An East-West transect through the Andes at 35°- 39°S

By

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Abstract

Volcanics from cinder cones and lava flows collected in the Barrancas region of northern Patagonia were analyzed for major and trace element concentrations, and for Sr, Nd, and Pb isotopic ratios. The analyses revealed that both an arc-like and intraplate-like geochemical signature occurs within this narrow geographic area, a 15km wide transect parallel to the Chile Trench. Several samples reflect the typical, yet muted characteristics of arc-type rocks displaying Nb-Ta negative anomalies, LILE enrichments and HFSE depletions. This manifestation suggests subduction flux transfer to a region of the mantle normally beyond the spatial extent of subduction related volcanism sometime within the last 3.5 Ma. Depletions of HREEs in other Barrancas rocks indicate that a component of deeper mantle plume material is also available for volcanics of this region. The analysis of geologic features across the Andes at 35-39°S in conjunction with geochemical profiles of regional centers allows to be presented here, a plausible mechanism for transport of both the IAB and OIB components to the mantle region below Barrancas.
1. Introduction

Arc volcanism is typically located 100 to 250km foreland of convergent plate margins (arc-trench gap) in subduction zone systems and exhibits a specific geochemical signature of LILE enrichment, Nb-Ta and HFSE depletions. However, researchers conducting geochemical studies between 36° and 38ºS in Argentina have detected an “arc like” signature in samples collected up to 500km east of the trench. Varekamp et al report rocks from the Copahue-Caviahue complex (347km to the east of the trench) as having enriched LILEs and depletions of Nb, Ta, P and Ti (HFSEs) as compared to N-MORB (Varekamp et al., 2006).

The REE patterns of these rocks also display an enrichment of LREE relative to the Nazca plate basalts but, similar flat MREE and HREE trends. Possible explanations of these “arc like” patterns include; incorporation of subducted sediment and or slab components into the mantle wedge because of volatile fluxing of the slab, eroded material of the overriding plate dragged down and or an increased crustal residence time of the melt resulting in assimilation of crustal material (Stern, 1991; Varekamp et al., 2006).

Since some rocks from the Copahue-Caviahue complex exhibit an “arc like” signature and are located 25km east of the current Andean volcanic front, two other studies were initiated to investigate volcanics further east. Hesse et al conducted a geochemical study in the Loncopue graben East-Northeast of Copahue-Caviahue (417kms from the trench) and this study of volcanics to the Northeast in the Barrancas region 450kms from the trench. In each of these subsequent studies, some rocks also
revealed an “arc like” signature with Nb-Ta and HFSE depletions in addition to enrichment in LILEs (Hesse et al., 2007) (Zareski, 2013 this study).

One control on arc volcanism is the subduction zone geometry (discussed in the following section). An arc signature beyond the usual arc-trench gap distance of 250 km suggests a variation of the accepted subduction zone geometry. The implication is; the location of the trench has changed, migrated east and then west to its current location since the Cretaceous, or that the angle of the subducting plate was shallower and has since steepened during this same period, or a combination of both has occurred.

The succeeding paragraphs will briefly describe the types of volcanism and their origins followed by a detailed overview of the continental arc volcanic setting - the setting associated with the volcanic products evaluated within this study. The last sections of this introduction will describe the controls on arc magmatism and the geochemical characteristics of arc volcanics.
1.1 Purpose of Study

The goal of this study is to investigate the volcanics of the Barrancas region for the presence of an arc signature. Modeling of the subducting Nazca plate to constrain the current subduction geometry between 35° and 39° south will assist in considering if the magmatism in this region was directly the result of subduction processes.

Chemical analyses of volcanic rocks collected in the Barrancas region and chemical analyses from a compiled database of selected regional volcanic centers are compared. These analyses are examined to identify any systematic geochemical across arc trends and extent of an arc signature due to variable subduction geometry.

This comparison can then be used to evaluate the contribution of the subduction complex (altered slab and subducted terrigenous sediments) to the mantle melting process and the proportional fractionation of these components with depth as the basis for cross-arc geochemical variations.
1.2 Volcanism

Volcanism is a geological process that transfers heat and mass from the interior of the Earth to its surface. This process is manifest as volcanoes and their products on the Earth’s surface. Several mechanisms are responsible for creation of the volcanic edifices at the surface; mantle plumes, rifting and subduction (Fig. 1.1). Formation of an isolated plume of hot mantle, with a possible origin at the core-mantle boundary, ascends to Earth’s surface causing intra-oceanic and intra-continental plate volcanism (hot spots) (Courtillot et al., 2003; Montelli et al., 2006). Possible examples are the Hawaii-Emperor seamount chain and the Yellowstone caldera complex (Smith et al., 1974). Secondly, rising mantle plumes may also thin and weaken an overlying plate to the point of rifting allowing upper asthenospheric mantle to ascend and fill the gap.

Since decreasing lithostatic pressure has the effect of decreasing melting temperatures of in situ rock, the asthenospheric mantle will melt upon ascension (decompressional melting) and create volcanism as exhibited at mid-ocean ridges and continental rift zones e.g. Mid Atlantic Ridge, East African Rift (White and McKenzie, 1989). Rifting may also be caused by the pull of a subducting plate which leads to thinning and decompressional melting such as that proposed at slab windows.

Lastly, subduction is the process found at convergent plate margins where one tectonic plate descends below another tectonic plate. Two types of plate subduction occur; oceanic-oceanic plate subduction, forming an ocean island arc and oceanic-continental plate, which construct continental arcs.
During the subduction process, the denser down-going plate (subducted plate), releases fluids from the breakdown of hydrous minerals as the result of increased temperatures. These fluids migrate to and depress the melting temperature (solidus) of the overlying asthenospheric/lithospheric mantle wedge causing partial melting. The created melts may then rise and solidify as an intrusive in the crust or continue ascending through the crust forming volcanic structures (Blake et al., 2001).

Figure 1.1 Cross section showing volcanic systems: 1- Island Arc, 1a-Continental Arc, 2-Hot spot, 3-Sea floor spreading center, 3a-Rift zone. After USGS
2. Continental Arcs

2.1 Magma Genesis in Continental Arcs

Continental Arc volcanism is a result of subduction at convergent oceanic-continental plate margins. Because of this process, magma is generated deep within the Earth’s interior (100-200 km) and erupted as lavas and pyroclastics forming volcanic structures on the surface of the continental margin (continental arc). Although both types of subduction (oceanic-oceanic plates, oceanic-continental plates) possess similarities in process and inherited components, oceanic-continental plate subduction has the additional component of a heterogeneous continental crust with which the magma may interact during its rise and ponding in the crust. This interaction produces volcanic rocks of a greater range of geochemical compositions than that produced by oceanic-oceanic plate subduction (Wilson, 1989). In both types of plate subduction, viscous coupling between the rigid subducting slab and plastic mantle wedge insures mantle flow (Fig.2.1). The hydrated mantle wedge subsequently is dragged downward to an environment where pressure-temperature conditions and volatile concentrations are sufficient to depress the mantle solidus and initiate partial melting. Upon descent, warming of the oceanic plate occurs through conduction, an effect of being in direct contact with the hotter mantle wedge. The oceanic plate additionally warms as it descends (oceanic geothermal gradient) and acquires heat produced by the frictional heating of plate slip. Increased heating in conjunction with the increased pressure of convergence causes the oceanic plate (and incorporated sediments) to undergo metamorphic reactions that transform the initial basaltic sea water altered oceanic crust into amphibolite-blueschist-eclogite rock
facies (predominantly high pressure-low temperature metamorphic rocks). During this pro-grade metamorphism, a series of dehydration reactions occur. Free water and other low boiling point volatiles are the first components released from the oceanic crust which then hydrate the overlying asthenospheric/lithospheric mantle wedge. Furthermore, volatile bearing mineral phases (Glaucophane/Amphibole-Phlogopite) in the subducting slab become unstable at high pressure-temperature conditions (≈100km) and undergo dehydration reactions which contribute additional volatiles to the mantle wedge (Figure 2.1, A and B).

**Figure 2.1** Model of subduction zone magmatism.
Blundy and Skora propose an alternative explanation of LILE transfer to the overlying mantle wedge. In their experiments, large volume melting of sediment (high LILE source) in the presence of external water (7-15% free water) was achieved at temperatures of 750-850°C and pressures of 3GPa (simulating under arc depths of ≈100km)(Blundy and Skora). In the absence of external water, lesser volume melts were observed and attributed to the breakdown of phengite + clinopyroxene + coesite.

However, anhydrous melt experiments conducted by Schmidt indicate that dehydration of amphibole, zoisite, and biotite, control melt production to ≤3GPa (80-90km). Whereas, phengite-K\((\text{AlMg})_2(\text{OH})_2(\text{SiAl})_4\text{O}_{10}\), a variation of muscovite but, with the addition of Mg, is stable at pressures greater than 3GPa and undergoes dehydration reactions at depths between 100 and 300km(Schmidt et al., 2004).

At these depths and with temperatures of ≈1000°C, hydrous melting of the mantle produces small volume melts. The less dense nature of these small volume melts create buoyancy driven mantle counter-flow which ascends toward the crust. Lithostatic pressure decreases on the counter-flow as it ascends thereby, decreasing mantle melting temperatures. When the rising counter-flow reaches approximately a depth of 60km, partial melting of the mantle ensues (decompressional melting) (Pearce, 1995; Stern, 2002).

Wilson (1989) proposed that metasomatizing partial melts from the subducting slab might also be sources of magma generation. Adakites, the volcanic products of slab partial melts require a thermal regime capable of melting cold oceanic crust, a condition not usually found in oceanic-continental plate subduction zones (Gutscher et al., 2000). However, Adakite signatures (high Sr/Y) have been identified in several excess heat flux
arcs with underlying subducted plate discontinuities (Zellmer, 2009). Alternative processes for the generation of adakite compositions are the partial melting of thickened lower crust (Atherton and al, 1993; Yumul et al., 2000) and high pressure fractional crystallization from parental hydrous basaltic magmas (Castillo et al., 1999; Macpherson et al., 2006).

Once the magma has formed in the mantle wedge, it has completed the first step of magma evolution due to the incorporation of fluid and dissolved compounds. The magma (primary melt) at this stage is less dense than the surrounding mantle and may:

- Ascend to the surface without any pause, erupting at the surface as basalt.
- Mix with other magmas in the mantle wedge and crust, erupting as a more evolved volcanic rock.
- Reach neutral buoyancy and solidify at the crust-mantle boundary under-plating the continental crust.
- Pond and react with the deep crust in any combination of processes collectively known as MASH (Melting, Assimilation, Storage and Homogenization) (Fig.2.2) (Hildreth and Moorbath, 1988).
Interaction of an ascending melt with a heterogeneous mantle will also modify the initial composition of the melt.

The transfer of material from the lowermost crust and/or uppermost mantle into the asthenosphere may create a regional heterogeneous mantle through the process of lithospheric delamination. A shallowing of the subducting plate angle may cause thinning and cooling of the mantle wedge. This cooling over time decreases the depth of the spinel–garnet transition, creating a thicker, denser and gravitationally unstable lowermost lithosphere which is likely to detach. Entrainment of these detached blocks should in part

be resorb into and alter the composition of the asthenospheric mantle wedge (Kay and Mahlburg Kay, 1993; Kay and Abbruzzi, 1996).

Researchers investigated cosmogenic Beryllium ($^{10}$Be) as a petro-genetic tracer of subducted sediment addition to the mantle wedge. With a half-life of $1.5 \times 10^6$ yrs, $^{10}$Be survives subduction time scales yet, is removed by radiogenic decay from geologic systems over greater time scales. $^{10}$Be concentrations were found to be higher in island arc (subduction regime) than in other basalts. Since it is formed by spallation reactions in the atmosphere and in rocks exposed to cosmic rays on the surface, it is probably subducted with sediment (terrigenous/pelagic) and then assimilated into the mantle by subduction processes (Brown et al., 1982; Deschamps et al., 2011; Morris et al., 1990).

Staudacher and Allegre suggest mantle heterogeneity may be demonstrated by the $^4$He/$^3$He systematics (Allègre et al., 1995; Staudacher et al., 1994). $^3$He is considered a primordial isotope of Helium trapped in the Earth’s interior during its formation and released to the surface by deep mantle plumes. Measured $^4$He/$^3$He ratios in MORB show it to be homogenous with a mean of 88,000 and a standard deviation of 9000. Measured OIB $^4$He/$^3$He ratios show a mean of $\approx 94,000$ but a much greater standard deviation 45,000 (Fig. 2.3). The greater dispersion in OIB values is attributed to a degassed upper mantle (high $^4$He/$^3$He >100,000) and to an un-degassed primitive lower mantle source (low $^4$He/$^3$He <30,000) (Allègre et al., 1983). Hilton et al. investigated Helium isotope characteristics of geothermal fluids and lavas in the Central and Southern Volcanic Zones of the Andes. Using MORB values as a benchmark for upper asthenospheric mantle, lower $^3$He/$^4$He were observed in arc rocks. This is attributed to of mixing of MORB- like
mantle and material derived from the lower crust containing high radiogenic Helium ($^{4}$He) (Hilton et al., 1993; Hoke et al., 1994)

However, Anderson proposed high $^{4}$He/$^{3}$He ratios are the result of primordial interplanetary dust particles (IDP’s) high in $^{3}$He, delivered to the Earth’s surface and subsequently incorporated into the mantle by subduction processes (Anderson, 1993).

![Figure 2.3](image)

**Figure 2.3** Histogram showing $^{4}$He/$^{3}$He ratio dispersion in OIB and relative homogeneity in MORB. (Allègre et al., 1995)

Subduction erosion of the overriding plate may be another cause of mantle heterogeneity. Shallow subduction angles provide greater contact of the subducting crust and the fore-arc crust and is typically greater during the subduction of seamounts and
ridges (Meschede and Barckhausen, 2000). This extended contact allows for greater continental crust material to be scraped off, subducted and integrated into a partial melt of the mantle wedge, imprinting a continental crustal signature (Stern, 1991).

In summary, a heterogeneous mantle may be produced by four processes of crustal material assimilation;

• Terrigenous/pelagic sediment input from the subduction complex as indicated by cosmogenic $^{10}$Be analyses
• The assimilation of material from a previously subducted plate as mantle magma ascends
• Subduction erosion of the continental plate imparting a local crustal signature
• Delamination of lower crust assimilated into the upper mantle

2.2 Arc Signature

The preceding descriptions show that intermingling of sources and magma generating processes, produce complex compositional variations in subduction zone volcanics. However, subduction zones produce volcanics with a geochemical signature that is dissimilar to the rocks of the other two volcanic regimes. These signatures are exemplified by: enrichment in fluid mobile LIL elements (Cs, K, Rb, Ba, Pb, Sr and U) facilitated by dehydration of the subducting oceanic plate and relative depletion of HFSE (fluid immobile elements Ti, Nb, Ta) due to retention in the residuum (Fig. 2.4) (Hawkesworth et al., 1993; Maury et al., 1992).
The isotopic signature of arc rocks vary due to the degree of crustal material incorporation, but characteristically arc rocks show higher $^{87}\text{Sr}/^{86}\text{Sr}$, $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{206}\text{Pb}/^{204}\text{Pb}$ ratios then that of OIB or N-MORB but a lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratio (Hawkesworth et al., 1982; Norman and Leeman, 1990; Saunders et al., 1988). Also, within a suite of arc rocks, a general trend towards more silicic magmas through Assimilation-Fractional Crystallization (AFC) is commonly observed.

While the subducting slab descends, it is progressively dehydrated, thereby reducing the amount of volatiles available for release to the mantle wedge at greater depths. The consequence of an early loss of volatiles and LILE’s is; once the slab reaches depths directly below the back-arc region these components may be already gone and not transported into back arc lavas or pyroclastics. So, the degree of enrichment of these fluid-mobile incompatible elements is dependent upon several factors: The amount of volatiles from dehydration of the oceanic slab and sediment; the degree of partial melting of the contaminated mantle wedge; the depth at which the partial melting takes place and the bulk rock additions from the melting of subducted slab/sediments.
Figure 2.4 Chondrite normalized incompatible element patterns of OIB-Ocean Island Basalt, IAB-Island Arc Basalt and MORB-Mid-Oceanic Ridge Basalt. IAB profile shows LILE (Ba, Rb, Th), LREE (La, Ce, Nd, Sm) enrichment, Nb-Ta anomaly and HFSE (Zr, Ti, Hf) depletion-characteristics of arc volcanism.
Two other groups of incompatible elements may be fractionated by the subduction process aiding in the identification of arc magmatism, the Rare Earth Elements (REEs, La through Lu) and the High Field Strength Elements (HFSEs). The REE are trace elements that have mainly $3^+$ ions with similar chemical and physical properties. Small differences in chemical behavior between these elements is due to a small, steady decrease in ionic radii (La>Lu) with increasing atomic number (La<Lu), referred to as the lanthanide contraction. The REE’s are grouped as light (LREE, La-Pm), middle (MREE, Ho-Sm) and heavy (HREE, Er-Lu) and become less incompatible with increasing atomic number because of their decreasing radius. This difference in size allows fractionation among the REE during melt formation in the subduction process. The LREE are the more incompatible of the REE’s and will leave the mineral structure for the melt before the heavier, less incompatible REEs.

This trend is scaled by partition coefficients which describe the equilibrium distribution of a trace element between a mineral and a melt. The partition coefficient is defined as:

$$K_d = \frac{C_i^{\text{mineral}}}{C_i^{\text{melt}}}$$

Where, $K_d$ is the Nernst partition coefficient and $C$ is the concentration of the trace element $i$ in ppm. Values greater than one indicate the trace element has a preference for the mineral phase (compatible), whereas values less than 1 indicate a preference for the melt (incompatible) (Blundy and Wood, 2003). Many researchers use partition coefficients for trace element modeling, however, composition, temperature, pressure and
oxygen fugacity of the melt have shown to influence $K_d$ values significantly (Drake and Weill, 1975; Green and Pearson, 1986).

The high field strength elements are high charge ions ($\text{Zr}^{4+}$, $\text{Hf}^{4+}$, $\text{Ti}^{4+}$, $\text{Nb}^{5+}$, and $\text{Ta}^{5+}$) with a smaller atomic radius and are less incompatible than the REEs. In contrast to the LILEs the HFSEs are immobile in aqueous fluids (Tatsumi and Eggins, 1995). During melting episodes Nb, Ta, and Ti are shown to be retained in refractory phases in the residuum such as hornblende and rutile (Brenan et al., 1994b; Defant and Drummond, 1990). Depletions in these elements are characterized as negative anomalies and are a typical signature found in arc volcanics.

2.3 Geophysical Controls on Arc Volcanism

Geometric relations between the subducting slab and the overriding plate are the primary controls on magmatic and volcanic activity in continental arc settings (Figure 2.5). The minimum subducting slab angles conducive for magma generation globally range from $\approx 20$-$30^\circ$. At these subduction angles, peridotite mantle will undergo hydration at $\approx 90$-$110$ km depths followed by small volume melting. If the slab is not completely dehydrated at depth, a second episode of mantle hydration may occur at $\approx 200$ km. Volcanoes will generally form 100 to 250 km inland from the initial point of subduction (trench). Shallow subduction angles of $10^\circ$ or less do not allow for the subduction process to attain the conditions necessary for partial melting; that is, not enough room for a mantle wedge between the subducting and overriding plate (Barazangi and Isacks, 1979).
Other geophysical factors affecting the petrogenesis of arc magmas:

- **The rate of subduction:** A fast rate allows a cold subducting plate to descend more quickly depressing the isotherms thereby delaying slab dehydration until greater depths. A slow rate allows more time for warming of the subducting plate at shallower depths thereby increasing the rate and degree of slab dehydration.
• **The age of the subduction zone:** In a young arc, the subduction system is hotter. In a mature arc, the isotherms are depressed because of a thick continental crust.

• **The age of the subducting slab:** An old slab will dehydrate before the slab reaches wet basalt solidus thus, precludes slab melt. A young slab is hotter and dehydrates after reaching wet basalt solidus which causes immediate slab partial melts (adakites).

• **The extent to which the subducting slab induces flow in the mantle wedge:**
  Increased mantle flow produces heat flux into wedge.

• **Oceanic plate features subducted:** Spreading ridge, aseismic ridges, seamounts-subduction of these creates slab windows or flat subduction. (Winter, 2010).

### 2.4 Geochemical Controls on Arc Volcanism

Several reservoirs are responsible for the geochemical signature of arc volcanics, however, the subducting slab complex (composed of the oceanic slab, continental and oceanic sediment) is the predominant source. Equally important is a medium that can facilitate the transfer of the slab components into the overlying mantle wedge, in subduction systems, it is available water. Since, it is generally accepted that arc magmas are formed in the overlying mantle wedge after flux/volatile transfer from the slab (Ringwood, 1974), the rate and amount of slab component added (LILEs) to a HFSE depleted MORB like mantle wedge has the ultimate control over the character of subduction zone magmas (McCulloch and Gamble, 1991).
3. Regional History

3.1 Pre-Andean Cordillera

Formation of the South American continental margin began with the break-up of the super-continent Rodinia approximately 825-740 Ma (Li et al., 2008). Zircon U-Pb age dating (Chew et al., 2007; Restrepo-Pace et al., 1997), indicate Grenville age basement terranes form a nearly continuous belt along the current western South American margin (Fig. 3.1) and an analogous belt that stretches from Labrador to Northeastern Mexico (Fuck et al., 2008). This suggests that rifting occurred, which created the western margin of Laurentia and the Amazonian proto-margin (Baldo et al., 2006; Loewy et al., 2003; Pankhurst et al., 2006). Following the fragmentation of Rodinia, alternating periods of extension, oceanic crust formation, subduction, continental arc formation, island arc, micro-continental and continental collisions, allochthonous and parautochthonous terrane accretion (Ramos, 2009), produced a complex amalgamated South American western margin (Fig. 3.2, 3.3). This complexity has contributed to the lack of a definitive explanation for the formation of South America’s western margin.

The terrane model forwarded by some researchers relies upon two findings; uplifted ophiolite sequences between the Gondwanian proto-margin and the accreted terranes suggesting a trapped remnant oceanic plate (Bahlburg and Hervé, 1997; Omarini et al., 1999; Ramos, 1988; Ramos et al., 2000). Other authors suggest terrane accretion was accomplished by a mobile belt during the Paleozoic. This model is primarily based on metamorphic crystallization ages and model ages for the Late Precambrian – Early Paleozoic metamorphic basement rocks (Lucassen et al., 2000; Viramonte et al., 1999).
By the end of the Paleozoic, varying tectonic regimes had shaped a continent that is similar to South America's present day configuration, with the exception of terranes accreted to northern South America in Late Tertiary times (Mpodozis et al., 1989).
Figure 3.1 Grenville U-Pb zircon ages in basement terranes of western South America (Ramos, 2009)
Figure 3.2 Schematic showing relationship between parautochthonous Famatian terrane, allochthonous Cuyania terrane and western Gondwana during the Ordovician (Ramos and Aleman, 2000). An alternate hypothesis proposes Cuyania accreted as result of a Laurentia-Gondwana collision (Dalla Salda et al., 1992)
The onset of the Andean Cordillera is associated with the break-up of Pangaea that began in the early to mid-Mesozoic. Initially two continents- Laurasia and Gondwana were created by the breakup, the western half of Gondwana being the parent landmass of South America and Africa (Scotese, 2004). This event was coincident with the initiation of Farallon Plate subduction beneath Gondwana’s western margin in the vicinity of the current trench location. The absolute motion of western Gondwana and the Farallon plate during this period was to the Northeast.
This created a scenario of extensional subduction dictated by plate roll back and variation in relative velocities between western Gondwana and the subducting Farallon plate that lasted until the Early Cretaceous (Ramos, 2000). Break-up of western Gondwana initiated a change in the absolute direction of South America, from a northeast motion in the Early Cretaceous to a west-northwest motion in the Late Cretaceous. This directional change also caused a conversion in tectonic regime, from extensional subduction in the early Jurassic to quiescence during the Aptian-Albian, followed by a compressional subduction regime in the Late Cretaceous, the latter, initiating the present tectonic setting of Andean uplift and crustal thickening (Ramos, 1999). This change in tectonic regimes is manifest in the magmatism of these periods. Early Triassic volcanics are Ocean Island Basalt (OIB) type rocks (Ramos and Kay, 1991) but, transition to Calc-Alkaline Basalt (CAB) type rocks representative of continental magmatic arcs, in the Late Cretaceous, (Franzese and Spalletti, 2001)

3.2.2 Late Cretaceous-Recent

The Andes are an 8000km non-collisional mountain range that extends from Columbia to southernmost Chile in South America. Their formation is due to tectonic interaction between the western margin of South America and several subducting oceanic plates of various origins, ages and consequently, compositions. The variations in these oceanic plate characteristics are reflected in the overriding South American plate and are subsequently used to identify segments of the Andean mountain belt.

Although a nearly contiguous range, Gansser was the first to correlate the geology of the Andes with plate tectonics, based on the presence of metamorphic rocks and ophiolite
belts of Andean age. Gansser subdivided the range into three segments (Fig. 3.8); the Northern (12°N-3°S), Central (3°S-46°S) and the Southern Andes (46°S-57°S) (Gansser, 1973).

From the onset of compressional subduction (Andean orogeny) in the Cretaceous, subduction involved the interaction of three plates – the subducting Farallón, Aluk and the overriding South American. Ramos, Kay and Somoza suggest the Aluk Plate was likely subducted and consumed beneath the western margin of central and southern South America during the Early Cenozoic (Ramos and Kay, 1992; Somoza, 2005). However, beginning in the Early Miocene, subduction along the western margin of South America involved two oceanic plates each with their own geomorphological evolutions.

In the Early Miocene (≈23Mya), the Farallón plate split into the Cocos and the Nazca plates because of greater slab pull in the northern portion of the Farallón plate beneath North America (Lonsdale, 2005; Menard, 1978). This division resulted in a change from an oblique to a nearly orthogonal convergence of the Nazca and South American plates, as well as a greater than two-fold increase in convergence rate (Pardo-Casas and Molnar, 1987; Somoza, 1998). This coincided with the formation of subsequent spreading systems in the region: CNS-2, 19.5–14.7 Ma; and CNS-3, 14.7 Ma (Meschede et al., 1998).
The general east-west axes of the Cocos–Nazca spreading centers produced new oceanic crust nearly orthogonal to the Pacific-Farallon spreading center. In proximity to the CNS is the Galapagos Hot Spot and a second unnamed volcanic center that produced material partially overprinting the newly formed Nazca crust (Meschede and Barckhausen, 2000)(Figure 3.4)

**Figure 3.4** Map view showing tectonic evolution and segment ages of the Cocos-Nazca spreading center from the Early Miocene to present day. (Meschede and Barckhausen, 2000)
These geologic processes created a complex, regional assemblage of subducting oceanic crust with incongruent ages and compositions that correlate to the Northern Andes (12°N-3°S) as designated by Gansser.

During the Miocene, the southern South American subduction zone was also undergoing a change in oceanic plate characteristics. Convergence of the Antarctic-Nazca spreading ridge (Chile Ridge) with the western margin of South America ≈14Mya created the Chile Triple Junction (Cande and Leslie, 1986) and marked the transition of a subducting Nazca Plate to a subducting Antarctic Plate regime near 46.5°S (Figure 3.5). The Chile Triple Junction migrated north 160mm/yr. (Boutonnet et al., 2010) during the Cenozoic from its origin near the southern tip of South America as a consequence of oblique east-northeast convergence of the Antarctic Plate to the northerly strike of the South American western margin.

**Figure 3.5** East-ward migration of the Chile ridge and northerly migration of the Chile Triple Junction between 18Mya and the present.

- Green circle: Triple junction origin
- Red circle: Current location of triple junction-Taitao Peninsula (After Cande and Leslie, 1986)
Convergence rates are nearly 4 times faster to the north of the triple junction than to the south (7.8 cm/yr. vs. 2 cm/yr.) and is exemplified by a more active volcanic arc north of the triple junction (Herve et al., 2000) (Figure 3.6).

Currently the position of the Chile Triple Junction is 46.5°S and delineates the northern boundary of the Southern Andes (Hervé et al., 2000).

The Nazca and Antarctic plates converging at the Chile Trench have an age of <1 Ma as it is not clear whether the ridge axis or the Taitao transform fault is being subducted. Northward from the Chile Ridge (46°S), the age of the Nazca Plate increases to approximately 37 Ma at 33°S (Tebbens et al., 1997) whereas, the Antarctic Plate from the

Figure 3.6 Tectonic map showing interaction of the Nazca-Antarctic and South American plates -the Chile triple junction (Thomson, 2002).
Chile Ridge southward increases in age to approximately 14-15Ma at 56°S (Cande and Leslie, 1986).

Subduction of the Chile Ridge causes shallowing of subduction angle, near trench magmatism, and a gap in the volcanic arc. These anomalous features are caused by elevated temperatures created by the subduction of hotter, thin, young oceanic crust. Elevated temperatures facilitate shallower slab dehydration and proximal trench magmatism, unusual in normal continental arc settings (DeLong et al., 1979). The results are magmatic rocks as those found in the Taitao Peninsula (Chile Triple Junction) and because of the unique early dehydration, a gap of volcanism in this segment of the Andean arc axis (Mpodozis M et al., 2010).

A second consequence of the Chile Ridge subduction is the formation of an ever widening gap between the two subducting plates flanking the ridge: the asthenospheric or slab window (Figure 3.7) (Gorring et al., 1997; Thorkelson, 1996). The slab window allows for asthenospheric mantle below the subducting plate to rise and undergo decompressional melting which interacts with the sub-continental asthenosphere and lithosphere as well as thermally eroding edges of the down-going slab (Thorkelson, 1996) producing adakitic magmas (Castillo, 2006). Furthermore, tearing of the subducting plate may also form a slab window. As the ridge approaches the trench, increased tectonic coupling occurs between the overriding and the subducting plate as the result of a hotter subduction regime and the more buoyant subducting plate (Boutonnet et al., 2010). While the near trench region of the subducting plate’s descent is slowed by coupling, the already subducted segment of the down-going plate continues to descend at a relatively faster rate. This difference in rates and thermal weakening between the two plate regions
may cause a slab tear parallel to the trench and may explain the accumulation of OIB magmatism in the Patagonian back-arc (Guivel et al., 2006). Additionally, divergence in flow between the westward asthenospheric mantle wedge and the global eastward flow of the asthenosphere may enhance sub-slab asthenospheric upwelling through the “window” (Bruni et al., 2008; Gorring et al., 2003).

Figure 3.7 Schematic of Chile Ridge subduction. Slab window is formed by oblique convergence of the Chile Ridge. The Nazca Plate (B) is subducting more quickly and at a steeper angle than the Antarctic Plate (C) below the South American Plate (A). Upon subduction, the transform faults convert from strike-slip the dip-slip to compensate for differential convergence rates and dips. Normal subduction forms calc-alkaline arc (grey volcanoes) whereas, tholeiitic-alkaline volcanoes (black volcanoes) form above proposed slab window. After Thorkelson, 1996

The Antarctic Plate associated with the Southern Andes also shows a variation in dip along its length. From the Chile Triple Junction to 49°S, the subduction angle of the
Antarctic Plate is estimated to be 16° by (Jarrard, 1986) and coincides with the lack of Quaternary volcanism (Patagonian Volcanic Gap) between the Southern and Austral volcanic zones (Ramos and Kay, 1992). The dip of the Antarctic Plate segment from 49°-56°S is poorly constrained, nonetheless Quaternary volcanism is evident in the Southern Andes (Hervé et al., 2000; Ramos, 1989) inferring a dip of greater than 20°.

In contrast to the complex tectonic regimes of the northern and southern Andes, the central Andes (3°S-46°S) are the result of a continuous non-collisional/igneous (“Andean type subduction”) orogeny caused by the subduction of a single oceanic plate since the late Cretaceous. The Central Andes are a range extending over 5000km and are comprised of three continuous main geological features that parallel the Peru-Chile trench: The Coastal Cordillera, the Cordillera Principal and the eastern Sub-Andean ranges. The latter two ranges transition from a ≈ 3000km north-south trend to a ≈2000km northwest-southeast trend near Arica, Chile. However, the metamorphic Coastal Cordillera disappears 850km to the northwest of Arica, where it intersects with the subducting Nazca Ridge (Gansser, 1973).

The Nazca plate varies in subduction angle along strike to the Central Andes as determined by Barazangi and Isacks (1976). Five segments, each displaying relatively uniform dips, have been identified using hypocenter locations (Benioff zone) as a proxy for the Nazca plate - South American plate interface.
Figure 3.8 South American western margin indicating Andes subdivisions, volcanic zones and geological structures used for segment designations (Ramos and Aleman, 2000).
These segments alternate consecutively between steeper (≈25-30°) and flatter dips (≈5-10°) which may be the result of a distorting Nazca Plate (Hasegawa and Sacks, 1981). Alternatively, Barazangi and Isacks (1979) suggest that tearing of the Nazca plate is the cause for the variable dips as observed by hypocenters delineating the Benioff zone at different depths in adjacent segments. The segments on the order of 500-1500km (Burbach et al., 1984) coincide with geologic features of the Nazca plate and are used to designate volcanic and non-volcanic zones of the Central Andes (Barazangi and Isacks, 1976).

The northern most segment of the Nazca plate is bounded by the Carnegie Ridge to the north and south by the Nazca Ridge (Fig. 3.8). Plate dip in this segment (2°S to 15°S - Peruvian Flat Slab zone) is between 5-10° with seismicity observed to be more frequent and at shallower depths (<100km) than adjoining segments with steeper subduction angles. Between 15° S and 25° S, the plate segment dip increases to ≈30°. Seismicity peaks in this region with most events occurring at depths of 100-130km but, no observed large shallow earthquakes over the last 100yrs (Kelleher, 1972).

At 27° S, The Easter Island –San Felix seamount chain extends from the East Pacific Rise to the Central Andes and delineates the northern boundary of the Pampean Flat Slab zone (27°S - 33°S) (González-Ferrán, 1985). This segment dips at ≈5-10° and displays seismicity similar to the Peruvian Flat Slab zone but, has experienced many large shallow earthquakes. The Juan Fernandez Ridge at 33°S and the Chile Triple Junction at 46°S delimit the southernmost segment. Here, the plate returns to a ≈25-30° dip and exhibits a steep inclined seismicity.
Seismicity also indicates a depth of slab with distance relationship eastward of the trench. Flat slab segments have earthquake foci at depths of 80-100km and range 200-600km from the trench axis, whereas segments with steeper dips have foci at depths of 80-100km but, range 100km to 400km from the trench axis (Isacks and Barazangi, 1977).

The differences of the seismic trends can be explained by the proximity of the subducting slab to the overriding continental plate. The two flat slab segments with shallower subduction angles may follow and grind the bottom contour of the South American plate as suggested by the occurrence of shallow seismicity extending to the foreland. The steeper segments on the other hand show shallow seismicity close to the trench axis but do not show shallow seismicity as far toward the foreland. This infers these Nazca plate segments are descending at a steeper angle under the South American plate.

Subducting-overriding plate geometry may control whether or not partial melting and volcanism occurs in arc environments. Barazangi and Isacks suggest shallow slab angles might not leave enough room for asthenospheric mantle between the subducting and overriding plates, a factor believed to be necessary for partial melting (Barazangi and Isacks, 1976). Since the current Andean arc was built by Quaternary volcanism above steeper slab segments, the shallowing of slab dip in the Peruvian and Pampean flat slab segments may account for the lack of volcanism during this period.

The Peru Flat Slab segment however had experienced significant volcanic activity in the Miocene and Pliocene (Giletti and Day, 1968). This intermittent volcanism may be explained if there is a correlation of shallow slab subduction with a lack of volcanism,
then the subduction angle in these flat slab regions may have been steeper during the Miocene and Pliocene (Barazangi and Isacks, 1976).

The segments of the Nazca plate with steeper dips display high seismic wave attenuation in a region that lies between the zone of seismicity in the upper 50km of the South America plate and the Benioff zone of the Nazca plate (Chinn et al., 1980). This attenuated region is perceived to be the upper mantle wedge beneath the South America plate (Barazangi and Isacks, 1976).

Discontinuity in Nazca plate segment ages and strike of axial magnetic anomalies occur at the Valdivia Fracture Zone-trench interface, ≈40°S (Fig. 3.9). To the south of 40°S, the subducting slab age is 18 Ma and was formed at the Chile Ridge whereas the segment to the north was formed at the East Pacific Rise and jumps to 26 Ma (Tebbens et al., 1997). The Valdivia Fracture Zone also demarcates a transition in crustal thickness. To the south crustal thickness is a fairly uniform 30km but north of this boundary crustal thickness increases to 55km.
Figure 3.9 Map of the Southern Volcanic Zone showing major transform faults and age of inbound Nazca Plate segments (linked colored circles). Volcanoes of the Andean arc are yellow triangles. (Tebbens et al., 1997)
3.3 Arc Migration

Changes in the subduction regime previously described also has an effect on location of the arc axis on the continent and is manifest as longitudinally aligned sets of volcanic/intrusive rocks observed in the Peruvian flat slab segment and in central Chile. Arc type rocks anomalously close (within 75km) and distant (≈500km) from the current trench location in the Peruvian Flat Slab segment suggests migration of the trench axis eastward from the Jurassic (JORDAN et al., 1983). In addition, researchers identified an almost complete lack of Mesozoic-Cenozoic arc-trench gap accretionary complexes at the Andean margin and infer that a significant volume of the missing oceanic and terrigenous sediment were subducted into the sub-Andean mantle (Kulm et al., 1977; Rutland, 1971; Schweller et al., 1981). Ziegler noted that extensive subduction erosion of material occurred along the inner trench wall north of 32°S (Ziegler et al., 1981).

During the early to mid-Miocene eastward migration of the arc front accelerated culminating at its eastern most extent during the late Tertiary, a result of a shallower subduction of the Nazca plate beneath South America (Ramos, 1988b) (Figure 3.10). The position of the volcanic front in the Quaternary occurs to the west of the Late Tertiary front between 38 and 39°S (Stern, 1988). Migration to the west is suggested to be a result of trench roll back, or a general steepening of the subduction angle in this region. This roll back is suggested to have produced retro-arc basaltic magmatism of alkaline composition in the Southern Central Andes (JORDAN et al., 1983; Muñoz B and Stern, 1988).
Figure 3.10 Migration of the arc front; the eastward migration from the Jurassic through the Cretaceous is related to subduction erosion of the continental margin (Ramos 1988b). Later, in the Tertiary advancement to the east was controlled by a shallowing of subduction angle (JORDAN et al., 1983).
3.4 Volcanic Zones and Geochemical Trends

The Andes are the result of a buildup of Quaternary volcanic edifices upon orogenic belts formed during the Paleozoic. Four active volcanic zones are associated with the Andean subduction zone; The Northern Volcanic Zone (5°N to 2°S), the Central Volcanic Zone (15°S to 25°S), the Southern Volcanic Zone (33°S to 46°S), which coincide with the more steeply dipping Nazca slab segments and the Austral Volcanic Zone (49°S to 55°S) (Stern and Kilian, 1996; Thorpe and Francis, 1979a).

The Southern Volcanic Zone can be subdivided into the Northern Southern Volcanic Zone (33°-34.5°S), the Transitional Southern Volcanic Zone (34.5°-37°S) and the Southern Southern Volcanic Zone (37°-46°S) (Tormey et al., 1991). The data compiled in this study are from volcanic centers which range in latitude from 36.4 to 38.7° S and thereby straddle the Transitional Southern and Southern Southern Volcanic Zone boundary.

Beneath each volcanic zone, there are differences in crustal thickness. Just south of the Northern Volcanic Zone (7°S) the crust has a thickness of approximately 40-45km. The thickness of the crust increases southward to the Central Volcanic Zone where it is at a maximum 65km (Fromm et al., 2004). The crust then thins southward to the Southern Volcanic Zone where it is a comparatively uniform thickness of ≈30km (Völker et al., 2011).

Erosion rates also vary between the volcanic zones as a result of climate differences, an important factor for transport of sediment to the mantle wedge.
Precipitation in the Atacama desert in northern Chile (≈23°S) is less than 0.01m annually (Pananont et al., 2004). This lack of precipitation precludes transport of sediment by rivers to the ocean and subsequently to the subduction channel.

Corroboration of a climate effect may be shown by a crosssection through the trench at 23°S. Here, the trench reaches depths of over 8km with steep inner and outer walls indicating low sediment fill. At 35°S annual rainfall approaches 4m facilitating large amounts of fluvial sediment transported to the trench. The profile of the trench at 23°S shows a flat topography over the axis, reclined trench walls and a depth of less 5.5km (Palmer et al., 1976).

Tormey, also observed a decrease in trench sediments to the north of 37°S and attribute this to greater subduction of sediment (Tormey et al., 1991). However, Ranero and Huene using multi-beam bathymetry, depth processed reflection and wide angle seismic data, imaged trench sediments 2.5km thick south of the San Juan Ridge (33°S) but only 0.5km to the north (Ranero et al., 2006; von Huene et al., 2009). This suggests that the San Juan Ridge is a barrier to northerly sediment transport in a northward deepening trench.

The subduction process along the 8000km Andean arc produces mostly calc-alkaline volcanics (Winter, 2010). These volcanic products are the possible result of fluid induced, sub-continental asthenospheric mantle melting, which reacts with overlying continental asthenosphere and lithosphere. Geochemical variations along strike of the arc may then be largely determined by local source reservoir compositions; ocean plate, altered oceanic crust, subducted continental sediment, and overriding plate. On the other hand, geochemical variations normal to the trench axis (across arc) are likely effected by
subduction processes, e.g. degrees of; melting, fluid/sediment input from the subducting slab, crustal assimilation and crystal fractionation.

The volcanic products of each zone are characterized by basaltic andesite in the northern, andesitic to dacite lavas and dacite to rhyolite ignimbrites in the central and high-alumina basalts, basaltic andesite and andesite in the southern zones (Thorpe and Francis, 1979b) (Table 3.1). Additionally, shoshonites and alkali basalt-trachyte volcanics can be found east of the arc axis at scattered locations.

Several researchers propose an association of increasing K concentration in calc-

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<td>0.4–2.8</td>
<td>1.4–5.4</td>
<td>1.4–2.2</td>
</tr>
</tbody>
</table>

Table 3.1 Tectonic and geological characteristics of the Andean volcanic zones. (Harmon et al., 1984b)

alkaline volcanics with distance from the trench (Gill, 1981; Kuno, 1959; Peccerillo and Taylor, 1976; Taylor, 1969). This observation was made while reviewing data from several arcs. The increasing K concentration also correlates with the increasing depth of the Benioff zone below a volcanic center. This is known as the K-h relationship.

Plotting volcanic data from the three Andean zones into Gill’s K₂O vs. SiO₂ diagram for subdividing subduction related rocks, shows the Northern Volcanic Zone volcanics plot within the Medium K field with 59-60wt% SiO₂, the Central Volcanic Zone
volcanics plot within the Medium K field with 53-71wt% SiO$_2$ and the Southern Volcanic Zone volcanics plot in the low boundary of the Medium K field with 51-63wt% SiO$_2$ (Fig.3.11).

Variation in LILE concentrations are also shown to differ between zones. The Central Volcanic Zone displays the greatest enrichment in LILE enrichment and resembles average upper continental crust incompatible element composition as presented by Taylor and McLennan (Taylor et al., 1981). The Southern Volcanic Zone shows the lowest LILE enrichment of all Andean zones and displays similarities to average island arc calc-alkaline basalts from destructive convergent margins (Gill, 1981). The Northern Volcanic Zone exhibits an intermediate incompatible element composition between the Central and Southern zones (Fig.3.11) (Harmon et al., 1984a). It also appears that the degree of LILE enrichment correlates with thickness of the continental crust. The thickest crust of the Central Zones shows the greatest enrichment of Rb, Th, U and K whereas, the Southern Zone displays the lowest enrichment with the thinnest crust and the Northern Zone exhibits an intermediate incompatible element composition and crust thickness (Table 3.1, Fig.3.12).
Figure 3.11 K2O vs. SiO2 diagram of rock data from three Andean volcanic zones distinguishing High-K, Medium-K and Low-K series. (See text). Differentiation within a series progresses left to right on x-axis, whereas, variation of primary magmas may be depicted by vertical variations in K2O wt. % at low SiO2.

The Central Volcanic Zone has the thickest/oldest crust likely allowing for greater crustal residence time of magmas to fractionate and may account for the highest K2O wt. %.

The Southern Volcanic zone on the other hand is the thinnest and youngest crust thereby limiting magma residence time for fractionation. Volcanics of the SVZ approach the low-K tholeiitic boundary indicative of shallow melting and low crustal assimilation (Harmon et al., 1984a).
Figure 3.12 Mantle normalized incompatible element diagram showing variation between the three Volcanic zones of the Andes (NVZ, CVZ, SVC) and comparison to upper crust (UC) (Taylor et al., 1981), island arc calc-alkaline basalt (IACAB) (Gill, 1981) and N-MORB (Harmon et al., 1984b; Sun and McDonough, 1989)
4. Analytical Methods

4.1 Major Element Concentrations using X-Ray Fluorescence

Eighteen rock samples were powdered in preparation for x-ray analysis at the Ronald B. Gilmore XRF Laboratory, University of Massachusetts- Amherst. Rock samples Barrancas were first reviewed for freshness and then cut on a diamond slab saw to remove any signs of alteration or weathering. The resulting 1 cm thick slices were then placed between two Lexan sheets and crushed by hammer impact reducing them to irregular shaped pieces of 1-3cm. An aluminum oxide ceramic jaw crusher was used to reduce the rock sample before placing 30-50cc splits in a ceramic shatter box. The product of this technique is a powder of approximately 200µ that was additionally processed by manual grinding with an agate mortar and pestle to a talc-powder like consistency. Two grams of each powdered sample were forwarded to the Ronald B. Gilmore XRF Laboratory, University of Massachusetts - Amherst where routine, high-quality major element analyses (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) are obtained from fused La-bearing lithium borate glass disks using a Siemens MRS-400 multi-channel, simultaneous X-ray spectrometer. The analytical methods are modified from those of Norrish and Hutton (1969).
4.2 Trace Element Concentrations using ICP-MS and ICP-AES

Aliquots of all sample powders derived from XRF preparation were sent to SGS Toronto, Canada for trace element ICP (Inductively Coupled Plasma) analysis (ICPMS-AES54). The technique for ICP analysis entails digestion of the sample powders by sodium peroxide fusion followed by dissolution in a dilute acid. This method allows for complete dissolution of numerous mineral phases. The majority of trace elements are analyzed by ICP-MS (ICP-Mass Spectrometer) however, Ba, Be, Cr, Cu, Li, Mn, Ni, P, Sc, Sr, V, Zn, and Zr are analyzed by ICP-AES (ICP- Atomic Emission Spectrometer). In addition the USGS standard BIR-1 was included in the sample group as a control. The average calculated error for ICP-AES is -.2% and -.58% for ICP-MS. Relatively high analytical errors were recorded for Pb, Sn, and Tm of 11-12% in duplicate analyses of RN 12A. Anomalously high analytical errors are numerous between certified BIR-1 and measured BIR-1 which range from 10-2300%. (Table 7.1)

4.3 Radiogenic Isotopes by MC-ICP-MS

Ten powdered samples were analyzed for $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at the University of Florida, Gainesville. Samples were analyzed using a Nu-Plasma Multi Collector-Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). The sample powders were dissolved in strong acids, dried, re-dissolved in acid and centrifuged. The resulting supernatant was injected into cation exchange columns and target elements were separated by adsorption (Rea, 2009). The
following standards were run with the samples; NBS 981 for Pb analysis, NBS 987 for Sr analysis and JNDi1 for Nd analysis. The analyses and analytical errors are shown in figures 7.1 to 7.3.
5. Sample locations and field description

Twenty nine volcanic samples were collected from lava flows and cinder cones along a 49km North-South (≈69.83°W) section of route 40 in the Ranquil del Norte – Barrancas region of Argentina. Sixteen samples were chosen for detailed analysis and are described in this section and the petrography section 6.1. Figure 5.1 below shows the collection sites of the Barrancas volcanics between ≈36.62°S and 37.03°S. Table 5.1 lists Barrancas samples, latitude, longitude, elevations and a brief site description.

Figure 5.1 Sample sites in the Barrancas region of western Argentina. (Image courtesy of Google Earth)
RN1:
-Northern most sample site, Thin (2m), rough lava flow broken into blocks located on the north side of route 40. Underlying topography telegraphs through flow. Hand sample has dark gray color (melanocratic), vesicles are rare. Plagioclase laths are abundant and visible (1-3mm) without hand lens. Olivine and possibly clinopyroxene are less abundant and <1mm.

RN2:
-Sample is from a road-cut on Rt. 40 through a large lava flow knoll. Flow is viscous as suggested by the formation of lobes built upon each other to form the knoll and vesicles more abundant on top of flow. Hand sample is melanocratic, fine grained and has vesicles filled with possibly zeolites.

RN3:
-This sample is from a road-cut 1km away from RN2 at km marker 2767 on Rt. 40. Hand sample color is light gray (mesocratic), phaneritic with plagioclase laths up to 5mm in a fine grained ground mass. Field assessment was andesite. (Photograph 5.1).

**Photograph 5.1** Road cut through lava formation. Yellow circle with cross indicates sample location.
RN7:  
-Small weathered out-crop protruding from relatively flat landscape across from gas station in Barrancas. Formation appears to be a melanocratic volcanic breccia. Hand sample displays moderate vesiculation, sharp fractured clasts and plagioclase laths in a dark fine groundmass.

RN11:  
-A thick cap-rock basalt exhibiting spectacular columnar jointing. Sample extracted from base of upper jointed sequence where hexagonal columns are 1 meter in diameter and 30 meters in height. This flow rests atop a 2 m unconformity consisting of sediment with imbedded basalt clasts overlying another columnar formation with 2 m diameter columns. Hand sample appears mesocratic with apparent olivine phenocrysts of 2 mm but widely dispersed in a very fine grained groundmass (Photograph 5.2).

Photograph 5.2 Massive basalt cap-rock flow showing colonnade and entablature.
RN12:
-Samples 12A and 12B were collected at the base of adjacent talus slopes. These slopes are a younger erosion feature as the result of the bisecting of a much older unnamed volcano by the Rio Colorado River. The left slope consisted predominantly of red scoria where the right slope was comprised of black scoria. Sample 12A is scoria retrieved from the right slope. Hand sample shows moderate elongated vesicles inferring trachytic texture and oxidation as evidence of alteration. 12B is a baseball sized piece of basalt from the left slope scoria slope. Since its character was not consistent with either slope, the association is unknown. Hand sample is predominantly aphanitic, melanocratic (Photograph 5.3).

Photograph 5.3 Talus slopes showing compositional variation in eruption episodes.
RN13:
- Thin lava flow capping the topography. Hand sample is melanocratic, porphyrytic with plagioclase up to 4mm phenocrysts.

RN15:
- Lava flow with associated cinder cone. Hand sample is melanocratic with moderate spherical vesiculation of 0.5-14mm and fine groundmass.

RN16A and RN16B:
- Samples are from two flows at the same road-cut location. 16A is the insitu top flow (1m thick) exhibiting plagioclase, some vesicles, in a fine melanocratic groundmass. Sample 16B is from rock piles near the road-cut and match characteristics of the underlying flow. Hand sample shows that 16b is mesocratic, plagioclase rich, contains more vesicles but, no apparent olivine. Both samples maybe associated with cinder cones visible to the south.

CV1, CV2, CV3:
The CV samples are from the area immediately around Cochiquito volcano (background in photograph 5.4).

CV1:
- Collected at the small lava flow outcrop (fore-ground labeled 1, photograph 5.4) north of Cochiquito. The sample is melanocratic and fine grained with olivine phenocrysts of 1mm.

CV2:
- Retrieved from the wall of a wash (1m depth), is similar in appearance to CV1-melanocratic, fine grained matrix but, slightly larger olivine phenocrysts (1-2mm). (Labeled 2 in middle of photograph 5.4).

CV3:
- Was collected at the south flank of Cochiquito. It is the darkest gray of all samples, fine grained and olivine as the visible phenocryst phase. (Labeled 3 in photograph 5.4).
CS1:
-An eroded cinder cone 5.85km due south of Cochiquito. The sample is taken from an outcrop at the top of the cone where, low volume vertical cross cutting dikes (<1m) also occur (Photograph 5.5). Hand sample is melanocratic, phaneritic, and has subtle flow banding and olivine phenocrysts of 1mm.

Photograph 5.4 Cochiquito Volcano: 1-Lava flow, 2- Oldest Cochiquito crater rampart, 3- Youngest Cochiquito Cone.

Photograph 5.5 Eroded cinder cone showing cross cutting dikes and out crops.
**BC1, BC3:**
- Field site is comprised of several cinder cones behind the town of Barrancas (Photograph 5.6). BC1 is leucocratic, phaneritic consisting of plagioclase phenocrysts of 2mm and a large phenocryst of aegerine-augite of 2cm and heavily oxidized. BC3 is mesocratic, exhibiting plagioclase phenocrysts of 1-5mm in a fine grained groundmass.

Photograph 5.6 Shows series of Basaltic-trachyandesite cinder cones behind the town of Barrancas.
6. Petrographic analysis

CV1- Basalt

Texture
Holocrystalline, porphyritic, glomeroporphyritic, vesicular, trachytic, consisting of orientated euhedral phenocrysts of fine (.5-1mm) plagioclase laths, subhedral to anhedral olive phenocrysts (1-2mm).

Groundmass
Holocrystalline; consisting of microcrystalline plagioclase phenocrysts and cryptocrystalline material intersperse with a subhedral isotropic oxide phase.

Abundances
Groundmass 75 %
Phenocrysts 15%
Vesicles 10%

Phenocrysts

Olivine
Euhedral - anhedral phenocrysts of 1-2mm, glomeroporphyritic. Hi birefringence, parallel extinction and nearly clear in plane light. Phenocrysts contain euhedral spinel and opaque oxide inclusions.

Plagioclase
Most abundant phenocrysts all of which are found in the ground mass, predominantly as euhedral microlites. Apatite within phenocrysts, occur as transparent stubby prismatic crystals.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and found as inclusions in olivine.

Spinel
Occur as light green euhedral to subhedral phenocryst in olivine.
Photograph 6.1 Sample CV1 (magnification - 4x). Glomeroporphyrtic olivine phenocrysts (Ol).

Photograph 6.2 Sample CV1 (magnification - 63x). Light green spinel inclusions within olivine phenocryst.
CV2-Basalt

Texture
Holocrystalline, porphyritic, glomeroporphyritic, vesicular, trachytic, consisting of euhedral to subhedral phenocrysts of medium grained olive (1-2mm) in a fine grained matrix of microcrystalline plagioclase laths.

Groundmass
Holocrystalline; consisting of microcrystalline plagioclase phenocrysts and cryptocrystalline material intersperse with a subhedral isotropic oxide phase.

Abundances
Groundmass 75 %
Phenocrysts 15%
Vesicles 10%

Phenocrysts

Olivine
Euhedral - anhedral phenocrysts of 1-2mm some glomeroporphyritic. High birefringence, parallel extinction and nearly clear in plane light. Phenocrysts contain euhedral – subhedral spinel and opaque oxide inclusions.

Plagioclase
Most abundant phenocryst that is found in ground mass only, predominantly euhedral microlites. Apatite within phenocrysts, occur as transparent stubby prismatic crystals.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and found as inclusions in olivine.
Photograph 6.3  Sample CV2 (magnification - 4x). Olivine phenocryst (Ol) adjacent to glomeroporphyrtic olivine (Og).

Photograph 6.4  Sample CV2 (magnification - 63x). Spinel inclusions within olivine phenocryst.
CV3-Basalt

Texture
Holocrystalline, porphyritic, glomeroporphyritic, locally trachytic, consisting of euhedral to subhedral phenocrysts of medium grained olive (1-2mm) and subhedral phenocrysts of medium grained (1-2mm) orthopyroxene set within a fine grained matrix of microcrystalline plagioclase laths.

Groundmass
Holocrystalline; consisting of microcrystalline plagioclase laths and cryptocrystalline material intersperse with a subhedral isotropic oxide phase.

Abundances
Groundmass 75 %
Phenocrysts 25%

Phenocrysts

Olivine
Euhedral - anhedral phenocrysts of 1-2mm some glomeroporphyritic. High birefringence, characteristic fracturing, parallel extinction and nearly clear in plane light. Phenocrysts contain euhedral – subhedral spinel and opaque oxide inclusions. Biaxial positive, 2v = 90°.

Plagioclase
Exists as euhedral microphenocrysts in ground mass. Apatite abundant within phenocrysts, occur as transparent elongate prismatic crystals.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and found as inclusions in olivine and orthopyroxene.
Photograph 6.5 Sample CV3 (magnification - 10x). Euhedral and sub-hedral olivine phenocrysts (Ol).

Photograph 6.6 Sample CV3 (magnification – 63x). Euhedral spinel inclusions (Sp) in euhedral olivine phenocryst (Ol).
RN1-Basaltic andesite

Texture
Holocrystalline, vesicles - uncommon, porphyritic, phaneritic, euhedral phenocrysts consisting of fine (<1mm) to medium grained (1-3mm) plagioclase laths and euhedral to anhedral phenocrysts of olivine (~1mm), clino-pyroxene (~1mm), ortho-pyroxene (1-2mm).

Groundmass
Holocrystalline; consisting of plagioclase microlites, cryptocrystalline material evenly intersperse with an isotropic oxide phase.

Abundances
Groundmass 60%
Phenocrysts 40%
Vesicles < 1%

Phenocrysts

Plagioclase
Exhibits the greatest modal abundance of phenocrysts, predominantly euhedral crystals (1-3mm) with rounded sieve cores and non-sieve rims, oscillatory zoning, carlsbad and albite twins common with some deformation twinning evident.

Olivine
Euhedral - anhedral phenocrysts (~1mm), high birefringence, iddingsite present in cracks and rims, most containing small numbers of euhedral to anhedral opaque oxide and spinel inclusions. Biaxial positive, 2v = 80°. Glass inclusions of ~15-30µ are visible in several phenocrysts.

Ortho-pyroxene
Subhedral to anhedral phenocrysts (1-2mm), light pale green in plane light, parallel extinction and no pleochroism.

Clino-pyroxene
Subhedral to anhedral phenocrysts (~1mm) exhibiting second order birefringence and inclined extinction.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass.
Photograph 6.7  Sample RN1 (magnification - 10x) showing a plagioclase phenocryst (Pl) with oscillatory zoned rims encasing resorbed core. X-polars.

Photograph 6.8  Sample RN1, (magnification - 63x, plane polarized light). Glass inclusion (Gl) with contraction bubble and spinel (Sp) in an olivine phenocryst (Ol).
RN2-Basaltic andesite

Texture
Holocrystalline, porphyritic, vesicles – uncommon, phaneritic, euhedral phenocrysts of fine (<1mm) to medium grained (1-3mm) plagioclase laths and euhedral to anhedral phenocrysts of olivine; (~1mm): clino-pyroxene (~1mm) and ortho-pyroxene (1-2mm).

Groundmass
Holocrystalline, consisting of plagioclase microlites, olivine microlites and cryptocrystalline material evenly interspersed with an isotropic oxide phase.

Abundances
Groundmass 65%
Phenocrysts 35%
Vesicles < 1%

Phenocrysts

Plagioclase
Exhibits the greatest modal abundance of phenocrystals and groundmass, predominantly euhedral crystals (1-3mm) with rounded sieve cores and non-sieve rims, oscillatory zoning, carlsbad and albite twins common with some deformation twinning evident.

Olivine
Euhedral to anhedral phenocrysts (~1mm) containing iddingsite along fractures. Many phenocrysts with several dark to light green spinel inclusions.

Ortho-pyroxene
Subhedral to anhedral phenocrysts (1-2mm), light pale green in plane light, parallel extinction and no pleochroism.

Clino-pyroxene
Subhedral to anhedral phenocrysts (~1mm) exhibiting 2nd order birefringence and inclined extinction, many twinned.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and found as inclusions in olivine.
Photograph 6.9  Sample RN2 (magnification-4x, crossed polars). Olivine phenocryst (Ol), twinned clinopyroxene (Cpx), oxide (ox) and plagioclase exhibiting resorption core (Pl).

Photograph 6.10  Sample RN2 (magnification-4x, crossed polars). Olivine Phenocryst-iddingsite rim (Id) and light brownish-green spinel inclusions (Sp).
RN3-Basaltic andesite

Texture
Holocrystalline, porphyritic, phaneritic euhedral phenocrysts of fine (<1mm) to medium grained (1-3mm) plagioclase laths, euhedral to anhedral phenocrysts of olivine (~1-3mm), glomeroporphyrtic clinopyroxene (~2mm) and orthopyroxene(1-2mm).

Groundmass
Holocrystalline; consisting of plagioclase and olivine microlites, cryptocrystalline material evenly intersperse with an isotropic oxide phase.

Abundances
Groundmass 70%
Phenocrysts 30%

Phenocrysts

Plagioclase
Exhibits the greatest modal abundance of phenocrysts and groundmass, predominantly euhedral crystals (1-3mm) with rounded sieve cores and non-sieve rims, oscillatory zoning, carlsbad and albite twins common with some deformation twinning evident. A second plagioclase phase of euhedral phenocrystals exists without resorption features, however these crystals are sparse.

Olivine
Euhedral to anhedral phenocrysts (~1mm) containing iddingsite along fractures. Many phenocrysts with several dark to light green spinel inclusions. Several ~120µ phenocrysts contain glass inclusions of 12-16µ.

Ortho-pyroxene
Subhedral to anhedral phenocrysts (1-2mm) and several glomeroporphyrtic phenocrysts, light pale green in plane light displaying parallel extinction and no pleochroism. Many twinned.

Clino-pyroxene
Individual subhedral to anhedral phenocrysts and several glomeroporphyrtic phenocrysts (~1mm), inclined extinction. Many twinned.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine.
Photograph 6.11  Sample RN3 (magnification-63x, plane polarized light). Olivine phenocryst (Ol) shows iddingsite (Id) along fractures and glass inclusion with an oxide romb inclusion (ox).

Photograph 6.12  Sample RN3 (magnification-4x, crossed polars). Glomeroporphyritic texture of cpx (Cpx) located in bottom center of photograph.
RN7-Basalt

**Texture**
Holocrystalline, amygdaloidal (calcite filled), microporphyritic, trachytic, consisting of euhedral phenocrysts of fine (<1mm) orientated plagioclase laths, subhedral to anhedral corroded olive phenocrysts (<1mm).

**Groundmass**
Holocrystalline, microphenocrysts of plagioclase and altered olivine mixed with interstitial cryptocrystalline material.

**Abundances**
Groundmass 37%
Phenocrysts 60%
Vesicles 3%

**Phenocrysts**

**Plagioclase**
Exhibits the greatest modal abundance of phenocrysts, predominantly euhedral crystals ranging from microlites to 1-2mm phenocrysts, exhibit oscillatory zoning, carlsbad twins common, lacking lamellar twinning but some deformation twinning evident.

**Olivine**
Euhedral to anhedral phenocrysts (~1mm) the largest embayed contains iddingsite along fractures. Biaxial positive, 2v = 80-90°. Many phenocrysts display several dark (Cr rich) to light green (Mg rich) spinel inclusions.

**Calcite**
Calcite filled Amygdales.

**Apatite**
Occurs as euhedral microphenocrysts in plagioclase and pyroxene.

**Oxides**
Subhedral to anhedral phenocrysts (.3mm) of oxide phase, evenly intersperse in groundmass and also found as inclusions in olivine.
Photograph 6.13  Sample RN7 (magnification - 10x). Embayed olivine (Ol) phenocryst. Note trachytic texture NW to SE in bottom left corner of photograph.

Photograph 6.14  Sample RN7 (magnification - 10x). Vesicles filled by latter stage calcite crystals (Cc), (Amygdaloidal).
RN 11A-Basalt

Texture
Holocrystalline, porphyritic, trachytic, phaneritic, glomeroporphyritic, consisting of randomly orientated euhedral phenocrysts of fine (.5-1mm) to medium grained (1-2mm) plagioclase laths, euhedral olivine phenocrysts (1-2mm), euhedral to subhedral clino-pyroxene and ortho-pyroxene phenocrysts (1-2mm).

Groundmass
Holocrystalline, trachytic; consisting of plagioclase microlites, cryptocrystalline material intersperse with an isotropic oxide phase.

Abundances
Groundmass 70 %
Phenocrysts 30%

Phenoocrysts

Plagioclase
Exhibits large modal abundance of phenocrysts in groundmass, predominantly euhedral crystals ranging from microlites (indicating trachytic texture) to 1-2mm phenocrysts, carlsbad, albite and deformation twinning evident.

Olivine
Present as the greatest modal abundance of phenocrysts, predominantly euhedral crystals (1-2mm), some phenocrysts with euhedral opaque oxide inclusions. Biaxial positive, 2v = 90°.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine and pyroxenes,
Photograph 6.15  Sample RN11 (magnification - 4x) Olivine (Ol), plagioclase (Pl) and ground mass exhibiting trachytic texture.

Photograph 6.16  Sample RN11 (magnification – 63x) Spinel (Sp) and glass (Gl) inclusions in olivine phenocryst (Ol).
RN 12A-Basaltic trachyandesite

Texture
Holocrystalline, microporphyritic, melanocractic, vesicular-(most vesicles elongated) with calcite, trachytic, consisting of orientated subhedral phenocrysts of fine grained (.5-1mm) plagioclase laths, euhedral to anhedral olive phenocrysts (<1mm).

Groundmass
Holocrystalline; consisting of plagioclase microlites, cryptocrystalline material intersperse with an isotropic oxide phase.

Abundances
Groundmass 30 %
Phenocrysts 60%
Vesicles 10%

Phenocrysts

Plagioclase
Exhibit the greatest modal abundance of crystals ranging from microlites to .5mm phenocrysts (phenocrysts rare). Largest phenocrysts contain inclusions of anhedral spinel, rutile.

Oxides
Euhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass.

Olivine
Occurrence is rare, euhedral phenocrysts, hi birefringence, parallel extinction.

Apatite
Rod shape phenocrysts in some larger plagioclase laths, hi relief, clear in crossed polars.
**Photograph 6.17** Sample 12A (magnification – 10x). Plagioclase phenocryst (Pl) in cryptocrystalline matrix.

**Photograph 6.18** Sample 12A (magnification - 10x). Olivine phenocryst (Ol).
RN 12B- Basaltic trachyandesite

Texture
Holocrystalline, microporphryritic, consisting of randomly orientated subhedral, heavily corroded plagioclase phenocrysts (~3mm), subhedral to anhedral partially altered olive phenocrysts (<1mm). Xenolithic fragment is also present consisting of iddingsite altered olivine with interstitial plagioclase laths.

Groundmass
Holocrystalline; consisting of plagioclase and olivine microlites mixed with cryptocrystalline material, intersperse with an isotropic oxide phase.

Abundances
Groundmass 90%
Phenocrysts 10%

Phenocrysts

Plagioclase
Exhibits the greatest modal abundance of phenocrysts, predominantly euhedral crystals ranging from microlites to 3mm phenocrysts, exhibit oscillatory zoning, carlsbad twins common.

Olivine
Euhedral to anhedral phenocrysts (<.5mm) containing iddingsite along fractures and rims, some phenocrysts with euhedral opaque oxide inclusions.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine.

Apatite
Rod shape phenocrysts in some larger plagioclase laths, hi relief, clear in crossed polars.
Photograph 6.19  Sample 12B (magnification – 4x, XP). Microporphyritic texture

Photograph 6.20  Sample CS (magnification – 10x). Olivine-Plagioclase xenolith (Xe) boundary with host rock (Hr).
RN13-Basalt

**Texture**
Holocrystalline, microporphryritic, poikilitic, ophitic and sub-ophitic, consisting of euhedral phenocrysts of fine (<1mm) to medium grained (1-2mm) plagioclase laths, subhedral to anhedral partially altered olivine phenocrysts (<1mm), oikocryst clinopyroxene and ortho-pyroxenes

**Groundmass**
Holocrystalline; consisting of plagioclase and olivine microlites, Cryptocrystalline material intersperse with an isotropic oxide phase.

**Abundances**
- Groundmass 30%
- Phenocrysts 60%
- Vesicles 10%

**Phenocrysts**

**Plagioclase**
Exhibit the greatest modal abundance of phenocrysts, predominantly euhedral crystals ranging from microlites to 1-2mm phenocrysts, exhibit oscillatory zoning, carlsbad twins common, lacking lamellar twinning but some deformation twinning evident.

**Olivine**
Euhedral to anhedral phenocrysts (<.5mm) contain iddingsite along fractures and rims, some phenocrysts with euhedral opaque oxide inclusions.

**Ortho-pyroxene**
Poikilitic phenocrysts (~1mm), light pale green in plane light, parallel extinction and no pleochroism.

**Clino-pyroxene**
Poikilitic phenocrysts (~1mm) with inclined extinction and light pale green in plane light.

**Apatite**
Euhedral microphenocrysts: in plagioclase and pyroxene.

**Oxides**
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine.
Photograph 6.21  Sample RN13 (magnification - 10x) Ophitic and subophitic texture.

Photograph 6.22  Sample RN13 (magnification - 63x). Transparent apatite crystals (Ap) embedded within plagioclase phenocryst.
RN15A-Basalt

Texture
Holocrystalline, porphyritic, phaneritic, moderate vesiculation, locally trachytic, consisting of euhedral phenocrysts of fine (<1mm) to medium grained (1-3mm) plagioclase laths, euhedral to anhedral phenocrysts of olivine (<1mm), subhedral phenocrysts of clinopyroxene (~2mm), and subhedral phenocrysts of orthopyroxene (1-2mm).

Groundmass
Holocrystalline; consisting of plagioclase microlites and olivine microphenocrysts, cryptocrystalline material evenly intersperse with an abundant isotropic oxide phase.

Abundances
Groundmass 65%
Phenocrysts 15%
Vesicles 20%

Phenocrysts

Plagioclase
Exhibit the greatest modal abundance of phenocrysts and groundmass, two generations- euhedral phenocrysts (1-3mm) with extensive sieve cores, A second plagioclase phase of euhedral – subhedral phenocrysts exists without resorption feature however these crystals are just slightly larger than the groundmass crystals. Oscillatory zoning, carlsbad and deformation twinning is evident in the latter generation.

Olivine
Euhedral to anhedral phenocrysts (<1mm), iddingsite along fractures and rims is evident, light green in plane light and hi birefringence, many phenocrysts contain several dark to light green spinel inclusions. Most phenocrysts show a reaction rim with a heavy mantle of an opaque oxide phase.

Ortho-pyroxene
Individual subhedral to anhedral phenocrysts (1-2mm), light pale green in plane light, parallel extinction and no pleochroism.

Clino-pyroxene
Anhedral phenocrysts (~1mm), twinned, inclined extinction, hi relief.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and found as inclusion and mantling olivine.
Photograph 6.23  Sample RN15A (magnification - 4x, XP). Olivine phenocryst (Ol) and resorbed Plagioclase (Pl)

RN 16A-Basalt

Texture
Holocrystalline, microporphyritic, vesicular, glomeroporphyrtic, locally trachytic, consisting of randomly orientated euhedral to subhedral phenocrysts of fine (.5-1mm) plagioclase laths, euhedral to anhedral slightly altered olive phenocrysts (<1mm), clino-pyroxene and ortho-pyroxenes phenocrysts (<1mm).

Groundmass
Holocrystalline; consisting of plagioclase microlites and cryptocrystalline material moderately interspersed with an isotropic oxide phase.

Abundances
Groundmass 55 %
Phenocrysts 30%
Vesicles 15%

Phenocrysts

Plagioclase
Exhibits the greatest modal abundance of phenocrysts, two phases- sieve (largest laths) and non-sieve, predominantly euhedral crystals ranging from microlites to 1mm phenocrysts, exhibit oscillatory zoning, carlsbad twins common, lacking lamellar twinning.

Olivine
Euhedral to anhedral phenocrysts (<.5mm), with iddingsite along fractures and rims, some phenocrysts show euhedral opaque oxide inclusions.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine.
Photograph 6.25  Sample RN16A (magnification - 4x, XP).

Photograph 6.26  Sample RN16A (magnification - 10x, XP). Subhedral plagioclase phenocryst (Pl) with albite twinning.
RN 16B-Basalt

Texture
Holocrystalline, microporphyritic, vesicular, glomeroporphyrtic, consisting of randomly orientated euhedral to subhedral phenocrysts of fine (.5-1mm) plagioclase laths, euhedral to anhedral olive phenocrysts (<1mm), clino-pyroxene and orthopyroxenes phenocrysts (<1mm).

Groundmass
Holocrystalline; consisting of plagioclase microlites and cryptocrystalline material moderately interspersed with an isotropic oxide phase.

Abundances
Groundmass 60 %
Phenocrysts 30%
Vesicles 10%

Phenocrysts

Plagioclase
Exhibits the greatest modal abundance of phenocrysts, two generations - sieve (largest laths) and non-sieve, predominantly euhedral crystals ranging from microlites to 1mm, exhibit oscillatory zoning, carlsbad twins common, lacking lamellar twinning.

Olivine
Euhedral to anhedral phenocrysts (<.5mm), colorless, some phenocrysts show euhedral opaque oxide inclusions.

Ortho-pyroxene
Glomeroporphyrtic, subhedral to anhedral phenocrysts (1-2mm) are colorless to light gray-green color in plane light and display parallel extinction with no pleochroism.

Clino-pyroxene
Glomeroporphyrtic subhedral to anhedral phenocrysts (~1mm), twinned, light gray-green in plane polarized light.

Oxides
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine.
Photograph 6.27  Sample RN16B (magnification - 4x).

Photograph 6.28  Sample RN13 (magnification - 10x). Orthopyroxene phenocryst (Opx) exhibiting chemical zoning.
**CS- Basalt**

**Texture**
Holocrystalline, porphyritic, occasionally glomeroporphyritic, consisting of euhedral to subhedral phenocrysts of medium grained plagioclase (1-3mm) some serritized, euhedral to subhedral medium grained olivine phenocrysts (1-2mm) in a fine grained matrix of microcrystalline plagioclase laths and olivine.

**Groundmass**
Holocrystalline; consisting of microphenocryst plagioclase laths and cryptocrystalline material interspersed with a subhedral to anhedral isotropic oxide phase.

**Abundances**
- Groundmass 60%
- Phenocrysts 35%
- Vesicles 5%

**Phenocrysts**

**Plagioclase**
Exhibit the greatest modal abundance of phenocrysts and groundmass, euhedral – subhedral phenocrysts exist with and without slight resorption features. Oscillatory zoning and carlsbad twinning is evident.

**Olivine**
Euhedral - anhedral phenocrysts (1-2mm) altered with iddingsite along fractures and rims, some glomeroporphyritic. Hi birefringence, parallel extinction and light green in plane light. Biaxial positive, \(2v = 80^\circ\). Phenocrysts contain euhedral – subhedral spinel and opaque oxide inclusions. Glass inclusions also present.

**Oxides**
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and also found as inclusions in olivine.

**Calcite**
Calcite- partially filled amygdales.
Photograph 6.29  Sample CS (magnification - 4x). Euhedral olivine phenocrysts (Ol) showing iddingsite (Id) alteration along fractures and rims.

Photograph 6.30  Sample CS (magnification - 63x). Olivine phenocryst with glass inclusion (Gl) showing euhedral spinel inclusion (Sp).
**BC3- Basaltic trachyandesite**

**Texture**  
Holocrystalline, porphyritic, glomeroporphyritic, vesicular, trachytic, consisting of euhedral to subhedral phenocrysts of medium grained plagioclase (1-5mm), euhedral to subhedral olivine phenocrysts (~.5mm) in a fine grained matrix of microcrystalline plagioclase laths.

**Groundmass**  
Holocrystalline; consisting of microcrystalline plagioclase phenocrysts and cryptocrystalline material intersperse with a subhedral-anhedral isotropic oxide phase.

**Abundances**  
Groundmass 75%  
Phenocrysts 20%  
Vesicles 5%

**Phenocrysts**

**Plagioclase**  
Exhibit the greatest modal abundance of phenocrysts and groundmass, two generations- euhedral phenocrysts (1-5mm) with extensive sieve cores, A second plagioclase phase of euhedral – subhedral phenocrysts exists without resorption feature however these crystals are just slightly larger than the groundmass crystals. Oscillatory zoning, carlsbad and deformation twinning is evident in the latter generation.

**Olivine**  
Euhedral - anhedral phenocrysts (~.5mm) altered with iddingsite along fractures and rims, some glomeroporphyritic. Hi birefringence, parallel extinction and light green in plane light. Phenocrysts contain euhedral – subhedral spinel and opaque oxide inclusions. Glass inclusions also present.

**Oxides**  
Subhedral to anhedral phenocrysts (.3mm) of oxide phase evenly intersperse in groundmass and found as inclusions in olivine.

**Apatite**  
Abundant rod shape phenocrysts in larger plagioclase laths, hi relief, clear in crossed polars.
Photograph 6.31  Sample BC3 (magnification - 10x, XP). Resorped Plagioclase (Pl).

Photograph 6.32  Sample BC3 (magnification - 4x, XP). Olivine (Ol) and plagioclase (Pl) in trachytic texture.
7. Results

7.1 Whole Rock Major Element Chemistry

Sixteen volcanic samples were collected at lava flows and cinder cones from a 49km Northeast-Southwest transect in the Ranquil del Norte – Barrancas region of Argentina. These samples were analyzed for major and trace element concentrations by XRF-UMASS (Table 7.1) and ICPMS60, ICPAES-SGS respectively (Table 7.2). Data is plotted in bivariate graphs to facilitate characterization and grouping of samples into rock type through-out the following chapters.

<table>
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<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3^+$</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
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<td>1.52</td>
<td>17.22</td>
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<td>0.19</td>
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<td>0.53</td>
<td>99.96</td>
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<td>7.89</td>
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<td>17.14</td>
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<td>6.99</td>
<td>9.03</td>
<td>3.14</td>
<td>0.81</td>
<td>0.28</td>
<td>100.19</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 7.1 XRF major element analyses of 16 samples collected in the Barrancas region of Argentina.
The Total Alkalis vs. Silica (TAS) diagram (Fig. 7.1a) of Le Maitre, classifies volcanic rock on the basis of wt. % total alkalis oxides (Na$_2$O + K$_2$O) versus wt. % SiO$_2$. The TAS diagram is subdivided into six fields based on silica content: Picrite (<45 wt.% SiO$_2$), Basalt (45-52 wt.% SiO$_2$), Basaltic Andesite (52-57 wt.% SiO$_2$), Andesite (57-61 wt.% SiO$_2$), Dacite (63-77 wt.% SiO$_2$) and Rhyolite (>77 wt.% SiO$_2$). The diagram field is additionally subdivided between the alkaline and sub-alkaline series reflecting a proportional relationship between (Na$_2$O+K$_2$O) and SiO$_2$ (Irvine and Baragar, 1971). The Barrancas samples range from basalt to basaltic trachy-andesite (Figure 7.1a), the majority nevertheless, is basaltic with SiO$_2$ content of 47 to 52 wt. % and Na$_2$O + K$_2$O content of 2 to 4.5 wt. %. Therefore, all samples are classed as sub-alkaline.

![Figure 7.1a Total Alkali vs. Silica diagram of the Barrancas samples showing classification of groups (Le Maitre, 1976).](image-url)
Although it may be argued that the Barrancas rocks form an overall fractionation trend, the TAS diagram reveals the Barrancas rock suite is comprised of three segregated groupings of rock types. The basaltic group (CV1, CV2, CV3, CS1, RN7, RN13, RN15A, RN16A, RN16B and RN11), the basaltic andesite group (RN1, RN2 and RN3) and the basaltic trachy-andesite group (BC3, RN12A and RN12B).

Since all the Barrancas samples are classified sub-alkaline, the total K₂O vs. SiO₂ diagram (Gill, 1981) can be used for further discrimination that distinguishes high and intermediate K₂O wt. % (calc-alkaline rock) from low K₂O wt. % (tholeiitic) volcanic rock. Most samples fall within the Medium K field, but the three Cochiquito cinder cone samples (CV1, 2, 3) and a cinder cone west of Barrancas (BC3) are shown to be marginally in the High K field of the diagram (Figure 7.1b).

**Figure 7.1b** Barrancas samples divided into sub-alkaline series classification. The sub grouping of the Barrancas suite is also apparent here.
Plotting of the Barrancas data in the SiO$_2$ vs. MgO bivariate diagram shows a rather narrow range of SiO$_2$ concentrations (47-55 wt. %) but, a wider range in MgO concentrations (3.5-11 wt. %). The general trend of the samples is increasing SiO$_2$ with decreasing MgO. However, upon closer examination, several segregated groupings of data plus one outlier-sample **RN11**, are also revealed. Two of the groups (most silica enriched) display tight compositional ranges (MgO-3.4 to 3.5 wt. % and 5.87 to 5.89 wt. %, left to right in diagram) but, the third group, consisting of majority of the Barrancas samples, shows a narrow range in SiO$_2$ but, a dispersed range of MgO concentrations (4-11 wt. %)(Fig. 7.2a).

**Figure 7.2a** SiO$_2$ vs. MgO bivariate diagram of Barrancas suite showing overall decreasing trend of MgO with increasing SiO$_2$. Segregation of data into several distinct groupings is also apparent.
If we accept, the supposition that the Barrancas suite is a compilation of several suites (CV, RN, and BC groups) the major element vs. MgO data plotted in Harker type diagrams (Fig.7.2-7.5) shows no coherent trends either within the segregated groups or between them. Additionally, the three Cochiquito Volcano samples CV1, CV2, and CV3, are regularly displayed as a tight assemblage of data in the bivariate diagrams and may be considered as another subgroup. However, these samples as a subgroup (CV1, CV2, and CV3) have similar intra-group but, variable major element concentrations as compared to the other members of the CV group. Sample RN11 is consistently an outlier in the major element vs. MgO plots and the most mafic of all with MgO concentration of 10.22 wt. %. The groups can be characterized as:

**BC group**

- Highest concentrations of SiO$_2$, K$_2$O, Na$_2$O, Al$_2$O$_3$, and P$_2$O$_5$
- Lowest concentrations of MgO, CaO, and Fe$_2$O$_3$
- Uniform major element concentrations intra-group
- No apparent enrichment trends

**RN group**

- Intermediate concentrations in all major elements
- Uniform major element concentrations intra-group
- No apparent enrichment trends

**CV group**

- Highest concentrations of CaO and Fe$_2$O$_3$ (CV1, 2, 3- highest P$_2$O$_5$)
- Generally the Lowest concentrations of SiO$_2$, K$_2$O, Na$_2$O, Al$_2$O$_3$
- Wide range in all major element concentrations
- No apparent enrichment trends
Figure 7.2b SiO$_2$ vs. MgO (top), K$_2$O vs. MgO (bottom) bivariate diagrams showing Barrancas rocks segregated into several distinct groupings. Cochiquito volcano samples are enclosed in yellow circle.
Figure 7.3 $\text{Al}_2\text{O}_3$ vs. MgO (top), Na$_2$O vs. MgO (bottom) bivariate diagrams showing Barrancas rocks segregated into several distinct groupings. Cochiquito volcano samples are enclosed in yellow circle.
Figure 7.4 CaO vs. MgO (top), Fe$_2$O$_3$ vs. MgO (bottom) bivariate diagrams showing Barrancas rocks segregated into several distinct groupings. Cochiquito volcano samples are enclosed in yellow circle.
Figure 7.5 TiO$_2$ vs. MgO (top), P$_2$O$_5$ vs. MgO (bottom) bivariate diagrams showing Barrancas rocks segregated into several distinct groupings. Cochiquito volcano samples are enclosed in yellow circle.
Although there is a range in rock type classification of the Barrancas samples, the three distinct groups correlate with a specific geographic location. The three basaltic-andesite samples are from lava flows located in the northern most section of the collection region (RN1, 2, 3) and the three basaltic trachy-andesite samples (BC3, RN12A+B) were collected within a three kilometer radius of Barrancas. The remaining basaltic samples appear to be concentrated to the east of and to the south of Barrancas (Figure 7.5)

Figure 7.5 Rock type groupings of Barrancas samples: Basaltic-andesite RN1, 2, 3, Basaltic trachy-andesite BC3, RN12A+B, Basaltic-all other samples.
7.2 Whole Rock Trace Element Chemistry

The 16 Barrancas samples analyzed for trace element abundance, are presented in table 7.2, and are plotted in Harker, REE abundance and incompatible element diagrams.

The elements Cr, Ni and Co are highly compatible in solid phases. They preferentially remain in the residua during melting processes and are taken-up in refractory minerals during the initial crystallization of the magma. This attribute makes them particularly useful in identifying magma source lineage and crystal fractionation processes.

Figure 7.6 Cr vs. MgO Harker diagram showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
The Barrancas samples considered as a rock suite show a strong linear trend in Cr, Ni, and Co indicating fractionation. However, the Barrancas samples were previously classified in TAS diagram as three subgroups CV, RN, and BC. As such, show no fractionation trends (Figures 7.6-7.7).

**Figure 7.7** Ni vs. MgO (top) and Co vs. MgO (bottom) Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
The LILE vs. MgO charts show no intra or inter group trends (Figs. 7.8, 7.9)

The groups can be characterized as:

**BC group**

- Highest concentrations of CS, Rb, Sr, and Ba
- Lowest MgO concentrations
- Similar LILE concentrations intra-group
- No apparent enrichment trends

**RN group**

- Intermediate concentrations in all LILE elements for a similar MgO value
- Uniform LILE concentrations intra-group
- No apparent enrichment trends

**CV group**

- Intermediate to lowest concentrations of CS, Rb, Sr, and Ba (except CV1, 2, 3)-which have a tight range and intermediate to high concentrations of CS, Rb, Sr, and Ba).
- Wide range in all LILE concentrations over wide range of MgO values
- RN11 consistent outlier
- No apparent enrichment trends
Figure 7.8 Cs vs. MgO (top) and Rb vs. MgO (bottom) Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
Figure 7.9 Ba vs. MgO (top) and Sr vs. MgO (bottom) Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
The light rare earth (LREE), mid rare earth (MREE) and the heavy rare earth (HREE) elements are represented by the elements La, Tb, and Y respectively in the following charts (Figs. 7.10, 7.11).

The groups can be characterized as:

**BC group**

- High concentrations of La, and Tb with lowest MgO,
- Variable range of Tb and Y for a given MgO value
- Similar concentrations in La
- No apparent enrichment trends

**RN group**

- Intermediate concentrations in all REE elements with intermediate MgO
- Variable range of Tb and Y for a given MgO value
- No apparent enrichment trends

**CV group**

- Generally, intermediate to low concentrations of La, Tb and Y with CV1, 2 and 3 have intermediate to high concentrations of La,
- Wide range in all trace element concentrations and MgO
- RN11 consistent outlier
- No apparent enrichment trends
Figure 7.10 La vs. MgO (top) and Tb vs. MgO (bottom) Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
The High Field Strength element (HFSE) diagrams (Figs. 7.12, 7.13) display similar relationships as seen in the previous trace element diagrams with three notable distinctions. 1; the BC group is the most enriched in HFSE (Th, Pb, U, and Zr). 2; the RN group exhibits a tighter range of HFSE concentrations with a similar MgO value except in Pb where the concentrations are more variable with a similar MgO value. 3; the CV group data forms a narrower horizontal array of values in the HFS diagrams whereas, in previous trace element diagrams, data was diffusely distributed with a wide range in trace element concentrations.

**Figure 7.11** Y vs. MgO Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
Figure 7.12 Th vs. MgO (top) and U vs. MgO (bottom) Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
Figure 7.13 Pb vs. MgO (top) and Zr vs. MgO (bottom) Harker diagrams showing grouped Barrancas sample data. Cochiquito volcano samples are enclosed in yellow circle.
The groups can be characterized in relation to the HFS elements as:

**BC group**

Highest concentrations of Th, Pb, U, and Zr with lowest MgO,

Variable range of Th, Pb, U, and Zr for a given MgO value

No apparent enrichment trends

**RN group**

Intermediate concentrations in all HFSE elements with intermediate MgO

Tight range of Th, U, and Zr for a given MgO value

Variable range of Pb for a given MgO value

No apparent enrichment trends

**CV group**

Generally, lowest concentrations of Th, U, and Zr

Intermediate concentrations of Pb

Wide range in all HFS element concentrations

RN11 consistent outlier

No apparent enrichment trends

Figure 7.14 shows the relationship of all Barrancas groups to end member compositions defined by La/Sm (Fluid/melt mobile elements) and Dy/Yb (Depth of melting). The Barrancas rocks are distributed between all three end members with the exception of BC3 and RN13 which, are firmly in the IAB and OIB fields, respectively.
Figure 7.14a La/Sm vs. Dy/Yb diagram shows the relationship of the Barrancas rocks to end members characterized by LREE (La/Sm) and HREE (Dy/Yb). The Barrancas rocks are situated between all three end-member fields, (IAB)-Island Arc Basalt, (OIB)-Ocean Island Basalt, (MORB)-Mid-Ocean Ridge Basalt.
Figures 7.14, 7.15 and 7.16 plot all Barrancas samples in primordial mantle normalized incompatible element diagrams. The samples are plotted as the three Subgroups defined by the TAS diagram in figure 7.6.

The RN subgroup displays moderate; LILE, K and Pb enrichment, Ta-Nb, Ti anomalies in comparison to OIB and parallel profiles between samples. Aside from deviations and minor depletions in some HFSEs (Ti, Hf) and HREEs (Tb, Y), the RN sub-group resembles OIB in trace element abundance and slope (Fig. 7.14, top).

The BC samples are the most enriched in trace elements of the Barrancas samples and show similar LILE, K, Pb enrichment and Ta-Nb, Ti anomalies to the RN sub-group. Additionally, the BC sub-group samples parallel the slope of the OIB pattern but, with slightly higher concentrations (Figure 7.14, bottom).

The remaining samples (CV sub-group) show a more widely distributed range of trace element values. Because of deviations from other CV group members in previously depicted trace element diagrams, the CV group is sub-divided into two sub-groups; CVa (CV1, CV2, CV3) and CVb (CS1, RN7, RN13, RN12A, RN16A, RN16B, RN11).

The CV1, CV2, CV3 samples are nearly identical in trace element patterns and display LILE enrichments, modest Ta-Nb and Ti negative anomalies(Figure 7.15, top). They are also the second highest group in overall trace element concentrations. Lacking in the CV profiles is a significant enrichment in Pb and P depletions seen in most Barrancas samples.
Figure 7.14 Primordial mantle normalized incompatible element diagrams comparing Barrancas RN sub-group (top) and Barrancas BC sub-group to representative OIB and MORB.
Figure 7.15 (bottom) displays the other members of the CV sub-group. Enrichment in the LILEs and LREE are somewhat variable between samples yet, are similar for the other trace elements. The most significant traits are the moderate Ta-Nb negative anomalies (most depleted of the Barrancas rocks) and the moderate spike in Pb. Ta and Pb concentrations were below detection limits for RN 7, RN11, RN16B and CS1, thereby creating the appearance of deviations from parallel trends. A steeper sloping pattern of HFSEs (Zr, Ti) and HREEs (Hf to Y) are apparent for these samples possibly indicating retention in a refractory mineral phase.
Figure 7.15 primordial mantle normalized incompatible element diagrams comparing Barrancas CV sub-group to representative OIB and MORB.
The only sample not exhibiting convincing arc characteristics (pronounced LILE enrichment, Ta-Nb, Ti, and P negative anomalies) is the Barrancas RN13 rock (Figure 7.16).

Figure 7.16 Primordial mantle normalized incompatible element diagram comparing the Barrancas RN13 sample (only sample lacking a distinct Ta-Nb anomaly) to representative OIB and MORB.
The rare earth element data for the Barrancas rocks is displayed in figures 7.17-7.18. Plotted along with the volcanic centers are the MORB and OIB REE patterns. A key feature distinguishing MORB from OIB is the enrichment of the HREEs (Er-Lu) in MORB relative to OIB.

The Barrancas RN sub-group exhibits intermediate values between MORB and OIB, is more similar to the OIB profile but, shallower in slope. The RN slopes slightly flatten in the HREEs and straddle the OIB profile in Er-Lu (Figure 7.17, top). There is some variation between the RN profiles in enrichment yet, they are roughly parallel. None of the RN sub-group samples display an Eu anomaly.

The Barrancas BC sub-group is: slightly more enriched in LREEs than the RN subgroup (BC sub-group is the most enriched of the barrancas rocks), shows no Eu anomalies and flattens in slope across the HREEs (Dy-Lu) (Figure 7.17, bottom). LREE and MREE values of the BC sub-group parallel the OIB values but, are lower. A transition in slope of the Barrancas rocks occurs in the HREEs to higher values than OIB.
Figure 7.17 Chondrite normalized rare earth element diagram comparing Barrancas RN sub-group (top) and BC sub-group samples (bottom) to representative OIB and MORB.
Figure 7.18 exhibits the CV sub-group in two diagrams. The top diagram shows that CV1, CV2, and CV3 (CVa sub-group) are nearly superimposed in REE values except for the shallow EU depletion in CV3. The CV slope is similar to but, depleted as compared to OIB and flattens in slope through the HREE. The other members of the CV sub-group (CVb) display LREE patterns that are distributed between MORB and OIB (Figure 7.18, bottom). They are the least enriched in LREEs as compared to OIB and all other Barrancas rocks. These patterns converge at the mid-REE Sm and flatten in slope through the HREEs. Exceptions to the general patterns of the CVb sub-group are RN13 and RN11 (the most mafic sample). RN13 and RN11 steepen in slope at the MREEs Gd and Tb respectively. They are the only Barrancas samples exhibiting REE abundances that are entirely depleted in relation to MORB and OIB.
Figure 7.18 Chondrite normalized rare earth element diagram comparing Barrancas CVa sub-group (top) and CVb sub-group samples (bottom) to representative OIB and MORB.
7.3 Barrancas Isotopes

Since there are small mass differences between isotopes of an element, isotopes are not fractionated by geological processes and reflect the initial composition of the source region. This characteristic allows for the identification of magma sources, degrees of magma mixing and lithospheric/crustal contamination.

In the Sm-Nd isotope system, the radioactive parent, $^{147}$Sm decays into its radiogenic daughter $^{143}$Nd. Both elements are LREEs and preferentially fractionate into liquid phases. Nd however, has a larger atomic radius than Sm which causes it to be concentrated slightly more in the melt relative to Sm. The abundance of $^{143}$Nd (initial and radiogenic) in rock is indicated by its relationship to $^{144}$Nd, a stable isotope in constant abundance in all rocks. Since Nd isotopes (and other LREEs) are preferentially removed during partial melting, rocks that show high Sm/Nd ratios (LREE depleted) produce higher $^{143}$Nd/$^{144}$Nd ratios with time whereas, rocks that show low Sm/Nd ratios (LREE enriched) produce lower $^{143}$Nd/$^{144}$Nd ratios.

Consequently, enriched continental crust has lower $^{143}$Nd/$^{144}$Nd ratios and lithospheric/asthenospheric mantle will have higher $^{143}$Nd/$^{144}$Nd ratios (Faure and Mensing, 2005). A drawback of the Sm-Nd isotope system is that the isotopic signature of a small amount of incorporated crustal material becomes overprinted when mixed with a large proportion of mantle (Rollinson and Data, 1993).

The Rb-Sr system works in the opposite sense, in that the radioactive parent $^{87}$Rb is more incompatible than its radiogenic daughter isotope $^{87}$Sr. Consequently, Rb is preferentially mobile in the presence of fluids and partial melting. Rocks that show
high Rb/Sr ratios (crustal input) produce higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios over time and rocks that show low Rb/Sr ratios (lithospheric mantle input) produce lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Figure 7.19 plots the Sm-Nd and Rb-Sr systematics with the mean mixing line of representative end members MORB (high $^{143}\text{Nd}/^{144}\text{Nd}$, low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) and PDS (low $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios).

**Figure 7.19** Bi-variate ratio diagram $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ showing representative rocks of the 3 Barrancas groups plotting to the right of a mixing line of MORB (NCR-North Chile Ridge) and PDS (Pacific Detrital Sediment). BSE-Bulk Silicate Earth.
Plotting of Barrancas data in figure 7.19 indicates that their compositions can be explained by the mixing of MORB and sediment sources (PDS) alone. Variations off the mean mix line are likely the result of a sediment or crustal component with higher $^{87}$Sr abundances.

Pb isotope systems are also a good indicator of crustal contamination. Pb may be produced by three decay reactions of Uranium and Thorium: $^{238}\text{U} \rightarrow ^{234}\text{U} \rightarrow ^{206}\text{Pb}$, $^{235}\text{U} \rightarrow ^{207}\text{Pb}$ and $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$. Each radioactive parent is an incompatible trace element and tends to fractionate into fluid/melt phases and subsequently, into the crust. Reservoirs with high concentrations of U and Th will with time, produce high $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Based on concentrations of U, Th, and Pb, three reservoirs have been characterized; upper crust, lower crust and upper mantle (Zartman and Doe, 1981). In the upper crust U, Th and Pb display high concentrations with Pb relatively depleted to U and Th. The upper crust thus produces radiogenic Pb. The lower crust is depleted in U and Th therefore; abundances are based on non-radiogenic Pb. The upper mantle contains lower U, Th, and Pb than the upper crust but, higher than the lower crust thereby producing intermediate radiogenic Pb values.

The $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 7.20, top) and $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 7.20, bottom) diagrams shows data is positioned along a mixing line of minimum values of MORB and PDS. Most Barrancas rocks form an array along the mix lines toward lower $^{208}\text{Pb}$, $^{207}\text{Pb}$ and $^{206}\text{Pb}$. Sample RN13 is positioned off the mix line indicating the mixing in of a possible third unknown low $^{206}\text{Pb}$ end member.
Figure 7.20 $^{208}\text{Pb}/^{204}\text{Pb}$ (top), $^{207}\text{Pb}/^{204}\text{Pb}$ (bottom) vs. $^{206}\text{Pb}/^{204}\text{Pb}$ Diagrams shows most Barrancas rocks along the mixing line of MORB and PDS, but sample RN13 is positioned to the left suggesting a mixing with a third low $^{206}\text{Pb}$ end member.
Figure 7.21 shows that all Barrancas rocks can be produced by the mixing of MORB and PDS.

*Figure 7.21* $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram shows Barrancas rocks plot along the mixing line of MORB and PDS with RN 13 displaying the lowest Pb values.

The $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 7.22, top) and $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 7.22, bottom) diagrams produce mirror images of each other depicting opposing source systematics that suggest the assimilation of a third low $^{206}\text{Pb}$ end member. The trend of the Barrancas rocks to the left of the mix line also shows that this third end member source is likely a non-sedimentary crustal reservoir as suggested by relatively higher Sr (crustal influence), lower Nd (also indicating crustal influence) and low Pb.
Figure 7.22 $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (top) and $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ (bottom) diagram shows some Barrancas rocks plot along the mix line of MORB and PDS, but most plot to the left of the mix line.
### Table 7.2 Whole rock trace element analyses of the 16 Barrancas samples.

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Aver. % Dev. | -0.50  | 67.30 |
Aver. % Dev.-AES | -0.20 | -4.96 |
Aver. % Dev.-MS | -0.58 | 93.10 |

Table 7.3 ICP-MS and ICP-AES precision determined by duplicate analysis. * Denotes cation %, all other trace elements reported in ppm.
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Table 7.4 Pb analyses.

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Table 7.5 Sr analyses with analytical precision.

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Table 7.6 Nd analyses with analytical precision.
8. Regional Setting of the Barrancas Rocks

8.1 Transect Centers

Since the Barrancas rocks as a suite display no coherent differentiation trends, the decision was made to include data from other volcanic centers in the region for comparative analyses. The volcanic centers chosen for this comparison Llaima, Talhuaca, Callaqui, Caviachue-Copahue complex, Loncopue-Las lajas, Tromen, and Payun Matru, form an East-West transect through the Southern Andes (Figure 8.1).

![Figure 8.1 Transect area indicating volcanic centers Llaima, Talhuaca, Callaqui, Caviachue-Copahue complex, Loncopue-Las Lajas, Tromen, and Payun Matru.](image-url)
The volcanoes Llaima, Talhuaca, Callaqui configure the arc axis in this region and are characterized as;

**Llaima:** the western and southern most center of this transect and is a stratovolcano of Holocene age. It is one of the largest and most active volcanoes of the southern Andes having erupted 50 times since 1750 and as recent as 2009 (GVP, 2013). Volcanics of Llaima are largely basaltic and basaltic andesite (Hickey et al., 1986).

**Talhuaca:** a late-Pleistocene to Holocene, basaltic-andesitic stratovolcano. Only fumarolic activity has occurred from this volcano during historical time.

**Callaqui:** a basaltic-andesitic, crater row/stratovolcano of late-Pleistocene to Holocene age (Muñoz B and Stern, 1988). It is constructed along an 11 km (7 mi) long fissure above a 1.2-0.3 million year old Pleistocene edifice. Primarily, fumarolic activity has been reported for this volcano but, a small phreatic ash eruption occurred in 1980 and several reports of ash plumes in 2009 and 2012 are recorded (GVP, 2013).

The remaining transect volcanic centers are located to the east of the volcanic arc and are characterized as:

**Caviahue-Copahue complex:** consists of a Quaternary stratovolcano (Copahue) that sits upon the southwest wall of an older Pliocene caldera (Caviahue) 30km east of the current arc front. Volcanic products of the complex range from basaltic andesite to rhyolite in the caldera walls whereas rocks from Copahue are classed as
basaltic trachyandesite and trachyandesite (Varekamp et al., 2006). Several additional traits distinguish Copahue from Caviahue compositions. The Copahue rocks are enriched in LILE and exhibit higher $^{87}\text{Sr}$ and higher Pb isotope ratios as compared to Caviahue.

**Loncopue-Las Lajas**: a 30-40km wide, 300km N-S striking graben, 60km east of the current volcanic front. It is proposed to be linked with Pliocene-Pleistocene extension (Ramos and Kay, 2006) with evidence of crustal thinning at this location (Yuan et al., 2006). Volcanics covering the graben are characterized as Pleistocene basaltic lavas with many Pleistocene-Holocene monogenetic cinder cones that produced alkali basalts and pyroclastic deposits possibly from the Copahue-Pino Hachado uplift to the west (Muñoz and Stern, 1989).

**Tromen**: an active (Pleistocene-recent) back-arc andesitic-to-rhyolitic volcanic complex 124km east of the current arc front. At the surface, the most voluminous products of Tromen are basaltic lava flows (Zöllner and Amos, 1973). An early geochemical analysis of Tromen lavas yielded a cal-calkaline signature (Llambí´as et al., 1982). Other studies indicated that the Tromen lavas are more alkaline and have intraplate-like signatures different from those of the main volcanic arc: they (Stern et al., 1990).

**Payun Matru**: a massive Holocene hawaiian-style shield volcano 186 km east of the current arc front. The high point of the massif is 3680-m-high Cerro Payún stratovolcano, constructed over the SW flank of the shield. Post-caldera basaltic eruptions produced more than 300 eruptive centers, mostly along E-W-trending
fissures that extend across the entire shield volcano. Numerous trachyandesite lava domes and basaltic lava flows were erupted contemporaneously with the basaltic fissure eruptions (Inbar and Risso, 2001; Pasquarè et al., 2008).

Insertions of data from the accompanying volcanic centers into the TAS and K₂O vs. Silica diagrams show that Llaima, Talhuaca, Callaqui (REA, 2009), (GeoRoc), Caviahue-Copahue (de Moor et al., 2003) Tromen (Kay and Copeland, 2006) and Payun Matru (Pasquarè et al., 2008) rocks have tight compositional ranges whereas the Barrancas, Loncopue and Las Lajas (LPE/LLB) have a wide compositional spread (Figure 8.2).

Copahue rocks are more silicic (≈ 57 wt. % SiO₂) than all Barrancas samples and exhibit slightly higher alkalis concentrations (≈ 6 wt. %). Caviahue volcanism predates Copahue development, shows a somewhat disperse linear trend from basalt to andesite and is slightly more silicic (≈ 52 wt. %) than most of the Barrancas samples (49.11-50.84 wt. % SiO₂). However, the Barrancas samples (RN1, 2, 3) and BC groups do show a resemblance to the Caviahue rocks. The (RN1, 2, 3) group has similar alkali and silica concentrations as compared to the lower end of the Caviahue trend and the BC group lies midway within the Caviahue trend but, with higher alkali concentrations.

Tromen, Payun Matru, Loncopue (LPE), and Barrancas sub-group CV are classified as basalts in the TAS diagram. However, Tromen, Payun Matru and Las Lajas (LLB) samples are slightly more alkallic than the Barrancas samples for a
similar SiO$_2$ concentration. The Loncopue data are the most similar to the basaltic Barrancas groups.

Figure 8.2 TAS diagram (Top) and sub-alkaline discrimination diagram (Bottom) displaying classification of volcanic rocks reviewed in this study.
The Las Lajas samples reveal no clear classification or trend as a rock series given the scattered distribution of data points between the basalt and trachy-basalt fields in the TAS diagram.

Irvine and Baragar’s (1971) boundary between alkaline and sub-alkaline on the TAS diagram, shows that Payun Matru, Tromen and some Las Lajas rocks are generally classified as alkaline whereas all the remaining volcanic centers are classified as sub-alkaline (Figure 8.2).

Major element Harker type diagrams (Figures 8.3 through 8.6) also portray Llaima, Talhuaca, Callaqui, Caviahue-Copahue, Tromen and Payun Matru data in

![SiO₂ vs. MgO Harker type diagram](image)

**Figure 8.3** SiO₂ vs. MgO Harker type diagram for all volcanic centers of this study. (Llaima, Callaqui and Talhuaca-trench proximal, Payun Matru-trench distal).
either tight compositional ranges or coherent trends whereas, the Barrancas and Loncopue/Las Lajas volcanic centers exhibit a much wider compositional spread. All volcanic centers of this study show a negative correlation of MgO with increasing SiO$_2$ except the Loncopue/Las Lajas volcanic centers which show no trend in SiO$_2$ concentration with decreasing MgO.

Two other trends are observed in the Harker type diagrams in regards to Llaima, Talhuaca, Callaqui, and Caviahue-Copahue (arc and near arc volcanoes); a trend of increasing SiO$_2$, K$_2$O, Na$_2$O, with decreasing MgO toward the foreland (Figures 8.3, 8.4) and the decrease of CaO, TiO$_2$, and Fe$_2$O$_3$ with decreasing MgO toward the foreland (Figures 8.5, 8.6). All volcanic centers show neither an increase nor decrease in Al$_2$O$_3$ with decreasing MgO toward the foreland.

A trend of K$_2$O and Na$_2$O enrichment with decreasing MgO is observed for all volcanic centers samples except Loncopue which shows no trend of K$_2$O and Na$_2$O (Figure 8.4). The majority of the Barrancas samples are less sodic than the comparative samples. Of the Barrancas samples, the BC group is the most enriched in Na$_2$O and has analogous values to the more evolved Copahue rocks. The Barrancas samples RN1, RN2, RN3 show the lowest Na$_2$O and a slight similarity to the values of the Tromen, Payun Matru and Las Lajas volcanic centers.

The BC group displays higher K$_2$O than Payun Matru, CS, (RN1, 2, 3), (RN7, 13), Loncopue and Caviahue samples but, a similarity in values to the Callaqui, Copahue and Las Lajas (some) samples.
The Al\textsubscript{2}O\textsubscript{3} data shows the majority of all samples are high alumina (≈17-21 wt. % Al\textsubscript{2}O\textsubscript{3}), a characteristic often detected in association with calc-alkaline basalts from subduction zones (Winter, 2010). In contrast, the majority of Las Lajas samples and some from Tromen, Copahue and Payun Matru are slightly below the lower limit of the high alumina range. The Loncopue data indicates increasing Al\textsubscript{2}O\textsubscript{3} with decreasing MgO and the Callaqui data show decreasing Al\textsubscript{2}O\textsubscript{3} with decreasing MgO (Figure 8.5, top) whereas all other volcanic centers lack trends.

A decreasing trend in CaO with decreasing MgO in can be seen in Llaima, Talhuaca, Callaqui, Caviahue-Copahue complex, but, most rocks from LLB, Tromen and Payun Matru are unaffected in CaO by decreases in MgO (Figure 8.5, bottom). The Barrancas rocks are widely scattered and show no intelligible trends.

In the TiO\textsubscript{2} vs. MgO Harker type diagram Llaima, Callaqui, LLB, and Payun Matru data show clear trends of TiO\textsubscript{2} enrichment with a corresponding depletion of MgO (Figure 8.6, top). Caviahue, Copahue, Loncopue, Tromen, and Barrancas rocks display data that is widely distributed, showing no general trends.

Fe\textsubscript{2}O\textsubscript{3} data exhibits ambiguous, if any, trends with the entire compiled data set. Copahue rocks show a rather tight range in Fe\textsubscript{2}O\textsubscript{3} and Caviahue may be revealing a trend of decreasing Fe\textsubscript{2}O\textsubscript{3} with decreasing MgO but there are a significant number of data points outside of this trend. All other volcanic centers show higher but, little variation in Fe\textsubscript{2}O\textsubscript{3} and no clear trends (Figure 8.6, bottom).
Figure 8.4 Harker type diagrams $K_2O$ vs. $MgO$ (top) and $Na_2O$ vs. $MgO$ (bottom) for all volcanic centers of this study.
Figure 8.5 Harker type diagrams $\text{Al}_2\text{O}_3$ vs. $\text{MgO}$ (top) and $\text{CaO}$ vs. $\text{MgO}$ (bottom) for all volcanic centers of this study.
Figure 8.6 Harker type diagrams TiO₂ vs. MgO (top, dashed lines indicating shallow level fractionation trends of Fe-Ti oxides) and Fe₂O₃ vs. MgO (bottom) for all volcanic centers of this study.
The $P_2O_5$ vs. MgO Harker type diagram reveals a strong linear trend of increasing $P_2O_5$ with decreasing MgO within the individual data sets of Llaima, Callaqui,(arc volcanoes) and most of the Barrancas rocks (Figure 8.7). The BC sub-group and the samples CV1, 2, 3 and RN11 appear not to be associated to the other Barrancas samples or to each other in this plot. The remaining centers, Payun Matru, Tromen, Las Lajas and Copahue-Caviahue, display their normal group assemblages as seen in previous bivariate diagrams but, no trends are apparent. Noteworthy, is that most arc rocks from Llaima, Talhuaca and Callaqui fall within a range of .15 and .27 wt. % $P_2O_5$, whereas, the more easterly centers of Caviahue, Copahue, Loncopue and Tromen, range between .27 and .37 wt. % $P_2O_5$.

Figure 8.7 Harker type diagram $P_2O_5$ vs. MgO for all volcanic centers of this study.
8.2 Transect Centers Summary

The addition of data from other regional volcanic centers into the TAS, subalkaline and Harker type diagrams show them to consist of trends or in tighter compositional ranges (except LPE, LLB and Tromen) than the Barrancas samples.

The comparative volcanic centers composition, range from basalt to trachyandesite. Payun Matru and some samples from LLB and Tromen are classified as alkaline rock whereas, all other are rocks classified as sub-alkaline. The sub-alkaline discrimination diagram shows the majority of the centers fall within the Medium K field. In contrast, Llaima approaches tholeiitic compositions and the Copahue rocks straddle the Medium K and High K boundary. Most rocks display a negative correlation of MgO with increasing SiO₂, a trend of K₂O and Na₂O enrichment with decreasing MgO, ambiguous trends in Al₂O₃, decreasing trends in CaO with decreasing MgO and decreasing TiO₂ with a corresponding decrease of MgO.

The Barrancas trace data are plotted together with data from regional volcanic centers in Harker, REE abundance and incompatible element diagrams throughout this chapter.

The following diagrams use a selection of trace elements from the data set as petrogenetic indicators of magma genesis for each volcanic center of this study.
Most of the comparative volcanic centers do not show any correlation of increasing Co with increasing MgO (Figure 8.8). However, they do show tight within suite compositional ranges. Conversely, LPE, Caviahue and Talhuaca show a strong linear trend of increasing Co (with increasing MgO) ranging from a low of ≈20 ppm to ≈38 ppm, suggesting olivine fractionation.

![Figure 8.8 Co vs. MgO Harker diagram showing comparative centers and grouped Barrancas samples.](image)

The data in the Cr vs. Mgo diagram follow the same general descriptions as the Co vs. Mgo diagram, where a wide range of values for the Barrancas, and LLB samples is evident but, for the other volcanic centers a tighter compositional range is
displayed. Caviahue may show the same strong trend of olivine fractionation but, cannot be confirmed due to lack of Cr data (Figure 8.9, top).

The most distinctive trends of compatible trace elements can be seen in the Ni vs. Mgo diagram. Payun Matru and the LLB samples exhibit a steep linear trend of decreasing Ni with decreasing MgO supporting the notion of olivine fractionation. Llaima, Talhuaca, Callaqui, Caviahue-Copahue, and LPE (Tromen lacks data) also participate in this linear trend but at a much shallower slope ranging from approximately 6 to 3.5wt.% Mgo (Figure 8.9, bottom). The Barrancas samples are scattered across the entire range of the other volcanic centers. This range forms a single quasi trend or a series of individual trends within the previously classified Barrancas sub-groups that, when linked together form what appears to be a larger continuous trend.
Figure 8.9 Cr vs. MgO (top) and Ni vs. MgO (bottom) Harker diagrams showing comparative centers and Barrancas sample data.
The LIL element data (Cs, Rb, Ba and Sr) from each center form a more diffuse assemblage of compositions but, the individuality of a rock suite is maintained (Figures 8.10, 8.11). Llaima and Payun Matru preserve their tighter compositional ranges in relation to the other centers and show little variation of LILE’s with decreasing MgO. The Cs, Rb, and Ba plots reveal no trends in the centers of Payun Matru, Tromen, LLB, LPE and Llaima but, do show trends within the rock suites of Talhuaca, Callaqui and Caviahue-Copahue. Llaima displays the lowest values and enrichment of Cs, Rb, and Ba with decreasing MgO, possibly due to the thinner crust in this region (Figures 8.10, 8.11, top). Steep trends of Cs, Rb, and Ba enrichment are seen in the centers Talhuaca, Callaqui and Caviahue-Copahue which also hold the highest amounts of these trace elements. The Barrancas samples have similar abundances in Cs and Rb to Llaima, Payun Matru, LLB and Tromen but, are significantly lower than Talhuaca, Callaqui and Caviahue-Copahue. A lack of any trend is obvious in the Barrancas samples for Ba and Sr, as the data plots over the entire range of all volcanic centers (Figure 8.10). The Sr vs. MgO diagram provides little information other than a dispersed range of group values though, still maintaining the identity of individual rock suites.
Figure 8.10 Cs vs. MgO (top) and Rb vs. MgO (bottom) Harker diagrams showing comparative centers and Barrancas sample data.
Figure 8.11 Ba vs. MgO (top) and Sr vs. MgO (bottom) Harker diagrams showing comparative centers and Barrancas sample data.
The following trace vs. MgO Harker diagrams display elements representing the light (La, Figure 8.12), mid (Sm, Figure 8.13) and heavy (Yb) REE’s (Figure 8.14). Two general characteristics are revealed in these diagrams; the most easterly centers Payun Matru, Barrancas, Copahue and LLB shown no correlations between the trace elements and MgO; all other centers (arc-near arc volcanoes) indicate variable but, clear correlations.

Payun Matru and the majority of LLB rocks maintain a similar compositional range. These two rock suites also maintain mid-range values of the light and mid REEs but, exhibit some of the lowest values in the heavy REEs (Figures 8.12, 8.13, 8.14).

In contrast to Payun Matru and LLB rocks, the Barrancas samples are widely distributed across the entire range of values. Nonetheless, an unusual grouping can be seen within the Barrancas samples. The CV1, 2, and 3 samples are consistently associated with the LLB and nearly as often with the Payun Matru rocks within the REE vs. MgO diagrams.

The second characteristic of these charts show Llaima, Talhuaca, Callaqui and Caviahue-Copahue forming a trace element enrichment trend west to east in the transect (This relationship, from this point on, shall be referred to as the Foreland Enrichment Trend or FET). The westernmost center (Llaima, closet to the trench), displays the lowest values in REEs. Traversing east, Talhuaca and Callaqui show consecutive increases in REEs. Lastly, the Caviahue-Copahue complex culminates the easterly trend with the highest enrichment in REEs.
Within this overall trend, individual volcanic centers display variable trends of trace element enrichment with decreasing MgO. Llaima and Talhuaca have the lowest abundances of LREEs (with shallow slopes) and MREEs but, transition to steepening enrichment slopes through the mid-REEs and HREEs. Callaqui and Caviahue show steep linear enrichment trends of LREEs, MREEs and HREEs with decreasing MgO. Copahue displays a more diffuse linear trend of LREE enrichment and appears to be a continuation of the Caviahue trend, exhibiting the highest values of LREEs, MREEs and HREEs (Figures 8.12, 8.13, 8.14).

LPE on the other hand displays decreasing trace elements with decreasing MgO in the LREEs and MREEs, while appearing to exhibit no trends in the HREEs.
**Figure 8.12** La vs. MgO diagram showing relationship of transect centers data to Barrancas sample data.

**Figure 8.13** Sm vs. MgO diagram showing relationship of transect centers data to Barrancas sample data.
The high field strength element (HFSE) diagrams show Payun Matru, Barrancas, LPE, LLB, Tromen and Llaima form a low contiguous assemblage of trace values that vary over a range of MgO abundances but, show no enrichment trends (Figures 8.15a, b). From this baseline Talhuaca, Callaqui and Caviahue are the only volcanic centers that display enrichment trends with decreasing MgO concentrations, all of which reach high values similar to those of Copahue. The Copahue rock suite shows no clear trend but does exhibit high values in all HFSE diagrams.

Figure 8.14 Yb vs. MgO diagram showing relationship of transect centers data to Barrancas sample data.
Figure 8.15a Th vs. MgO (top) and U vs. MgO (bottom) Harker diagrams showing comparative centers and Barrancas sample data.
Figure 8.15b Pb vs. MgO (top) and Zr vs. MgO (bottom) Harker diagrams showing comparative centers and Barrancas sample data.
Linear correlations within rock suites are best seen in Ni, Cr, and Co. There are additional correlations within and between rock suites throughout the trace element vs. MgO diagrams however, they are slightly less coherent.

Generally, Payun Matru rocks are shown as a suite with tight compositional ranges exhibiting no enrichment or depletion trends. They are intermediate in trace concentration values with associated higher MgO compared to all other rocks but, are the highest in Co, Cr, and Ni.

Barrancas trace data show MgO concentrations that range across the entire spectrum of values for all the centers, and nearly so for all trace element concentrations. The recurrent sub-groupings of this suite are apparent in most plots (as indicated in the Co vs. MgO diagram, Fig 8.8) and fall within specific MgO concentrations of 3-5wt. % (BC sub-group), 5-7 wt.% (RN sub-group) and 8-9 wt.% (CV sub-group). No enrichment or depletion trends are discernible either within the Barrancas suite or within individual sub-groups.

Tromen data is missing in most bi-variate plots but, does show ambiguous depletion trends in Cr, Ni, and the LILE with decreasing MgO.

LPE displays decreasing trace elements with decreasing MgO in the LREEs and MREEs and appears to exhibit no trends in the HREEs or HFSE.

The LLB rocks show a wide distribution similar to Barrancas with no apparent trends. However, in each trace diagram the LLB rocks seem to be closely associated with Payun Matru.
In contrast, the near trench volcanos Talhuaca, Callaqui, and Caviahue-Copahue: show quasi-linear enrichment trends with decreasing MgO while maintaining the tightest compositional identity of all rocks. They also show the lowest values in compatible elements, (Co, Cr, and Ni). Llaima data displays the tightest compositional range of all groups and exhibits low to intermediate trace values except in the HREE (high Yb).

The Llaima rocks also show their most linear enrichment patterns in Cr, Ni, MREE and HREE. An overall characteristic of these charts show Llaima, Talhuaca, Callaqui and Caviahue-Copahue form a trend of increasing trace element concentrations with distance from the trench (lowest in the westernmost center-Llaima, increasing to high trace concentrations eastward across the arc to Caviahue-Copahue). Barrancas, LPE, LLB, Tromen and Payun Matru form data assemblages independent of this trend.
8.3 Transect Trace Element Ratio Diagrams

Trace ratio bi-variate diagrams are used as petrogenetic indicators for the rock suites in this study as compared to the three end-member sources - MORB, OIB, and IAB. Selection of specific trace element pairs with similar chemical behavior can identify: depth of melt source region, element transport mechanisms, mixing of source regions and degrees of trace element enrichment and depletion.

The Th-Nb pair was selected as a proxy for crustal contamination because of their similar chemical behavior during petrogenetic processes and general immobility through weathering and lower amphibolite facies metamorphism (Pearce, 2008).

![Figure 8.16 Th/Yb vs. Nb/Yb diagram showing that oceanic rocks (MORB, OIB) plot in a narrow array. Rocks resulting from an interaction of ascending magmas with crustal components plot above the array.](image)

Figure 8.16 Th/Yb vs. Nb/Yb diagram showing that oceanic rocks (MORB, OIB) plot in a narrow array. Rocks resulting from an interaction of ascending magmas with crustal components plot above the array.
Although similar in chemical behavior within processes, slight differences in size/charge cause Th to be more incompatible and thus more mobile than Nb.

In Figure 8.16, plotting of the present day ratios (Th/Yb, Nb/Yb) for oceanic rocks form a narrow diagonal array that ranges from high % melts and depleted Th in N-MORB to smaller % melts and Th enrichment in oceanic OIB. Lavas that have crustal assimilation by: subduction components, direct crustal input or inherited subduction components (crustal recycling) in the lithosphere tend to plot above the MORB-OIB field.

Nearly all rocks considered in this study plot above the MORB-OIB array however, the arc rocks display the highest enrichment of Th whereas, the Barrancas and LLB rocks form an intermediate array. Similar to previous bi-variation diagrams, patterns of tight compositional ranges in Llaima, Talhuaca, Callaqui, Caviahue-Copahue and Payun Matru are also observed here as are the widely distributed ranges of the Barrancas and LLB rocks. The Barrancas rocks however, do not display segregation into subgroups. The FET (Foreland Enrichment Trend) of the arc rocks is also displayed in figure 8.16 (red dashed oval) where enrichment of Th increases across the arc axis from west (Llaima) to east (Caviahue-Copahue).
TiO$_2$/Yb vs. Nb/Yb can be used as a proxy to identify depth of melting for the volcanic centers of this study. Both Ti and Yb have similar partition coefficients in spinel peridotite (stable phase at 30-80km in depth) but, Yb is preferentially partitioned into garnet peridotite (stable phase at 80-400km in depth). Retention of Yb in garnet residue thereby infers depth of melting.

Llaima, Talhuaca, Callaqui, Caviahue-Copahue display tight assemblages in the MORB array, indicative of shallow melts (Figure 8.17). Also displayed is a trend of decreasing % melt volume from the near trench volcanoes (Llaima, Talhuaca) eastward to Caviahue-Copahue as indicated by increasing Nb/Yb ratio values.

**Figure 8.17** TiO$_2$/Yb vs. Nb/Yb diagram showing Llaima, Talhuaca, Callaqui, Caviahue-Copahue plot within the shallow melt MORB fields. The Barrancas and LLB rocks however, straddle the E-MORB-OIB fields. Payun Matru data plots entirely within the OIB field. (Dashed black line passes through Nb/Yb chondrite (C1) ratio of 1.45 and delimits N-MORB from E-MORB)
The recurring dispersed ranges of the Barrancas and LLB rocks form individual data assemblages that plot between the OIB and MORB fields whereas, Payun Matru displays a linear negative correlation of TiO$_2$ with Nb, possibly demonstrating shallower yet higher melt volumes.

Figure 8.18 plots all volcanic center data and displays their relationship to the three end-member rock suites based on REE trace element ratios La/Sm and Dy/Yb.

![Figure 8.18](image)

**Figure 8.18** Diagram shows the relationship of the Barrancas rocks to end members in LREE (La/Sm) and HREE (Dy/Yb). Higher La/Sm ratio values indicate rocks enriched in fluid mobile LREE. Higher Dy/Yb ratio values indicate Yb retained in garnet residuum at depth. Morb field is a reference for shallower melting and OIB field for melting at greater depths. Note the Barrancas rocks are situated between all three end-member fields, (IAB)-Island Arc Basalt, (OIB)-Ocean Island Basalt, (MORB)-Mid-Ocean Ridge Basalt.
The La/Sm ratio is a measure of LREE enrichment in the presence of fluid/melts and Dy/Yb, depth of melting. The arc rocks Llaima, Talhuaca, Callaqui, Caviahue-Copahue plot firmly within the island arc field.

Also apparent is the FET (Foreland Enrichment Trend) indicated by low La/Sm for the nearer trench Llaima rocks, intermediate La/Sm eastward across the arc in the Talhuaca and Callaqui rocks then, peaking in the Caviahue-Copahue rocks nearer the foreland. Payun Matru and several LLB samples plot within the OIB field but the majority of LLB and the Barrancas rocks are diffusely grouped between the IAB and OIB fields.

The niobium-tantalum anomaly is a prominent geochemical trait of volcanic rocks created in subduction zones (Pearce, 1982). There are two schools of thought regarding Nb-Ta anomalies. Nb and Ta have lower solubility in subduction fluids than all other incompatible trace elements; consequently there is the preferential enrichment of all other incompatible elements into a HFSE depleted mantle wedge, creating the appearance of a depletion in Nb-Ta (Hawkesworth et al., 1994; Tatsumi et al., 1986).

The second suggests that Nb and Ta are retained in amphibole, rutile, ilmenite and other titanate minerals but, there are arguments for and against the stability of these phases during subduction dehydration/melt processes (Baier et al., 2008; Brenan et al., 1994a; Ryerson and Watson, 1987).
The degree of niobium depletion can be displayed by calculating the deviation of niobium concentration from its nearest neighbor trace elements (Uranium-U and Potassium-K) as sequenced in the Primordial Mantle normalized trace element diagram figure 8.21.

![Figure 8.19 Dy/Yb vs. Nb/Nb* plot showing Nb depletion (Nb/Nb*) in volcanic centers where values ≥ 1 indicate no depletion and values < 1 indicate the degree of depletion. Dy/Yb indicates depth of melting as it reflects Yb retention in garnet residue at depth.](image)

The rocks of Llaima, Talhuaca, Callaqui, Caviahue-Copahue display a narrow range of Nb/Nb*values from .08 to .19 indicating similar depletion in Nb (Figure 8.19). Coincident with this narrow range is the FET however, in this instance the enrichment of Dy is relative, a consequence of Yb retention. Another attribute of this
trend is that the Nb concentration remains nearly constant regardless of the melting depth (Dy/Yb melt depth proxy) beneath these volcanic centers.

To the east of Caviahue-Copahue, progressive decreases in the negative Nb anomaly with a correlating increase in melt depth and distance from the trench are observed in the volcanic rocks of Loncopue (Nb/Nb*≈.24-.37), Barrancas (Nb/Nb*≈.31-.52), Las Lajas (Nb/Nb*≈.4-.8) and Payun Matru (Nb/Nb*≈.58-.92).

Figure 8.20 highlights the decreasing flux of subduction components across the arc. Ba/Nb represents the transport/enrichment of fluid mobile LILEs and Nb/Zr as the mantle heterogeneity and degree of partial melting proxy. The volcanic centers nearest the trench Llaima, Talhuaca and Callaqui show a wide distribution of Ba/Nb with Low Nb/Zr that transition to lower Ba/Nb but higher Nb/Zr eastward across the arc to Caviahue-Copahue (arc distal field). Traversing further east, the back-arc samples from LLB and Payun Matru display lower Ba/Nb and higher Nb/Zr. The Barrancas region which is geographically between the back-arc and Caviahue-Copahue, have Ba/Nb and Nb/Zr values similar to both the arc distal and back-arc fields.

The slab window rocks from 46ºS (subducting Chile Ridge) display the lowest Ba/Nb but the highest Nb/Zr and plot largely in the mantle field possibly inferring a pure mantle source( Figures 8.20).
Figure 8.20 Ba/Nb vs. Nb/Zr graph shows high Ba/Nb in Llaima and Talhuaca samples (80-170), intermediate at Copahue-Caviahue (Ba/Nb = 35-75) lower in the back-arc basalts/Barrancas area and lowest in the slab window rocks of the subducting Chile ridge (Ba/Nb = 7-15).
Trace element ratio plots identify characteristics of the volcanic center rocks included in this study.

Figure 8.16 highlights crustal input by the Th-Nb proxy where the greater incompatibility of Th allows for preferential transport into the crust. Llaima, Talhuaca, Callaqui, Caviahue-Copahue plot above the oceanic MORB-OIB field and firmly within the IAB field. The LLB, LPE and Barrancas rocks plot midway between the MORB-OIB and IAB fields, whereas Payun Matru rocks straddle the IAB-OIB boundary.

Depth of melting is displayed in the TiO$_2$/Yb vs. Nb/Yb diagram (Figure 8.17). Llaima, Talhuaca, Callaqui and Caviahue-Copahue plot in the shallow melt MORB array while the Barrancas, LPE, and LLB straddle the deep melting OIB and the shallow melting MORB boundary.

Enrichment of fluid mobile LREEs are depicted in the La/Sm vs. Dy/Yb chart (Figure 8.18). Llaima, Talhuaca, Callaqui and most of the Caviahue-Copahue rocks plot within the IAB field. An enrichment trend is apparent across the arc as indicated by the low La/Sm in the nearer trench Llaima rocks, increasing eastward to high La/Sm in the Copahue rocks. The Barrancas, LPE and LLB rocks show wide distribution of La/Sm that ranges from IAB to OIB compositions. Payun Matru rocks however are located solely within the OIB field.

Ta and Nb depletions(Ta-Nb anomaly) are distinguishing traits of arc rock geochemistry. The depth of the niobium anomaly is represented by Nb/Nb* in Figure 8.19. Llaima, Talhuaca, Callaqui, Caviahue-Copahue show similar depletions in Nb.
but, with varying melting depths. A trend of decreasing Nb depletion begins with the LPE and Barrancas rocks (east of Caviahue-Copahue) and transitions to lesser depletion through the LLB and Payun Matru volcanic centers.

A progressive decrease in subduction component transfer (LILEs and H$_2$O) east across the arc are displayed in Figure 8.20. The nearer trench volcanoes Llaima, Talhuaca and Callaqui show the greatest enrichment but, Ba/Nb gradually decreases with increasing distance from the trench.

Although these trace element diagrams were intended to identify specific processes, the Barrancas rocks consistently display traits of both the OIB and IAB type rocks.

### 8.4 Transect Incompatible Element Diagrams

To avoid clutter within the primordial mantle normalized incompatible element diagrams, volcanic center data is divided geographically into across the arc front and behind arc representations (Figure 8.21).

The across arc volcanoes (Llaima, Talhuaca, Callaqui, Caviahue-Copahue) display similar profiles with characteristic patterns of LILE (Cs, Rb, Ba, Th) and Pb (Laima no Pb data) enrichment with distinct Nb-Ta, P, and Ti depletions compared to OIB. A correlation of decreasing Nb depletion with distance from the trench is seen in Figure 8.21 (top). Llaima displays the lowest values of Nb, but increase steadily (eastward) through Talhuaca, Callaqui and Caviahue-Copahue. A representative sample of the Barrancas rocks-CV2 is also plotted with the arc rocks for comparison.
Figure 8.21 Primordial mantle normalized incompatible element diagrams comparing across arc volcanoes-Llaima, Talhuaca, Callaqui, Caviahue-Copahue (top) and behind arc centers-LPE, LLB, Tromen, Payun Matru (bottom) to representative OIB, MORB and Barrancas CV2 sample.
CV2 shows intermediate values for most incompatible elements, but the highest values of Nb, P, Sr and Ti.

The behind arc volcanic centers also show similar patterns to each other, but enrichments and depletions are less pronounced than in the arc patterns (Figure 8.21, bottom). They also exhibit a narrow range in abundance of incompatible elements and show no Pb enrichment except in the LLB rocks. LPE and Tromen show a slight P depletion whereas, the LLB and Payun Matru rocks do not.

The rare earth element data is also divided geographically into arc centers and behind arc centers (Figure 8.22). Plotted along with the volcanic centers are the MORB and OIB REE patterns. A key feature distinguishing MORB from OIB is the enrichment of the HREEs (Er-Lu) in MORB relative to OIB. A nearly systematic enrichment in LREEs and MREEs is seen between the arc center profiles (Figure 8.22, top). Eu depletion is seen in all arc centers possibly caused by Eu$^{2+}$ for Ca$^{2+}$ replacement during plagioclase fractionation in reducing conditions. The slope of the LREE (La-Sm) incrementally increases from Llaima through Talhuaca, Callaqui and Caviahue-Copahue. This steepening in slope is correlated with increasing distance from the trench, defining an FET (Foreland Enrichment Trend) in the rare earths. The steep LREE trends abruptly flatten at Tb and become more variable between centers through Lu. In contrast, the profile slope of Llaima does not break at Tb but continues on through Yb.
Figure 8.22 Chondrite normalized rare earth element diagram comparing across arc volcanoes-Llaima, Talhuaca, Callaqui, Caviahue-Copahue (top) and behind arc centers-LPE, LLB, Tromen, Payun Matru (bottom) to representative OIB, MORB and Barrancas CV2 sample.
The representative sample CV2 from the Barrancas rocks shows a constant slope from La to Tm, the lowest values of HREEs and no Eu anomaly as compared to the arc rocks. Generally, the arc rocks are more enriched than MORB in elements La to Dy but, less than OIB and show HREE patterns that overlap both MORB and OIB.

The behind arc rocks of LPE and CV2 display moderate slopes that tend to flatten in the HREEs (Figure 8.22, bottom). Tromen is lacking HREE data causing the profile to be unintelligible. The Barrancas, LLB and Payun Matru rocks are nearly identical in profile to one another, parallel LPE and Tromen but, are more enriched. All arc rock profiles in this diagram are less enriched than, but resemble the OIB pattern.

Several volcanic center REE patterns are more similar to the OIB profile than they are to all other profiles (Figure 8.23). These are the behind arc centers Payun Matru, Barrancas RN11, RN13, LLB and LPE all of which are parallel in slope but are depleted in all REEs as compared to OIB. Payun Matru, Barrancas RN13 and LLB are the least depleted and show no pronounced relative enrichment or depletions. Barrancas RN11, and LPE display a Dy and Tm anomaly and are the most depleted.
Figure 8.24 plots the Sm-Nd and Rb-Sr systematics with a mean mixing line of representative end members MORB (high $^{143}\text{Nd}/^{144}\text{Nd}$, low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios) and PDS (low $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios). In addition to transect volcano data, slab window rock data from the triple junction region at 46ºS is included in the following isotope charts for comparison. Plotting of all volcanic centers indicates that their compositions can be explained by the mixing of MORB and sediment sources (PDS). However, variations to the right of the mean mix line are likely the result of a sediment or crustal component with higher $^{87}\text{Sr}$ abundances. Variations to the left of

8.5 Transect Isotopes

Figure 8.23 Chondrite normalized rare earth element diagram comparing behind arc rocks Payun Matru, Barrancas RN11, RN13, LLB and LPE to representative OIB and MORB.
the mean mix line indicates a source with little or no crustal/sediment input. LPE, LLB, Tromen and Payun Matru rocks form linear trends on or very close to the MORB-PDS mixing line, whereas Llaima, Callaqui, and Barrancas rocks form coherent trends oblique to the mix line.

Caviahue-Copahue lack data for interpretation. Nearly all transect volcanic data are bounded by \(^{87}\text{Sr}/^{86}\text{Sr}\) values of 0.7035 to 0.7043 and \(^{143}\text{Nd}/^{144}\text{Nd}\) values of 0.5000 to 0.5129. These values also bound volcanic data from the TSVZ and SSVZ (Figure 8.25).

**Figure 8.24** Bi-variate ratio diagram \(^{143}\text{Nd}/^{144}\text{Nd}\) vs. \(^{87}\text{Sr}/^{86}\text{Sr}\) showing all Southern Volcanic Zones (Southern, Transitional and Northern) and volcanic centers in this study plotting along a mixing line of MORB (NCR-North Chile Ridge) and PDS (Pacific Detrital Sediment) BSE-Bulk Silicate Earth.
Figure 8.25 Closer view of volcanic data in figure 8.24 in relation to MORB-PDS mix line.
Pb isotope systems are also a good indicator of crustal contamination. Pb may be produced by three decay reactions of Uranium and Thorium: $^{238}\text{U} \rightarrow ^{234}\text{U} \rightarrow ^{206}\text{Pb}$, $^{235}\text{U} \rightarrow ^{207}\text{Pb}$ and $^{232}\text{Th} \rightarrow ^{208}\text{Pb}$. Each radioactive parent is an incompatible trace element and tends to fractionate into fluid/melt phases and subsequently, into the crust. Reservoirs with high concentrations of U, Th will with time, produce high $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Three reservoirs have been characterized based on concentrations of U, Th, and Pb; upper crust, lower crust and upper mantle (Zartman and Doe, 1981). In the upper crust high concentrations of U, Th and Pb are observed with Pb relatively depleted to U and Th. The upper crust thus produces radiogenic Pb. The lower crust is depleted in U and Th therefore; abundances are based on non-radiogenic Pb. The upper mantle contains lower U, Th, and Pb than the upper crust but, higher than the lower crust thereby producing intermediate radiogenic Pb values.

The $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Figure 8.26) shows most data is positioned along a mixing line between minimum values of MORB and PDS.

Llaima rocks show a tight compositional range positioned on the mix line while the LPE, LLB and Barrancas rocks form arrays that deviate slightly off the mix line towards lower $^{208}\text{Pb}$ and $^{206}\text{Pb}$. The slab window rocks have similar $^{208}\text{Pb}$ values to the IAB field however, they show a strong trend towards very low $^{206}\text{Pb}$ indicating the mixing in of a possible third unknown low $^{206}\text{Pb}$ end member.
Figure 8.27 shows similar positioning of data indicating all centers can be produced from the mixing of MORB and PDS end members. Tight compositional ranges are seen in the arc volcanoes Llaima and Callaqui and are located on the mix line. Conversely, the LPE, LLB, Barrancas and slab window rocks exhibit dispersed trends toward lower $^{207}$Pb and $^{206}$Pb and although most slab window rocks can be produced from mixing of MORB and PDS, several rocks cannot.

Figure 8.26 $^{208}$Pb/$^{204}$Pb vs. $^{206}$Pb/$^{204}$Pb Diagram shows most rocks plot along a mixing line of MORB and PDS whereas, some LLB, Barrancas and the slab window rocks suggest a mixing with a third low Pb end member.
In general, the IAB show the highest values of $^{207}\text{Pb}$ and $^{206}\text{Pb}$, the arc rocks Llaima, Callaqui, Caviahue-Copahue display values similar to the low end of the IAB range, and the LPE, LLB, Barrancas and slab window rocks exhibit the lowest values.

The rocks of Llaima, Callaqui, Caviahue and Tromen form tight assemblages in the $^{208}\text{Pb}$ vs. $^{207}\text{Pb}$ diagram and are found slightly below the IAB values on the MORB-PDS mixing line (Figure 8.28). LPE, LLB and the Barrancas rocks have some values similar to that assemblage but, they also form linear trends of decreasing $^{208}\text{Pb}$ with decreasing $^{207}\text{Pb}$ parallel to the mean mix line. The slab window rocks form a
distinct linear correlation of decreasing $^{208}$Pb with decreasing $^{207}$Pb, and contain some of the highest $^{208}$Pb values and lowest $^{207}$Pb. Here again all rocks can be derived from a mix of MORB and PDS (with the exception of several slab window rocks).

Figure 8.28 $^{208}$Pb/$^{204}$Pb vs. $^{207}$Pb/$^{204}$Pb Diagram shows nearly all rocks plot along a mixing line of MORB and PDS whereas, the slab window rocks are suggesting a mixture with a third end member low in $^{207}$Pb.

Figure 8.29 shows the nearer arc volcanos Llaima, Callaqui, and the majority of IAB samples plot to the right of the minimum mix line and have a similarity in Nd and Pb values. Caviahue-Copahue and some LLB rocks also plot to the right of the mix line and display similar values.
The LPE and Tromen centers plot slightly to the left but, near the mix line whereas, the Barrancas, slab window and some LLB rocks show a pronounced trend towards an unknown low Nd-Pb end member.

Figure 8.29 $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram shows rocks plot along a mixing line of MORB and PDS whereas, the slab window and Barrancas rocks suggest a mix with a third end member low in Nd and Pb.

The $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram also show the rocks of Llaima, Callaqui, and IAB are tightly grouped to the right of the MORB-PDS minimum mixing line at approximately 97% MORB (Figure 8.30). Caviahue-Copahue and several samples of LLB are positioned closely to these rocks as well. To the left of the mixing line at similar Sr but, slightly less Pb values, lies the LPE, LLB, Tromen, and Barrancas
rocks. The LLB rocks show a diffuse grouping while, the LPE rocks display a correlation of decreasing Sr with decreasing Pb. The Barrancas rocks show a slight trend of Sr enrichment with decreasing Pb suggesting the mixing with a low $^{206}\text{Pb}$ end member. Similarly, the slab window rocks exhibit a pronounced trend of decreasing Pb suggesting the mixing with a low $^{206}\text{Pb}$ end member with no change in Sr but, display the highest values of Sr.

![Figure 8.30](image)

**Figure 8.30** $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram shows rocks plot along a mixing line of MORB and PDS whereas, the slab window and Barrancas rocks suggest a mix with a third end member low in Pb.
8.6 Subduction Zone Modeling between 35° and 39° South

As described in the introduction, a requirement for arc volcanism is the specific geometric relationship of subducting plate to that of the overriding plate and formation of volcanic edifices at the surface. Specifically, that surface volcanic structures overlie the magma source region by 100-200km and 100-250km inland from the trench. A question for this study thus becomes, could the Nazca-South American Plate subduction zone between 35° and 39°S have produced arc type volcanic rock in the Barrancas region, some 445km inland of the trench.

Estimation of the subduction zone geometry can be achieved by geographically plotting earthquake hypocenters (origin of earthquake) in ArcGIS for the region between 35° to 39°S and 66° to 76°W. This technique uses the location of the hypocenters as a proxy for identifying the brittle subducting plate. An assumption here is that the earthquakes are the result of slip fractures within the plate and extensional fractures on the upper surface of the plate as it is pulled into the sub-continental mantle. The majority of the earthquakes occur as a planar band in the diagram and the upper surface of this planar band represents with some interpretation, the surface of the subducting plate (Figure 8.31). Planar arrangements of these earthquakes are known as the Wadati-Benioff Zone named after the investigators who identified this feature.

Hypocenter data was acquired from two databases, the USGS national earthquake information center (NEIC) (2000 hypocenters) and a higher resolution database (150 hypocenters) compiled by Robert Engdahl, Rob van der Hilst, and
Raymond Buland (EHB) (Engdahl et al., 1998). Hypocenters with magnitudes of 3 to 9 and recorded from 1964 to 1995 were plotted in the region previously defined.

**Figure 8.31** Plotting of hypocenters to identify the Wadati-Benioff zone (between red lines) and the stress regimes in the subducting oceanic slab; compressional stress as the subducting plate collides with the continental plate, compressional stress on the lower section of the subducting plate as it bends downward and tensional stress on the subducting plate as it is pulled into the mantle. After USGS
The following block diagrams illustrate the subduction zone of the western South American convergent margin encompassing the area between 35° to 39°S and 66° to 76°W (400km x600km).

The geographical plotting of hypocenters from the two catalog databases produces similar Wadati-Benioff zones. The NEIC (National Earthquake Data Center) hypocenter database consists of 2000 earthquake events which plot as a diffuse downward curving planar feature of approximately 30-40 km in thickness that extends to a depth of 210km (Figure 8.32).

**Figure 8.32** 3D block diagram showing plotted NEIC hypocenters (2000) forming the Wadati-Benioff Zone between 66° and 76°W.
The Engdahl, E.R., R. van der Hilst, and R. Buland (EHB) hypocenter database consists of a smaller number of earthquake events. The higher resolution data set better approximates the Wadati-Benioff Zone (10-20km thick) but, there is a lack of data below 150km (Figure 8.33).

![Figure 8.33 3D block diagram showing plotted EHB hypocenters (150) forming the Wadati-Benioff Zone between 66° and 76°W.](image)

To resolve the surface of the subducting plate an inverse distance weighting interpolation algorithm (Spatial Analyst in Arc GIS) was used to convert the hypocenters into a plane (Figure 8.34). The conversion of each hypocenter database into a plane produces a similar feature. A draw-back to this method places the interpolated plane within the body of the hypocenter data set and therefore does not identify the top of the subducting plate. In addition, inconsistencies in fault plane location and geometry (particularly in depth) can cause hypocenter location errors of
up to 30km in the NEIC database (Engdahl et al., 1998). Therefore, the relationship of the subducting Nazca plate to the overlying South American plate regarding actual depth could be significantly incorrect. However, Subduction angle of the Nazca Plate in both models is nearly parallel (Figure 8.35).

**Figure 8.34** Top image - 2nd order global polynomial interpolation algorithm through the NEIC hypocenters. Bottom image - 3rd order global polynomial interpolation algorithm through the EHB hypocenters.
Volcanic centers within the study area are plotted in the block diagram using their geographic coordinates. Their positions on the surface are extrapolated down until intersection with the subducting plate model, establishing the subduction zone geometry (Figure 8.36). The depth from the frontal arc (Llaima, Talhuaca, Callaqui and Caviahue-Copahue complex) to each interpolated plane is approximately 100km.

Although the current subduction geometry is conducive for volcanic activity at Copahue, Caviahue is one of the oldest centers (Pliocene) in the transect and may have produced volcanism from a different subduction geometry. The volcanic centers behind the arc-Tromen, Loncopue and Barrancas are located about 180-200km above the interpolated planes and fall within the subduction geometry required for mantle melting. Payun Matru is beyond the limits of the plane.
interpolations however; by extrapolating the position of Payun Matru to the modeled subduction planes, the indicated depth would be below 250km.

Hayes (2009) used a probability density function method to model the South American subduction zone geometry at 36°S. The volcano Nevado de Longavi (36.2°S) is used as an indexing point for a comparison of the Hayes and the ArcGIS model. The comparison of the two models indicates good agreement on the depth (125km vs. 110km) of the Nazca Plate and subduction angle (∼30°) at that location (Figure 8.37).

Figure 8.36 Block diagram showing depth from volcanic centers to interpolated subducting plates. The first four red vertical bars (from left) indicate the volcanic centers (Llaima, Talhuaca, Callaqui, Caviahue-Copahue) in the current arc axis. These volcanoes lie approximately 110 km above the interpolated plates and 280 km inland from the trench axis. Volcanic centers left to right (red vertical bars) are Llaima, Talhuaca, Callaqui, Caviahue-Copahue complex, Loncopue-Las lajas, Tromen, Barrancas (green vertical bars) and Payun Matru.
Figure 8.37 (Top) Block diagram indicating position of Nevado de Longavi at 36°S Latitude and 300km inland of the Chile trench (ArcGIS model). Extrapolation of position down to interpolated Nazca Plate model surface indicates a depth of approximately 110km. (Bottom) Modeled cross-section through the Andean subduction zone at 36°S using a probability density function method (Hayes and Wald, 2009). Depth from a position 300km inland at 36°S Latitude (Nevado de Longavi) to the modeled Nazca Plate surface (red dashed line) is approximately 125km, a difference in depth of 15km from the ArcGis model.
9. Phosphorus

9.1 Introduction

A typical geochemical characteristic of continental arc volcanoes is the depletion of Phosphorus and to varying degrees; this depletion is seen in several of the volcanic centers included in this study. The incompatible element diagrams in chapter 8 (Figure 8.21) show negative Phosphorus (P) anomalies in Llaima, Talhuaca, Callaqui, Caviahue-Copahue complex, Tromen and LPE samples. In contrast, several Barrancas, LLB and the behind arc volcano Payun Matru samples reveal slight to no negative P anomalies. Since there is a difference in P abundance between these two groups, an investigation of the disparity is warranted. The following paragraphs will first describe the general geochemical characteristics of P and then address the geochemical characteristics of P in arc rocks.

Phosphorus is an incompatible minor element present in most geologic systems comprising approximately .19% of the bulk continental crust and .02% of the mantle (Sun and McDonough, 1989). The majority however, was fractionated into the core as a result of its siderophilic nature during earth’s formation (Sun, 1984).

All basic to intermediate volcanic and plutonic rocks generally contain < 1% wt.% P$_2$O$_5$ (Le Maitre, 1976). MORB normally ranges between .05 and .25 wt. % P$_2$O$_5$ (Klein, 2003; Le Maitre, 1976; Workman and Hart, 2005). Island arc basalts (IAB) and andesite exhibit .1 to .7 wt. %(Condie, 1993; Plank and Langmuir, 1998)
and continental alkali-rich basalts (OIB) have concentrations from .5 to 1.6 wt. % (Farmer, 2003; Le Maitre, 1976).

Peridotite melting models along with observed characteristics of basic lavas suggest P concentrations in the upper mantle (200ppm) are much less than chondrite values (900 ppm) (Watson, 1980). This indicates that higher P abundances in a melt must be the result of an enriched source or assimilation of P rich material or both (Exley and Smith, 1982).

Magmatic rocks (lamproites, lamprophyres and kimberlites) with an origin depth in the lithospheric and asthenospheric mantle (∼150km) contain abundant apatite in their groundmass that may produce P₂O₅ concentrations of 1 to 3 wt.% (Mitchell, 1995; Mitchell and Bergman, 1991).

The assimilation of partially melted subducted sediments into the mantle wedge may also be a source of P enrichment (Plank, 2005; Rosenbaum et al., 1997).

In the natural environment, phosphorus exists as phosphate PO₄³⁻, predominantly in the mineral Apatite [Ca₅(PO₄)₃(OH, F, Cl)]. Flourapatite [Ca₅(PO₄)₃F], is the most common of the apatite compounds found in igneous, metamorphic and sedimentary systems but, Clorapatite [Ca₅(PO₄)₃Cl] and Hydroxyapatite [Ca₅(PO₄)₃OH] may also be present in small amounts (Dawson and Hinton, 2003; Piccoli and Candela, 2002; Seifert et al., 2000).

Not only is apatite the main repository of phosphorus, it may contain nearly the entire REE and Sr budget of a rock (Fourcade and Allegre, 1981; Peter Gromet and Silver, 1983; Sorensen and Grossman, 1989).
Apatite structure allows for cation substitutions (K, Na, Mn, Ni, Cu, Co, Zn, Sr, Ba, Pb, Cd, Sb, Y, REEs, Th and U) for Ca, and anionic complexes $\text{AsO}_4^{3-}$, $\text{SO}_4^{2-}$, $\text{CO}_3^{2-}$, and $\text{SiO}_4^{4-}$ that replace $\text{PO}_4^{3-}$ (Belousova et al., 2002; Dawson and Hinton, 2003; Dawson et al., 1996; Fleet and Pan, 1997).

Experimental studies have demonstrated the stability of apatite at high temperatures (1275-1350°C) and pressures (8-25 kbar), simulating conditions in the upper mantle (Watson, 1980). Apatite in the presence of a hydrous phase was also shown to be stable and insoluble except when in association with acids, i.e. HCL and HF (Ayers and Watson, 1991). Although apatite remains a stable phase at mantle temperatures, pressures and in the presence of aqueous fluids, the question arises of whether or not it is a residuum after a melting event.

Researchers have investigated the solubility/saturation of apatite in igneous systems (Ayers and Watson, 1991; Harrison and Watson, 1984; Pichavant et al., 1992). Experiments cover a wide range of compositions from ultramafic to rhyolite and have determined the solubility of apatite in melts increases; with increasing temperature and de-polymerization/decreasing $\text{SiO}_2$ concentration (London et al., 1999). Watson conducted solubility experiments on fluoroapatite in basic magmatic liquids. It was observed that under upper mantle pressures (apatite solubility is not affected by pressure above 8 kbar) and a temperature of 1250°C, molten basalt (50 wt. % $\text{SiO}_2$) will dissolve 3-4 wt. % $\text{P}_2\text{O}_5$ before saturation in apatite is reached (Figure 9.1) (Watson, 1980).
Figure 9.1 $P_2O_5$ vs. $SiO_2$ plot for experimental melts saturated in apatite at 1 to 25 kbar. Dashed isotherm lines from the 1kbar plot are shown for reference. "P", "F" and "H" designate runs in which phosphate, $MgF_2$ and 3 wt. % $H_2O$, respectively, where added. Behavior of apatite solubility at high and low pressure is similar.
Since most silicate melts contain less than 1 wt. % $\text{P}_2\text{O}_5$ (Mysen et al., 1981), the occurrence of residual apatite in mantle melt source regions is unlikely. If a melt is produced at lower temperatures ($1100^\circ\text{C}$) as a result of an added flux to the system, or it has a $\text{SiO}_2$ concentration of 60 wt. %, apatite saturation is $< 2$ wt. %. Given these conditions apatite might survive as a residuum but, in very small amounts (Watson, 1980). Monazite-(Ce, La, Th)PO$_4$ (less soluble than apatite) and Xenotime-YPO$_4$, are also phosphate minerals however; they contribute negligible P to the melt (Montel, 1986; Wolf and London, 1995).

In addition to apatite, the mineral phases of olivine, clinopyroxene, plagioclase and garnet can accommodate significant P in their crystal lattice yet, retention and concentration are dependent upon $P$, $T$, oxygen fugacity and $\text{SiO}_2$ concentration in the coexisting melt (Bindeman et al., 1998; Milman-Barris et al., 2008).

As olivine and plagioclase undergo high pressure metamorphism, P is expelled from their lattice structure. Some of this freed P is taken up in clinopyroxene and garnet but, at pressures of $< 2\text{GPa}$, the bulk of P is redistributed into apatite formation in excess of that inherited from the parent rock (Konzett and Frost, 2009).

Eclogite, a high pressure- low temperature metamorphosed basalt (oceanic crust) found in subduction zones world-wide is shown to contain apatite as an extremely common accessory mineral (Aulbach et al., 2007; Brueckner et al., 1998; Spandler et al., 2008; Sun et al., 2007). It is primarily composed of omphacite (Na-Al pyroxene) and pyrope-rich garnet (Mg-Al garnet), formed at pressures of approximately 1GPa and is stable to higher pressures and temperatures (Frisch et al., 2011). At pressures
above 3GPa (105km depth), garnet preferentially begins to host P at the expense of apatite, which undergoes continual decreases in modal % as it approaches breakdown to tuite \( \gamma-\text{Ca}_3(\text{PO}_4)_2 \) at approximately 7.5GPa (Konzett and Frost, 2009).

### 9.2 Data/Observations

Major element vs. \( \text{P}_2\text{O}_5 \) (wt.%) plots show diffuse linear trends in the rocks of Llaima, Callaqui, Caviahue-Copahue, LPE, and LLB. These trends can be characterized as; decreasing CaO with increasing \( \text{P}_2\text{O}_5 \), decreasing MgO with increasing \( \text{P}_2\text{O}_5 \), and increasing NaO with increasing \( \text{P}_2\text{O}_5 \). No apparent correlations are seen in the SiO\(_2\), Al\(_2\)O\(_3\) or Fe\(_2\)O\(_3\), vs. \( \text{P}_2\text{O}_5 \) diagrams with these centers. The Barrancas and Payun Matru rocks display a wide distribution of values and usually no coherent trends in the major element diagrams. However, the MgO, TiO\(_2\) and K\(_2\)O vs. \( \text{P}_2\text{O}_5 \) plots display distinctive within and between group trends.

Figure 9.2 shows end member bulk \( \text{P}_2\text{O}_5 \) concentrations range from .05-.49 wt. % for MORB; .046-1.08 wt. % for OIB and .05 to .55 wt. % for IAB (from compiled data in this study). In comparison, the volcanic centers of the transect show \( \text{P}_2\text{O}_5 \) values of .17-.28 wt. % (Llaima), .18-.2 wt. % (Talhuaca), .2-.3 wt. % (Callaqui), .21-.34 wt. % (Caviahue-Copahue), .2-.4 wt. % (LPE), .3-.8 wt. % (LLB), .2-.38 wt. % (Tromen) and .3-.46 wt. % (Payun Matru).

These centers also display a generally lower MgO content than either MORB or OIB. Llaima, Caviahue and Copahue exhibit a somewhat tight range of values and well within the IAB field whereas, Talhuaca and LPE display a counter trend of
decreasing MgO with decreasing $P_2O_5$. Callaqui shows a distinct linear trend of increasing $P_2O_5$ with a corresponding decrease in MgO. The LLB, Payun Matru and the majority of Barrancas rocks exhibit a diffuse assemblage of data points within the OIB field but no coherent trends are visible.

Figure 9.2 Bivariate major element diagrams $P_2O_5$ vs. MgO showing concentrated data assemblage of nearer trench volcanic centers in the IAB field whereas the behind arc centers LLB, Barrancas, and Payun Matru rocks exhibit diffuse linear arrays.

The recurring pattern of a foreland enrichment trend (FET) seen in previous diagrams is observed here as well. In this instance it is demonstrated by progressive increases in P concentration, from the lowest abundance in the Llaima rocks (arc...
axis), through Callaqui and Caviahue-Copahue to several Barrancas samples exhibiting the highest P concentration, east of the arc axis.

In the TiO$_2$ vs. P$_2$O$_5$ diagram, the nearer trench centers exhibit a positive correlation of TiO$_2$ with P$_2$O$_5$ (Figure 9.3, top). Llaima, Talhuaca, Callaqui, Caviahue-Copahue, and LPE; parallel each other in slope, display progressive increases in TiO$_2$ and P$_2$O$_5$ concentrations and also correlate to a foreland enrichment trend. Furthermore, these centers are positioned within the IAB field and consist of TiO$_2$ concentrations lower than LLB, Tromen, Barrancas and Payun Matru rocks. The Payun Matru rocks show a somewhat linear trend of increasing TiO$_2$ with P$_2$O$_5$ outside of the three end-member classification fields but, the Barrancas, Tromen and LLB rocks show a wide range of concentrations plus, ambiguous patterns. Although the nearer trench rocks are positioned firmly within the IAB field not all the centers display correlations as seen in the TiO$_2$ vs. P$_2$O$_5$ diagram.

Callaqui and Caviahue display a positive correlation between K$_2$O and P$_2$O$_5$, a trend that continues outside of the IAB field (Figure 9.3 bottom). Some Callaqui and Caviahue rocks are horizontally aligned with the Copahue rocks at 2 wt. % K$_2$O and .3 to .35 wt. % P$_2$O$_5$. Llaima and Talhuaca plot within the IAB field but show no correlation and a counter trend in K$_2$O, respectively. The Tromen and LPE rocks show a wide distribution in concentrations but, no decipherable trends. Payun Matru data forms a low slope linear array along the upper OIB boundary line ranging from .26 to .50 P$_2$O$_5$ wt. %. Dissimilar, is the diffuse linear trend displayed by the
Barrancas and LLB rocks originating in the IAB field (.24 wt. % K$_2$O, .26 wt. % P$_2$O$_5$) and progressing to the highest P$_2$O$_5$ values (2.3 wt. % K$_2$O, .7 wt. %P$_2$O$_5$).
Figure 9.3 Bivariate major element diagrams TiO$_2$ vs. P$_2$O$_5$ (top) and K$_2$O vs. P$_2$O$_5$ (bottom) showing concentrated data assemblage of nearer trench volcanic centers in the IAB field whereas the behind arc centers LLB, Barrancas, and Payun Matru rocks exhibit diffuse linear arrays.
The incompatible element diagrams (Figures 9.4 and 9.5) reveal the presence or absence of negative Phosphorus (P) anomalies. This feature separates all samples of this study into two groups. The first group consists of the volcanoes Llaima, Talhuaca, Callaqui and Caviahue-Copahue which display a moderate depletion in P and the behind arc centers LPE and Tromen (Figures 9.4). The second group includes LLB and Payun Matru displaying negligible P depletions (Figure 9.4 bottom). The Barrancas rocks can be divided between both groups. Four members of the CV sub-group CV1, CV2, CV3 and RN13 and two members of the BC sub-group (BC3 and RN12A) display small to negligible P depletions (Figure 9.5)
Figure 9.4 Incompatible element diagrams showing relative Phosphorus depletions in across arc centers (top) and behind arc centers (bottom).
A quantitative comparison of the degree of P depletion is achieved by calculating $P/P^*$, the actual P concentration of the sample divided by what P should be as related to its adjacent neighbor elements in the spider diagrams. This relationship is represented by the equation:

$$\frac{P}{P^*} = \frac{P}{10^{\log(Sr_n)^{.5}}+\log(Nd_n)^{.5}}$$

The $P/P^*$ (anomaly depth) of the first group as determined in the spider diagrams (Llaima, Talhuaca, Callaqui and Caviahue-Copahue) display a moderate depletion in P ($P/P^* \approx .47$ to $61$) as well as and the behind arc centers LPE and Tromen which also show moderate depletions ($P/P^* \approx .6$). The second group consisting of LLB and...
Payun Matru, display minor P depletions (P/P* .8 to .93). The Barrancas rocks can be divided between both groups. Four members of the CV sub-group CV1, CV2, CV3 (P/P* ≈ .97) and RN13 (P/P* .87) and two members of the BC sub-group (BC3 and RN12A) (P/P* .99 and .87) display small to negligible P depletions. The remaining Barrancas samples display P/P* in a range of .63 to .83.

Figure 9.6 (top) shows subduction fluxing/partial melting (LREE enrichment) versus the P anomaly, La/Sm vs. P/P*. The rocks from Llaima, Talhuaca, Callaqui, and Caviahue-Copahue exhibit an enrichment trend of LREEs between centers with no appreciable change in Phosphorus (Figure 9.6 top, black dash field). In contrast, Llaima rocks shows a range of P/P* from .50 to .84 but, no enrichment of LREEs. Tromen lacks data. LPE, LLB, Tromen, Barrancas, and Payun Matru rocks exhibit diffuse arrays of increasing La/Sm with increasing P/P*(Figure 9.6 top, yellow dash field).

Figure 9.6 (bottom) illustrates the relationship of the melting depth proxy Dy/Yb to the depth of the P anomaly (P/P*). Generally, each volcanic center displays a linear array of increasing P/P* without significant variation in Dy/Yb. The Copahue rocks overlap values of Llaima and Talhuaca while maintaining a diffuse linear array. A similar effect is seen in the Barrancas rocks overlapping the LLB rocks and vice versa. A second correlation seen is the FET (Foreland Enrichment Trend) of increasing Dy/Yb and P/P* with distance eastward from the trench. Llaima, Talhuaca, Callaqui, the nearest centers to the trench exhibit the lowest values Dy/Yb and P/P*.
Figure 9.6 Bivariate diagrams showing P depletion (P/P* < 1) in relation to LREE enrichment, La/Sm (top) and depth of melting, Dy/Yb (bottom) proxies. Shaded oval- Llaima, Talhuaca, Callaqui, shaded arrow- Foreland Enrichment Trend across the arc. Dashed lines infer uniform relative melt depth of respective volcanic center.
Dy/Yb and P/P* values increase eastward, arguably, through Caviahue-Copahue, LPE, LLB, Tromen, Barrancas and Payun Matru.

In the following trace vs. P$_2$O$_5$ diagrams, pairs of elements are selected to represent the light (La and Nd), (Figure 9.7), mid (Sm and Tb), (Figure 9.8) and heavy (Er and Yb), (Figure 9.7) REE’s. Although a number of within volcanic center enrichment trends are observable throughout these diagrams, the focus will be on two major trends; enrichment trends between centers and the bifurcation of Llaima, Talhuaca, Callaqui and Caviahue-Copahue from LPE, LLB, Barrancas and Payun Matru data.

Figure 9.7 (top) shows a progressive enrichment of La across the arc. Llaima, trench proximal, exhibits the lowest concentrations of La (7 ppm) and Copahue (arc axis eastern flank) the highest (31 ppm). This increase in La across the arc is complemented by an a doubling of P$_2$O$_5$ concentration from Llaima, (.16 wt. %) through Talhuaca (.2 wt. %), Callaqui (.3 wt. %), Caviahue (.34 wt. %) to Copahue (.35 wt. %). These centers are positioned entirely within the arc field but, form an enrichment trend oblique to the MORB-OIB array. In contrast the LPE, LLB, Barrancas and Payun Matru data demonstrate; distinct positive correlations of La and P$_2$O$_5$, plotting within the OIB field, within volcanic center enrichments but, no apparent between center enrichment trends.

The trends observed in the La vs. P$_2$O$_5$ diagram are also seen in the Nd vs. P$_2$O$_5$ plot (Figure 9.7, bottom) however, a subtle change in the behind arc rock trend occurs with this less incompatible LREE. The LPE, LLB, Barrancas and Payun Matru
trend axes are nearly parallel to the MORB-OIB axis in the La vs. P₂O₅ diagram whereas, in the Nd vs. P₂O₅ plot these centers begin to show a depletion (axes shift) relative to the MORB-OIB array. This depletion is demonstrated by the arrow emanating from the MORB-OIB axis (orange and black cross hair symbol) in Figure 9.7 (bottom). The trend of increasing depletion with decreasing incompatibility is persistent through the MREE (Figure 9.8) and HREE (Figure 9.9).
Figure 9.7 La vs. $P_2O_5$ (top) and Nd vs. $P_2O_5$ (bottom) diagrams showing enrichment trends of trench proximal and behind arc volcanic centers. Addition of .5% $P_2O_5$ (Igpet mix) to most depleted samples (Llaima, Callaqui) produces some compositions similar to LLB rocks (top). $\otimes$ - MORB-OIB axis, $\downarrow$ - relative REE depletion.
Figure 9.8 Sm vs. \( P_2O_5 \) (top) and Tb vs. \( P_2O_5 \) (bottom) diagrams showing increasing depletions of MREE in behind arc centers. Addition of .5% \( P_2O_5 \) (Igpet mix) to most depleted samples (Llaima, Callaqui) produces some compositions similar to LLB and SW rocks (top). X - MORB-OIB axis, \( \sim \) - relative REE depletion.
Figure 9.9 Er vs. $P_2O_5$ (top) and Yb vs. $P_2O_5$ (bottom) diagrams showing increasing depletions of MREE in behind arc centers. Addition of .5% $P_2O_5$ (Igpet mix) to most depleted samples (Llaima, Callaqui) produces some compositions similar to LLB and SW rocks (top). ▼ - OIB axis, ▼ - relative REE depletion
10. Discussion

10.1 Volcanic Center Associations

XFR data indicate the Barrancas samples are mafic to slightly intermediate in composition with ranges of 47-55 wt. % SiO$_2$ and 3.5-10.0 wt. % MgO. Although the samples fall within a somewhat tight range of SiO$_2$ values, there are three distinct sub-groups as seen in the TAS and sub-alkaline discrimination diagrams (Figure 10.1). The sub-groups can be categorized as follows; the BC sub-group, basaltic trachy-andesite (samples BC3, RN12A and RN12B), the RN sub-group (samples RN1, RN2, RN3) and the CV sub-group, basalt (all other Barrancas samples).

It is likely the three sub-groups are products of independent volcanic events inferring the sub-groups are unrelated to each other in source region or magmatic process. This is illustrated by the lack of transitional compositions between the groups and wide-ranging differences in geochemical traits (Figures 7.6-7.10 and 8.1-8.9). In contrast, the other transect volcanic centers often show distinct fractionation trends and a much tighter compositional range in values.

If it is acknowledged that the Barrancas suite is actually a compilation of several sub-groups, each sub-group has more geochemical characteristics in common with other volcanic centers than to each other. Figures 10.2, 10.3, 10.4 and 10.5 are representative of alkaline, major, Large Ion Lithophile (LILEs) and Rare Earth (REEs) element plots (of all data) that exhibit these relationships.
Figure 10.1 Total Alkaline vs. Silica diagram (top) shows a tight assemblage of data points suggesting three distinct rock types. Sub-alkaline discrimination diagram (bottom) also identifies the sub-groups and classifies the majority of Barrancas rocks as medium K-calc-alkaline.
Figure 10.2 displays all volcanic center data in the Total Alkaline vs. Silica diagram. Most of the transect rocks plot in a tight range with SiO$_2$ concentrations of 47-53 wt. % and (Na$_2$O+K$_2$O) of 3-6 wt. %. Several centers exhibit linear trends that cross rock classification boundaries indicating differentiation to more silicic compositions within the magma chambers. These centers are the arc volcanoes Llaima, Talhuaca and Callaqui. On the eastern flanks of the current arc axis, Caviahue and Copahue display similar differentiation trends however; they are more alkaline likely due to their position above thicker crust. Tromen appears to have two diverging trends; a trend of increasing SiO$_2$ with increasing Na$_2$O and K$_2$O (calc-alkaline character, figure 10.2, top), and a second trend of increasing Na$_2$O and K$_2$O with no appreciable enrichment in SiO$_2$ (Figure 10.2, bottom). The LPE rocks show an enrichment trend similar to Tromen (increasing SiO$_2$ with increasing Na$_2$O and K$_2$O). Payun Matru displays a tight range of compositions and is consistent with OIB type rocks (GeoRoc database). The majority of the LLB rocks exhibit compositions similar to Payun Matru and the OIB like rocks of Tromen but, others are among the highest concentrations of K$_2$O. The Barrancas rocks show vague associations to the other centers in the TAS and the sub-alkaline discrimination diagrams.

Major element diagrams (Figure 10.3) reveal clear geochemical associations of the Barrancas sub-groups to other specific volcanic centers in the transect.

The BC sub-group exhibits SiO$_2$ and Na$_2$O concentrations close to the evolved Copahue and Callaqui rocks but with slightly lower MgO.
Figure 10.2 Total Alkaline vs. Silica (top, all data) and sub-alkaline discrimination diagrams (bottom) show the wide compositional range of the Barrancas rocks and their affiliation to the other transect centers which display tight assemblages of data or distinct trends.
The RN sub-group resembles Caviahue and Llaima rocks with corresponding values of SiO$_2$, Na$_2$O and MgO. The remaining CV sub-group displays a more diffuse similarity in the SiO$_2$ vs. MgO diagram but, coincides with SiO$_2$, Na$_2$O and MgO values of Payun Matru and LLB rocks. In these plots, RN11 is depicted as an outlier and has no clear association to the other transect rocks. Its physical characteristic of thick flood basalt (22m) with a well-developed colonnade-entablature structure (Figure 3.2) also distinguishes it from the other Barrancas volcanics that consist of samples from cinder cones, dikes and thin lava flows.

The associations between each Barrancas sub-group and their respective transect volcanic centers seen in the major element plots, are also revealed in the representative LILE (Figure 10.4) and REE plots (Figure 10.5).

In each of the plots, the rocks of Llaima, Talhuaca, Callaqui, and Caviahue, show distinct enrichment trends of LILE and REE with decreasing MgO, inferring fractionation processes.

Generally, Copahue, Callaqui, Talhuaca and the BC sub-group display the greatest enrichment in the incompatible elements, particularly in the LILE’s and LREE’s (Figures 10.2 through 10.5). These preferential enrichments may infer smaller degrees of melting from a decreased flux of subduction fluids, a source region enriched in incompatible elements or an increased assimilation of crustal material.

The Llaima, RN sub-group and several Caviahue rocks usually show slightly lower enrichment in the incompatible elements which may be the result of greater degrees of partial melting.
Figure 10.3 Major element plots displaying similarities of Barrancas sub-groups to other volcanic centers in this study. Ellipses represent affiliations to respective Barrancas group.
Figure 10.4 Large Ion Lithophile element plots displaying similarities of Barrancas sub-groups to other volcanic centers in this study. Ellipses represent affiliations to respective Barrancas group.
Figure 10.5 Rare Earth Element plots displaying similarities of Barrancas sub-groups to other volcanic centers in this study. Ellipses represent affiliations to respective Barrancas group.
The Payun Matru, LLB and CV sub-group rocks show no differentiation trends and little variation of incompatible element concentrations with values ranging slightly above or below Llaima values. The incompatible element diagrams also show overlapping compositions in Payun Matru, LLB and CV sub-group rocks. Most Payun Matru rocks display lower Y concentrations suggesting garnet phase retention at depth (Figure 10.5 bottom).

10.2 Magmatic Processes of Transect Volcanics

The variation in volcanic products across the transect can be explained in part by two mechanisms of magma generation: subduction and intra-plate volcanism (OIB).

Active subduction zones are complex systems and can generate magmas because of several tectonic processes. Magmas may be produced the dehydration of mineral phases in the descending oceanic plate/sediments in subduction zones thereby creating a flux of fluid mobile LILEs into the overlying mantle wedge. Volatiles migrate to and depress the melting temperature (solidus) of the overlying asthenospheric/lithospheric mantle wedge causing partial melting at the proper conditions of pressure and temperature. This melting process produces calc-alkaline magmas, typical products of arc volcanoes formed above subduction zones.

A second magmatic process related to subduction zones is the result of oceanic –continental plate coupling at the margin and subsequent trench/plate roll back (Figure 10.6). A compressional regime created by either the added mass of the arc edifice, horizontal plate motion or both at an oceanic –continental plate boundary causes the
Figure 10.6 Schematic showing coupling between an old, cold, and dense oceanic plate and the less dense continental plate at an active continental margin. Since an old oceanic plate is denser, gravity pulls it down at a steep angle promoting rollback and because of the coupling, the attached continental crust behind the arc stretches, creating a back-arc basin (After Frisch, 2011).
A subducting oceanic plate that is young, therefore hotter and less dense is buoyant in the underlying mantle creating upward compression. This causes greater horizontal stress (strong coupling) in the continental plate that is manifest as earthquakes, fold and thrust belts deep into the interior (Uyeda and Kanamori, 1979). Magmas generated in this type of a compressional regime are normally trapped in the crust as intrusions or melt adjacent crustal rock producing silicic volcanoes (Figure 10.7) (Frisch et al., 2011).

Figure 10.7 Schematic showing coupling between the young, hot, restless and buoyant oceanic plate and the less dense continental plate at an active continental margin. (After Frisch, 2011).
The presence of a deep mantle plume in close proximity to or a direct interaction with back-arc extension/riifting may also be a magma source. In this case, characteristics of OIB and MORB sources may be detected in the resulting volcanics.

Although individual magmas would have a source region with a locally derived composition; their interaction with other magmas/components and the residence time in the crust and or mantle allows for differentiation of that composition.

Each volcanic center in the transect can be characterized as a product of one the several magma generation mechanisms previously described.

In the westernmost end of the transect Llaima, Talhuaca, and Callaqui conform to the criteria of subduction volcanism; having the proper subduction zone geometry and geochemical characteristics of LILE enrichment, Nb-Ta negative anomalies and HFSE depletions.

At the easternmost end of the transect is Payun Matru. Positioned 483 km from the trench, presumably is beyond the influence of subduction processes and lacks proper subduction geometry. Its geochemical profile differs from the arc volcanos; displaying a decreased enrichment of LILEs, lack of an Nb-Ta negative anomaly and no depletions in HFSEs. Therefore, it exhibits the characteristics of an intra-plate OIB like source.

The remaining centers (intermediate); Caviahue-Copahue complex, Loncopue-Las Lajas, Tromen, and Barrancas, are geographically located (west-east) between the arc volcanos and Payun Matru (Figure 10.8).
The Caviahue-Copahue complex is located just 30 km east of the current arc front and displays the most arc-like signature of this intermediate group of volcanic centers (Figures 10.8, 10.9).
Loncopue-Las Lajas, Tromen, and Barrancas are positioned within extensional troughs and exhibit progressive increases in LILE (arc-like) west to east (Figures 10.8, 10.9). A similar pattern is seen in the REEs (Figure 10.9, bottom) but, there is

![Image of incompatible element (top) and rare earth element diagrams of intermediate group volcanic centers]

**Figure 10.9** Incompatible element (top) and rare earth element diagrams of intermediate group volcanic centers
greater variability (overlap) of individual trace elements between the profiles and sparse data for Tromen.

A close review of the troughs in figure 10.8 reveals a difference in volcano types and size. The Loncopue and Sierra De Reyes troughs are relatively narrow (22km) and host predominately, small monogenetic cinder cones. The Las Loicas trough however, is twice the width (50km) and contains several (7) very large (10-25km dia.) caldera and volcanic field complexes. This variation in trough geomorphic character posits the question; is there a correlation between the width of extensional structures, the thickness of the crust after extension and the resulting volume of magma produced from decompressional melting?

Trace element variability, decreased arc-like signature and similar to but, not an exact OIB end member profile, infers the magmas of these intermediate volcanic centers are produced by the mixing an arc derived flux, depleted sub-continental mantle and intra-plate deep mantle.

Previous authors have proposed periods of slab shallowing in this region during the Miocene as the mechanism for an easterly arc front migration and a subducted flux- arc signature deep into the foreland (Kay et al., 2006; Kay and Coira, 2009; Ramos and Folguera, 2009; Spagnuolo et al., 2012). The following illustrations (Figures 10.10 and 10.11) present possible variations on this theme.

During “normal” Andean type subduction (compressional regime), volatiles are continually migrating from the slab to the mantle upon descent until the appropriate depth for the production of hydrous melts is reached. The shallowing of the slab from
this “normal” position causes the appropriate depth for the production of hydrous melts to shift eastward (Figure 10.10). This shift may push the arc forward or not, given the possible range from the trench (100-250km) of edifice formation above the melt region. The volatiles from the slab complex at the maximum depth limits of dehydration, on the other hand, are likely to reach further east in the mantle. The volatiles from these lower limits may or may not have enough volume, buoyancy or heat to breach the surface but, will be transferred into the mantle wedge.

Figure 10.10 Cartoon depicting sources of melt and potential interaction within the mantle at the subduction zone between 36°-39°S. Slab shallowing creates the possibility of hydrous melts shifting toward the foreland (eastward) in keeping with the proper geometry required for subduction magmatism.
The proximity of a deep mantle plume to a subduction zone also has the potential to add melt to the mantle wedge through plume erosion. Here, the plume tail may be eroded by mantle flow (in this case westward, under continental South America), assimilated into the mantle and transferred to a region above the dehydration zone of the subducting plate (Figure 10.10). If all parameters are right, mixing of a rising hydrous melt and eroded, deep mantle plume material may occur.

Steepening of the slab, because of a change in tectonic regime, creates thinning of the crust behind the arc axis which is compensated by the upwelling of mantle asthenosphere. Upwelling may create a pull on the mantle that intercepts the rising melts from the slab, eroded plume and or mixed melts (Figure 10.11, top).

Continued steepening allows for decompressional melting and episodic volcanism to occur. The volcanic products may then be pulses of magma that have an arc-like signature, the degree depending on position of the overlying edifice in relation to the depth and volume of hydrous melting (Figure 10.11, bottom, Label \(A\) or \(B\)). They may also be more of an intra-plate signature if the melt is predominantly eroded plume or sub-continental mantle (Figure 10.11, bottom, Label \(C\)). Lastly, any combination of \(A\), \(B\), and or \(C\) (Figure 10.11, bottom) may explain the varying degrees of arc-like and OIB-like character in the Caviahue-Copahue complex, Loncopue-Las Lajas, Tromen, and Barrancas rocks.
Figure 10.11 Schematic showing convergences of melts during extension. A- Primary hydrated melt. B- Secondary hydrated melt. C- Eroded plume.
10.3 Potential Magma Reservoirs of Transect Volcanics

Chapter 7 describes the usefulness of radioactive parent-radiogenic daughter element pairs in distinguishing magma source regions. Several researchers using Nd, Sr, and Pb isotopes have characterized five mantle (Zindler and Hart, 1986) and three crustal (Taylor and McLennan, 1985) reservoirs (Figure 10.12, Table 10.1). The five mantle reservoirs are classified as:

**Depleted Mantle (DM)** - high $^{143}\text{Nd}/^{144}\text{Nd}$ (0.1530-0.1533), low $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70240-0.702256) and low $^{206}\text{Pb}/^{204}\text{Pb}$ (17.98 – 18.50). DM is the source rock of many MORBS.

**Prevalent Mantle (PREMA)** - $^{143}\text{Nd}/^{144}\text{Nd} = 0.1530$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7033$ and $^{206}\text{Pb}/^{204}\text{Pb} = 18.2 – 18.5$. End member consists of oceanic island arc, oceanic and continental basalts.

**Mantle with High Mu (HIMU)** - Mu ($\mu$) = $^{238}\text{U}/^{204}\text{Pb}$, high $^{206}\text{Pb}/^{204}\text{Pb}$, high $^{208}\text{Pb}/^{204}\text{Pb}$, intermediate $^{143}\text{Nd}/^{144}\text{Nd}$ (0.5129) and low $^{87}\text{Sr}/^{86}\text{Sr} \approx (0.7030)$. This suggests an enrichment of U and Th without a corresponding enrichment in Rb/Sr.

**Enriched Mantle I** - low $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{207}\text{Pb}/^{204}\text{Pb}$, and high $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$.

**Enriched Mantle II** - high $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{207}\text{Pb}/^{204}\text{Pb}$, and high $^{208}\text{Pb}/^{204}\text{Pb}$ at a given $^{206}\text{Pb}/^{204}\text{Pb}$.
The Bulk Silicate Earth (BSE) designation is a proposed homogenous primitive mantle composition minus core material and before the formation of continents. Currently, there is no geochemical data suggesting this reservoir still exists (Hart and Zindler, 1986).

Currently, there is no geochemical data suggesting this reservoir still exists (Hart and Zindler, 1986).

![Figure 10.12](image-url)

**Figure 10.12** $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ diagram showing the five end-member isotopic reservoirs of the mantle as characterized by Zindler and Hart (1986). DM-depleted Mantle, PREMA (Prevalent Mantle)-commonly observed mantle compositions, HIMU-high U/Pb mantle compositions, EMI and EMII-enriched mantle and BSE-Bulk Silicate Earth (see text). Barrancas rocks are shown to be positioned within the mantle array. After Zindler and Hart (1986).

The three crustal isotopic reservoirs characterized by Taylor et al. 1984 possibly assimilated by magma bodies are displayed in (Table 10.1). Generally, the upper crust contains high $^{87}\text{Sr}/^{86}\text{Sr}$, low $^{143}\text{Nd}/^{144}\text{Nd}$, high $^{207}\text{Pb}/^{204}\text{Pb}$, high $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ with decreasing isotopic ratios with depth through the mid and lower crustal regions.
Lead isotope data (Figures 8.25-8.28) show the Barrancas, Loncopue (LPE) and Las Lajas (LLB) rocks have lower values than the arc rocks.

The $^{143}$Nd/$^{144}$Nd ratios of the Barrancas samples show a tight range of values (.512804-.512837) and are depicted as a horizontal array with a range of $^{87}$Sr/$^{86}$Sr values of .703851 to .704270 (Figure 10.9). This indicates a similar mantle source ($^{143}$Nd/$^{144}$Nd) for the samples but, varying degrees of a crustal signature ($^{87}$Sr/$^{86}$Sr) possibly from a prolonged crustal residence time of the magma or sediment input from subduction processes.

Unfortunately isotope data is deficient for many volcanic centers in the transect but, the arc volcano Callaqui and maybe Llaima (given only two data points) display a tighter range of $^{143}$Nd/$^{144}$Nd values. Callaqui exhibits $^{87}$Sr/$^{86}$Sr values that form an array straddling the Morb-Pacific Detrital Sediment mean mix line. This array, like the Barrancas array may be the result of the same processes. However,
alternative explanations may be; increased sediment transfer to the trench, relative magma enrichment due to crystal fractionation or tapping of other $^{87}\text{Sr}$ enriched/depleted asthenospheric source regions.

Somewhat perplexing is the position of Payun Matru data along the Morb-Pacific Detrital Sediment mean mix line (Figure 10.13) since it is characterized as an alkaline OIB-type intra-plate shield volcano (Pasquarè et al., 2008; Ramos and Folguera, 2011; Søager et al., 2013). The occurrence of Payun Matru volcanics along the mix line is likely a coincidence and the trend may actually be the result of tapping different regions of the asthenosphere. The LLB and LPE rocks also lay along the mix line and may be the result of the same source regions.

**Figure 10.13** $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ diagram showing available volcanic data of transect centers plotted in relation to the mean mix line of the North Chile Ridge (NCR) and Pacific Detrital Sediment (PDS).
10.4 The Subduction Zone Phosphorus Dilemma

Depletion of P is commonly seen in arc rock incompatible element diagrams but, is poorly explained in the literature.

Figure 9.4 (top) shows progressive shallowing of the negative P anomaly of the arc rocks eastward from Llaima to Talhuaca and Callaqui. The Caviahue-Copahue complex, LPE and Tromen rocks also show depletions in P however, they are not as pronounced as in the arc rocks (Figure 9.4, bottom).

The Barrancas samples as a group display variation of P depletions but, segregated into the sub-groups: the BC and RN group and several rocks of the CV group show modest P depletions (Figure 10.14). The remaining samples of the CV group display distinct depletions in P that resemble the arc rocks (Figure 10.15).

A plausible explanation for this progressive increase in P across the arc and into the foreland is the transport of detrital apatite through the subduction zone. The stability of apatite under subduction zone conditions (P, T, volatiles) as described in chapter 9 allows for survival of detrital apatite. In addition, apatite formed by the release of PO$_4^{3-}$ during the high pressure metamorphism of olivine, plagioclase and clinopyroxene, prevents P from migrating into the overlying mantle. The retention of P in apatite formed during metamorphic reactions early on in slab descent may cause the depletions seen in the arc rocks (Figure 9.2) but, is released with increased solubility at depth. Supporting the premise of apatite formation creating P depletion in arc rocks is the correlating retention of LREE.
Figure 10.14 Incompatible element chart shows most Barrancas samples with minor P depletions.
Apatite as a compatible host for most REE may incorporate mobilized incompatible elements into its structure from dehydration reactions of the slab. Figure 9.7 depicts the greatest depletion of LREE in the nearer trench arc rocks of Llaima but increases eastward through Talhuaca, Callaqui and Caviahue-Copahue, inferring retention with supposition, in apatite.

A number of rocks from LLB and Barrancas (and some Payun Matru) show increasing P with an increase in LREE. This could be explained by the addition of LREE enriched apatite formed during subduction to the melt schematic presented in figures 10.10, 10.11 and 10.16. To corroborate an LREE enriched apatite, the arc rocks and back-arc rocks display a systematic decrease in MREE and HREE Figures 9.7-9.9).
Figure 10.16 Schematic of detrital apatite transport through the subduction zone.
11. Conclusions

This overview of the geochemical characteristics of the Barrancas rocks and their relationship to the transect centers in this study has shown that: (1) the volcanic centers located between arc axis volcanos and the intra-plate shield volcano Payun Matru (Caviahue-Copahue, Loncopue-Las Lajas, Tromen and Barrancas) exhibit diminished traits of both an intra-plate like and an arc-like character, and (2) may be explained by slab geometry oscillations as a result of fluctuations in tectonic regime during the Miocene.

- The Barrancas rocks are likely the products of several different spatial and temporal volcanic events rather than a coherent rock suite produced from a single magmatic process.
- The Barrancas subgroup CV has greater geochemical affinity to the Arc volcano Callaqui and the near arc volcano Copahue than to other Barrancas samples
- The Barrancas subgroup RN has greater geochemical affinity to the Arc volcano Llaima and the near arc volcano Caviahue than to other Barrancas samples
- The Barrancas subgroup RN has greater geochemical affinity to the intra-plate volcano Payun Matru and the back-arc volcanics of LLB than to other Barrancas samples
• Nazca Plate modeling (current position) supports proper subduction geometry for generation of arc volcanism at Llaima, Talhuaca, Callaqui and Copahue, but at Loncopue-Las Lajas, Tromen and Barrancas, edifices are formed above the maximum dehydration depth where LILEs and LREEs have already been expelled from the subduction complex thereby exhibiting a diminished arc signature

• Progressive West to East enrichment of incompatible elements (major and trace) across the arc (FET)

• Nazca Plate model supports proper geometry for current arc volcanism

• Shallowing slab angle over time accounts for Caviahue being similar in geochemical composition to Llaima and back arc volcanics with arc-like signature

• Increasing REE concentrations correlated with increasing P across the arc inferring retention of P and LREEs in slab/continental plate detrital apatite until solution at depth

• Several Barrancas samples display an abundance of apatite supporting P retention

• The LLB, Barrancas and slab window rocks show a progressive decrease in REE with increasing atomic number and increasing P, a result of partial melting or a depleted mantle source
• Propose arc like signature east of the current front is result of a slab flux enriched mantle dragged upward during extensional episodes during the Miocene
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