Oxidation state of Paleozoic subcontinental lithospheric mantle below the Pali Aike volcanic field in southernmost Patagonia

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A B S T R A C T

Mantle xenoliths in the Quaternary Pali Aike alkaline basalts of southernmost Patagonia include lherzolites and harzburgites with and without garnet. The values of fO2 for all xenoliths range from 0.33 logarithmic unit below the fayalite–magnetite–quartz buffer (FMQ−0.33) to FMQ+0.75, which overlap those for abyssal peridotites. The fO2 data, together with the bulk rock and mineral compositions, suggest that the subcontinental lithospheric mantle (SCLM) below Pali Aike formed through the accretion of oceanic lithosphere. The oceanic accretion likely occurred in mid to late Paleozoic time when the southern Patagonian terrane formed along the southwest margin of Gondwana. Relict spinel inclusions in garnet suggest that garnet-facies peridotites formed from spinel-facies peridotites most likely in response to pressure increase during the accretion. Comparable fO2 for garnet- and spinel-facies peridotites suggests that this spinel-garnet transformation was not accompanied by changes in fO2.

Metasomatism by asthenospheric-derived melt through a slab window resulted in the formation of Ti-bearing minerals, and lowering of Mg and enrichment of Ti in bulk rocks and minerals. The replacement of olivine by orthopyroxene formed orthopyroxenites in extreme cases. No significant change in fO2 is associated with this metasomatism since similar oxidation state is observed between un-metasomatized (FMQ−0.23 to +0.48) and metasomatized (FMQ−0.33 to +0.75) samples. This is explained by the fO2 of the asthenospheric melt (~FMQ−0.50) similar to the SCLM prior to the metasomatism.

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1. Introduction

Mantle oxidation state is important in controlling the composition and nature of partial melt. For example, diamond forms in reduced subcontinental lithospheric mantle (SCLM) beneath old cratons and remains stable during transportation to surface by kimberlites (McCammon et al., 2001). In contrast, oxidized sub-arc mantle is conducive to forming high sulfur magmas (DeHoog et al., 2004) and large Au and Cu deposits because metals can be effectively partitioned to partial melt under oxidized conditions (Hattori and Keith, 2001; Mungall, 2002). Furthermore, the amount of V in partial melt may be affected by the oxidation state of the mantle source (Canil, 2002).

A significant variation is observed in fO2 in lithospheric upper mantle, but its causes are still not well understood. Partial melting is generally considered to result in low fO2 in the residual mantle as Fe3+ is preferentially incorporated in melt (e.g., Canil et al., 1994). This is supported by low fO2 in refractory peridotites beneath ancient cratons that show high Cr# (atomic ratio of Cr/[Cr+Al]) in spinel (e.g., Woodland and Koch, 2003). In contrast, a positive correlation between fO2 and Cr# in spinel is observed in sub-arc mantle peridotites and this is explained by the infiltration of oxidizing fluids from slabs (e.g., Ballhaus, 1993; Parkinson and Arculus, 1999).

Previous studies on the oxidation state of SCLM focused on those underlying Archean continents, such as Kaapvaal craton (South Africa; Daniels and Gurney, 1991; McCammon et al., 2001; Woodland and Koch, 2003) and Slave province of the Canadian Shield (e.g., McCammon and Kopylova, 2004). Studies on oxidation state of Phanerozoic SCLM have thus far not been reported. Southern Patagonia in the southernmost part of South America is considered to have docked with Gondwana to form the South American continent in the Paleozoic (e.g., Rapalini, 2005; Pankhurst et al., 2006). Subsequently, the SCLM below the Patagonian terrane underwent metasomatism by melt derived from the underlying asthenosphere (Kempton et al., 1999a,b; Stern et al., 1999). Therefore, mantle xenoliths from Patagonian basalts contain information relevant to the formation and later modification of the Phanerozoic SCLM of the Patagonian terrane. This paper reports the bulk rock compositions, mineral chemistry, and the oxidation conditions of representative...
mantle peridotite xenoliths from the Quaternary Pali Aike basalts, southernmost Patagonia (Fig. 1), and discusses the origin and evolution of this relatively young SCLM.

2. Tectonic setting

There is considerable debate regarding the origin and tectonic evolution of the southern portion of the Patagonian terrane, and its relations with Gondwana (e.g., Ramos, 1986; Von Gosen, 2002; Pankhurst et al., 2003; Rapalini, 2005; Pankhurst et al., 2006). Pali Aike is located south of the Deseado Massif, the main part of southern Patagonia. The Deseado Massif consists in part of metasedimentary rocks of Neoproterozoic age (580 Ma; Pankhurst et al., 2003, 2006), which were rifted from Gondwana in the late Proterozoic to early Cambrian. It was later united again with northern Patagonia through the subduction of an intervening oceanic lithosphere during the late Paleozoic. Metamorphosed basement from Tierra del Fuego, ~100 km south of Pali Aike, has been dated at 529 Ma by U-Th-Pb zircons (Söllner et al., 2000). Thus the basement below Pali Aike may be either part of this Deseado Massif, or may have been accreted to the Deseado Massif in Paleozoic time. Either way, the basement and SCLM below the Pali Aike area is clearly not Archean or early Proterozoic, but relatively young accretionary lithosphere of Phanerozoic age.

During the late Jurassic break-up of Gondwana, voluminous riftogenic volcanism formed the Chon Aike Formation in southern Patagonia (Bruhn et al., 1978; Kay et al., 1989). Since the late Jurassic or early Cretaceous, the area has been dominated by subsidence and sedimentation, forming the Magallanes basin, whereas the eastward subduction of oceanic plates beneath the western margin of South America produced the Andes on the western margin of the South America.

The Chile ridge between the Nazca and Antarctic Plates collided with the trench near the southern tip of South America at ~14–15 Ma, forming a triple junction (Cande and Leslie, 1986) which has since migrated northward to its present position at 46.5° S (Fig. 1). Ridge subduction was responsible for Neogene uplift of the southernmost sector of the Andes, and formation of the Patagonian fold-thrust belt (Ramos, 1989; Hasschke et al., 2006). Ridge subduction also resulted in upwelling of underlying asthenospheric mantle through a slab window, which produced extensive alkaline plateau basaltic rocks in southern Patagonia (Goring et al., 1997; D’Orazio et al., 2000). These plateau basalts range in age from late Miocene to Recent and systematically young to the northeast following the track of the subducted ridge. The Pali Aike volcanic field, which covers 4500 km², is the southernmost among the Patagonian plateau basalts (Fig. 1; D’Orazio et al., 2000). The subduction of Antarctic plate, west of the subducted ridge, is producing the adakitic andesite stratovolcanoes of the Andean Austra Volcanic Zone, ~250 km west of the Pali Aike area (Fig. 1; Stern and Kilian, 1996).

3. Samples

The Pali Aike volcanic field contains lavas as well as pyroclastic rocks, including tuff breccias associated with maars as well as both spatter and scoria cones, of alkaline basaltic composition. Some of the basaltic lavas and pyroclastic rocks contain peridotite and pyroxenite xenoliths (Stern et al., 1999). Mantle xenoliths used in this study were collected from a small scoria cone (samples BN and BNC; 52°02′23″ S and 70°04′08″ W) within a tuff ring around a large maar (samples BNH). These sample sites are located at the southeast end of a SE–NW trending chain of maars and cones, just north of the north branch (Brazo Norte) of the dry river (Rio Seco). Mantle xenolith samples were also collected from the maar enclosing Timone Lake (samples TM; 52°00′58″ S and 70°12′16″ W) to the northwest along this same chain. Other samples were collected from the tuff ring around Laguna Salida (now called Laguna Ana: samples LS; 52°04′30″ S and 69°47′18″ W) maar, and another tuff ring (samples PAK and PA; 52°06′06″ S and 69°43′48″ W) to the southeast along the fissure that also includes the Pali Aike cone.

We examined a total of thirty-two mantle xenoliths ranging in size from 3 to 2 cm in the longest dimension. Samples are rounded and show no evidence of weathering and serpentinitization, but the rims of several samples show the evidence of interaction with host basaltic magma. These parts were removed before preparing samples for bulk rock analysis. Six samples (LS33, BN50, TM15, TM0, TM2, and LS1) were described previously by Stern et al. (1999). In this study, we have re-analyzed major element compositions for these six samples and further determined mineral compositions together with the other twenty-six new samples.

### Table 1

<table>
<thead>
<tr>
<th>Xenoliths group</th>
<th>Rock type</th>
<th>Assemblage</th>
<th>Samples*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peridotites</strong></td>
<td>Grt lherzolite</td>
<td>Ol+Opx+Cpx+Grt</td>
<td>LS33, TM0, TM2, LS50, BN73, LS1, BN32</td>
</tr>
<tr>
<td></td>
<td>Grt-Spl lherzolite</td>
<td>Ol+Opx+Cpx+Grt+Spl</td>
<td>TM14, TM15, BN92, BN50, PAK0, PAHk1, BN45, BN31</td>
</tr>
<tr>
<td></td>
<td>Spl Iherzolite</td>
<td>Ol+Opx+Cpx+Spl</td>
<td>PA64, PAKT</td>
</tr>
<tr>
<td></td>
<td>Spl harzburgite</td>
<td>Ol+Opx+Spl+Cpx</td>
<td>L55, PAK2, PK31, 01RN, BN41, LS100, PAK5</td>
</tr>
<tr>
<td><strong>Pyroxenite</strong></td>
<td>Grt orthopyroxenite</td>
<td>Opx+Grt+Ilm+Ti-Phl+Ti-Am±Ol±Cpx</td>
<td>BN113, BN2C, BN43, BN93, BS0, BN31, BN95, BN46</td>
</tr>
</tbody>
</table>

Abbreviations: Cpx = clinopyroxene, Grt = garnet, Ol = olivine, Opx = orthopyroxene, Spl = spinel, Ti-Phl = Ti-phlogopite, Ti-Am = Ti-amphibole, Ilm = ilmenite.

*Bold = samples affected by cryptic metasomatism showing low Mg# and high Ti in minerals and bulk rock compositions.

*Underlined bold = modally metasomatized samples containing Ti-Am, Ti-Phl, or Mg-Ilm.
The mantle xenoliths are divided into two types; peridotites (lherzolites and harzburgites) and pyroxenites. Their mineralogy is listed in Table 1. Peridotites are further divided into five subtypes based on the presence of garnet and/or spinel: garnet lherzolite (n=1), garnet-spinel lherzolite (n=6), spinel lherzolite (n=2), garnet-spinel harzburgite (n=8), and spinel harzburgite (n=7). Pyroxenite xenoliths are orthopyroxenites and minor websterites. This paper focuses on peridotite samples.

Garnet-bearing lherzolites consist mainly of olivine (50–70 vol.%), orthopyroxene (15–30 vol.%), clinopyroxene (5–20 vol.%), garnet (5–15 vol.%) and spinel (≤2 vol.%). They show coarse-grained (1–4 mm) equigranular to porphyroblastic textures (Fig. 2a). Garnet-spinel harzburgites show porphyroblastic to equigranular (1–4 mm) texture (Fig. 2b) and contain olivine (50–70 vol.%), orthopyroxene (25–30 vol. %), and garnet (5–10 vol.%) with minor spinel (≤2 vol.) and clinopyroxene (≤0.5 vol.%). Garnet (1–6 mm) shows a symplectic rim (≥50 µm), which consists of a mixture of fine-grained pyroxenes and spinel, that was most likely formed during the ascent of the xenoliths. Relict spinel (up to 2 mm) with reaction rims are common in garnet (Fig. 2c), suggesting that garnet is a reaction product of spinel. Spinel also forms inclusions (0.2–0.3 mm) and intergrowth with olivine and pyroxene (up to 2 mm) in garnet-bearing peridotites.

Spinel peridotites show grain sizes and mineral assemblages similar to garnet-bearing peridotites.

Orthopyroxenite (n=8) occurs either as discrete xenoliths or veinlets (>5 mm) in garnet-bearing harzburgites (Fig. 2d). Discrete orthopyroxenite xenoliths commonly contain small angular dunite and/or harzburgite fragments (5–10 mm in size) with diffuse boundaries. Orthopyroxenites show equigranular and/or porphyroblastic texture with coarse garnet (up to 5 mm) and orthopyroxene (up to 4 mm). They are composed of orthopyroxene (≥85 vol.%), garnet, olivine, Ti-phlogopite, Ti-amphibole, Mg-ilmenite, and minor sulphide minerals (pentlandite and pyrrhotite), with or without minor clinopyroxene. The veinlets of orthopyroxenite contain the same mineral assemblage as orthopyroxenite xenoliths and are accompanied by halos of secondary orthopyroxene (Fig. 2d).

4. Analytical methods and calculation of $fO_2$

4.1. Microprobe analysis

Mineral compositions were determined using the Camebax MBX electron probe at Carleton University in Ottawa and the JEOL 8900 Super probe at McGill University in Montreal. Camebax MBX electron
samples in mantle peridotites from Pali Aike. Ratios of \( \frac{\text{Fe}^{3+}}{\sum \text{Fe}} \) assuming stoichiometry of spinel compositions and each point represent an average of 5–8 grains in each sample. Calibrated ratios, \( \frac{\text{Fe}^{3+}}{\sum \text{Fe}} \), were obtained using four spinel standard samples (KLB8304, KLB8311, MBB8305 and KLB8316) with known \( \text{Fe}^{3+} \) contents following the method described by Wood and Virgo (1989).  

\[
\log f_{\text{O}_{2}} = \log(100\text{f}_{\text{O}_{2}}) = P_{\text{O}_{2}} - 29800T + 0.35P_{\text{O}_{2}} + 12\log(100\text{f}_{\text{O}_{2}}) + 0.0369P_{\text{O}_{2}}T^{-1} \quad \text{K, bar} 
\]

where the term in parentheses refers to total atomic concentration of \( \text{Fe}^{2+}, \text{Cr} \), and \( \text{Al} \) in spinel on a four oxygen basis.

4.2. Bulk rock analysis

For the bulk rock composition analysis, rims and veins were removed before grinding samples. Major and minor elements were determined using Camebax MBX and JEOL 8900 probes, respectively. A suite of well characterized natural and synthetic minerals were used as standards in both probes. A suite of well characterized natural and synthetic minerals were used as standards in both probes.

4.3. Calculation of \( f_{\text{O}_{2}} \)

The \( f_{\text{O}_{2}} \) values are calculated using the following reaction equilibrium:

\[
6\text{Fe}_2\text{SiO}_4(\text{olivine}) + \text{O}_2 \rightarrow 3\text{Fe}_2\text{SiO}_6(\text{orthopyroxene}) + 2\text{Fe}_2\text{O}_3(\text{spinel}) \quad (1)
\]

The \( \text{Fe}^{3+} \) contents are converted to activities of \( \text{Fe}_3\text{O}_4 \) using the formula of Nell and Wood (1991):

\[
\log a_{\text{Fe}_{3}\text{O}_4} = \log((\text{Fe}^{3+})^4) - 1/4 + 1/4 \log(100\text{Al})^2 + 653(\text{Mg})(\text{Al}) - 299(\text{Cr})^2 - 199(\text{Al})(\text{Cr}) + 346(\text{Mg})(\text{Cr}) \quad (2)
\]

where the term in parentheses refers to total atomic concentration of Mg, Fe\(^{2+}, \text{Cr} \), and \( \text{Al} \) in spinel on a four oxygen basis.

The \( f_{\text{O}_{2}} \) is estimated relative to the FMQ buffer, as follows:

\[
\log(f_{\text{O}_{2}})_{\text{FMQ}} = \log(f_{\text{O}_{2}})_{\text{FMQ}} + 220/T - 0.35 - 0.0369P_{\text{O}_{2}}/T - 12\log(X_{\text{Fe}^{2+}}^{\text{Ox}})/2 - 2620(X_{\text{Fe}^{2+}}^{\text{Ox}})^2/T + 3\log(X_{\text{Mg}^{2+}}^{\text{Ox}})/X_{\text{Fe}^{2+}}^{\text{Ox}} - 2\log(f_{\text{O}_{2}})_{\text{FMQ}} \quad (3)
\]

where \( P \) is bar, \( T \) is K, \( X_{\text{Fe}^{2+}}^{\text{Ox}} \) and \( X_{\text{Mg}^{2+}}^{\text{Ox}} \) refer to the \( \text{Fe}^{2+}/(\text{Fe}^{2+}+\text{Mg}) \) and \( \text{Mg}/(\text{Fe}^{2+}+\text{Mg}) \) ratios in olivine, and \( (X_{\text{Fe}^{2+}}^{\text{M2}})_{\text{Ox}} \) and \( (X_{\text{Mg}^{2+}}^{\text{M2}})_{\text{Ox}} \) refer to the atomic fractions of Fe in M1 and M2 sites of orthopyroxene (Wood, 1990).

The uncertainty in the calculated \( f_{\text{O}_{2}} \) originates from analytical errors and errors associated with activity estimates of components in Eq. (1). Analytical errors in silicate compositions contribute little to the \( f_{\text{O}_{2}} \) uncertainty. For example, the olivine composition has an error of less than ±0.003 in \( X_{\text{Fe}^{2+}} \), which translates into an uncertainty of ±0.15 log units in \( f_{\text{O}_{2}} \). Orthopyroxene grains are more heterogeneous in composition than olivine in individual samples; however, propagated uncertainties from this heterogeneity are also small, on the order of 0.1 log units in \( f_{\text{O}_{2}} \) or less.

Inaccurate \( \text{Fe}^{3+} \) contents in spinel are the major cause of error in the calculated \( f_{\text{O}_{2}} \) (O’Neill and Wall, 1987; Wood and Virgo, 1989). To alleviate this error, four secondary spinel standards with known \( \text{Fe}^{3+} \) contents were used to estimate \( \text{Fe}^{3+}/\sum \text{Fe} \) of samples following the method by Wood and Virgo (1989). In this study, the calibrated \( \text{Fe}^{3+}/\sum \text{Fe} \) ratios are systematically higher than those calculated assuming stoichiometric composition and charge balance (Fig. 3). We determined \( \text{Fe}^{3+} \) in the same way as Woodland et al. (1992), therefore we believe the uncertainty in \( \text{Fe}^{3+}/\sum \text{Fe} \) is similar to their value, ±0.025.

Combing the analytical error and error associated with using an activity model for \( \text{Fe}_3\text{O}_4 \) in spinel (see Eq. (2)), determination of spinel produces \( f_{\text{O}_{2}} \) uncertainty of 0.3–0.4 log units.

The calculation of \( f_{\text{O}_{2}} \) requires \( P \) and \( T \), but estimates of \( P \) for spinel peridotites have large uncertainties because of no well-established
5. Mineral chemistry and bulk compositions of xenoliths

5.1. Olivine

Olivine in garnet-spinel lherzolite has higher Fo (89–91) than that in garnet-spinel harzburgites (87–89) (Appendix 1), which is not consistent with the general interpretation that harzburgite is more refractory than lherzolite, and so low Fo values in harzburgites are attributed to metasomatism. Similar Fo values are observed in spinel lherzolite and spinel harzburgite, 90–91 and 86–92, respectively (Appendix 2). Relict olivine in orthopyroxenites shows low Fo, 83–87 (Appendix 3).

5.1.2. Orthopyroxene

As with olivine, the values of Mg# (Mg/(Mg+Fe)) for orthopyroxene are higher (0.90–0.91) in lherzolite and lower (0.87–0.92) in harzburgites (Appendices 1 and 2). High Ti in orthopyroxene in harzburgites (0.13–0.35 wt.%) is another indication that harzburgites have been metasomatized. Orthopyroxene contains orthopyroxene with low Mg# (0.85–0.89) and relatively high TiO2 (0.20–0.59 wt.%) (Appendix 3). The Mg# of orthopyroxene is similar or slightly greater than that of olivine, confirming the equilibration between the two (Von Seckendorff and O’Neill, 1993).

5.1.3. Clinopyroxene

As in olivine and orthopyroxene, clinopyroxene in garnet-spinel harzburgites shows slightly lower Mg# (0.88–0.89), but significantly higher TiO2 (0.90–1.26 wt.%) than that of garnet-spinel lherzolites (Mg# = 0.89–0.91; 0.11–0.64 wt.% TiO2) (Appendix 1), again confirming that the harzburgites were metasomatized. Relict clinopyroxene occurs in secondary orthopyroxene in orthopyroxenites, but contains high TiO2 (0.65–1.59 wt.%) and low Mg# (0.83–0.91) compared to that in peridotites (Appendix 3).

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lherzolites and spinel harzburgites have similar major element compositions as abyssal peridotites (Fig. 6).

Most garnet-bearing harzburgites have higher SiO₂, Al₂O₃, TiO₂ and lower Mg# than that of spinel harzburgites (Fig. 6). Furthermore, they contain higher TiO₂ and lower Mg# than garnet-bearing lherzolites (Fig. 6a, c, d), suggesting that they were metasomatized. Three spinel harzburgite samples also show higher TiO₂ and lower Mg# than spinel lherzolites (Fig. 6c–d), suggesting that spinel harzburgites were also affected by similar metasomatism as in garnet-bearing harzburgites.

Garnet orthopyroxenites contain high SiO₂ (48.8–53.95 wt.%), Al₂O₃ (3.62–11.34 wt.%) and TiO₂ (up to 2.0 wt.%), and low Mg# (0.85–0.88) compared to peridotite xenoliths (Fig. 6).

5.3. Metasomatism

Metasomatic minerals are common in garnet-bearing samples (Table 1). Several garnet-bearing harzburgites contain veinlets of orthopyroxenite with halos of Ti minerals and secondary orthopyroxene (Fig. 2d). These veinlets have identical mineralogy and mineral chemistry as discrete garnet orthopyroxenite xenoliths, suggesting that these xenoliths were likely brought from wide veins of orthopyroxenites in the mantle. The orthopyroxenites are interpreted to be the products of extensive metasomatism of harzburgites based on the presence of relict olivine (Fig. 2e), mineral and bulk compositions. One orthopyroxenite contains relict clinopyroxene enclosed in orthopyroxene and is interpreted to have originated from lherzolite (Fig. 2f). Although it is difficult to evaluate the abundance of orthopyroxenite in the mantle, it is probably minor in the mantle considering that both veined xenoliths and orthopyroxenites comprise <10% of all xenoliths. Olivine has low Fo and plots outside or on the margin of the olivine-spinel mantle array of Arai (1994) (Fig. 7).

Cryptic metasomatism is expressed as low Mg# and elevated TiO₂ in minerals and bulk rock compositions (Figs. 6c–d and 8). Lower Mg# and higher TiO₂ in olivine and pyroxenes in harzburgites than those in lherzolites suggest prevalent metasomatism in harzburgites (Fig. 8). Metasomatism in spinel peridotites is not as common as in garnet-bearing peridotites. Only one spinel lherzolite sample (PA64) contains a websterite veinlet, and two spinel harzburgites (PAK5, LS100) show high

Fig. 6. Bulk chemical compositions of mantle xenoliths from the Pali Aike area. Plots of (a) CaO vs. SiO₂, (b) Cr vs. Al₂O₃, (c) TiO₂ vs. Mg# and (d) Al₂O₃ vs. Mg# for bulk compositions of mantle xenoliths from Pali Aike. Filled star depicted with PM refers to the primitive mantle composition (McDonough and Sun, 1995). Fields for abyssal peridotites are based on the data of Niu (2004). Other symbols are the same as in Fig. 4. Note that garnet orthopyroxenites show a wide compositional variation; spinel harzburgite shows a wide compositional variation in subpanels (c) and (d).
The two-pyroxene thermometry of Brey and Köhler (1990) yielded systematically lower T than that by Wells (1977) for garnet-free samples when compared with garnet-bearing samples and did not yield a continuous geotherm. The geotherm based on garnet-bearing peridotites is much higher than those of ancient cratons, such as South Africa, Siberia and Namibia (Fig. 9), but similar to oceanic geotherm and those of off-craton areas affected by upwelling asthenospheric mantle, such as Vitim, Russia (Ionov et al., 1993) and SE China (Qi et al., 1995) (Fig. 9). Stern et al. (1999) suggested that this high geotherm was a relic inherited from the late Jurassic rifting related to the break-up of Gondwana and the opening of the southern Atlantic ocean. On the other hand, Kempton et al. (1999b) suggested that high geotherm in the region is linked to a late Tertiary–Neogene event. We suggest that the observed high geotherm defined by garnet-bearing peridotites is most likely related to hot asthenospheric upwelling through a slab window in the area since Tertiary.

The calculated fO2 values of peridotites range from FMQ +0.33 to FMQ +0.75 and the majority of samples are slightly more oxidized than the FMQ buffer, with the median value of FMQ +0.30 (n = 24) (Table 4). Garnet-bearing lherzolite and harzburgite show similar mean fO2 values of FMQ +0.13 ± 0.32 (n = 6) and FMQ +0.22 ± 0.19 (n = 8), respectively. Orthopyroxenite sample BNC2 shows relatively reduced fO2 value of FMQ −0.50.

7. Discussion

7.1. Origin and evolution of the mantle below southern Patagonia

7.1.1. Formation of SCLM below Pali Aike

Several possible processes have been proposed for the formation of SCLM, including formation of highly refractory lithospheric mantle above mantle plumes (Herzberg, 1999), formation of highly refractory mantle in mantle wedges (Parman et al., 2004), and accretion of oceanic lithosphere (Boyd, 1989; Niu and O’Hara, 2003). The oceanic

![Fig. 7. Fo component of olivine and Cr# of spinel in peridotite xenoliths from Pali Aike. Symbols are the same as Fig. 4. Note that all garnet-spinel harzburgites, two spinel harzburgites and one orthopyroxenite (BNC2) plot outside the olivine-spinel mantle array (OSMA) defined by Arai (1994), suggesting that they are not primary mantle peridotites. It also shows the field of abyssal peridotite as a shaded area (Arai, 1994).](image)

![Fig. 8. Plots of TiO2 in pyroxenes and Fo in olivine in mantle xenoliths from the Pali Aike area. Symbols for samples are the same as in Fig. 4. Note that orthopyroxenites, garnet-spinel harzburgites and several spinel harzburgites show low Fo in olivine and high TiO2 contents in clinopyroxene and orthopyroxene compared with their lherzolite counterparts. The variation bars shown in orthopyroxenites and garnet-spinel harzburgites are based on 3–5 analyses.](image)
lithosphere accretion model involves the thickening of lithosphere mantle by stacking oceanic lithosphere during subduction (Boyd, 1989; Niu and O’Hara, 2003). The mantle plume model involves upwelling of hot asthenospheric mantle plume followed by high degree of partial melting above plume heads to form buoyant refractory lithospheric mantle. The mantle wedge model suggests that continents and underlying lithospheric mantle may be formed from refractory wedge mantle (Parman et al., 2004). This model explains the occurrence of subduction-related igneous rocks in ancient continents (Canil, 2004), the Si-enrichment in SCLM (Kelemen et al., 1998), and small volumes of volcanic rocks to mass balance the refractory composition of SCLM. The model also explains the enrichment of incompatible trace elements in continental rocks (Carlson et al., 2005).

Both “hot plume” and “mantle wedge” models require partial melting to form refractory SCLM and the age of SCLM should be older than or similar to voluminous igneous rocks on the overlying continent. However, Pali Aike peridotites are not as refractory as most ancient SCLM. Peridotites from ancient SCLM, such as Kaapvaal and Siberian cratons, commonly show high Fo of olivine with an average of 93 (Boyd, 1989; Boyd et al., 1997) and high Cr#, 0.49–0.79, in spinel (Woodland and Koch, 2003). The data suggest that these two models may not be applicable to the formation of the SCLM underlying Pali Aike.

The degrees of partial melting and origin of peridotites can be evaluated by examining the ratios of Mg/Si and Al/Si of bulk rock compositions (e.g., Hattori and Guillot, 2007). Un-metasomatized Pali Aike peridotites show lower Mg/Si and higher Al/Si than refractory sub-arc peridotites and plot in the field of abyssal peridotites (Fig. 10). The degree of depletion due to melt extraction in the residual mantle can also be illustrated in a diagram of Al2O3 in orthopyroxene vs Cr# in spinel (Fig. 11). Preferential incorporation of Al in melt lowers Al2O3 in orthopyroxene and increases Cr# in spinel in the residues. Un-metasomatized garnet-bearing lherzolites and most spinel peridotides in Pali Aike show Al2O3 contents in Opx and Cr# in spinel overall overlapping with the field of abyssal peridotites, and notably higher Al in Opx and lower Cr in spinel than sub-arc peridotites, such as Mariana (Bloomer and Hawkins, 1983; Parkinson and Pearce, 1998), Tonga (Bloomer and Fisher, 1987), and south Kamchatka (Arai et al., 2003). In addition, compositions of spinel in anhydrous peridotite xenoliths plot in the field of abyssal peridotites in both the binary (Mg#–Cr#) and ternary (Fe2+–Cr3+–Al3+) diagrams (Figs. 4 and 5).

Therefore, our data support the suggestion that the SCLM beneath the Pali Aike formed from an oceanic lithosphere. This interpretation is also supported by similar abundance and normalized patterns of REE and Sr–Nd isotope compositions between garnet lherzolites and abyssal peridotites (Stern et al., 1999; Kempton et al., 1999b). Considering the Re–Os model ages of 531 Ma (sample TM2) and 860 Ma (sample LS33) for Pali Aike garnet peridotites (Stern et al., 1999), the SCLM beneath Pali Aike may have formed from oceanic lithosphere that was produced at a ridge in late Proterozoic–early Paleozoic time (Fig. 12).

The Pali Aike area occurs south of the Deseado Massif of southern Patagonia. There are arc igneous rocks of Siluro-Devonian time along

---

### Table 3

Temperature and pressure estimates for the peridotite xenoliths from Pali Aike area, southern Patagonia

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rock type</th>
<th>Temperature (°C)</th>
<th>P (kb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS33</td>
<td>Grt-Spl lherzolite</td>
<td>1110</td>
<td>1209</td>
</tr>
<tr>
<td>TM0</td>
<td></td>
<td>959</td>
<td>1011</td>
</tr>
<tr>
<td>TM2</td>
<td></td>
<td>964</td>
<td>1040</td>
</tr>
<tr>
<td>LS50</td>
<td></td>
<td>1015</td>
<td>1099</td>
</tr>
<tr>
<td>BN73</td>
<td></td>
<td>1055</td>
<td>1133</td>
</tr>
<tr>
<td>LS1</td>
<td></td>
<td>1074</td>
<td>1127</td>
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<td>BN32</td>
<td></td>
<td>1001</td>
<td>1053</td>
</tr>
<tr>
<td>TM14</td>
<td>Grt-Spl harzburgite</td>
<td>959</td>
<td>1027</td>
</tr>
<tr>
<td>TM15</td>
<td></td>
<td>965</td>
<td>902</td>
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<td>1006</td>
<td>1073</td>
</tr>
<tr>
<td>BN50</td>
<td></td>
<td>980</td>
<td>1061</td>
</tr>
<tr>
<td>PAH1K</td>
<td>1010</td>
<td>938</td>
<td>23.0</td>
</tr>
<tr>
<td>PAK6</td>
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<td>993</td>
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</tr>
<tr>
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<td>Spl harzburgite</td>
<td>997</td>
<td>944</td>
</tr>
<tr>
<td>PK2</td>
<td>997</td>
<td>1030</td>
<td>1018</td>
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<tr>
<td>PK3</td>
<td>1024</td>
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<td>1010</td>
</tr>
<tr>
<td>LS100</td>
<td>108</td>
<td>975</td>
<td>17.8</td>
</tr>
<tr>
<td>PK5</td>
<td>1025</td>
<td>1057</td>
<td>16.8</td>
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<tr>
<td>01BN</td>
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<td>1005</td>
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<tr>
<td>BN46</td>
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<td>1079</td>
<td>1033</td>
</tr>
<tr>
<td>BNH5</td>
<td>1064</td>
<td>1170</td>
<td>984</td>
</tr>
<tr>
<td>BN43</td>
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<tr>
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<td>1002</td>
</tr>
<tr>
<td>BNC2</td>
<td>1002</td>
<td>22.48</td>
<td></td>
</tr>
</tbody>
</table>

a Wells (1977) two-pyroxene thermometer.
b Brey and Köhler (1990) two-pyroxene thermometer.
Fig. 9. Results of thermobarometries of peridotite xenoliths in this study. Symbols are the
same as in Fig. 4. Our data of garnet-bearing samples define a continuous geotherm,
close to the oceanic geotherm for 60 Ma old plate. Oceanic geotherm, Precambrian
shield geotherm, and fields for Archean SCLM at S. Africa, Siberia and Namibia are from
Nickel and Green (1985). Data for Phanerozoic SCLM at Vitim, Russia is from Ionov et al.
(1993). Data for Phanerozoic SCLM at SE China is from Qj et al. (1995). The location of
graphite-diamond phase transition is from Kennedy and Kennedy (1976). The spinel-
garnet transitional zone is based on this study.

the southeastern margin of the Deseado massif (Pankhurst et al.,
2006), suggesting the development of a subduction complex in
response to the northern subduction of oceanic lithosphere along
the southern margin of the Deseado Massif (Fig. 12a). Like many oceanic
subduction zones, this oceanic subduction zone was likely accompa-
nied by an accretionary prism of sediments and a stack of
underplated oceanic lithosphere (Fig. 12b), which we suggest became
the SCLM below Pali Aike. The proposed scenario is consistent with
Re–Os model ages of late Proterozoic and early Paleozoic age of mantle
xenolith samples (Stern et al., 1999; Schilling et al., 2008).

Subduction of the Nazca plate resulted in the formation of a
continental arc along the west coast of southernmost South America
in Miocene time (Fig. 12c). This was followed by the collision of Chile
ridge with the trench at ~14–15 Ma (Cande and Leslie, 1986; Fig. 12d).
The ridge subduction resulted in the formation of a slab window and the
extensive eruption of plateau lavas from late Miocene to Recent (e.g.,
Goring et al., 1997; D’Orazio et al., 2000). Asthenospheric mantle-
derived melt infiltrated the lower portions of overlying SCLM and
metasomatized garnet-bearing peridotites (Fig. 12d).

7.1.2. Origin of garnet-bearing peridotites

Two possible processes are proposed to explain the common
occurrence of relict spinel in garnet (Fig. 2c); cooling or P increase.
Either cooling or P increase results in the isochemochemical reaction of
spinel + orthopyroxene + clinopyroxene forming garnet + olivine (Obata
and Morten, 1987). Stern et al. (1999) suggested cooling greater than
175 °C based on core-to-rim compositional zoning in clinopyroxene
from Pali Aike spinel lherzolites, and suggested that this cooling
caus ed spinel break-down to form garnet and olivine either in the late
Proterozoic or early Paleozoic, or after the late Jurassic opening of the
southern Atlantic ocean. Granulite xenoliths in the Pali Aike basalt
considered to have formed during the Jurassic event associated with
the opening of the southern Atlantic ocean underwent similar post-
crystallization cooling (Selverstone and Stern, 1983). Most likely
explanation for the occurrence of relic spinel in garnet is a pressure
increase during subduction/accretion of oceanic lithosphere. The
subduction and accretion of oceanic lithosphere results in pressure
increase which led to the transformation from spinel- to garnet-facies
peridotites (Fig. 12b).

7.2. Possible processes controlling the oxidation states of mantle rocks

The variable lithologies, a range in Cr# in spinel and the evidence of
metasomatism in our samples suggest that the redox state may have
been influenced by both partial melting in the original suboceanic
lithosphere and the subsequent metasomatism associated with the
generation of the Pali Aike basalts. Partial melting is considered to
result in reduction of fO2 in the residual mantle as Fe3+ is preferentially
incorporated in partial melt (Canil et al., 1994). However, our spinel-
facies xenolith samples, which are in general free of metasomatism,
do not show any correlation between fO2 and Cr# of spinel (Fig. 13),
suggesting that their fO2 did not change during partial melting. Our
results are consistent with comparable fO2 values between mid-
oceanic ridge basalts and the abyssal peridotites (Christie et al., 1986;
Bézos and Humler, 2005). This conclusion is also supported by the
experimental result of Amundsen and Neumann (1992), who showed
that garnet-facies mantle peridotites produce a partial melt with
comparable Fe3+/ΣFe ratios.

Fig. 10. Weight ratio of Mg/Si vs. Al/Si of peridotites in Pali Aike area. The large solid star
represents primitive mantle value from McDonough and Sun (1995). The fields for
abyssal peridotites, Himalaya peridotites, and Mariana forearc peridotites are from
Hartto and Guillot (2007). The compositional variation expected during partial melting
is shown with arrows. Residues have higher Mg/Si and lower Al/Si, whereas melt has a
lower Mg/Si and higher Al/Si. Symbols are the same as in Fig. 4. Note that un-
metasomatized peridotites overall overlap with the field of abyssal peridotites.

Fig. 11. Plot of Al2O3 in Opx (wt.%) vs. Cr# in spinel for peridotites in Pali Aike area. The
field for abyssal peridotites is based on the samples from North Atlantic oceanic
peridotites by Michael and Bonatti (1985). Data source for arc mantle peridotites
includes Mariana (Bloomer and Hawkins, 1983; Parkinson and Pearce, 1998), Tonga
(Bloomer and Fisher, 1987), and south Kamchatka (Arai et al., 2003). The mineral
compositional variation expected during partial melting is shown with arrows.
Residues have higher Cr# in spinel and lower Al2O3 in Opx. Symbols are the same as
in Fig. 4. Note the spinel peridotites and un-metasomatized garnet-spinel peridotites
in Pali Aike overall overlap with the field of abyssal peridotites, and show notable high Al
in Opx and low Cr in spinel compared with mantle wedge peridotites.
Table 4
Estimates of oxygen fugacity values for the mantle xenoliths from Pali Aike, southern Patagonia

<table>
<thead>
<tr>
<th>Lithology sample</th>
<th>Grt-Spl lherzolite</th>
<th>Grt-Spl harzburgite</th>
<th>Spl lherzolite</th>
<th>Spl harzburgite</th>
<th>Grt orthopyroxenite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TM0</td>
<td>TM2</td>
<td>LS50</td>
<td>BN73</td>
<td>LS1</td>
</tr>
<tr>
<td>Olivine</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X_{Fe})</td>
<td>0.11</td>
<td>0.10</td>
<td>0.10</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>(X_{Mg})</td>
<td>0.89</td>
<td>0.90</td>
<td>0.90</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>Orthopyroxene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1(Fe)(^{a})</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>M2(Fe)(^{a})</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>Spinel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr#</td>
<td>0.28</td>
<td>0.30</td>
<td>0.37</td>
<td>0.34</td>
<td>0.36</td>
</tr>
<tr>
<td>(Fe^{3+}/(2Fe^{2+}))</td>
<td>0.29</td>
<td>0.29</td>
<td>0.30</td>
<td>0.34</td>
<td>0.31</td>
</tr>
<tr>
<td>Mg/(Mg+Fe(^{2+}))</td>
<td>0.75</td>
<td>0.74</td>
<td>0.72</td>
<td>0.77</td>
<td>0.74</td>
</tr>
<tr>
<td>log (F_O2/^{96})</td>
<td>-1.74</td>
<td>-1.77</td>
<td>-1.86</td>
<td>-1.87</td>
<td>-1.70</td>
</tr>
<tr>
<td>P (kbar)(^{c})</td>
<td>19.6</td>
<td>20.8</td>
<td>22.0</td>
<td>22.1</td>
<td>22.7</td>
</tr>
<tr>
<td>T (°C)(^{d})</td>
<td>959</td>
<td>964</td>
<td>1015</td>
<td>1060</td>
<td>1074</td>
</tr>
<tr>
<td>Δlog((F_O2/^{FMQ}))</td>
<td>0.27</td>
<td>0.32</td>
<td>0.35</td>
<td>0.39</td>
<td>0.23</td>
</tr>
</tbody>
</table>

\(^{a}\) M1(Fe), M2(Fe) = fractions of Fe at M1 and M2 sites, calculated following the method in Wood (1990).

\(^{b}\) Calibrated using the four spinel grains with known Fe\(^{3+}\) contents.

\(^{c}\) For garnet-bearing xenoliths, P is calculated based on Al-in-Opx barometer of Nickel and Green (1985) and for garnet-free xenoliths P is assumed as 1.5 Gpa in \(F_O2\) calculation.

\(^{d}\) For xenoliths containing both Opx and Cpx, T is calculated based on two-pyroxene thermometer (Wells, 1977), and for samples without Cpx, T is calculated based on Ca-in-Opx thermometry (Brey and Köhler, 1990).

\(^{e}\) Calculated based on Ol-Spl Fe–Mg exchange thermometer of Ballhaus et al. (1991).

\(^{f}\) \(F_O2\) estimates following the method of Ballhaus et al. (1991) using Fe\(^{3+}\) contents of spinel calculated from its stoichiometric composition.

\(^{g}\) \(F_O2\) estimates following the method of Nell and Wood (1991) using the calibrated contents of Fe\(^{3+}\).
Orthopyroxenites represent the products of extensive metasomatism by melts. Therefore, $f_{O_2}$ value of orthopyroxenites likely reflects the oxidation state of these metasomatizing melts. One orthopyroxenite (BNC2) yielded $f_{O_2}$ of FMQ$-0.50$ based on spinel+orthopyroxene+olivine oxybarometry. Low contents of Fe$^{3+}$ in ilmenite and clinopyroxene also support relatively reduced $f_{O_2}$ for the metasomatizing agent for the formation of orthopyroxenites. Hematite components

![Schematic diagrams showing the formation and later modifications of SCLM beneath Pali Aike, southern Patagonia.](image)

**Fig. 12.** Schematic diagrams showing the formation and later modifications of SCLM beneath Pali Aike, southern Patagonia. (a) An oceanic plate was subducted beneath the southeastern margin of Deseado Massif, South Patagonia during the Mid Paleozoic producing arc-type igneous rocks. The subduction resulted in the formation of accretionary prism. (b) Oceanic lithosphere was accreted to the southeastern margin of Deseado Massif by underthrusting and the SCLM beneath Pali Aike was established by late Paleozoic. (c) Eastward subduction Chile ridge collided with the trench at middle Miocene, ~14–15 Ma. (d) Chile ridge subducted beneath the Pali Aike volcanic field forming a slab window from which asthenospheric melt infiltrated the lower portions of overlying SCLM and erupted to the surface as Pali Aike volcanic rocks.

![Values of $f_{O_2}$ relative to FMQ buffer ($\Delta f_{O_2}$ (FMQ)) vs. Cr# in spinel for peridotites from Pali Aike compared with abyssal peridotites (Bryndzia and Wood, 1990) and sub-arc mantle peridotites.](image)

**Fig. 13.** Values of $f_{O_2}$ relative to FMQ buffer ($\Delta f_{O_2}$ (FMQ)) vs. Cr# in spinel for peridotites from Pali Aike compared with abyssal peridotites (Bryndzia and Wood, 1990) and sub-arc mantle peridotites. Symbols are the same as Fig. 4. Sub-arc mantle peridotites include those from Ichinomegata in Japan, Marelava in Vanuatu arc, Grenada in Lesser Antilles arc, Santa Isabel and San Jorge in Solomon islands and the Simcoe area in Cascade arc (Wood and Virgo, 1989; Ballhaus et al., 1991; Brandon and Draper, 1996; Parkinson and Arculus, 1999; Parkinson et al., 2003).

![Oxidation state for mantle xenoliths from Pali Aike in comparison with those for other mantle peridotites.](image)

**Fig. 14.** Oxidation state for mantle xenoliths from Pali Aike in comparison with those for other mantle peridotites. Data source: abyssal peridotite (Bryndzia and Wood, 1990); Baikal rift zone, Dariganga, and Sikhote-Alin ridge (Ionov and Wood, 1992); Kilbourne Hole, San Carlos and Ichinomegata (Wood and Virgo, 1989); Avacha (Arai et al., 2003); Simcoe (Parkinson and Arculus, 1999). The vertical bar indicates the mean $\Delta \log f_{O_2}$ (FMQ) value for a particular region.
in ilmenite range from 0.01 to 0.024, suggesting a relatively reduced FeO, and relatively reduced Fe3+/Fe2+ (Amundsen, 2003). The metasomatized melt is characterized by high A12O3, SiO2, TiO2 and spinel-facies transformed to garnet-facies peridotites during the upper asthenospheric mantle, which is slightly reduced compared to the FMQ buffer (McCanta et al., 2004). Furthermore, the oxidation state of the upper asthenospheric mantle, which is slightly reduced compared to the FMQ buffer as indicated by the data from abyssal peridotites (Bryndzia and Wood, 1990) and mantle peridotites in continental rifts that have been affected by asthenosphere-derived melts (Ionov and Wood, 1992).

The values of FeO for spinel-facies and garnet-facies peridotites are similar ranging from FMQ – 0.33 to +0.75, suggesting that the transformation from spinel- to garnet-facieswas not accompanied by FeO changes. The ranges of FeO for metasomatized (FMQ – 0.33 to +0.75), un-metasomatized (FMQ – 0.23 to +0.75) samples are also similar, suggesting that the later infiltration of asthenospheric melt did not alter FeO (Table 4; Fig. 13).

8. Conclusions

Pali Aike xenoliths show FeO values, FMQ – 0.33 to +0.75, slightly elevated, but comparable to abyssal peridotites and other SCLM affected by asthenospheric mantle melt, such as Baikal rift zone in Russia (Ionov and Wood, 1992), Dariganga in Mongolia (Ionov and Wood, 1992), Kilbourne Hole and San Carlos in USA (Wood and Virgo, 1989), and western Victoria in Australia (Chen et al., 1991) (Figs. 13 and 14). The values are distinctly higher than FeO values of ancient SCLM underlying cratons. The FeO data together with bulk rock compositions of not-metasomatized samples support the formation of SCLM underlying the southern Patagonia through the accretion of oceanic lithosphere. Relict spinel in garnet-bearing peridotites suggests spinel-facies transformed to garnet-facies peridotites during the accretion. The formation of a slab window since late Tertiary resulted in the upwelling of asthenospheric-derived melt and extensive metasomatism of the peridotites, especially garnet-bearing facies. The metasomatized melt is characterized by high Al2O3, SiO2, TiO2, and FeO, and relatively reduced FeO, from FMQ – 0.50. This metasomatizing melt did not significantly change the oxidation state of Pali Aike peridotites because their FeO values are comparable to that of the metasomatising melt.

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Appendix A. Supplementary data


References


Chen, Y.D., Pearson, N.J., O’Reilly, S.Y., Grif

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