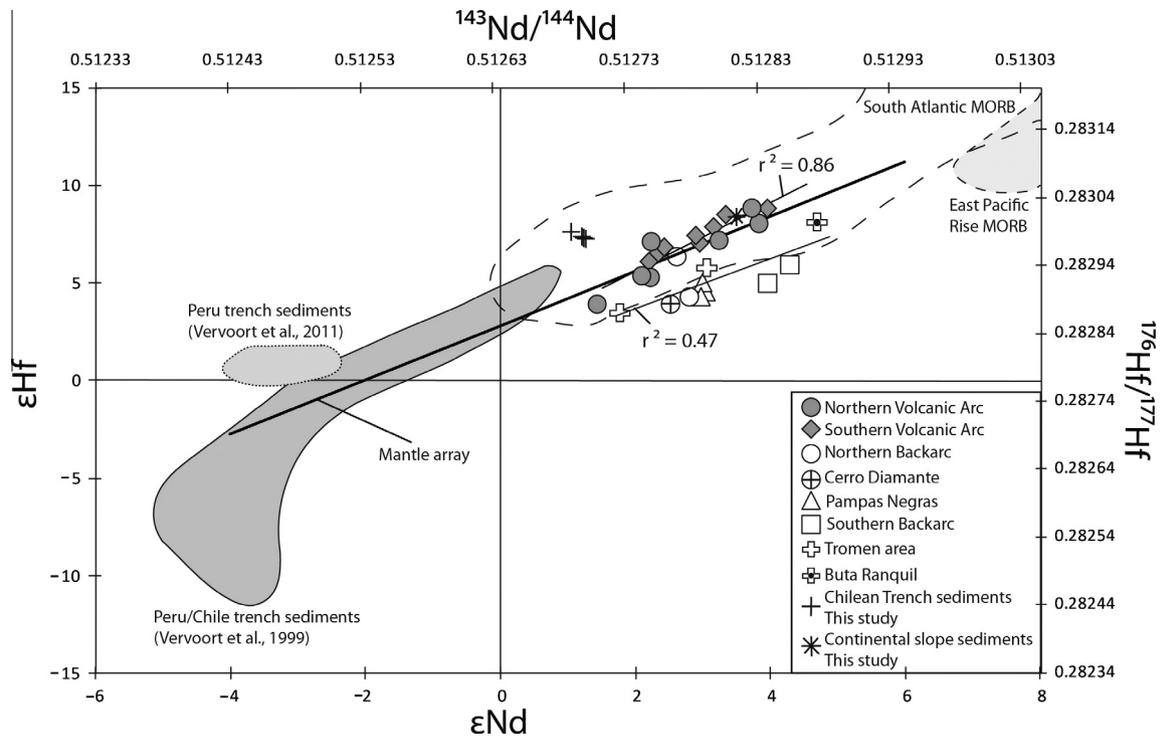


Fig. 8.  $\epsilon\text{Nd}$  versus  $\epsilon\text{Hf}$ . The VA and BA samples form separate subparallel positive correlations with correlation coefficients ( $r^2$ ) of 0.86 and 0.47, respectively. VA samples have higher  $\epsilon\text{Hf}$  than the BA for a given  $\epsilon\text{Nd}$ . The thick black line represents the mantle array (Geldmacher and Hoernle (2006)). Data sources are the same as in Fig. 5. The Peru/Chile trench sediments are from Vervoort et al. (1999) and Vervoort et al. (2011).

in dacitic and rhyodacitic rocks at the Azufre–Planchón–Peteroa complex at the volcanic front, as did Hildreth et al. (2010) for the Laguna del Maule area in the rear arc. Davidson et al. (1987, 1988) studied the Tatara–San Pedro–Pellado complex in detail. They suggested that although the sub-arc asthenospheric mantle was the principle source of basalts, and their LILE enrichments were largely from slab fluids, the more evolved rocks were affected by crustal assimilation during crystal fractionation. Dungan et al. (2001) and Dungan and Davidson (2004) proposed that assimilation of mafic plutonic roots occurs sometimes in San Pedro, primarily affecting the major and trace element contents of the magmas with little effect on the radiogenic isotopic composition. Therefore, it is essential to evaluate if these processes affected the geochemistry of our samples.

We analysed the most mafic of the youngest samples that we could find at each edifice, mostly with olivine phenocrysts, because most studies of the SVZ between 34.5°S and 43°S have concluded that the olivine basalts in the SVZ were not significantly crustally contaminated (e.g. Hickey et al., 1984, 1986; Futa and Stern, 1988; Hickey-Vargas et al., 1989; Sigmarsson et al., 1990; Hickey-Vargas et al., 1989, 2003; Sigmarsson et al., 2002). We also avoided xenocrystic and xenolithic material during sampling and sample preparation. Our VA samples can be divided into a mafic group with  $\text{MgO} > 5 \text{ wt.}\%$  and  $\text{SiO}_2 < 54 \text{ wt.}\%$ , and a differentiated group with lower  $\text{MgO}$  and higher  $\text{SiO}_2$  content. The differentiated group

consists of three samples from Tinguiririca, three from San Pedro, two from Longaví, two from Antuco, one from Callaqui and one from Copahue. There is no difference between the average of mafic and evolved groups in trace element ratios or in any isotope ratio (Fig. 9) and the most-evolved high-K calc-alkalic Tinguiririca samples do not have the highest Sr or lowest Nd isotope ratios (Figs. 5 and 9b and c). Neither the VA nor BA shows systematic variations with  $\text{SiO}_2$  or  $\text{MgO}$  (not shown). Due to the high Pb concentrations in most crustal rocks, Pb isotopes are a very sensitive indicator of crustal assimilation. The end member VA samples, with the most radiogenic Pb isotope ratios, fall below (have lower  $^{207}\text{Pb}/^{204}\text{Pb}$  than) all basement rocks with similar  $^{206}\text{Pb}/^{204}\text{Pb}$  on the uraniumogenic Pb isotope diagram (Fig. 6a; basement data from Lucassen et al., 2004; 36–41°S). Since neither the VA nor BA end member falls within the fields for the crustal basement rocks, the very tight correlations in our high-precision Pb isotope ratios preclude significant crustal assimilation having affected any of these samples. Furthermore, there is no correlation between any isotope ratio and  $\delta^{18}\text{O}$  (for example, Figs. 6c and 13). Thus, radiogenic isotopes show no evidence of crustal assimilation of older basement rocks, even in the andesites.

Variations in O isotope values in volcanic rocks can be used to constrain the amount of assimilation of isotopically diverse components (e.g. Bindeman, 2008). However, the  $\delta^{18}\text{O}_{\text{olivine}}$  in the volcanic rocks from the VA overlap the range of mantle olivine (5.0–5.4‰, Matthey et al., 1994)

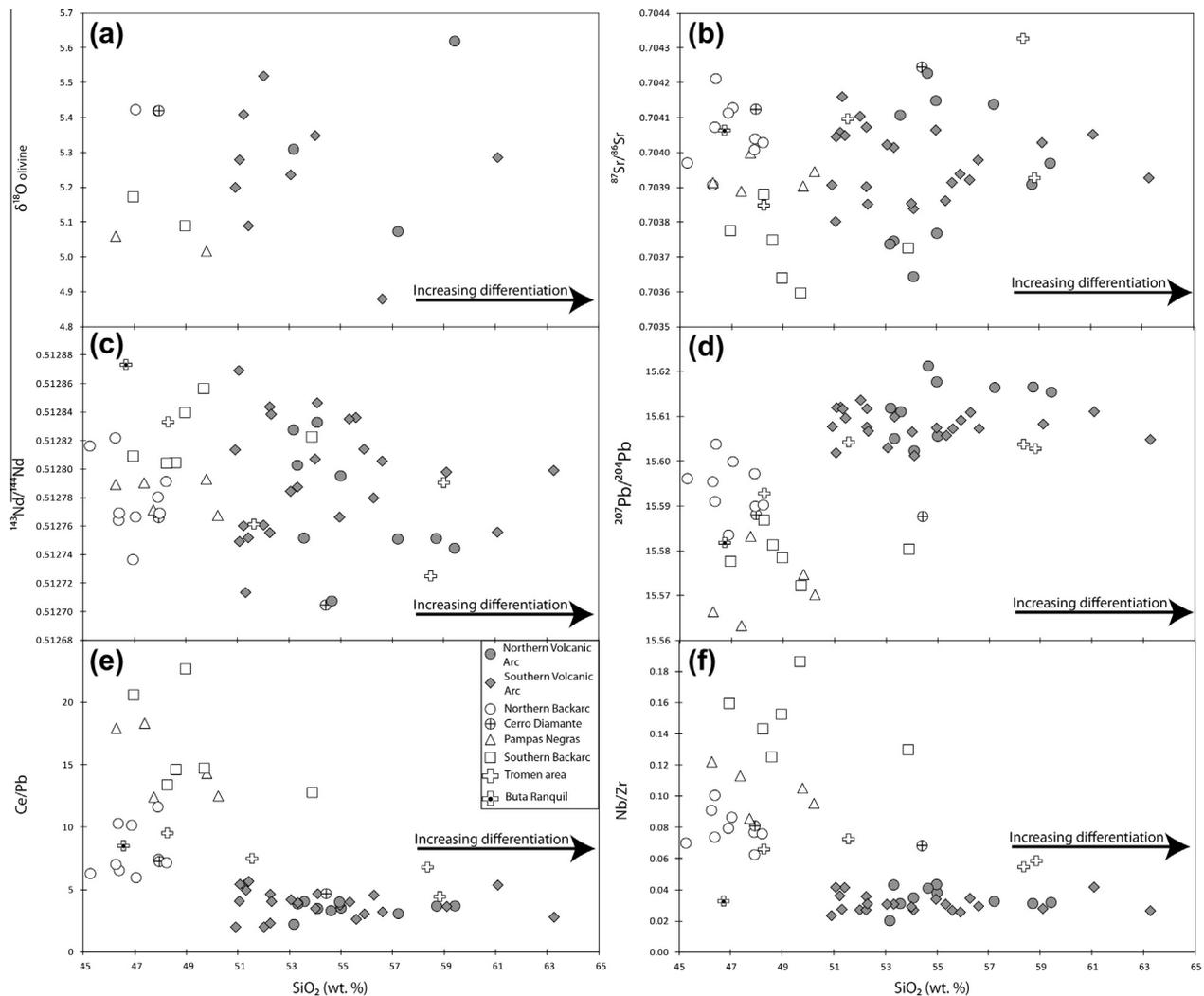


Fig. 9.  $\text{SiO}_2$  versus (a) Ce/Pb, (b) Nb/Zr, (c)  $^{87}\text{Sr}/^{86}\text{Sr}$ , (d)  $^{143}\text{Nd}/^{144}\text{Nd}$ , (e)  $^{207}\text{Pb}/^{204}\text{Pb}$  and (f)  $\delta^{18}\text{O}_{\text{olivine}}$ . There is no clear correlation for the VA or BA samples between  $\text{SiO}_2$  and isotopes or trace element ratios used in this paper indicating that assimilation of old sialic crust during differentiation does not significantly modify these isotopes and trace element ratios in our samples.

and extend to only slightly higher values (5.5‰ if the most evolved sample is excluded) and lower values (4.9‰) (Fig. 6c), which could reflect slightly variable contributions from lower  $\delta^{18}\text{O}$  subduction fluids from the lower oceanic crust, or higher  $\delta^{18}\text{O}$  subduction melts from the seawater-altered upper crust (e.g. Bindeman et al., 2005; Martin et al., 2011). The BA samples (5.02–5.42‰) are within the mantle range. In both the VA or BA samples,  $\delta^{18}\text{O}$  ratios do not correlate with indices of differentiation (for example  $\text{SiO}_2$ , Fig. 9a) or other isotope ratios, such as  $^{207}\text{Pb}/^{204}\text{Pb}$  (not shown), which are discriminatively higher in Andean basement rocks (Lucassen et al., 2004, Fig. 6). Moreover,  $\delta^{18}\text{O}$  values are within the typical range for subduction zone volcanic rocks lacking other evidence for crustal assimilation (e.g. Central America: see Heydolph et al., 2012). They are also within the range for oceanic arcs where there is less potential for crustal assimilation. The Mariana arc has whole rock  $\delta^{18}\text{O}$  values between 5.5‰ and 6.6‰ (Wade et al., 2005), and Tonga arc values are between 5.6‰ and 6.8‰ (Ewart and Hawkesworth, 1987; Vallier

et al., 1991; Turner et al., 2009). We corrected our VA phenocryst  $\delta^{18}\text{O}$  values to equilibrium melt following Bindeman et al. (2004) who calculate the  $\Delta(\text{min.-melt})$  based on the  $\text{SiO}_2$  content of the whole rock. This correction, however, needs to be applied with caution, since the linear equation is based on the liquid line of descent for Kamchatka magmas. If the liquid line of descent of the Andean magmas is different, it can decrease or increase the  $\Delta(\text{min.-melt})$  and therefore change the range in  $\delta^{18}\text{O}$ . Our corrected VA phenocryst  $\delta^{18}\text{O}$  values yield a similar average range of 5.9–6.6‰ (excluding the most evolved sample CL 576 with  $\delta^{18}\text{O}$  melt of 7.1) (Electronic Annex: Table 2). It has been proposed that whole rock  $\delta^{18}\text{O}$  up to  $\sim 6.6\text{‰}$  can be inherited from a slab component (Eiler et al., 2005) or metasomatized mantle containing pyroxenitic veins from earlier arc volcanism (Heydolph et al., 2012), or a preexisting subduction enrichment (Auer et al., 2009; Martin et al., 2011).

The low  $\delta^{18}\text{O}$  value for CL 531 from Longaví (4.88‰) could be explained by assimilation of hydrothermally altered mafic rocks, such as in the lower crust (with

Table 3

Sediment (SED), altered oceanic crust (AOC) and depleted MORB Mantle (DMM) compositions used for the Arc Basalt Simulator 3 calculations. South Atlantic MORB – depleted (SAM-D) – enriched (SAM-E). (\*) See Table 4 for values used in calculation of the slab melt composition.

	AOC	SED	Slab melt 60SED:40AOC(*)	SAM-D DMM	SAM-E E-DMM
Rb	13.7	44.7	16.7	0.050	0.108
Ba	15.6	1238	1286	0.563	1.22
Th	0.173	5.70	5.64	0.008	0.016
U	0.390	3.21	3.48	0.003	0.005
Nb	2.89	4.63	1.01	0.149	0.246
Ta	0.210	0.350	0.081	0.010	0.016
K	5147	17483	6476	80.0	120
La	3.40	13.5	11.0	0.192	0.253
Ce	11.4	32.4	31.7	0.550	0.726
Pb	0.437	17.5	18.7	0.018	0.024
Pr	2.06	3.93	4.15	0.107	0.132
Sr	109	257	311	7.66	9.72
Nd	11.3	16.3	16.8	0.581	0.703
Sm	3.95	3.65	2.72	0.239	0.273
Zr	112	123	84.4	5.08	6.09
Hf	3.00	3.40	2.36	0.157	0.186
Eu	1.34	0.905	0.614	0.096	0.108
Gd	5.55	3.51	1.58	0.358	0.397
Tb	1.01	0.547	0.164	0.070	0.076
Dy	6.56	3.32	0.750	0.505	0.543
Y	40.7	18.1	3.15	2.66	3.55
Ho	1.43	0.674	0.112	0.115	0.123
Er	4.09	1.88	0.290	0.348	0.369
Tm	4.02	0.290	0.141	0.055	0.055
Yb	0.636	1.97	0.110	0.365	0.382
Lu	3.07	0.298	0.081	0.058	0.060
<sup>87</sup> Sr/ <sup>86</sup> Sr	0.704769	0.705637	0.705480	0.703300	0.704200
<sup>143</sup> Nd/ <sup>144</sup> Nd	0.513153	0.512673	0.512946	0.512940	0.512690
<sup>206</sup> Pb/ <sup>204</sup> Pb	18.54	18.71	18.71	18.15	18.25
<sup>207</sup> Pb/ <sup>204</sup> Pb	15.45	15.63	15.63	15.54	15.55
<sup>208</sup> Pb/ <sup>204</sup> Pb	37.70	38.65	38.64	38.00	38.10
δ <sup>18</sup> O (‰)	2	9	6.2	5.25	5.25

δ<sup>18</sup>O = 0–6‰, Bindeman et al., 2005, and references therein), as proposed by Dungan and Davidson (2004) for San Pedro. Our samples from San Pedro do not have low δ<sup>18</sup>O<sub>olivine</sub>, however. Alternatively, the low δ<sup>18</sup>O at Longaví could possibly reflect the derivation of fluids from serpentinite associated with the Mocha Fracture Zone subducting beneath Longaví.

In summary, our isotope data show no clear evidence that assimilation of old sialic crust affected our TSVZ basalt to andesite samples. Even if there was assimilation of the mafic roots of the volcanoes in some of our more differentiated samples, it would only add potential for sampling greater Sr–Nd–Hf–Pb isotope mantle heterogeneity throughout the Cenozoic in the vicinity of the volcanoes, and would not affect our conclusion that the primary isotopic diversity comes from the mantle, not the sialic crust.

## 5.2. The mantle wedge and subcontinental lithosphere

BA basalts have less subducted component signature in their trace element abundance patterns (Fig. 4b) than the VA samples and are displaced the most from sediment in their Pb isotopic compositions (Fig. 6a and b). Indeed,

those from the southern and central BA extend to MORB–OIB (Ocean Island Basalt) Ce/Pb, Nd/Pb, Nb/U, and Nb/Th ratios (Hofmann et al., 1986) with little if any evidence for slab-derived Pb, U or Th (Figs. 7a,b and 10 and 11). Therefore, we propose that BA basalts in general, and the SBA and Pampas Negras basalts in particular, best represent the geochemical character of the TSVZ BA mantle source.

On the uraniumogenic Pb isotope diagram (Fig. 6a), the BA array lies above the Pacific MORB field. An extension of the BA trend does not intersect the Pacific MORB field but does intersect the enriched part of the South Atlantic MORB field, which has elevated <sup>207</sup>Pb/<sup>204</sup>Pb at <sup>206</sup>Pb/<sup>204</sup>Pb between 17.6 and 18.2. Consequently, the BA mantle source has South Atlantic rather than East Pacific Rise affinity. This is in agreement with the work of Husson et al. (2012) that modelled the flow of South Atlantic mantle beneath South America. They modelled westward mantle convection beneath South America as a counterflow above the subducting Nazca plate. Therefore, this convection brings South Atlantic Ridge mantle beneath the Andes.

Many of our BA basalts, and especially those from the SBA and Pampas Negras, are enriched in HFSE with

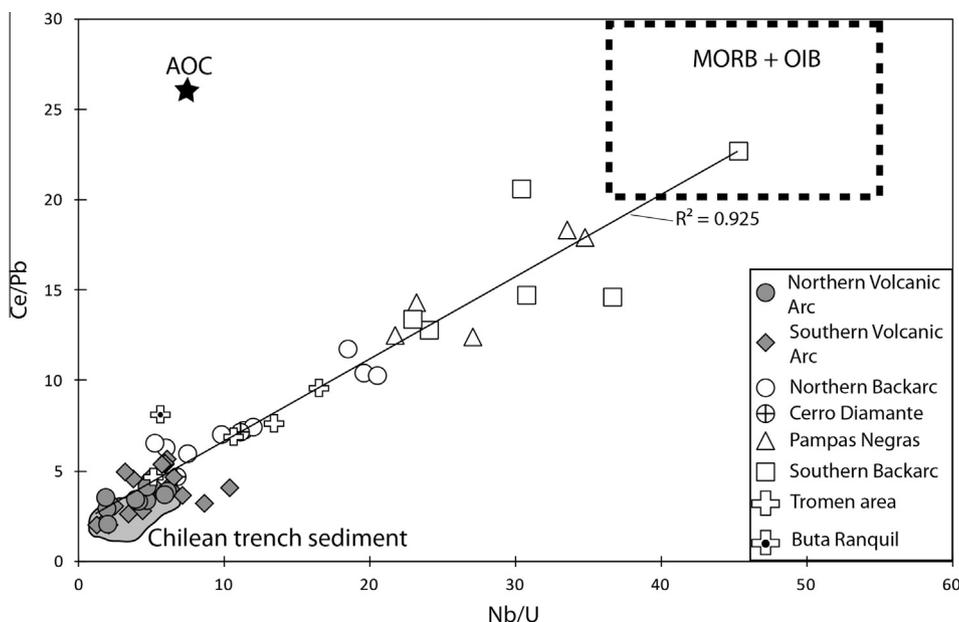


Fig. 10. Nb/U versus Ce/Pb. The VA and BA samples form an array from the trench sediments field to the MORB–OIB mantle field represented by the dashed line box (range in average values for MORB and OIB from Hofmann et al., 1986). The correlation ( $r^2 = 0.925$ ) indicates the presence of variable amounts of a uniform slab component in all samples, but least at the SBA and Pampas Negras. Trench sediments are from this study and Lucassen et al. (2010). AOC is from Tollstrup et al. (2010).

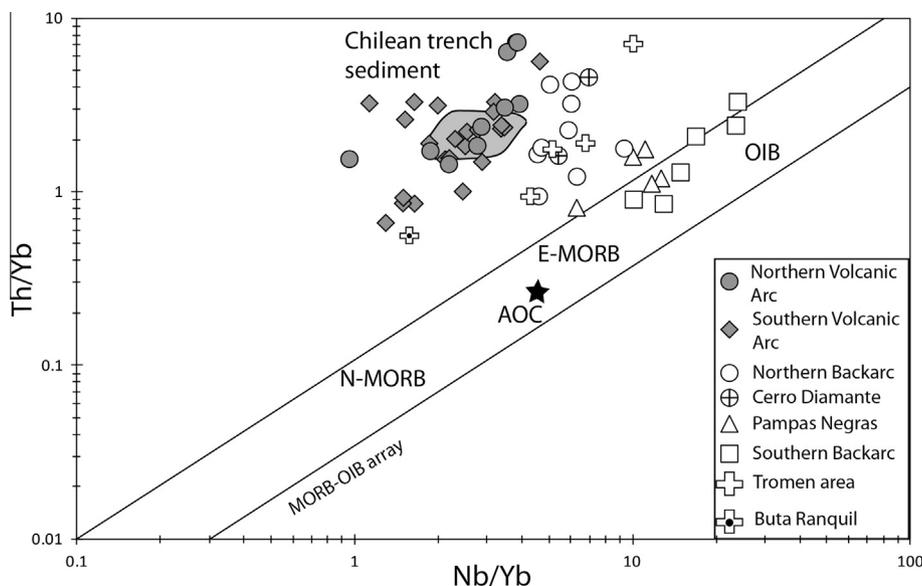


Fig. 11. Nb/Yb versus Th/Yb, after Pearce (2008). MORB and OIB define the positive trend labeled MORB–OIB array, reflecting greater mantle enrichment at higher ratios. VA and NBA samples lie above this array due to the addition of a Th-bearing slab component whereas most BA samples from Pampas Negras and the SBA lie within the mantle array or straddle its boundary and therefore lack slab-derived Th. The VA samples overlap, but show a larger range, than the trench sediments (grey field). Data sources are the same as in Fig. 10.

Nb/Yb > 10, like alkalic OIB (Fig. 11), and plot beneath the field for South Atlantic MORB on the Hf versus Nd isotope ratio diagram (Fig. 8). Therefore, the TSVZ BA mantle may contain OIB or EMORB-type components. In contrast, VA basalts have lower Nb/Yb (Fig. 11) and Nb/Zr (Fig. 7c) indicating that the VA mantle source is more depleted, or has experienced higher degrees of melting or both, than the BA source. Increasing source depletion

closer to the VA may reflect progressive extraction of small degree melts as a result of corner flow in the mantle wedge (Hochstaedter et al., 2001). Increasing percent melting beneath the VA is consistent with a higher mass fraction of slab flux there.

The Sr and Nd isotopes of most VA and BA basalts lie within the enriched portion of the South Atlantic MORB (SAM) field (Fig. 5). In detail, those from the SBA and

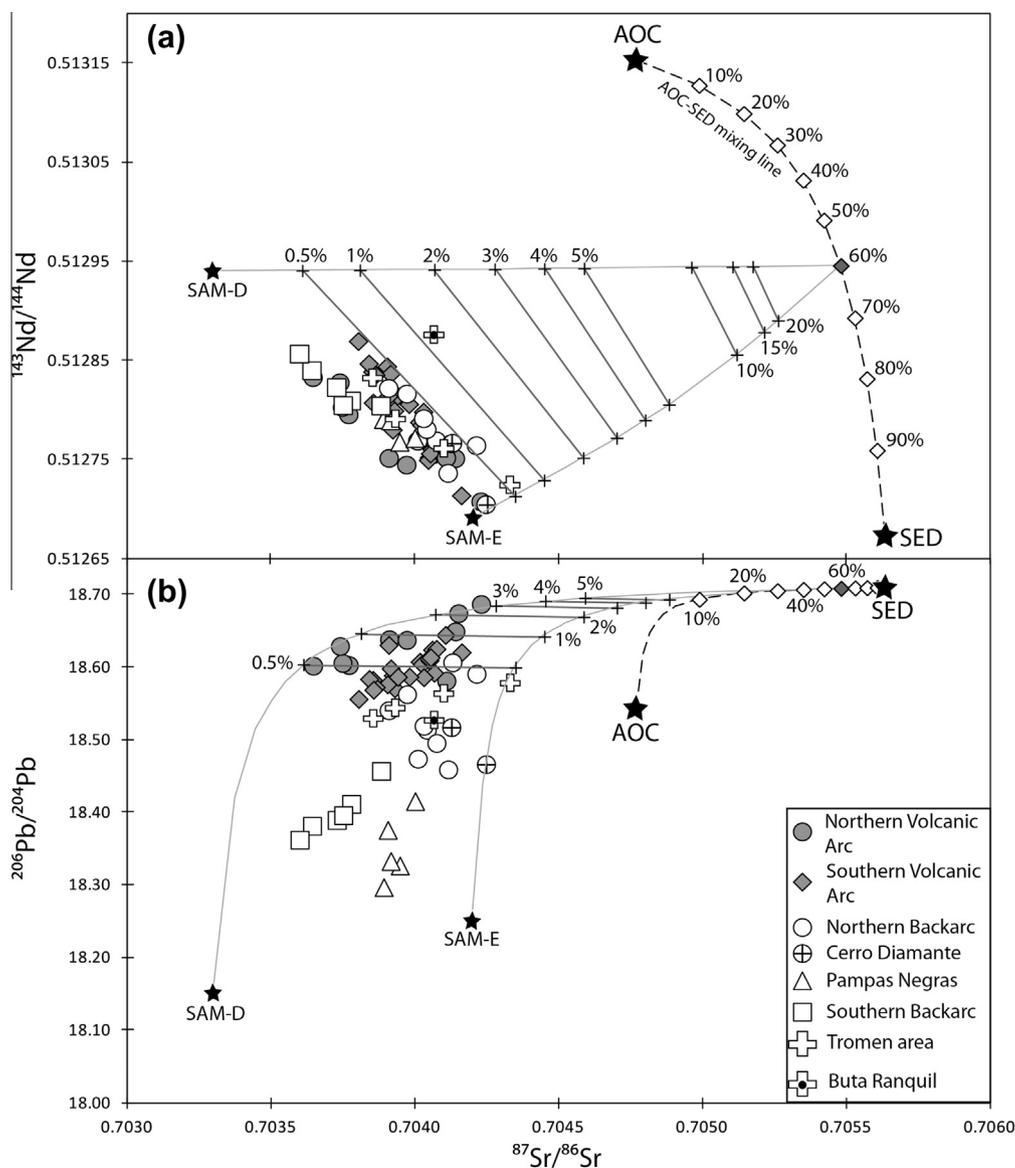


Fig. 12. (a)  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$  and (b)  $^{206}\text{Pb}/^{204}\text{Pb}$ . The mixing lines are from the Arc Basalt Simulator 3.10 models for the VA. The dashed line represents mixing between altered oceanic crust (AOC) and sediment (SED). The thin lines represent mixing between a melt of a 60:40 SED:AOC source with South Atlantic MORB, and depleted (SAM-D) or enriched (SAM-E) mantle (the two stars). The labeled tick marks show the amount of slab component added to the mantle. Source compositions are in Table 3. Slab and mantle melting conditions are described in the text and summarized in Table 4. For partition coefficients and melting modes for the slab and mantle see Kimura et al. (2010). AOC is from Tollstrup et al. (2010).

Pampas Negras (36–38°S), which show no evidence for the addition of slab-derived Th (Fig. 11) and little addition of U and Pb (Fig. 7a and b), span a range of Sr and Nd isotopes that we attribute to the mantle source. These rocks form a negative array on the Sr–Nd isotope diagram and plot at the left edge of the TSVZ VA field, having less radiogenic  $^{87}\text{Sr}/^{86}\text{Sr}$  at a given  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope ratio. Basalts from the Resolana and Los Hornos cones near Cerro Azul and from Tinguiririca in the northern VA (34.5–36°S) overlap the range for the southern BA lavas, excluding the Buta Ranquil sample. Therefore, the TSVZ mantle is heterogeneous in Sr and Nd, and contains both depleted (SAM-D) and enriched (SAM-E) components (Fig. 12a).

Although VA and BA samples overlap almost completely on the Sr–Nd isotope diagram (Fig. 5), the same is not true for Pb (Fig. 6a and b) or Hf isotope ratios (Fig. 8). This can be seen most easily by combining Sr and Pb isotope ratios (Fig. 12b), where the northern and southern VA groups, the central and southern BA groups, and perhaps even NBA samples seem to define different mixing trends between a slab component (trench sediment ± altered oceanic crust (AOC)) and variable mantle components. The northern and southern VA groups could be derived through mixing of the same end members (slab component + SAM-D) with different Pb/Sr ratios in one or both of the end members, or through mixing of slab

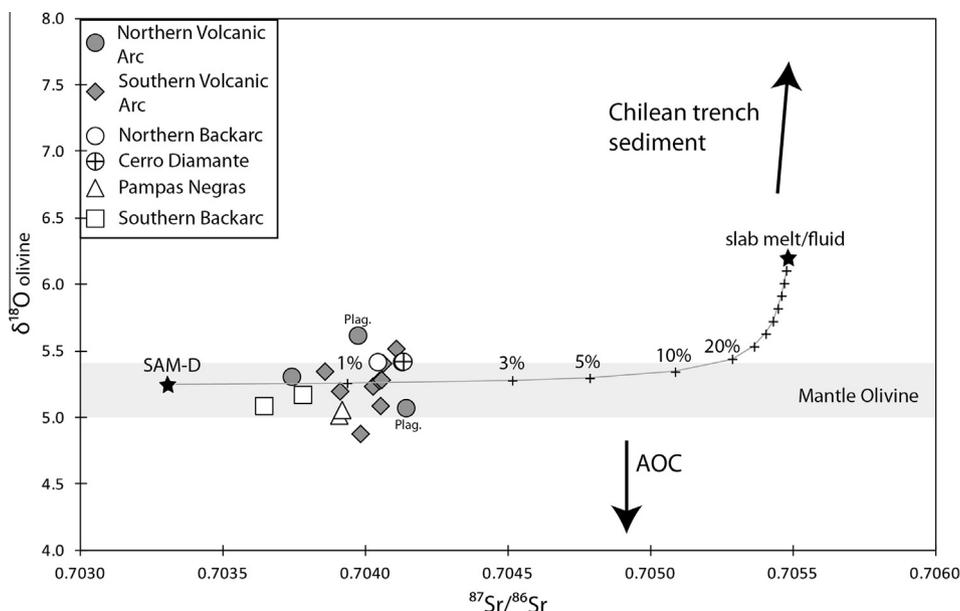


Fig. 13.  $\delta^{18}\text{O}_{\text{olivine}}$  versus  $^{87}\text{Sr}/^{86}\text{Sr}$ . The mixing lines are from the Arc Basalt Simulator 3.10 models for the VA. The thin line represents the mixing between a slab component of 60:40 SED:AOC source on one hand and depleted (SAM-D) mantle (stars) on the other. The labeled tick marks show the amount of slab component added to the mantle. Source compositions are in Table 3. The isotope ratios of the slab component (60% SED and 40% AOC) are calculated from the data in Table 3.

and/or mantle components with slightly different compositions. The BA groups require a spatially heterogeneous mantle source with the addition of less slab component than at the VA. The SBA and Pampas Negras mantle end members most closely approximate the SAM-D and SAM-E components, respectively.

This explanation, however, does not easily apply to the variation between Hf and Nd isotopes. The VA and BA groups define subparallel and offset positive correlations between Hf and Nd isotopes (Fig. 8). Within the VA, the depleted end (with highest Nd and Hf ratios) consists of the Resolana/Los Hornitos cones that have the least radiogenic Sr and most radiogenic Nd isotope ratios and are the closest to the depleted mantle component (SAM-D in Fig. 12). The more enriched VA samples do not lie on a mixing line between the depleted end and trench sediment as is the case on the  $^{87}\text{Sr}/^{86}\text{Sr}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  isotope diagram (Fig. 12b). Instead they define a mixing array slightly steeper than the mantle Hf–Nd array (Geldmacher and Hoernle, 2006) such as observed in South Pacific backarc basalts (Todd et al., 2011). This mixing array is most easily explained by mantle heterogeneity. The completely offset BA Hf–Nd array is without precedent in subduction zones to our knowledge. Apart from Central America where some BA samples also plot beneath the VA array (Heydolph et al., 2012), in no other arc do VA and BA samples define separate subparallel trends. All of these BA basalts have typical mantle Hf/Nd concentration ratios. The more depleted end of the BA Hf–Nd isotope array (SBA) also extends to the lowest Sr and Pb isotope ratios. The more enriched end of the BA array (NBA and Tromen) is not offset toward subducting sediment in Nd and Hf isotopes. We

think that the BA Hf–Nd trend also reflects mixing between depleted and enriched mantle components. Because the BA array is without precedent in oceanic arcs and lies below the field of South Atlantic MORB, we believe that both of its mantle components may lie within South American Proterozoic subcontinental lithosphere. Similarly low Hf with respect to Nd isotopes have been observed within continental basalts and attributed to mixing between components in subcontinental lithospheric mantle elsewhere (e.g. Zhang et al., 2009).

The restricted and mantle-like range in  $\delta^{18}\text{O}$  (5.0–5.4‰) of the BA rocks suggests a source within the sub-continental lithospheric mantle. Its enriched end member may be the EM1-type mantle identified by Varekamp et al. (2010) in the Loncopue graben (37.5–39°S, Neuquén, Argentina) that they also attributed to the subcontinental lithospheric mantle. The difference in Nb/Yb ratios between BA and VA could reflect trenchward advection and depletion of asthenospheric mantle but could also reflect a contrast between VA melts primarily derived from the asthenosphere versus BA melts that are in part from subcontinental lithospheric mantle beneath the BA. The latter may exist as delaminated old heterogeneities with lower solidi that melt out as mantle advects trenchward (Hochstaedter et al., 2001).

We also note the inconsistent correlation between trace element and isotope ratio measures of mantle enrichment and depletion. Nb/Yb and Nb/Zr ratios form crude positive correlations with  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  in the BA basalts (not shown), opposite to what is generally observed for the mantle (e.g. Douglass, 2002; Andres et al., 2002; Kinglsey, 2002; Kinglsey et al., 2007). Therefore, melting effects are superimposed on source effects within

the BA basalts. The SBA basalts are farthest from the VA and reflect the lowest percent melting, because the amount of slab component fluxing is least.

Kay et al. (2004, 2005, 2006a,b), Kay and Copeland 2006, and references therein) proposed that magmatism in the southern Mendoza and Neuquén provinces (which overlap and extend further south than our BA area) resulted from melting of hydrated mantle after two temporary flat subduction episodes in the late Miocene that moved the volcanic front eastward and produced large stratovolcanoes like Tromen and Cerro Diamante. The NBA and Tromen groups exhibit more arc affinities than the rest of our BA samples by: (1) having greater positive anomalies in fluid-mobile elements (Pb, K) and negative anomalies in HFSEs (Nb, Ta), (2) plotting closest to the VA in the Ce/Pb versus Nb/U diagram (Fig. 10), (3) plotting above the mantle array and close to the VA on the Nb/Yb versus Th/Yb diagram (Fig. 11), (4) having higher La/Ta, Ba/Ta and Th/Hf ratios than the other BA rocks which are most similar to the VA, and (5) having Pb isotope ratios most similar to the VA rocks. This could reflect residual slab components in the lithospheric mantle and/or crust beneath this part of the BA left over from when it was near the VA in the late Miocene/Early Pliocene, or more current input of slab components beneath these parts of the BA. The addition of Paleozoic crust to the mantle wedge as a result of forearc erosion in the late Miocene (Kay et al., 2005) cannot explain the more arc-like composition of the NBA because the addition of Paleozoic metamorphic or igneous crust would increase  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios in the NBA, yet they tend to be lower (not higher) at a given  $^{206}\text{Pb}/^{204}\text{Pb}$  compared to the VA and other BA basalts (Fig. 6a).

### 5.3. The slab component

In general, fluids and/or melts can be produced by dehydration and/or melting of the slab during subduction beneath the VA and BA. Possible slab sources include the sediments, AOC, and the underlying lithospheric mantle that may have been serpentized at bend faults and/or fracture zones. In this section we will attribute features that cannot otherwise be accounted for by crustal assimilation or mantle heterogeneity to a slab-derived component, and explore the nature of that component.

#### 5.3.1. Sources of the slab component

The incompatible element ratios of trench sediments almost completely overlap those of VA volcanic rocks in part because the former are almost entirely derived from the latter. Nonetheless, their similarity in Fig. 4a means that the currently subducting sediments may be responsible for the trace element pattern of the currently erupting magmas. Pb isotopes confirm this observation because most of the Pb in the volcanic rocks is from the slab component. On both the uranogenic and thorogenic Pb isotope diagrams (Fig. 6a and b), the TSVZ data form excellent positive correlations ( $r^2 = 0.94$  and  $r^2 = 0.97$ , respectively, if the Buta Ranquil sample is excluded), with the VA samples falling at the radiogenic end of the Pb isotope arrays and covering most of the sediment range in  $^{206}\text{Pb}/^{204}\text{Pb}$ . Therefore, most

of the fluid-mobile Pb must come from the sediment. This is confirmed by the overlap between VA and sediment in Fig. 7.

However, there is permissive evidence that some of the Pb also comes from the AOC slab component. The most radiogenic VA samples plot at the base of or just below the sediment field, suggesting that some of the Pb comes from an AOC component with lower  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ . We cannot constrain this tightly because of uncertainty in the Pb isotopic composition of all components and the circularity of argument about whether the sediments control the VA magmas or vice versa. However, the subducting crust is from the East Pacific Rise and should have a composition similar to Pacific MORB. Therefore more oceanic crust in the slab component will decrease its  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  relative to  $^{206}\text{Pb}/^{204}\text{Pb}$  ratios. This argument takes advantage of the difference in Pb isotopes between the subducting altered oceanic crust (Pacific-type) versus mantle wedge (South Atlantic-type) sources. The NBA samples have lower  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios than VA samples with similar  $^{206}\text{Pb}/^{204}\text{Pb}$ , suggesting a greater AOC slab component in these lavas than in the VA. The Buta Ranquil sample near Tromen may have the most AOC slab component which could explain the high  $^{143}\text{Nd}/^{144}\text{Nd}$  isotope ratio on Fig. 5 and why this sample has the lowest  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  at a given  $^{206}\text{Pb}/^{204}\text{Pb}$ . This sample also plots closer to the AOC end member on Figs. 7, 10 and 11 than do the other NBA and Tromen samples.

Other isotopes are more ambiguous because of the extensive overlap between the mantle and trench sediments. Although Sr and Nd isotopes for a few samples from the northern VA lie within the field defined by BA samples with the least evidence of a slab component (SBA and Pampas Negras), most are displaced to higher Sr but not lower Nd ratios (Fig. 5, 12a). This kind of offset is consistent with both elements being derived in part from AOC as well as sediment, and a higher mass fraction of slab component at the VA (Fig. 12b).  $\delta^{18}\text{O}_{\text{olivine}}$  is virtually constant across the range of Sr and Pb isotopes (e.g. Figs. 6c and 13), indicating that variation in Sr and Pb isotope ratios in rocks as mafic as ours reflects source mixing between depleted upper mantle and an enriched component, such as sedimentary material or fluids/melts from subducted sediments, rather than crustal assimilation.

Hf–Nd isotopes are not helpful in this regard, because there is so much variation within the mantle and the general immobility of Hf and to a lesser extent Nd in most slab components. However, all analyses of Chilean trench sediments from 35–40°S have  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios overlapping those of the arc, none of the arc rocks are offset toward a more pelagic sediment composition, and a mixture of sediment and AOC may lie within the Hf–Nd VA array. Neither VA nor BA samples define the steep positive correlation between  $^{176}\text{Hf}/^{177}\text{Hf}$  and LREE/Hf ratios that is common in oceanic arcs and can be attributed to addition of LREE > Hf in the slab component (e.g. Todd et al., 2011).

In conclusion, Pb, Sr, and Nd isotopes are most easily explained by mixing with a slab component that includes a significant mass fraction of AOC as well sediment.

### 5.3.2. Nature of the slab component: solid, fluid, or melt?

The slab component could be added to the overlying mantle wedge via subduction erosion, a fluid derived from the dehydration of the slab (e.g. Elliot et al., 1997), or a melt if the slab temperature exceeds the solidus of sediment (e.g. van Keken et al., 2011) and/or AOC (e.g. Tollstrup et al., 2010). In the previous section, we argued that the Pb isotope data rule out subduction erosion of Paleozoic or older crust. Therefore, fluids and/or melts from the subducting slab, or from a solid diapir carrying sediments and possibly some AOC from the subducting slab (e.g. Hall and Kincaid, 2001; Behn et al., 2011), probably carry the slab component into the mantle wedge beneath the TSVZ. The VA and BA volcanic rocks display an excellent positive correlation between Nb/U and Ce/Pb ( $r^2 = 0.93$ ), extending from average MORB and OIB values of 45 for Nb/U and 25 for Ce/Pb (Hofmann et al., 1986) in the BA to values of 1 for Nb/U and 2 for Ce/Pb in the VA, which overlap values for trench sediments (Fig. 10). The correlation suggests that two components dominate the geochemistry of the TSVZ rocks: a homogeneous slab component rich in fluid-mobile elements, such as Pb and U, and a decompressive partial melt of the mantle wedge that has the usual mantle values for these ratios.

The slab component must also contain Th and LREE, because all VA and NBA samples are displaced above the usual MORB–OIB array in Nb/Yb versus Th/Yb (Fig. 11) and La/Yb diagrams (not shown). This rules out a fluid slab component, because Th and LREE partition strongly into the liquid component only at temperatures above the AOC or sediment solidus (Johnson and Plank, 1999; Kessel et al., 2005). Partial melts, on the other hand, can fractionate and transport Th and LREE (Kessel et al., 2005). Moreover, the VA samples overlap the trench sediment in Nb/Yb and extend to higher Th/Yb and La/Yb ratios, which means that the slab component is preferentially enriched in Th and La relative to Yb. Therefore, melting involving equilibrium with minerals such as garnet is required.

Pb isotope ratios (e.g.  $^{206}\text{Pb}/^{204}\text{Pb}$ ) form good inverse correlations with Nb/Zr ( $r^2 = 0.70$ ), Nb/U ( $r^2 = 0.84$ ), Ce/Pb ( $r^2 = 0.81$ ), and Nb/Ba ( $r^2 = 0.75$ ) (Fig. 7, not all ratios shown). Although the latter correlations could be explained by adding a slab-derived fluid to the mantle, it is unlikely that fluid can transport enough Zr to explain the correlation. Instead, we attribute the variation to mixing with a slab-derived melt.

We noted earlier that the Mocha Fracture Zone may project under Longaví. We looked for evidence of greater than usual slab component at Longaví that might result from greater slab hydration at the fracture zone, as proposed by Sellés et al. (2004). However, we found no such evidence. Typical fluid-mobile to fluid-immobile trace elements ratios (e.g. U/Th, Pb/Ce, Ba/Nb, not shown) are relatively constant along this portion of the arc.

In summary, we conclude that the slab component is a melt of both trench sediment and AOC that it is homogeneous throughout the TSVZ, and that it is ubiquitous at the VA but less and variable in the BA – most in the NBA and Tromen and least at the SBA. The slab surface temperature beneath the TSVZ VA has been inferred to

be  $\sim 830$  °C (van Keken et al., 2011), which is only hot enough to melt AOC and sediment at the depth of the slab beneath the VA under water saturated conditions (Hermann and Spandler, 2008; Klimm et al., 2008). This conclusion is true for most subduction zones and requires a ubiquitous source of water external to any remaining hydrous minerals in the sediment or AOC themselves. Serpentinite in the underlying subducting mantle, possibly produced during bend-faulting at the outer rise (e.g. Rüpke et al., 2002; Ranero et al., 2003; Rüpke et al., 2004; Contreras-Reyes et al., 2007; Grevenmeyer et al., 2007), is an obvious candidate for the water source. Bend-faults, which provide deep reaching pathways, can be observed in the seafloor bathymetry in the incoming plate outboard of the TSVZ (Ranero et al., 2005; Ranero et al., 2006).

### 5.4. Quantitative flux melting model

We quantified some of our arguments by using the Arc Basalt Simulator version 3.10 of Kimura et al. (2009, 2010) to which the reader is referred for full details of the method. Briefly, ABS calculates forward mass balance models for the trace element and isotopic composition of arc basalts using assumed values for input parameters (AOC, sediment, mantle), the local P-T conditions of the slab from Syracuse et al. (2010), temperature-dependent trace element partitioning from Kessel et al. (2005), the integrated dehydration history of the slab from van Keken et al. (2011), and PMELTS-based flux mantle melting from Katz et al. (2003). As in most papers, successful models are subjective judgments about the fit between model prediction and representative basalts for extended trace element patterns and isotope ratios (e.g. Fig. 12).

Tables 3 and 4 contain: (1) our assumed compositions for the mantle, AOC and sediment; (2) the pressure of the slab surface beneath the volcanic front (4 GPa) from Syracuse and Abers (2009); (3) the temperature of the slab surface at this depth for Central Chile (830 °C) from Syracuse et al. (2010); (4) the modal mineralogy of basalt and sediment at these P-T conditions as calculated within ABS using *Perple\_X*, following van Keken et al. (2011); and (5) the percent of water-saturated melting at this P-T (18%) from Hermann and Spandler (2008). Table 4 also gives the bulk partition coefficients for these modal mineralogies for Sr, Nd, and Pb at 830 °C that are used for the mixing model in Fig. 12. They are based on Kessel et al. (2005) for garnet and clinopyroxene, and Green and Adam (2003) for phengite.  $D$ 's are assumed to be zero for the  $\text{SiO}_2$  phase and rutile except for rutile  $D_{\text{Nd}} = 0.7$  (from Ayers and Watson, 1993). Table 4 also gives the P-T-F conditions of melting in the mantle wedge that results in the best match of the shape of the REE pattern of a representative volcanic arc basalt (CL575 from San Pedro), and the corresponding bulk partition coefficients based on Green et al. (2000). At these P-T conditions, each percent of slab melt added to the mantle results in about one percent of mantle melting based on Katz et al. (2003). Between 0.5% and 1.5% slab melt yields the best match for most trace elements and isotopes (Fig. 12), and the resulting primitive basalts contain about 3 wt.% water. ABS version 3 does not include the sequential

Table 4

Mixing and results parameters from the Arc Basalt Simulator 3. AOC, altered oceanic crust, SED, sediment.

			Sr	Nd	Pb
Slab	P (Gpa)	4			
	T (°C)	827			
AOC	Melting (%)	18			
	Xgar	45.8			
	Xcpx	42.8			
	Xphen	1.04			
	Xrut	1.28			
	Bulk D		0.034	0.404	0.029
SED	Melting (%)	18			
	Xgar	24.7			
	Xcpx	15.8			
	Xphen	28.9			
	Xrut	0.80			
	Bulk D		0.404	1.63	0.297
Mantle	P (Gpa)	2.1			
	T (°C)	1270			
	Slab component added (%)	0.5–1			
	Mantle melting (%)	1–1.2			
	Bulk D		0.022	0.028	0.017

effects of dehydration in all layers of the slab or residual accessory minerals besides rutile. Although our model is only heuristic, predicted and observed isotope ratios agree well, and trace element concentrations agree to within 10–20% for most elements except for Ba and U that are over-predicted, perhaps because of the sediment values assumed.

Although this approach is easier for a homogeneous mantle, we adapted it for the heterogeneity that we infer for the TSVZ VA by using two South Atlantic MORB type mantle compositions – Depleted (SAM-D) and Enriched (SAM-E) – that bracket the VA samples in Sr, Nd, and Pb isotopes. We assume that SAM-D and SAM-E have the trace element concentrations of the DMM and E-DMM of *Workman and Hart (2005)*, respectively. However, the difference in concentrations between N-MORB and E-MORB sources has no effect on the mixing model because the slab melts are so much more enriched than the mantle wedge.

We also assumed a uniform slab component derived from both sediment and AOC for reasons given earlier. A sediment:AOC ratio of 60:40 gave the most satisfactory results but we have little independent control for this parameter. The isotopic composition of the sediment in *Table 3* is from *Lucassen et al. (2010)* and the trace element composition is from our sample SO210-#5-B as explained earlier. The AOC composition is from ODP Site 1149 in the western Pacific (*Kelley et al., 2003; Hauff et al., 2003*) as compiled by *Tollstrup et al. (2010)*.

*Fig. 12* shows the Sr–Nd–Pb isotope ratios for the resulting mixtures. They bracket all the Sr–Nd–Pb isotope data for the TSVZ when 0.5–1% of slab component is added to the depleted to enriched mantles except for two northern VA samples requiring 2–3% slab component. The separation between VA and BA is greater for Pb than Sr–Nd isotopes. A mixed-source slab component, slab melt-

ing, and a heterogeneous mantle all are required. Little or no slab component is needed for Sr and Nd in the SBA and Pampas Negras BA and Resolana/Los Hornitos VA basalts, but some slab-derived Pb is necessary for Resolana/Los Hornitos. Assuming an average  $\delta^{18}\text{O}$  value of 9‰ for sediment (*Electronic Annex: Table 2*) plus 2‰ (for hydrothermally-altered lower AOC) and 5.25‰ (for mantle wedge) (see *Bindeman et al., 2005*, and references therein), the model shown in *Fig. 13* predicts little if any change in O isotopes from the slab contribution to the VA mantle source.

Although some volcanic centers and regions define slopes that are shallower than the mixing lines, we attribute this to the heuristic generality of our model. All mixing components are likely to be heterogeneous in an area as large as this. Local variations in the isotopic composition of the mantle or subducted sediment or both, and in the P-T conditions of the slab component, all will affect the slope of mixing lines in *Fig. 12*. For example, two samples (CL 323/CL 325) plot close to SAM-E on the Sr versus Nd isotope diagram (*Fig. 12a*) but seem to mix to SAM-D on the Sr versus Pb isotope diagram (*Fig. 12b*). More generally, our model predicts slightly more slab component when using Pb isotopes than when using Nd isotopes. This may reflect a more fluid-like slab component with higher Pb/Nd than the melt calculated using ABS3.10. Our model could be fine-tuned to any subset of samples but our goal is to create a framework with which such tuning can start.

### 5.5. Regional and global comparisons

Although lying on relatively thick continental crust (ca. 40 km), the TSVZ differs from the CVZ in Peru and northern Chile (14–27°S) where the crust is ca. 70 km thick. There, crustal contamination plays a fundamental role in

the magma genesis (e.g. Davidson et al., 1991, Francis and Hawkesworth, 1994, Lindsay et al., 2001, Schmitt et al., 2001, 2002). In the CVZ, Sr, Nd and O isotopes correlate with increasing SiO<sub>2</sub> content, and Pb isotopes show correlations with the local Andean basement (e.g. Francis et al., 1985; Feeley and Davidson, 1994, Wörner et al., 1992, 1994; Aitchison et al., 1995). The TSVZ also differs from the NSVZ where the crust is also thick but where enriched Sr–Nd isotopic compositions have been observed and interpreted as the result of either crustal assimilation (Hildreth and Moorbath, 1988) or subduction erosion (Kay et al., 2005). Our TSVZ study reaches different conclusions about the crustal influence than previous large-scale studies (e.g. Hildreth and Moorbath, 1988; Tormey et al., 1991) or single-volcano studies (e.g. Tormey et al., 1995; Dungan et al., 2001) because we found no correlations between isotopes and differentiation indices and no mixing of Pb isotopes toward the local basement. Our O isotope data also show a typical subduction zone signature within and slightly above the mantle range.

Instead, the sediment-dominated slab component in the TSVZ is a feature more similar to the CSVZ to the south. There, previous studies have shown that basalts were formed by melting of the subarc mantle contaminated by fluids derived from the dehydration of the subducting oceanic lithosphere including sediments (e.g. Hickey et al., 1984, 1986; Hickey-Vargas et al., 1989; Morris et al., 1990; Sigmarsson et al., 1990; Hickey-Vargas et al., 2003; Sigmarsson et al., 2002). However, we conclude that both the subducting oceanic crust and the sediments melt. Our conclusion that the mass fraction of slab component and the degree of mantle melting both decrease eastward into the back arc agrees with previous studies (e.g. Hickey et al., 1986; Futa and Stern, 1988; Hickey-Vargas et al., 1989).

While most previous studies of the TSVZ showed a transition between a slab component in the CSVZ and a crustal component in the NSVZ, we show rather than the TSVZ segment can be interpreted as a “baseline” of subduction input, and that the mantle wedge is heterogeneous in its trace element and isotope ratios.

## 5.6. Conclusions

We use new major and trace element and Sr–Nd–Hf–Pb–O isotope data for basalts from the volcanic arc and backarc of the Transitional Southern Volcanic Zone (34.4–38°S) of Chile, and adjacent trench sediments, to evaluate the origin of the arc magmas. We conclude the following.

- (1) Major assimilation of pre-Cenozoic sialic crust is inconsistent with our isotopic data for basalts to andesites despite their ascent through 35–45 km thick crust.
- (2) The mantle is heterogeneous within and between the volcanic arc and backarc. The range is similar to the South Atlantic MORB field in Sr and Nd, but not in Pb and Hf isotopes. Mixing between a slab component and South Atlantic MORB can explain the Pb isotope data. Pb isotopes in the VA, NBA, and Tromen are dominated by subducting sediments. We attribute the

difference between VA and BA in Hf isotopes to the presence of subcontinental lithosphere beneath the backarc, but cannot constrain if it is presently located within the lithospheric mantle or has been delaminated and is presently in the asthenospheric mantle wedge.

- (3) All samples from the volcanic arc, and most from the backarc, contain a slab-derived component. The mass fraction of this component is less in the backarc and negligible in the SBA basalts farthest from the volcanic arc.
- (4) The slab component is homogeneous and drawn from subequal amounts of subducted sediment and altered oceanic crust. It must be a melt in order to transport Th, Zr and LREE, and to fractionate them so much from HREE. For melting to occur at the depth of the slab beneath the volcanic arc, the slab must be water-saturated at least locally, which requires an external source of water such as from dehydrating underlying serpentinite within the subducting plate, possibly formed through the access of water into the uppermost lithospheric mantle as a result of bend-faulting preceding subduction.
- (5) Trace element patterns and Sr–Nd–Pb isotope ratios are best modelled by adding 0.5–1% of a slab melt (except for two rear arc samples which require 2–3% slab melt) derived from a 60:40 sediment:AOC source to slightly depleted and isotopically heterogeneous mantle.
- (6) Addition of a few percent of this slab component causes an equivalent amount of melting of the mantle at about 2 GPa beneath the VA, with more melting beneath the volcanic arc than backarc. This is consistent with the larger magma flux observed at the volcanic arc.

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## APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2013.05.016>.

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