

## Chapter 1- INTRODUCTION

### 1.1. Mantle Rocks

This study is dedicated to mantle rocks derived from two different mantle domains: (1) Suboceanic convecting mantle of the south-east Pacific Ocean represented by peridotites from the Taitao ophiolite, derived from the suboceanic upper mantle and emplaced to the continent only 5 to 6 Ma ago at the Taitao Peninsula (46°S), Chile; and (2) Subcontinental lithospheric mantle of southern South America represented by mantle xenoliths derived from the lithospheric mantle root of the continent, and carried to the surface by deep-generated basaltic alkaline magmas of Eocene to recent ages at the modern back arc region of the southern Andes, Chile and Argentina. Figure 1.1 shows the location of the studied mantle rocks and a scheme representing the interaction between tectonic plates associated to the Chile Ridge subduction (modified from Gorrington and Kay, 2001).

Regarding the suboceanic mantle, the Taitao ophiolite offers the great possibility to study a relatively young and complete oceanic lithospheric section formed under the southeast Pacific Ocean. The examination of Os isotopes, HSE abundances and corresponding Sr, Nd, and O isotopic variability within the ophiolite, and particularly within the ultramafic unit, can contribute to deconvolute the history of mantle processes like partial melting and metasomatism but also some crustal processes that acted on these rocks, like crustal contamination and metamorphism including water-rock interactions.

In the other hand, mantle xenoliths can be used to recognize processes recorded at the subcontinental lithospheric mantle at different scales of space and time. The petrographic, chemical, and Sr, Nd and Pb isotopic characteristics of mantle xenoliths derived from the same locality can be used to decipher processes occurred in the sampled mantle section. Using this methodology is possible to recognize events occurred at the subcontinental mantle, like partial melting, metasomatism related to mantle melts and/or fluids, and the interaction with the host basalt infiltration.

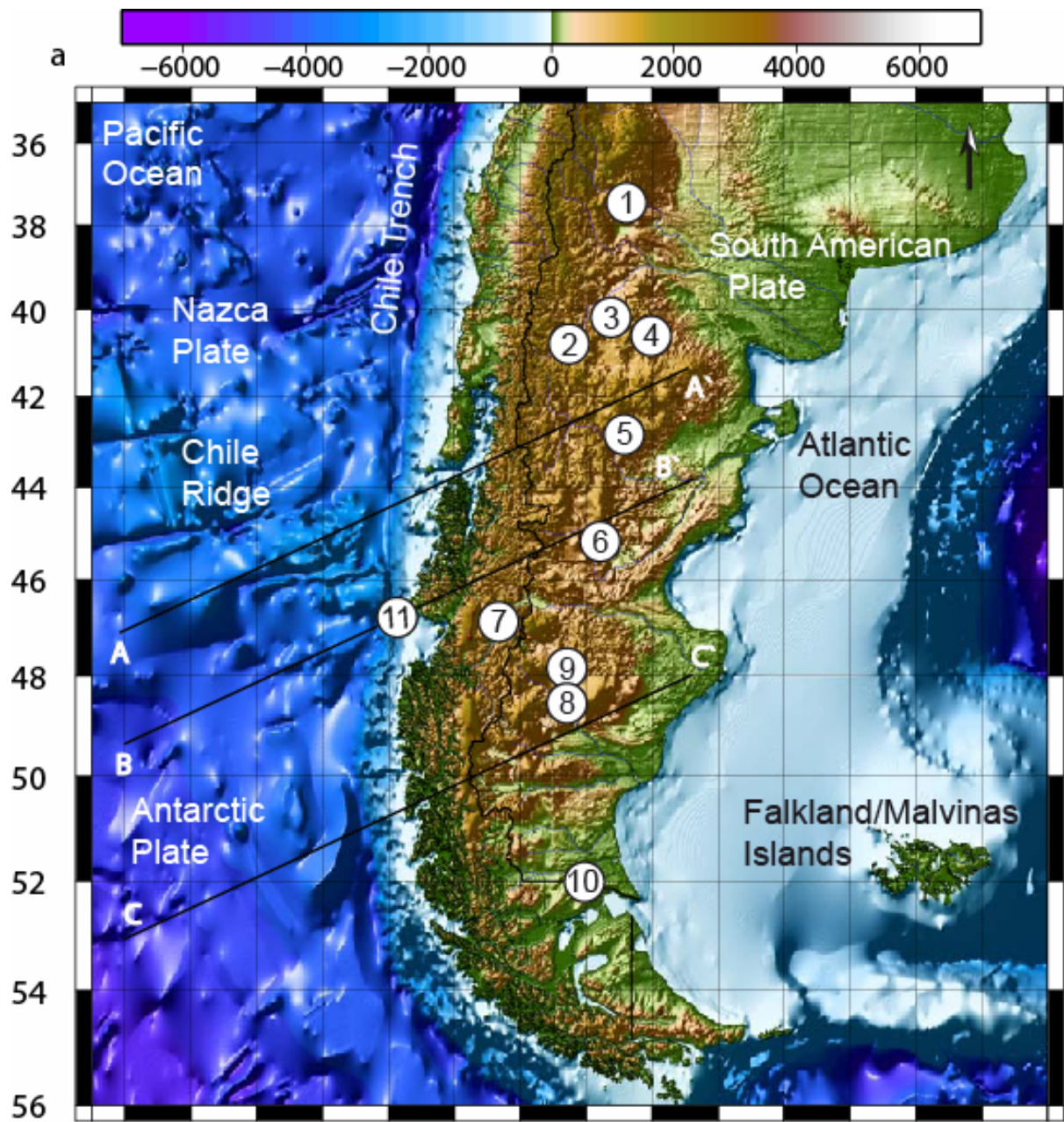
Also, the study of mantle xenoliths derived from different localities can be utilized to recognize regional heterogeneities in the subcontinental lithospheric mantle. The Re-Os isotopic system is particularly useful to study mantle rocks because it is able to record the time of partial melting events in the mantle, process that is generally related to the formation of the lithospheric mantle itself. Thus, the determination of Os isotopic compositions of widespread mantle

xenoliths can finally contribute to the better understanding of the geological history of the studied region. This kind of works can be strongly complemented by geophysical studies based on the physical properties of the lithosphere.

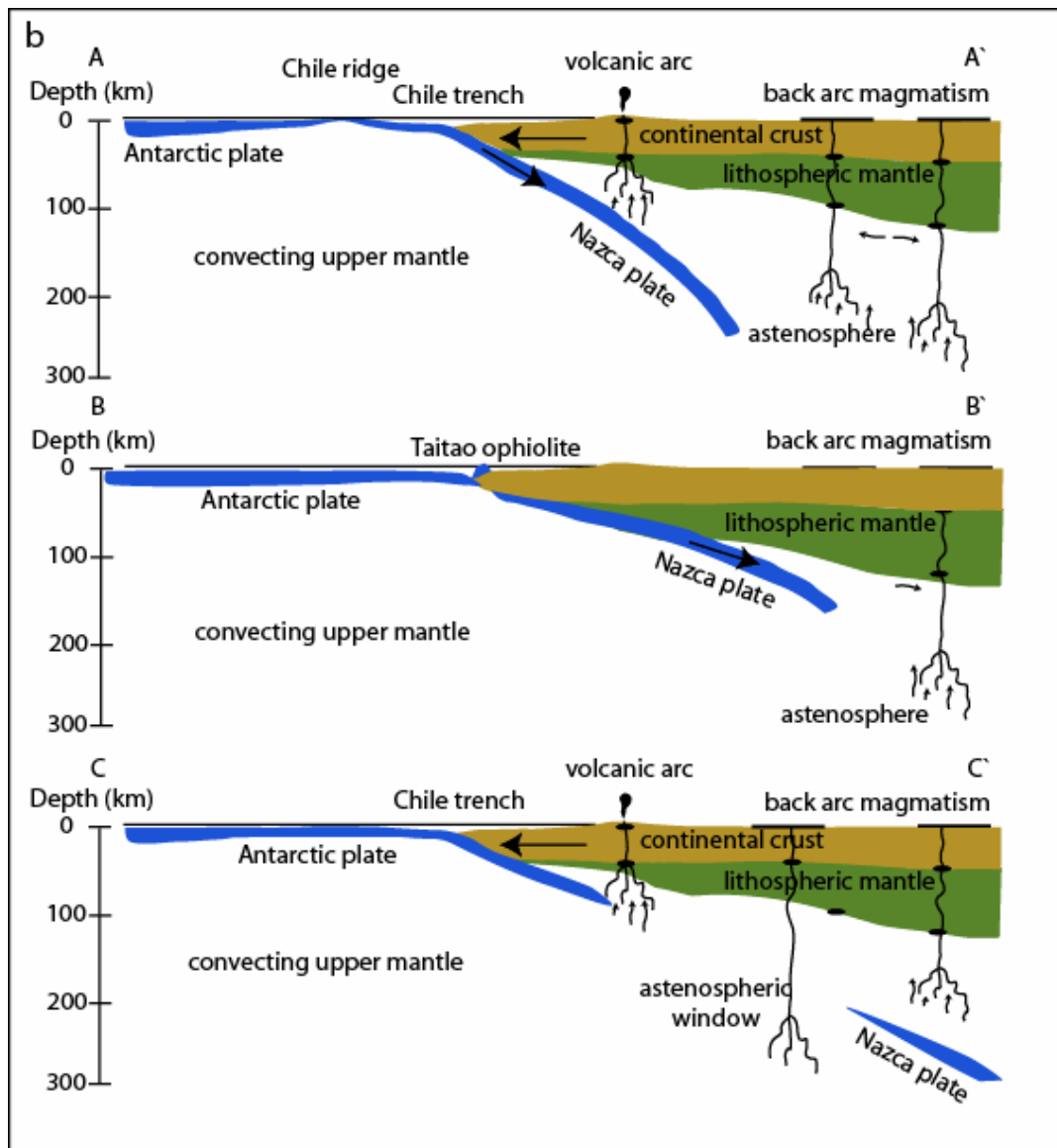
Next, a broad overview is presented describing some aspects about the mantle geology and geodynamics with the existing models for their formation and evolution. It is also introduced a brief review of the geochemistry, the Sr-Nd-Pb isotopic compositions, and the particular behavior of the HSE and the Re-Os isotopic system in mantle rocks, tools that will be utilized in the present work. For a complete review the reader is referred to the vol. 2 of *Treatise on Geochemistry, The mantle and the core* (2003), and the recent review presented by Carlson (2005) about the application of the Re-Os isotopic system to the mantle geochemistry and geochronology. Finally, at the end of this chapter, the objectives of this study and a broad outlay of the dissertation are exposed.

Considering that almost all the Earth's interior lies inaccessible beneath our feet, the relatively scarce occurrences of mantle rocks are of great importance to the understanding of the mantle composition and evolution. Mantle rocks presently found at the Earth's surface can be fragments emplaced tectonically into the continental crust (ophiolites and massif peridotites), or transported by deeply derived magmas to the surface (mantle xenoliths). These mantle-derived rocks are very important because they allow us to study directly the mineralogical, chemical, and physical properties of the mantle, characteristics that are related to its long history.

The seismic response of the mantle suggests that with broad bounds, an isochemical mantle with composition similar to that inferred from upper mantle rocks is consistent with the seismic properties of the whole mantle (Bina, 2003). This composition is predominantly a type of rock called peridotite that at upper mantle conditions is composed predominantly of the magnesium-rich silicates olivine and orthopyroxene with lesser amounts of calcium-bearing clinopyroxene and an aluminum-rich mineral that changes from plagioclase to spinel to garnet with increasing pressure.



**Figure 1.1.** a) Topographic map of southern South America and surrounding areas showing major geological features. The Taitao ophiolite (11) was studied on Chapter 2. Mantle xenoliths from Cerro Redondo (8) are the focus of Chapter 3 and were also studied in Chapter 4 together with xenoliths from: 1, Agua Poca; 2, Cerro del Mojón; 3, Estancia Alvarez; 4, Prahuaniyeu; 5, Paso de Indios; 6, Cerro de los Chenques; 7, Chile Chico; 9, Estancia Lote 17; and 10, Pali-Aike.



**Figure 1.1.** b) The cartoon illustrates the subduction of the oceanic lithosphere (Nazca and Antarctic plates) under the continental crust at different regions (modified from Gorring and Kay, 2001). The sequence can also be seen as approximately the last 14 Ma of evolution of any place located south of the present triple junction: A-A') The NW-directed Chile Ridge approximating to the Chile trench; B-B') The Chile Ridge arrives at the Chile trench that at the Taitao peninsula resulted in the obduction of a suboceanic lithospheric sequence (the Taitao ophiolite); C-C') The Chile ridge was already subducted and an asthenospheric window is formed. The schemes also show the magmatic activity of the volcanic arc and the basaltic alkali magmatism of the back arc region.

Seismology, together with experimental petrology, studies on meteorites, and mathematical models have allowed to know the deep Earth's structure and chemistry, characterized by a metal core composed mainly by iron, nickel, and sulfur, and divided in a solid inner core and an outer liquid core, which is the main candidate to be responsible of the Earth's magnetic field. The mantle-core transition occurs ~2800 km deep. The seismic response also distinguishes seismic discontinuities at 410 km and 660 km depth that mark the expected phase transformations as upper mantle olivine changes first into spinel and then into perovskite structured high-pressure polymorphs. Finally, the crust is a compositionally distinct layer overlying the mantle that concentrates preferentially the incompatible elements derived by partial melting of the mantle during the Earth's history. Seismology also recognizes a rigid conductive thermal boundary layer at the top of the convecting mantle that consist of both crust and that portion of the mantle that move together as a tectonic plate known as lithosphere. The lithosphere has higher shear wave velocities compared with the convecting mantle and has variable thickness depending on the geological setting context. In the ocean basins the base of the oceanic lithosphere is marked by a strong decrease in the shear wave velocities at depths generally less than 100 km beneath the crust (Carlson et al., 2005). Unlike the oceanic lithosphere, the base of the continental lithosphere is not well defined by seismological data: with increasing depth the high seismic velocities of the stable lithosphere gradually approach those of the convecting mantle across a broad transition zone. This zone of velocity transition, in general not well resolved, ranges from 200 to perhaps 400 km deep beneath the oldest continents known as cratons. Under younger continental regions or where old continents have suffered important tectonomagmatic activity, the thickness of the lithosphere generally reaches lesser depths than in cratonic areas, in some cases with similar thickness to those of the oceanic lithosphere (Carlson et al., 2005). Essentially all studies, whether based on seismic velocity, heat flow, gravity, or mantle xenoliths, indicate that the continental lithosphere, especially on cratons, is much colder than the oceanic lithosphere.

Significant differences exist between the oceanic and continental lithospheres. The oceanic crust is formed at the oceanic ridges by partial melting of the depleted mantle (Fig. 1.1), and during the migration of the oceanic crust away from the ridge, the underlying shallow mantle is cooled by conduction of heat into the oceans, what causes that the underlying mantle becomes mechanically coupled to the overlying plate to form the lithosphere. As the plate ages, oceanic lithosphere cools and thickens, becoming progressively more dense so that at some point it becomes gravitationally unstable and descends back into the mantle in the process known as plate

subduction. Unlike in the ocean basins where the shallow mantle eventually contributes to the destruction of the overlying crust, the shallow mantle beneath continents serves as a stiff, buoyant “root” whose presence may be essential to the long-term survival of continental crust at the Earth’s surface, particularly on cratons (Carlson et al., 2005). These distinct roles for subcrustal mantle come about because the subcontinental mantle consists of a thick section of material left behind after extensive partial melt extraction, possibly from the wedge of mantle overlying a subducting oceanic plate. Most melts finally reach the surface contributing to the crustal growth but the melt removal causes the continental lithospheric mantle to become cold and strong but also buoyant compared to convecting mantle, characteristic caused by the loss of heavy elements as Fe and Ca. These characteristics allow thick sections of cold mantle to persist beneath continental crust in some cases for over 3 billion years. A significant difference between old and young continental lithospheres is that the lithospheric mantle under Archean cratons is formed by thicker sections (> 200 km) conformed by highly depleted residues produced by very high degrees of partial melting under the high geothermal gradients that predominated during the initial stages of the planet. However, the thinner lithospheric mantle sections (approximately 100 to 150 km) formed under younger continental crust are the product of lower degrees and amounts of partial melting predominantly of mantle wedges (Pearson et al., 2003), primarily reflecting a secular decline in mantle temperature.

The principal division of the Earth into core, mantle, and crust is the result of two fundamental processes. (i) The formation of a metal core very early in the history of the Earth. Core formation ended at ~30 million years after the beginning of the solar system (Kleine et al., 2002). (ii) The formation of the continental crust by partial melting of the silicate mantle. This process has occurred with variable intensity throughout the history of the Earth. After the fractionation of the metal core, the mantle acquires a particular composition that has not been affected by the extraction of partial melts during crust formation, what is the concept of “*primitive mantle*” (PM). The Earth dynamics is marked by the constant motion of the Earth’s interior as a consequence of the internal heat liberation, which results in the mantle convection and the continual creation of new crust at ocean ridges, and their consequent destruction by subduction into the mantle at convergent margins (Fig. 1.1). This motion drives a slow two-way exchange of material between the Earth’s surface and interior, resulting finally in the continental crust formation. The creation of the crust and the constant recycling of oceanic crust and continental materials into the mantle have developed heterogeneous mantle domains with

particular mineralogical, physical, chemical, and isotopic characteristics. The long-term removal of oceanic crust by partial melting of the convecting mantle has resulted in its depletion of the most incompatible elements. This mantle domain is commonly referred as the depleted mantle source of MORBs (DMM). Another end member is the enriched mantle domain known as HIMU given their high U/Pb ratios, whose characteristics are generally accepted to be inherited from the recycling of the subducted oceanic crust into the mantle. Also the enriched mantle type I and type II (EMI and EMII, respectively) are recognized, which are inferred to be the result of the subduction and remixing into the mantle of subcontinental lithosphere and continental sediments, respectively. The study of mantle-derived basaltic melts has been crucial to identify these heterogeneous mantle domains. Nevertheless, great debate continues between geochemists about the origin and characteristics of those and others mantle domains, a subject which is out of the scope of the present work.

Different geological occurrences of rocks and rock fragments derived from the Earth's mantle can be found at the surface. "Tectonically emplaced" mantle rocks include subcontinental, suboceanic, and subarc mantle rocks that were tectonically exhumed from the upper mantle and correspond to ophiolites and massif peridotites. Compared with mantle xenoliths (see below), a disadvantage of some tectonically emplaced mantle rocks for representing mantle compositions is that their original geodynamic setting is not always clearly known and their significance is sometimes a subject of speculation. In addition, the mantle structures and mineralogical compositions of tectonically emplaced mantle rocks may be obscured by deformation and metamorphic recrystallization during shallow upwelling, exhumation, and tectonic emplacement (Bodiner and Godard, 2003). Metamorphic processes range from high-temperature recrystallization in the stability field of plagioclase peridotites (Rampone et al., 1993) to complete serpentinization (e.g. Burkhard and O'Neill, 1988).

**Orogenic peridotite massifs or Alpine peridotites** are dispersed ultramafic bodies, a few meters to kilometers in size, emplaced in suture zones and mountain belts (Thayer, 1960; Den Tex, 1969). With few exceptions, orogenic peridotite massifs are characterized by the predominance of lherzolites equilibrated at any of the garnet-, spinel, or plagioclase-peridotite facies (Bodiner and Godard, 2003). These terms are presently more restricted to the lherzolite massifs unrelated with ophiolitic oceanic crust (Menzies and Dupuy, 1991). The well known Lherz peridotite body, in the French Pyrenees, is now viewed as a typical "orogenic lherzolite" massif (= "truly alpine-

type peridotite”), considered to represent subcontinental lithospheric mantle (Fabriès et al., 1991). The orogenic massifs are generally associated with platform of sediments or continental rocks recording extreme metamorphic conditions, from high temperature at intermediate or low pressure to high or ultrahigh pressure at variable temperature conditions (Bodiner and Godard, 2003).

**Ophiolites** represent slivers of ancient oceanic lithosphere obducted onto continental or oceanic crust. Ophiolite suites are observed in all major orogenic belts as a consequence of the Earth’s geodynamics. Ophiolites provide a unique opportunity to observe the structure of the oceanic crust and upper mantle (Bodiner and Godard, 2003). At the Penrose Conference in 1972, a world wide agreement was reached among geologist on the definition of what is an ophiolite (e.g., Coleman, 1977; Dilek et al., 2000). After years of controversy, the participants of the Penrose Conference stated that in a completely developed ophiolite, the rock types occur in the following sequence, starting from bottom and working up: ultramafic complex, gabbroic complex, mafic sheeted dike complex, mafic volcanic complex, commonly pillowed. Ophiolites are overlain by a sedimentary section. They may contain podiform bodies of chromite associated with dunite, and sodic felsic intrusive and extrusive rocks. An ophiolite may be incomplete, dismembered, or metamorphosed. Peridotites are commonly strongly serpentinized but usually conserve rare mineralogical relics of the primary lithologies that are used to constrain original mantle characteristics.

**Abyssal peridotites** are dredged from the ocean floor or recovered from drill cores (e.g. Prinz et al., 1976). They provide direct information on the uppermost mantle in the present-day oceanic settings (e.g. Fisher and Engel, 1969). However, mantle exposures are rare on the sea floor, and limited to specific areas. All abyssal peridotites are serpentinized, generally to a large extent (e.g. Snow and Dick, 1995). The serpentine protoliths are mostly harzburgites and, less commonly, lherzolites. This predominantly refractory composition is consistent with significant amounts of melt extraction by the oceanic crust formation. Dunites, wherlites, and pyroxenites are subordinate rock types (e.g., review in Karson, 1998).



**Mantle xenoliths** are fragments of the Earth's mantle that range up to sizes in excess of 1 m across, frequently transported to the surface via volcanic rocks that are dominantly alkaline in nature. Mantle xenoliths provide snapshots of the lithospheric mantle beneath particular regions at the time of their eruption and hence are crucial direct evidence of the nature of the mantle beneath continental regions where no samples have been exposed by tectonic activity (Pearson et al., 2003). One obvious contrast between the mantle samples provided by xenoliths and those provided by tectonically emplaced peridotites is the lack of field relationships available for xenoliths. Other drawbacks include the small size of many xenoliths. This makes accurate estimation of bulk compositions difficult and accentuates modal heterogeneities. The frequent infiltration of the host magma also complicates their chemical signature. Despite these drawbacks, xenoliths are of immense value, being the only samples of mantle available beneath many areas. Because they are erupted rapidly, they freeze in the mineralogical and chemical signatures of their depth of origin, in contrast to peridotite massifs which tend to re-equilibrate extensively during emplacement into the crust. Most mantle xenoliths occur in continental areas but few occurrences on oceanic volcanic rocks (e.g. Jackson and Wright, 1970; Neuman et al., 1995) and in subduction zone environments (e.g. Brandon et al., 1999; McInnes and Cameron, 1994) have been reported.

## **1.2. Major and trace element geochemistry of mantle rocks**

The chemistry of the mantle peridotites is characterized by contents of MgO in the range of 35-50 wt.% and SiO<sub>2</sub> from 40 wt.% to 48 wt.%, remarkably constant abundances of FeO ( $8 \pm 1$  wt. %), only lower in most depleted cratonic peridotites (Fig. 1.2), Cr<sub>2</sub>O<sub>3</sub> ( $0.4 \pm 0.1$  wt. %) and Co ( $100 \pm 10$  ppm). Bulk rock magnesium numbers are generally  $\geq 0.89$ . The comparative high contents of nickel ( $2,200 \pm 500$  ppm), a siderophile element, and of iridium ( $3.2 \pm 0.3$  ppb), a compatible highly siderophile element, are diagnostic of mantle rocks (Palme and O'Neill, 2003).

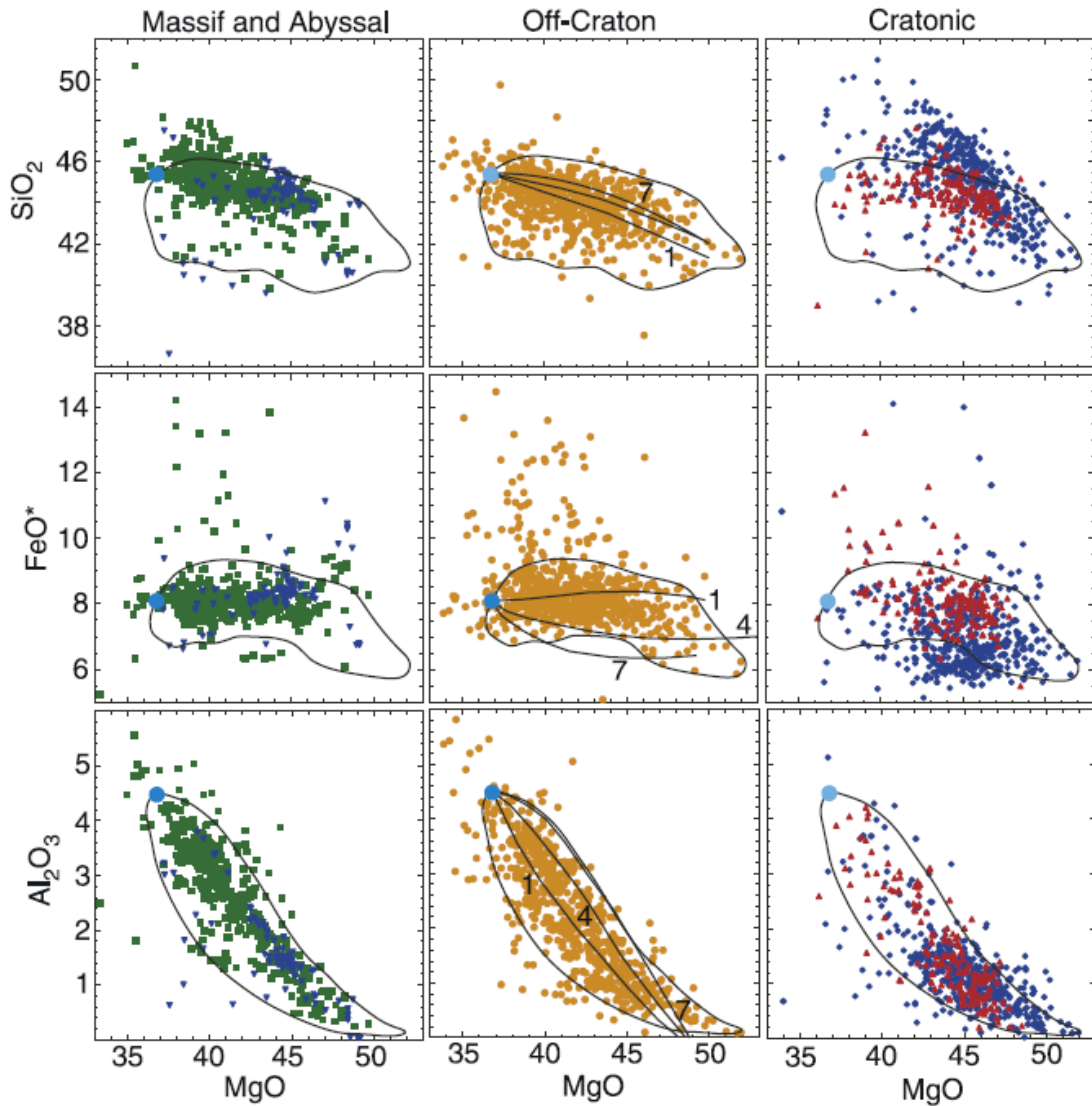
In Table 1.1 are presented some major element estimations of the composition of the primitive mantle before any melting has occurred, together with the averages of peridotites from different tectonic settings presented by Carlson et al. (2005). In presenting these averages it is important to recognize that each setting displays a wide range about the median values reported in Table 1.1. Nevertheless, some clearly distinguishable features are apparent. Both, massif peridotites, and mantle xenoliths from off-craton localities range to more fertile compositions (see below) than either oceanic peridotites or xenoliths erupted from beneath Archean crustal

terrains, which correspond to residues left after higher degrees of partial melting. This is because when melting occurs in the mantle, certain elements such as calcium and aluminum are concentrated into the melt and are removed with it while other elements, particularly magnesium, selectively remain behind in the solid residue (Fig.1.2). Those elements that concentrate in the melts are known as “incompatible” elements while the elements that remain in the solid residue are known as “compatible” elements. Mantle peridotites with compositions close to that of the primitive mantle are often termed as “fertile”, emphasizing their ability to produce basalts on melting. On the other hand, peridotites with lower contents of incompatible elements and higher contents of compatible elements are referred as “depleted”. The mineralogical expression of the transition from fertile to depleted peridotite is the loss first of clinopyroxene and garnet, the main host for incompatible elements in the mantle, and then orthopyroxene, resulting in the rock name transition from lherzolite (olivine + orthopyroxene + clinopyroxene +garnet or spinel) to harzburgite (olivine + orthopyroxene) to dunite (just olivine). A critical result of this mineralogical transition is that depleted peridotite is less dense than fertile peridotite at the same temperature. Peridotites bulk rock concentrations of  $\text{Al}_2\text{O}_3$ , CaO, and also Ti, Sc and the heavy REE from worldwide localities are negatively correlated with MgO (Fig. 1.2; McDonough, 1990; BVSP, 1981; McDonough and Sun, 1995). Peridotites with the lowest MgO contents have, in general, the highest concentrations of  $\text{Al}_2\text{O}_3$ , CaO, and other incompatible elements. Most peridotites are, however, depleted to various extents in incompatible elements, i.e., they have lower contents of CaO,  $\text{Al}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$ , etc., than a fertile mantle would have. By contrast, an element compatible with olivine, such as nickel, increases with increasing MgO contents. It is particularly noteworthy that trends for xenoliths and massive peridotites are statistically indistinguishable (McDonough and Sun, 1995). This geochemical behavior has been interpreted as reflecting various degrees of melt extraction (e.g. Frey et al., 1985), however, more complex hypothesis have been proposed to explain these mantle characteristics as well (Palme and O’Naill, 2003; and references therein).

Table 1.1. The first five columns are different estimations of the composition of the primitive mantle, and the other five columns are averages of the mantle at different tectonic settings. The cratonic mantle is commonly divided into high and low temperature, because their particular geological characteristics.

	<b>HZ86</b>	<b>J79</b>	<b>PN85</b>	<b>MS95</b>	<b>PO03</b>	<b>Oceanic</b>	<b>Massif</b>	<b>Off-Craton</b>	<b>low T Craton</b>	<b>high T Craton</b>
SiO <sub>2</sub>	45.96	45.14	46.20	44.92	45.40	44.66	44.98	44.47	44.18	44.51
TiO <sub>2</sub>	0.18	0.22	0.23	0.20	0.22	0.01	0.08	0.09	0.02	0.11
Al <sub>2</sub> O <sub>3</sub>	4.06	3.97	4.75	4.44	4.49	0.98	2.72	2.50	1.04	0.84
FeO*	7.54	7.82	7.70	8.05	8.10	8.28	8.02	8.19	6.72	8.08
MgO	37.78	38.30	35.50	37.80	36.77	45.13	41.15	41.63	46.12	44.76
CaO	3.21	3.50	4.36	3.54	3.65	0.65	2.53	2.44	0.54	1.08
Ni	0.28	0.27	0.23	0.25	0.24	0.32	0.27	0.28	0.28	0.27
Cr	0.47	0.46	0.43	0.38	0.37	0.41		0.40	0.36	0.38
Mg#	0.90	0.90	0.89	0.89	0.890	0.907	0.902	0.899	0.925	0.908

HZ86: Hart and Zindler, 1986; J79: Jagoutz et al., 1979; PN85: Palme and Nickel, 1985; MS95: McDonough and Sun, 1995; PO03: Palme and O'Neill, 2003. Other averages were estimated by Carlson et al. (2005) from the data of McDonough (1990).



**Figure 1.2.** Major element ranges observed for peridotites from a variety of tectonic settings including (left) ocean basins (dark blue points) and mantle sections tectonically obducted onto continental crust (massif peridotites (green points)), (middle) peridotite xenoliths (primarily spinel peridotites) erupted in tectonomagmatically active areas away from cratons, and (right) peridotite xenoliths carried by kimberlites erupting through both Archean and middle to Early Proterozoic crust. In the right column the blue points are for low-T peridotites, and the red points are for high-T samples. The field shown on all plots outlines the majority of the data for off-craton peridotite xenoliths to serve as a reference. The large light blue dot in all plots is an estimate of fertile mantle composition. Peridotite data are from the compilation of McDonough [1990] and figure from Carlson et al (2005).

Considering that peridotites are residues from melt extraction, the majority of mantle xenolith peridotites should contain pyroxenes and garnets that have LREE-depleted compositions. However, only a small proportion of peridotite xenolith minerals still reflect this depleted history because of either metasomatism, or because some minerals have crystallized from melts passing through the peridotite following initial depletion (Shimizu, 1999; Shimizu et al., 1997; Simon et al., 2003). Thus, metasomatism re-enriches the rocks in incompatible components subsequent to depletion by melt extraction. Where this is obvious (e.g., in reaction zones adjacent to later dikes) it may be avoided easily; but often the metasomatism is cryptic, in that it has enriched the peridotite in incompatible trace elements without significantly affecting major-elements chemistry. In those cases where infiltration occurs over wide areas by porous flow, the changes on the chemical characteristics can be more dramatic.

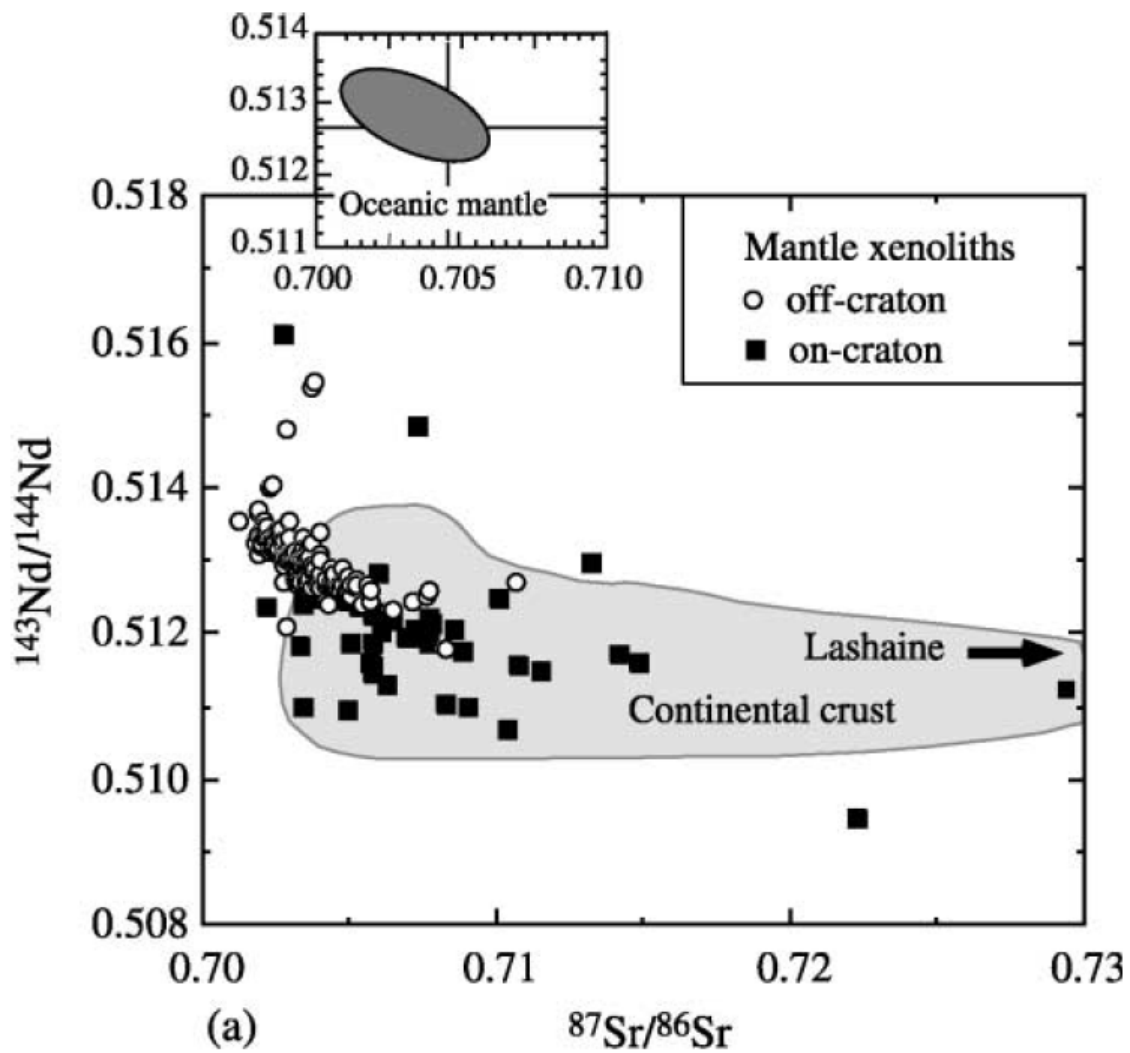
The thermobarometry based on the chemistry of minerals equilibrated under mantle conditions, is a useful tool commonly applied to the mantle rocks. This is because at the high temperatures present in the mantle, diffusion of elements between minerals is relatively rapid, so the constituent minerals of mantle rocks maintain compositions that are consistent with chemical equilibrium between the phases under the extant pressure and temperature conditions. Some of the elemental exchange reactions between minerals are temperature sensitive, and others are pressure sensitive (Finnerty and Boyd, 1987; Brey et al., 1990). Given the rapid ascent to the surface of mantle xenoliths and the conservation of their mineral compositions at mantle conditions, they are widely used to reconstruct the temperature profile for the whole depth column from which the xenoliths were derived.

### **1.3. Sr-Nd-Pb radiogenic isotope geochemistry of mantle rocks**

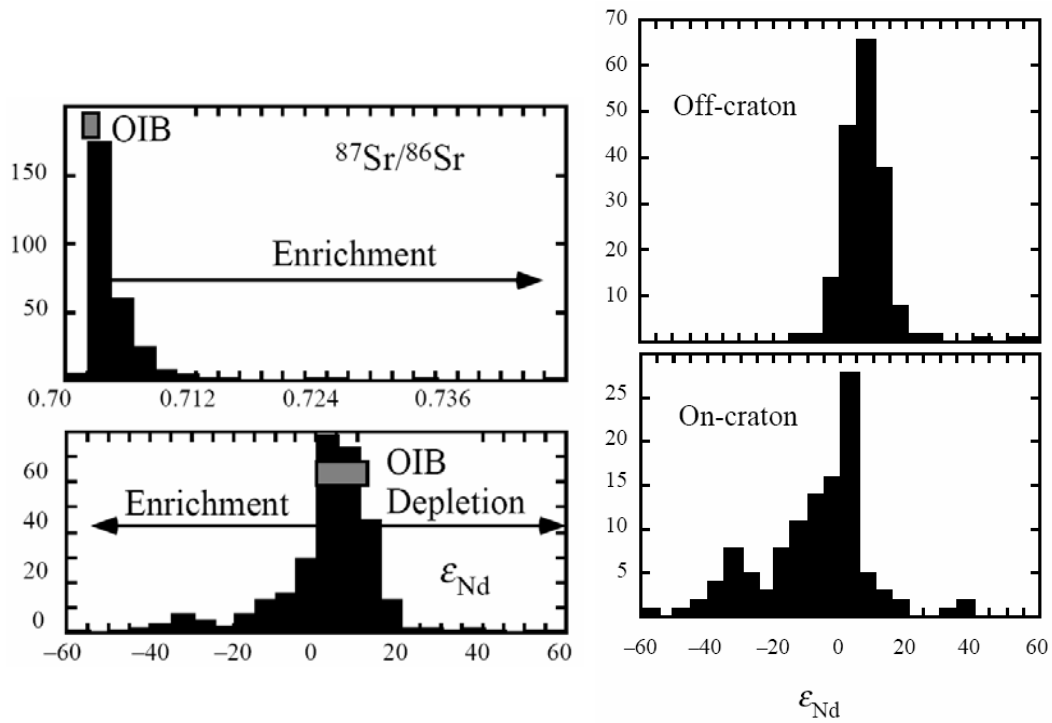
This section presents a brief introduction about the Sr-Nd-Pb systematics on mantle rocks, with emphasis on mantle xenoliths considering that these elements are strongly modified by secondary processes on suboceanic mantle rocks. Mantle xenoliths represent lithosphere-derived fragments and generally have major-element compositions reflecting an origin as melt-residues (Pearson et al., 2003). However, compilation of their strontium and neodymium mineral isotopic compositions reveals that very few samples show the characteristics of ancient melt residues (the exception to this are the osmium isotopes as we will see in the next section). The huge isotopic diversity shown by peridotite Nd-Sr systematics (Fig. 1.3) is a reflection of the diverse parent-daughter elemental fractionation shown by mantle silicate minerals coupled with ancient,

multiple-stage histories involving melt depletion and subsequent interaction with melts passing through the lithospheric mantle. Peridotite xenoliths from continental regions show substantial overlap with oceanic mantle for isotopic compositions of lithophile elements such as strontium and neodymium (Fig. 1.3). The frequency distribution for neodymium isotopes in peridotite xenoliths that represent the continental lithospheric mantle ranges from highly radiogenic compositions (relatively high values of  $^{143}\text{Nd}/^{144}\text{Nd}$ ; high  $\epsilon_{\text{Nd}}$ ), indicative of long-term parent-daughter depletion, to highly enriched compositions (relatively low values of  $^{143}\text{Nd}/^{144}\text{Nd}$ ; low  $\epsilon_{\text{Nd}}$ ) that require ancient parent-daughter enrichment. The dominant neodymium isotopic characteristic of the continental lithospheric mantle (mean  $\epsilon_{\text{Nd}}$  value of 1.8) is not “enriched” but close to, or slightly more depleted than the bulk Earth (or enriched compared to the DMM). The most extreme enriched neodymium isotope compositions are consistently found in ancient cratons (Fig. 1.4). The strontium isotope frequency distribution has a long tail out to very radiogenic (“enriched”) compositions but the mean  $^{87}\text{Sr}/^{86}\text{Sr}$  is 0.7047; very close to estimates of bulk Earth (Fig. 1.4). It is important to bear in mind that this statistical view of continental lithospheric mantle geochemistry could be heavily influenced by samples that have geochemical signatures dominated by their host magmas; i.e., the xenolith sample set could be very biased and the real continental lithospheric mantle composition grossly different.

From the diversity of observed isotopic compositions a number of different metasomatic agents have been inferred, that are thought to produce shifts of Nd-Sr isotope systematics in different directions. The three main enrichment processes thought to affect the lithospheric mantle, identifiable from petrographic evidence are silicate melt addition,  $\text{H}_2\text{O}$ -fluid-rich metasomatism, which may result in phlogopite/amphibole metasomatism and may ultimately be linked to silicate melt intrusion (Ionov et al., 1997), and carbonate metasomatism (Pearson et al., 2003). The reader is referred to Menzies and Hawkesworth (1987) and Menzies and Chazot (1995) for reviews. Ionov et al. (2002a, b) have noted that chromatographic effects related to porous flow during melt percolation can decouple strontium from neodymium isotopes in peridotite xenoliths, creating enrichment in  $^{87}\text{Sr}/^{86}\text{Sr}$  at relatively constant neodymium isotope compositions. These authors argue that the frequently observed decoupling of strontium from neodymium isotopes, which is often attributed to metasomatism by subduction-related fluids, can



**Figure 1.3.** Nd–Sr isotope variation of clinopyroxenes and garnet in peridotite xenoliths. Comparison of cratonic and noncratonic peridotite xenoliths with continental crust. Inset shows restricted field for oceanic mantle (from Pearson et al., 2003).

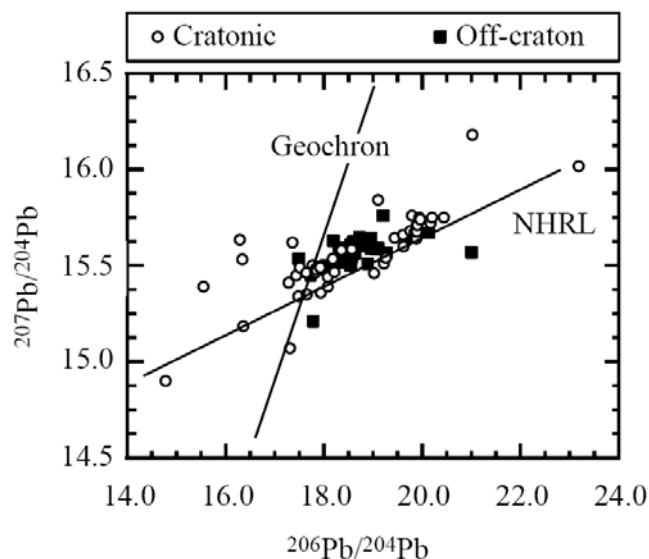


**Figure 1.4.** Frequency distribution plots for Sr and Nd isotope compositions of cratonic and noncratonic peridotite xenoliths. Plots give the range for ocean island basalts (OIB) and arrows show the direction of isotopic evolution for melt depletion and enrichment events. Figures from Pearson et al. (2003).



be a signature only of silicate melt percolation without the need for subduction zone fluids. Hence, as with trace-element signatures, it may be dangerous to identify the nature of a metasomatic agent solely on isotope criteria. Coupled petrographic, mineral chemical, elemental and isotopic studies are required to fully understand these processes.

As with strontium and neodymium isotopes, lead isotopic compositions are extremely variable in mantle xenoliths (Fig. 1.5). Peridotites and their metasomatized variants show most of the heterogeneity while pyroxenites and megacrysts have more constant compositions that relate closely to the host magmas and suggest a genetic link (Ben Othman et al., 1990; Tatsumoto et al., 1992). As expected from their greater antiquity, cratonic xenoliths show considerable more lead isotope variations than their noncratonic counterparts (Fig. 1.5). The isotopic variability is such that the end-member mantle “components” HIMU, EMI and EMII are all strongly developed in some xenolith suites. HIMU-type lead isotope characteristics seem to be restricted to cratonic peridotites despite the high measured U/Pb and Th/Pb ratios of some noncratonic peridotites (Meijer et al., 1990). This is further indication of the decoupling of parent-daughter ratios from isotopic composition in xenoliths, probably due to recent processes. Many noncratonic peridotite xenoliths show well developed EMI and /or EMII characteristics (Tatsumoto et al., 1992).



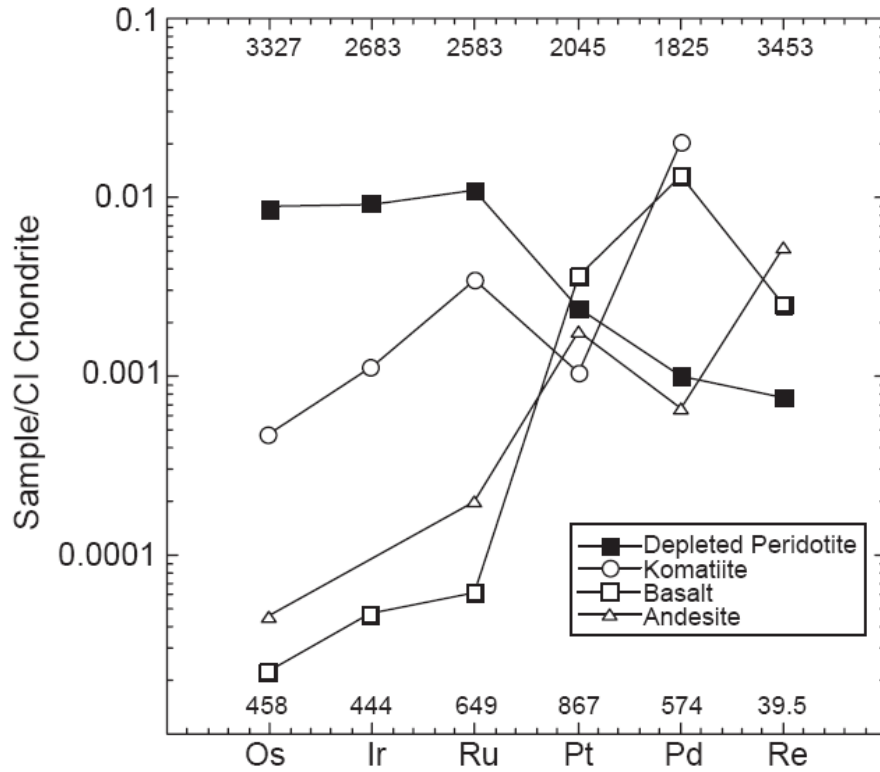
**Figure 1.5.**  $^{207}\text{Pb}/^{204}\text{Pb}$  versus  $^{206}\text{Pb}/^{204}\text{Pb}$  isotope plot of cratonic and noncratonic peridotite xenoliths minerals. For cratonic peridotites, only clinopyroxenes are plotted. For noncratonic peridotites, amphibole or clinopyroxene are plotted. NHRL = Northern Hemisphere Reference Line.

#### 1.4. Highly siderophile elements in the mantle

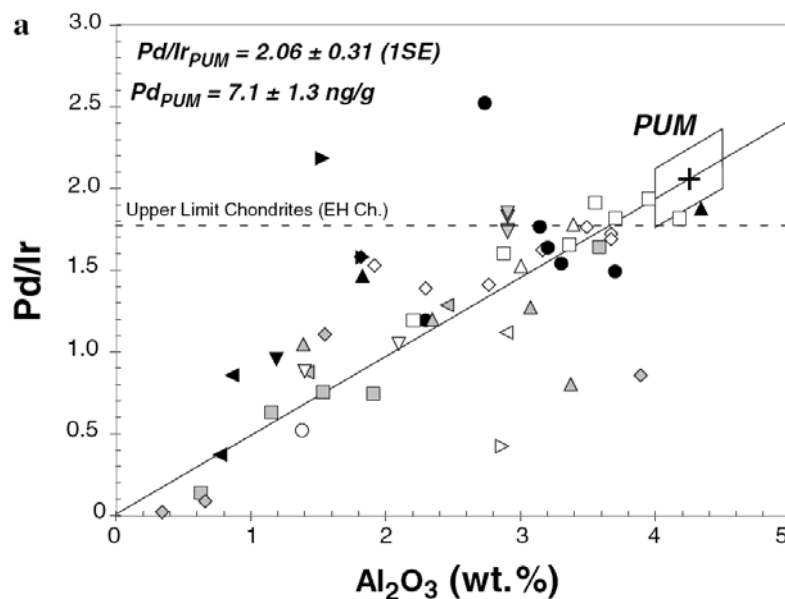
The highly siderophile elements (HSE) comprise the platinum group elements (PGE), Os, Ir, Ru, Rh, Pt and Pd, plus Re and Au. This definition reflects the fact that these elements strongly prefer iron metal over silicates, what means a completely different geochemical behavior compared to lithophile elements. In other words, their distribution coefficients between metal and silicate are greater than  $10^4$  (Holzheid et al., 2000; Fortenfant et al., 2003). When iron metal is not present, these elements partition strongly into sulfides (they behave as calcophile elements), but their partition coefficients vary widely. Consequently, the PGE are dominantly contained in trace sulfide phases in fertile peridotites, while the major silicate minerals and spinel in peridotites contain only 6% to 50% of the total inventory of the PGE in mantle peridotites (e.g. Luguet et al., 2004). Rhenium, on the other hand, is distributed through the silicate phases in the mantle, with olivine, orthopyroxene, garnet and phlogopite all having significant Re concentrations (Burton et al., 2000; Luguet et al., 2004). In a variety of mafic-ultramafic magmatic systems, Re appears to have a melt-solid distribution coefficient similar to Al (Reisberg and Lorand, 1995) or the heavy REE (Hauri and Hart, 1997; Sun et al., 2003) during both mantle melting and crystal fractionation. Os is concentrated and Re depleted in chromite (McCandless et al., 1999; Walker et al., 2002), but as in the case of silicate minerals, whether this reflects Os compatibility in chromite or co-crystallization of chromite and a PGE-rich phase is not clear (Carlson, 2005). Nevertheless, when sulfides or alloys are not present, chromite can be a major carrier for Os. For Re-Os systematics, chromite has the added advantage that it is resistant to weathering, which, coupled with its commonly very low Re/Os ratio makes it an excellent mineral for determining initial Os isotopic compositions in rocks as diverse as ophiolitic peridotites (Walker et al., 2002) and layered mafic cumulates (McCandless et al., 1999; Marques et al., 2003). In general, Ni-rich sulfides such as pentlandite and pyrrhotite concentrate Os, Ir, and Ru over Re, Pt, Rh and Pd, whereas Re, Pd, Rh and Pt abundances are enhanced in Cu-rich sulfides such as chalcopyrite (Li et al., 1992; Ballhaus et al., 2001; Brenan, 2002). When sufficiently concentrated in sulfide, or as sulfide is consumed during partial melting (see below), Pt, Os, Ir and Ru may exsolve to form their own alloy metal phases (Legendre and Auge, 1986; Talkington and Lipin, 1986).

During partial melting in the mantle, the Fe-Ni sulfides are rapidly consumed, and consequently, the PGE are selectively partitioned into the melt, caused by different melt-residue distribution coefficients, increasing in the order Re, Pd, Pt, Rh, Ru, Ir, Os with transition between

moderately incompatible and compatible occurring at Rh. This is reflected in the chondrite normalized HSE patterns of (Fig. 1.6), showing a typical depleted mantle peridotite and a variety of melt compositions. These chondrite-normalized HSE patterns illustrate the complementary enrichment of melts in Re, Pd and Pt and the depletion of these elements in the melt residue. In contrast, Ir, Ru, and Os are depleted in the melt and enriched in the residue. Some studied peridotite sets, show positive trends of Al versus Pd contents and Pd/Ir ratios, characteristics usually ascribed to mantle melting, where the most depleted peridotites show the lowest Al and Pd contents and the lowest Pd/Ir ratios (Fig. 1.7). Congruently, metasomatized peridotites show enrichments in Re, Pd, and Pt, with relatively high Re/Ir, Pd/Ir and Pt/Ir ratios, compared to unmetasomatized peridotites (e.g. Rehkämper et al., 1999; Becker et al., 2006). The order of incompatibility of the PGE matches the order of melting temperatures of the pure metals of this elements, suggesting that these elements exist as small clusters of metal included in mantle phases rather than as discrete elements in the lattice of the sulfide (Tredoux et al., 1995). Whether or not this is an accurate description of the PGE carriers in the mantle, what is clear is that the sulfides that concentrate the PGE in the mantle must experience some poorly understood compositional transformation during the melting process so that even while sulfur is being consumed by the melt, the compatible PGE (Ir, Os, Ru) remain behind in the residue (Carlson, 2005). However, there are clear evidences that the Cu-rich component in the monosulfide-solid-solution (Mss) that is the stable phase under mantle conditions (Ballhaus et al., 2001; Brenan, 2002), is the first to be consumed by the melt, and along with it, the Re, Pd, and Pt. The sulphides remaining behind become more Ni, Ir, and Os rich eventually reaching the stage where the remaining PGE form alloys of their own. This process has been reproduced experimentally where it was shown that Cu- and Ni-bearing Mss melted to produce a Cu-Ni-Pd-rich liquid leaving an Fe-rich Mss and Fe-Ir-Pt alloy (Peregoedova et al., 2004).



**Figure 1.6.** Re and PGE concentrations for an arc basalt and andesite (Woodland et al., 2002), a komatiite (Puchtel and Humayun, 2001), and a depleted peridotite xenolith (Irvine et al., 2003) normalized by the abundances in the CI chondrite Orgueil (Horan et al., 2003). The numbers above the x-axis give the CI concentrations in ng/g. The numbers at the top of the figure are the melting temperatures of the pure metals of these elements in degrees K (Emsley, 1991). Figure from Carlson (2005).



**Figure 1.7.** Pd/Ir–Al<sub>2</sub>O<sub>3</sub> diagram of peridotites analysed by Becker et al. (2006) to estimate the HSE contents of the Primitive Upper Mantle. The good positive correlation suggests that Pd is incompatible, similar to Re.

The fact that HSE are highly concentrated in sulfides (they constitute less than 0.05% by weight of the bulk rock and contains essentially all of the HSE in the rock) implies that the diffusion of HSE in the mantle is small considering the spatial separation of the very rare carrier phases of the HSE. Individual sulfide/alloy grains in the mantle thus can retain chemical and isotopic evidences of the distinct events that led to their initial formations (Alard et al., 2002; Pearson et al., 2002; Griffin et al., 2004).

The abundances of HSE in the Earth’s mantle are considerably higher than estimations based on models of core formation (Jones and Walker, 1991), what should concentrate almost the entire HSE budget of the Earth. Moreover, the chondritic abundances of HSE in the mantle, together with the chondritic Os isotopic composition, strongly support the “late veneer” hypothesis, in which a small fraction (~1 % by mass) of Earth’s mantle accreted after core formation. The small amount of added chondritic material, because of its very high HSE abundances, would raise the HSE concentrations and impart a chondritic relative HSE abundance pattern on a mantle that had effectively been stripped of these elements by core formation. Another hypothesis considered to explain the high HSE abundance of the Earth’s mantle arguments differences on metal-silicate distribution coefficients for HSE that may be

dramatically different under high pressure and temperature conditions (Murthy, 1991; Righter and Drake, 1999). Nevertheless, recent results for the PGE cast doubt on whether pressure and temperature effects on partitioning can explain the Re and PGE abundance pattern in the mantle (Holzheid et al., 2000; Fortenfant et al., 2003).

### 1.5. The Re-Os isotopic system in mantle rocks

Because the particular behavior of the HSE, the Re-Os isotopic system ( $^{187}\text{Re} \rightarrow ^{187}\text{Os} + \beta^-$ ;  $\lambda = 1.666 \times 10^{-11}\text{yr}^{-1}$ , Smoliar et al., 1996) trace geochemical processes that can be quite different from those recorded by most other radiometric systems that are based on lithophile elements, whose geochemistry is controlled by the silicates of Earth's crust and mantle. Another particular feature of the Re-Os system is that Os is preferentially retained in the mantle, while Re is moderately incompatible during mantle melt generation, in contrast to all other radiometric systems (e.g. Rb-Sr, Sm-Nd, Lu-Hf, U-Th-Pb) where both parent and daughter elements are strongly concentrated in the melt during mantle melting. Mantle melts are therefore enriched in Re and depleted in Os relative to mantle sources. Conversely, generation and extraction of mafic melts leads to Re depletion and retardation in the growth of  $^{187}\text{Os}/^{188}\text{Os}$  in the residue. As a result, the Re-Os isotopic system can provide age constraints on the timing of melt depletion. The high abundance of Os in the mantle residue, and the low Os abundances of most mantle melts, makes this system relatively impervious to the effects of secondary metasomatic processes.

Similar to other radiometric systems, the Re-Os mantle model age equation is defined as:

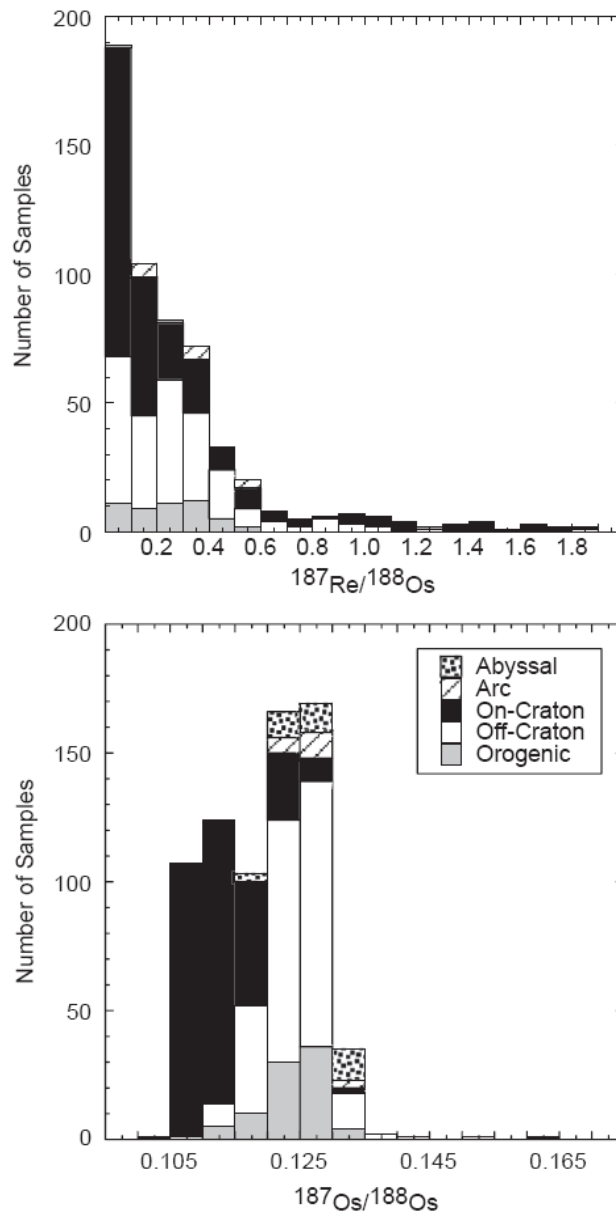
$$T_{MA} = (1/\lambda) * \ln(((^{187}\text{Os}/^{188}\text{Os})_{SA} - (^{187}\text{Os}/^{188}\text{Os})_{BSE}) / ((^{187}\text{Re}/^{188}\text{Os})_{SA} - (^{187}\text{Re}/^{188}\text{Os})_{BSE}) + 1)$$

where both sample (SA) and bulk silicate earth (BSE) parameters are present day values. The most commonly used values for the BSE are estimated from measurements of primitive mantle peridotites (present day  $^{187}\text{Re}/^{188}\text{Os} = 0.4353$ ,  $^{187}\text{Os}/^{188}\text{Os} = 0.1296$ ; Meisel et al., 2001).

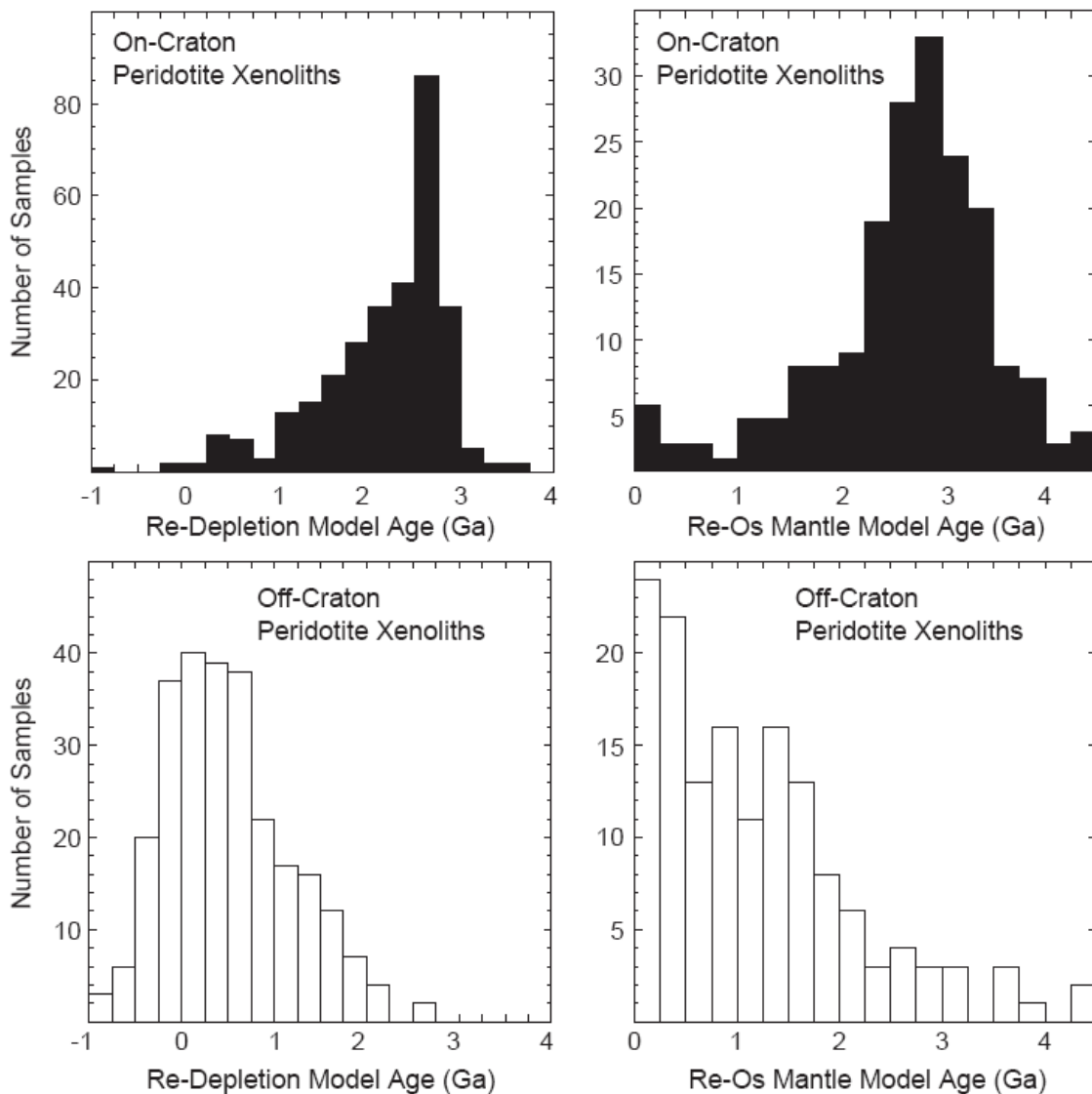
Another model age approach used in the Re-Os system is called the Re-depletion model age, or  $T_{RD}$  (Walker et al., 1989), which assumes that the Re/Os ratio of the sample is zero and is thus expressed as:

$$T_{RD} = (1/\lambda) * \ln(((^{187}\text{Os}/^{188}\text{Os})_{SA} - (^{187}\text{Os}/^{188}\text{Os})_{BSE}) / (^{187}\text{Re}/^{188}\text{Os})_{BSE} + 1)$$

In this case, the timing of melt depletion is estimated comparing the  $^{187}\text{Os}/^{188}\text{Os}$  of the sample corrected using the measured  $\text{Re}/\text{Os}$  to the time of xenolith host eruption to a mantle evolution model. If all of the  $\text{Re}$  was removed at the time of melting, then the  $T_{\text{RD}}$  age should equal the  $T_{\text{MA}}$  age (assuming no  $\text{Re}$  addition).  $T_{\text{RD}}$  ages are good approximations to the time of melting for highly refractory peridotites, such as cratonic xenoliths, but in less refractory material, where some  $\text{Re}$  remains in the residue,  $T_{\text{RD}}$  ages are minimum ages.  $T_{\text{RD}}$  was defined in an attempt to overcome the common problem of excess  $\text{Re}$  in peridotitic mantle xenoliths caused by infiltration of xenoliths by their commonly  $\text{Re}$ -rich host magmas.



**Figure 1.8.** Histograms of  $^{187}\text{Re}/^{188}\text{Os}$  and  $^{187}\text{Os}/^{188}\text{Os}$  for mantle peridotites. Figure and references from Carlson (2005).



**Figure 1.9.** Re depletion and mantle model ages for peridotite xenoliths contained in kimberlites erupted through Archean cratons (upper panels) and for those contained in a variety of composition magmas erupted through off-craton (post-Archean) crustal sections. The Re-depletion age will underestimate the true age of a depletion event both for fertile samples and for those affected by Re addition well prior to xenolith eruption. Mantle model ages will overestimate the true differentiation age for those samples affected by Re addition occurring close in time to the xenolith eruption. The smaller number of data shown on the mantle model age figures reflects the exclusion of those samples that either did not have measured Re/Os ratios, or that had negative ages or ages greater than the age of the Earth as a result of Re addition. Figure and references from Carlson (2005).



Most mantle-derived samples are the residues of varying degrees of partial melt extraction (Bodiner and Godard, 2003; Pearson et al., 2003). As discussed above, the melt depleted mantle should have low Re/Os and with time, low  $^{187}\text{Os}/^{188}\text{Os}$ . Figure 1.8 shows the results of Re-Os analyses of a large number of peridotites including both xenoliths and orogenic and abyssal peridotites, where most samples have low Re/Os ratios, with values lower than the estimation of the primitive mantle. Some cratonic samples have Re/Os ratios higher than estimated for the bulk mantle, but  $^{187}\text{Os}/^{188}\text{Os}$  less than bulk mantle. This is an obvious sign of recent introduction of Re, but minimal to no modification of Os isotopic composition. As seen in Fig. 1.8, most mantle samples have Os isotopic compositions ranging from close to chondritic to substantially below chondritic, particularly on cratonic peridotites, what is consistent with ancient Re-depletion. Figure 1.9 shows the model ages calculated using the Os isotopic compositions. These histograms illustrate the dramatic distinction in mean age for the mantle beneath sections of continent of different age. In general, Re-Os age data for subcontinental mantle peridotites show a reasonable correspondence between mantle lithosphere age and the age of the overlying crust (Pearson et al., 1995a,b, 2002; Handler et al., 1997; Carlson et al., 1999a; Griffin et al., 2002; Carlson and Moore, 2004). However, in some cases, the mantle is younger than the overlying crust, probably as the result of either magmatic reprocessing of the mantle (Carlson et al., 1999b) or tectonic delamination (Lee et al., 2000; Gao et al., 2002), and also mantle that apparently is older than the overlying crust (Peslier et al., 2000; Handler et al., 2003).

## **1.6. Purpose and methodologies of this work**

This PhD Thesis is devoted to the study of two different occurrences of mantle rocks: the suboceanic convecting upper mantle at the south-east Pacific Ocean (Taitao ophiolite), and the subcontinental lithospheric mantle of southern South America (mantle xenoliths). The main objective of this work is to contribute to the understanding of the different processes that controlled the evolution of the mantle under and around the southern South America continent and their time of occurrence.

In order to satisfy the main objective, the following specific objectives will be attained:

- Determine the platinum group elements (PGEs) variability on the modern convective depleted mantle source of MORB (DMM) under the southeast region of the Chile ridge, represented by the Taitao ophiolite. This data will complement the petrographic, chemical and isotopic analyses performed by Shulte (2007) on samples derived from this ophiolite (see below).
- Place geochronological constraints about the time of partial melting events occurred in the DMM under the region of the Chile ridge.
- Identify the occurrence of secondary processes and their implications on the chemical properties of the studied convecting upper mantle.
- Determine the petrographic, chemical, and isotopic variations of the subcontinental lithospheric mantle under the southwest of the Deseado Massif: the case of Cerro Redondo mantle xenoliths.
- Identify the processes responsible for the heterogeneities of the subcontinental lithospheric mantle under southern South America.
- Place geochronological constraints about the age of formation for the subcontinental lithospheric mantle under southern South America.

### **Suboceanic mantle**

The approach to study the suboceanic mantle presented in Chapter 2, consists on a detailed chemical analysis of variably serpentinized peridotites and mafic rocks sampled from the Taitao ophiolite. The data includes a detailed petrographic description, whole rock major and trace element compositions, mineral chemistry, HSE contents (Ir, Os, Ru, Pt, Pd and Re), Os isotopes of whole rocks and selected chromites, and O, Nd and Sr isotopes of selected samples. The studied samples from the Taitao ophiolite were obtained during two field works on the Taitao peninsula, southern Chile, realized during years 2000-2001 and 2002-2003, which were supported by the Science Research Project no. 13373004 (to R. Anma) from the Ministry of Education, Culture, Sport, Science and Technology, Japan. MS was one of the ten members of the second expedition to the peninsula, during which the transition zone between the ultramafic unit and the overlying gabbros unit was mapped and detailed described. Later, Professor Ryo Anma from the Tsukuba University, Japan, supplied some samples to collaborate with Professor Richar J. Walker who had recently obtained financial support (the NSF grant 0335933) to

characterize chemically the Taitao ophiolite. The Os isotopic characterization of the Taitao ophiolite was the core of the Master Thesis of Ruth Shulte from the University of Maryland under the guidance of Professor Richard J. Walker. As part of this research, Shulte also analyzed whole rock major and trace elements, mineral chemistry of some relict olivine crystals, whole rock oxygen isotope measurements, and Sr-Nd isotopic analysis on selected samples. Consequently, she is the first author of the manuscript that corresponds to Chapter 2 of the present thesis.

Since May to August, 2005, MS was invited by Professor Richard J. Walker to work on the Laboratory of Isotopic Geology of the University of Maryland, to be trained on the analytical techniques to measure the contents of the platinum group elements (PGEs) on peridotites. The HSE measurements on Taitao peridotites were performed utilizing high-precision analytical techniques by isotope dilution.

### **Subcontinental mantle**

This study of the subcontinental lithospheric mantle is based on the analysis of mantle xenoliths carried to the surface by basaltic alkali magmatism of Eocene to recent age, covering a wide area of the continental plate of southern South America (36 to 52° S). The collection of most xenoliths was done in three different campaigns. The first one achieved on January 2001 was directed by Dr. Yuji Orihashi and supported by the Science Research Project no. 13373004 (to R. Anma) from the Ministry of Education, Culture, Sport, Science and Technology, Japan. This field trip had as main objective the sampling of young (Pliocene to recent) alkali basalts from Patagonia and had as a consequence the discovery of the mantle xenoliths from Co. Redondo, 60 km south of Gobernador Gregores, in Santa Cruz province, Argentine. During years 2002 and 2004, two field works were organized exclusively to collect mantle xenoliths from over 20 localities on the back arc region of the southern Andes, Argentine, as part of a multinational project dedicated to the study of the subcontinental mantle under South America led by Dr. Rommulo V. Conceição from the Universidad Federal do Rio Grande do Sul. The location of the mantle xenoliths was possible by the helpful guidance of C.A. Cingolani. The sample from Chile Chico analyzed in Chapter 4 was supplied by Dr. Diego Morata and Dr. Felipe Espinoza from the Universidad de Chile and two samples from Agua Poca were supplied by Dr. Gustavo W. Bertotto from the Universidad Nacional de la Pampa.

Three chapters are dedicated here to the subcontinental lithospheric mantle of southern South America and are based on different and complementary methodologies:

Chapter 3 presents a detailed characterization of the petrographic, geochemical, and Sr-Nd-Pd isotopic compositions of six mantle xenoliths and their host alkali-basalt from sampled at Cerro Redondo (49° S), Santa Cruz Province, Argentina. These mantle rocks represent the subcontinental lithospheric mantle under the southwest corner of the Deseado Massif but do not represent the whole lithospheric mantle of southern South America, as will be clearly demonstrated on Chapter 4. This article began as the Graduation Thesis of MS (Schilling, 2002) that consisted in a detailed petrographic description, and mineral and whole rock chemical determinations of three mantle xenoliths from the Cerro Redondo. To complement that work, three more samples were analyzed and the Sr, Nd and Pd isotopic compositions of all samples were determined at the Laboratorio de Geologia Isotopica, on the Universidad Federal do Rio Grande do Sul, Porto Alegre, Brasil, under the management of Dr. Rommulo V. Conceição and Dr. Edinei Koester.

Chapter 4 consists on a Re-Os isotopic study of 29 mantle xenoliths derived from 10 localities covering a wide area on southern South America. The petrographic descriptions, as well as analyses of whole rock and mineral phases of mantle xenoliths studied in the Chapter 4 had been previously done as part of different works including under and postgraduate thesis, congress abstracts and publications on specialized journals. The Re-Os analysis of those samples were done under the direction of Dr. Richard W. Carlson at the Department of Terrestrial Magnetism (DTM) of the Carnegie Institution of Washington, USA, during August and September 2005, just after the training of M. Schilling on the analytical techniques for the determination of the PGEs contents at the University of Maryland, under the guidance of Professor R.J. Walker.

Chapter 5 combine the Os isotopic results obtained in Chapter 4 with a geophysical study performed by Tassara et al. (2007) based on the estimation of the elastic thickness ( $T_e$ ) over South America and its surrounding plates. This interdisciplinary approach is used to determine and recognize differences on physical, chemical, and chronological characteristics on the lithospheric mantle of the region.

Finally, Chapter 6 presents an overview of the main results of all previous chapters, where the principal conclusions and implications on the geodynamic evolution of the subcontinental lithospheric mantle of southern South America and its surrounding convecting upper mantle are discussed.

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