



Evidence of South American lithosphere mantle beneath the Chile mid-ocean ridge

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ABSTRACT

Numerous geochemical studies on mid-ocean ridge basalts have established the presence of both compositional and lithological heterogeneities in the upper mantle. These studies have successfully constrained the composition and age of the chemical heterogeneities within the Earth's upper mantle. However, the origin of those heterogeneities remains highly debated. The Chile Mid-Ocean Ridge in the southeast Pacific Ocean, located far away from any hotspot, is colliding and subducting under the South America plate promoting the formation of a slab window. Comprehensive geochemical data (major, trace, volatile element contents and Sr, Nd, Hf and Pb isotope ratios) on Chile Ridge submarine glasses collected over the 1000 km ridge length demonstrate significant mantle compositional variability. Four main mantle components have been recognized: the typical Pacific MORB mantle, an enriched mantle (e.g., EM-1), a Subduction Modified mantle, and an anciently depleted mantle with unusually high Hf isotope ratios. Surprisingly, despite the large compositional variability, all glasses – including those with a subduction signature – have volatile-refractory element ratios within the range of the Pacific normal MORB. We propose that the Patagonia sub-continental lithospheric mantle, variably metasomatized since the Early Paleozoic, is eroded and incorporated into an asthenosphere with a south Atlantic MORB mantle composition that is flowing westward across the slab window from South America to the Chile Ridge. This scenario contrasts with a well-accepted geodynamic model that predicts the opposite direction of mantle flow. We speculate that the westward mantle flow across the slab window might be a counter-flow response to the opening of the Drake passage and the eastward movement of Pacific mantle since ~30 Ma ago.

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1. Introduction

Much of our understanding of the chemical composition of the Earth's upper mantle comes from the study of the Mid-Ocean Ridge basalts (MORB). Numerous studies, in particular those presenting radiogenic isotope ratios in combination with major, trace and volatile element contents, have established that the source region of MORB is compositionally heterogeneous at variable length scales (e.g., Agranier et al., 2005). In some cases, these heterogeneities are clearly produced by the interaction of the mid-ocean ridge with deep mantle plumes [e.g., Iceland (Schilling et al., 1983); the Azores (Dosso et al., 1999)]. In other cases, the hetero-

geneities are attributed to the recycling of the oceanic lithosphere at subduction zones (Donnelly et al., 2004; Shimizu et al., 2016). However, unraveling the true origin of the upper mantle heterogeneities has been a challenging task.

The Chile Mid-Ocean Ridge (Chile Ridge) is a unique spreading center that has a well-constrained tectonic framework allowing us to investigate the origin of the mantle heterogeneities beneath the ridge and potential mantle flow across the slab window produced by its subduction under the South America plate. The ~1000 km long NW-SE trending Chile Ridge is a divergent plate boundary between the Nazca and the Antarctic plates (Fig. 1). The Chile Ridge is an intermediate spreading center with relatively uniform half spreading rate of ~31 mm/yr, generally characterized by deep valley floor (3400–4300 m) (Bach et al., 1996; Klein and Karsten, 1995). To the north, ~35° S, the Chile Ridge forms a triple junc-

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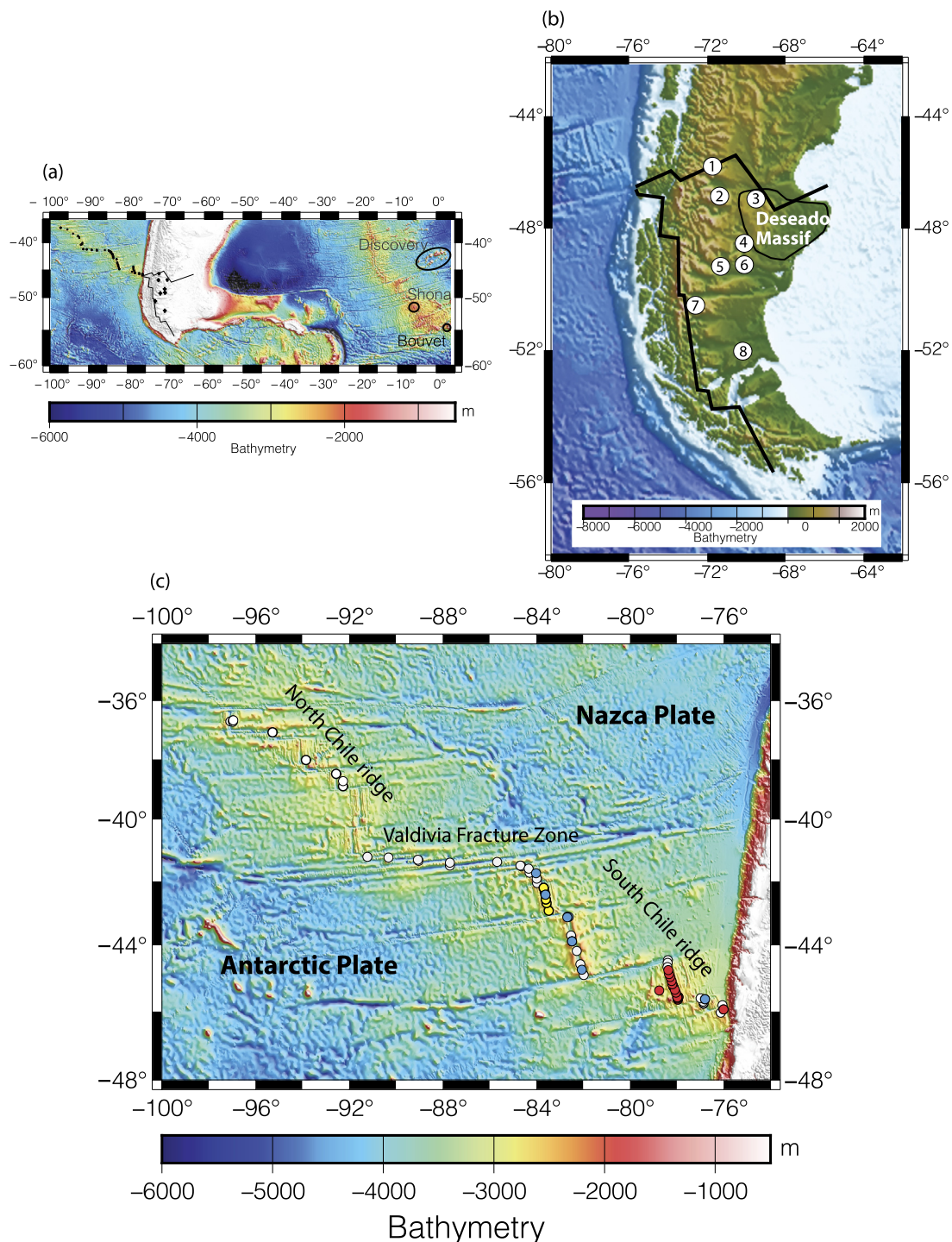


Fig. 1. (a) Regional map showing the location of the Chile Ridge relative to Patagonia and the south Atlantic ridge with Discovery, Shona and Bouvet hotspots. (b) Locations for the southern Patagonia mantle xenoliths with existing isotope measurements shown as white circles with number referring to the xenolith locations. Surface expression of the present-day slab window in Patagonia is indicated by the black line (Breitsprecher and Thorkelson, 2009). (c) Detail sample locations in the expanded Chile Ridge map. White (typical Pacific MORB composition) and colored circles (red – subduction modified, cyan – EM1, and yellow – residual lithosphere) representing the location of the Chile Ridge submarine glasses analyzed. Note that three of the four components are present in the Chile Ridge segment south of the Valdivia fracture zone, whereas only typical Pacific MORB composition is present within and north of the Valdivia fracture zone. Xenolith locations: 1 – Coyhaique, 2 – Sol de Mayo, 3 – Don Camilo, 4 – Gobernador Gregores, 5 – Tres Lagos, 6 – Cerro Redondo, 7 – Cerro de Fraile, 8 – Pali Aike.

tion between the Pacific, Antarctica and Nazca plates. To the south, $\sim 46^\circ$ S, the spreading center has been subducting beneath the westward-moving South American plate since about 18 Ma creating a gap in an otherwise continuous subducting oceanic lithosphere termed “slab window”; the slab window provides an opening for communication between the mantle above and below the subducting oceanic plate (Breitsprecher and Thorkelson, 2009). The

~ 600 km long Valdivia Fracture Zone (VFZ) divides the Chile Ridge system roughly around midpoint into two major sections – the northern ($36\text{--}39^\circ$ S) and the southern ($41\text{--}46^\circ$ S) Chile Ridge. The lavas along the Chile Ridge were sampled by three expeditions: Sonne 40 in 1985 (Bach et al., 1996), the Southern CROSS Expedition in 1993 (Klein and Karsten, 1995) and the Valdivia/Pan4 Expedition in 1998 (Howell et al., 2016).

Klein and Karsten (1995) and later Sturm et al. (1999) presented geochemical evidence for the presence, in addition to the Pacific MORB mantle, of two enriched mantle components: one closer to the trench (ridge segment 1 and 3) characterized by an unusual subduction trace element signature (e.g., low Nb/U ratios) associated with highly radiogenic Sr, Pb, He and unradiogenic Nd isotope ratios; and the other component south of the VFZ (ridge segment 4) with radiogenic Sr and unradiogenic Nd isotope ratios that is associated with high $\Delta 7/4$ – $\Delta 8/4$ at low $^{206}\text{Pb}/^{204}\text{Pb}$ ratios characteristic of the denominated EM1 mantle composition (Hart, 1984). Given the geographical proximity of the Chile Ridge to the Chile Trench they raised the possibility that the sub-oceanic mantle in this region has become contaminated with material derived directly from the adjacent Andean subduction zone, either from the slab itself or from the slab-contaminated sub-arc mantle. These authors proposed a recent (< 20 Ma) introduction of slab-derived fragments of subducted sediment and altered oceanic crust into the sub-ridge mantle for the segment 1 lavas with subduction signature. However, they could not explain the extreme Pb isotope ratios of segment 3 lava with subduction signature by a similar process. In contrast, the authors concluded that lavas from segment 3 represent small plume of mantle carrying a ~ 2 Ga mixture of recycled terrigenous sediment and altered crust material, in which case it would have nothing to do with the modern tectonic setting. Finally, for segment 4 lavas the authors argue for a complex history involving several stages of variable mantle enrichments over hundreds to billions of years. These authors presented different origins for lavas erupting in distinct ridge segments, but unfortunately there was no single geologically reasonable model that could explain all of these observations together.

We present here a full geochemical characterization (major, trace and volatile – H_2O , CO_2 , Cl, F, S – element contents and Sr, Nd, Hf and Pb isotope ratios, Table S1) of 123 submarine glasses collected from the entire ~ 1000 km long Chile Ridge to constrain the origin of the mantle heterogeneities beneath the Chile Ridge and the mantle flow through a slab window region. We show that the mantle source composition of the Chile Ridge lavas can be explained by the Patagonia sub-continental lithospheric mantle, variably metasomatized since the Early Paleozoic, eroded and incorporated into a South Atlantic asthenosphere that is flowing westward across the slab window.

2. Materials and methods

We have picked large, clean (devoid of any alteration) Chile Ridge submarine glasses under the binocular microscope. We prepared 1-inch round indium mounts for in situ analysis of major, trace and volatile elements of all samples including the ones with previously published data (Bach et al., 1996; Klein and Karsten, 1995; Sturm et al., 1999). We did it to obtain full geochemical data on the same glass chips, avoiding uncertainties related to analyzing different elements in different glass fractions. All reported elemental concentrations for the glasses are the average of 3–4 glass chips analyzed for each sample.

Quantitative major element analysis of basaltic glass was performed on the Brown University Cameca SX-100 electron microprobe. Operating conditions of the instrument consisted of 15 kV voltage, 10 nA current and a 20-micron diameter, defocused beam. Counting times were 30 seconds for on peak, and half that time for backgrounds, for all elements except Na, which was counted for 20 seconds. The data were calculated using the PAP correction procedures. Standards used for the basaltic glass analysis included USGS AGV-2 andesite glass (Si); USGS BIR-1G Iceland basalt glass (Al, Ca); synthetic Fo97 forsterite, University of Rhode Island (Mg); Rockport, Massachusetts fayalite, NMNH 85,276 (Fe); Amelia albite, Purdue University (Na); rhodonite, AMNH 104738 (Mn); synthetic

orthoclase OR-1, AMNH (K); synthetic rutile, Brown University, (Ti); and berlinite, synthetic, AMNH G. Harlow (P). The electron microprobe is equipped with extra-large diffracting crystals (LTAP, LLIF, LPET) that generate roughly five times the count rate of standard-sized diffracting crystals. Extra-large crystals were used in the analysis of Na, Al, K, P, Mn and Fe. Standard-sized crystals were used for Si, Mg, Ca, and Ti. Na and K were analyzed using a loss routine to account for any mobilization of the elements under the beam. Repeated measurement on a MORB glass (519-4-1) during the analytical session yields a reproducibility (2σ , $n = 15$) of $\sim 2\%$ for SiO_2 , Al_2O_3 , CaO , MgO , FeO and 7–8% for Na_2O , TiO_2 and $\sim 14\%$ for K_2O , MnO and P_2O_5 .

Trace element concentrations of the glasses were determined with a 193 nm wavelength excimer Analyte G2 laser ablation system coupled to a Thermo Scientific X-Series II quadrupole ICP-MS at the Mass Spectrometer Analytical Facility, Brown University. ICP-MS was tuned to optimize the signal on La using NIST 612 glass with a 65 μm spot and 2 $\mu\text{m}/\text{sec}$ scan speed on a line. During tuning ThO/Th was monitored to minimize the oxide production below 1%, and Th/U ratio was kept close to 1 to minimize the fractionation. Samples were analyzed with 140 μm spot with 20 Hz repetition rate and a laser frequency of 3.78 J/cm^2 at 50% energy level. Each analysis consisted of 30 s of gas background followed by 20 s of ablation. USGS glass standards (BHVO2-G, BIR1-G, and BCR2-G) were used as calibration standards and their concentrations are taken from GeoRem database. ^{43}Ca was used as an internal standard to normalize the raw counts and then reduced to concentrations using VBA based Excel macro developed by J. Sparks, Boston University. Analytical reproducibility for the majority of the elements is better than 10% (2σ , $n = 10$), based on repeated measurement on a MORB glass (519-4-1).

Concentrations of H_2O , CO_2 , F, Cl, S were measured on a Cameca IMS 1280 ion probe at the Northeast National Ion Microprobe Facility (Woods Hole Oceanographic Institution). A 10 nA $^{133}\text{Cs}^+$ primary beam was accelerated at 10 kV, focused and rastered to a diameter of 30–40 μm . Secondary $^{12}\text{C}^-$, $^{16}\text{OH}^-$, $^{19}\text{F}^-$, $^{30}\text{Si}^-$, ^{32}S , and $^{35}\text{Cl}^-$ ions were extracted at a -10 kV voltage potential. Entrance and exit slit widths were set to achieve a mass resolving power > 6000 , sufficient to separate $^{16}\text{OH}^-$ from $^{17}\text{O}^-$, $^{32}\text{S}^-$ from $^{31}\text{P}^-$ and $^{16}\text{O}_2$, and all elements from potential hydride interferences. A 400 μm secondary ion field aperture was applied to ~ 100 times magnified secondary image to minimize transmission of ions from outside the innermost ~ 4 μm of the sputtering crater, thereby minimizing the contribution of background volatile elements to the measurements. Each mass was measured on an ETP electron multiplier for count times ranging from 5–10 seconds within each measurement cycle, over a total of 5 cycles. Linear calibrations for each volatile element were obtained by analyzing 9 natural basaltic glasses of known volatile composition as standards – 46D, D52-5, D51-3, 519-4-1, 1649-3, D20-3, JD17H, 6001, 1654-3, D20-3. Volatile abundances were obtained on three to four glass chips previously analyzed for major and trace elements from each sample and the average is taken as a representative concentration of the sample. We have monitored the secondary images to avoid any inclusions and cracks (bright feature on the ^{12}C image) and crystals (dark feature on the ^{32}S image). On each mount, Suprasil 3002 was measured to characterize and correct for H_2O , CO_2 , F and S background, and Herasil 102 was measured to characterize and correct for Cl background. The background for F, and S is estimated to be ≤ 0.1 ppm, for Cl ~ 0.6 ppm, for $\text{CO}_2 \leq 1$ ppm, for $\text{H}_2\text{O} \leq 10$ ppm. Basaltic glass 519-4-1 was analyzed periodically to assess the reproducibility which is typically $< 5\%$ (2σ , $n = 33$) for all volatile elements.

Sr, Nd, Hf, and Pb isotopic compositions were measured on a Thermo Scientific NEPTUNE PLUS MC-ICP-MS at the Mass Spectrometer Analytical Facility, Brown University. Pb, Sr, Nd and Hf

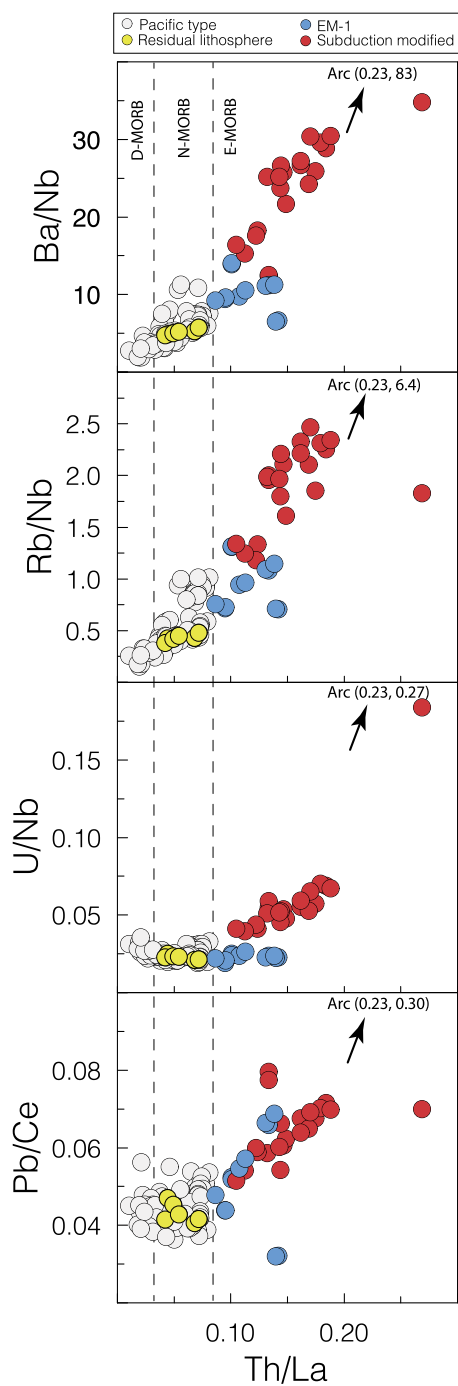


Fig. 2. Selected incompatible trace element ratio plots for the Chile Ridge glasses. The panels distinctly show the EMORB samples with and without subduction modified mantle signature. The former is characterized by high U/Nb, Pb/Ce, Ba/Nb, Rb/Nb and Th/La composition, whereas the latter has normal U/Nb but range to high Pb/Ce, Ba/Nb, Rb/Nb and Th/La compared to the N and DMORB lavas. Symbols and colors for the Chile Ridge glasses as in Fig. 1. The arrow points towards the average values of lavas from the Andes Southern Volcanic Zone (Jacques et al., 2013, 2014).

were introduced in the plasma using a PFA nebulizer with a flow rate of $\sim 50 \mu\text{l}/\text{min}$ coupled to an APEX-IR introduction system. The mass spectrometer was equipped with an H-skimmer cone and H-sampler cone. The baseline measurement was taken at -0.5 amu . $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ were corrected for instrumental mass fractionation using an $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$, $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ and $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ respectively with an exponential law. Sample Pb solution was spiked

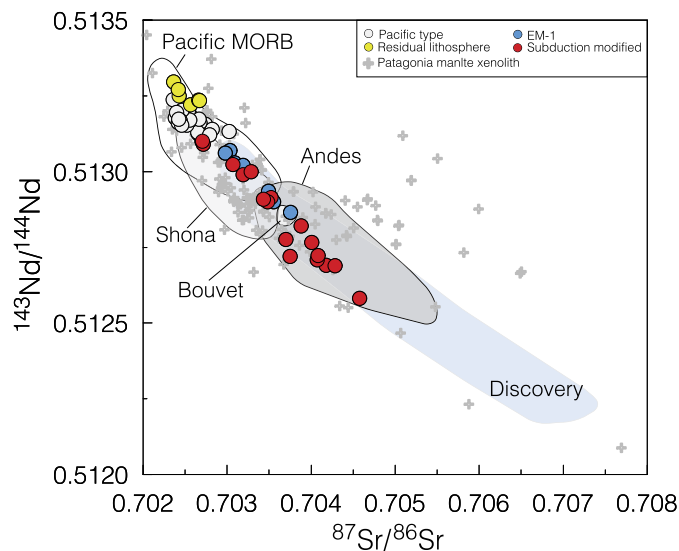


Fig. 3. Sr and Nd isotopic compositions of the Chile Ridge glasses. Chile Ridge glasses carrying the EM-1 and subduction signature are characterized by radiogenic Sr and unradiogenic Nd isotopes, overlapping with the compositions of the Andes Southern Volcanic Zone, the Discovery, Shona, Bouvet plume basalts and plume modified South Atlantic MORB, whereas the remaining Chile Ridge glasses overlap with the Pacific MORB field (Gale et al., 2013; Mallick et al., 2019; Shimizu et al., 2016; Stracke, 2012). Note that the southern Patagonia mantle xenoliths (gray cross) cover the entire Sr and Nd isotope variation of the Chile Ridge glasses. Data for Andes lavas from (Jacques et al., 2013, 2014), for Discovery, Shona, Bouvet from (Andres et al., 2002; Barry et al., 2006; Douglass et al., 1999; Janney et al., 2005; le Roux et al., 2002; Schwindrofska et al., 2016) and for Patagonia mantle xenoliths from (Conceicao et al., 2005; Gorrington and Kay, 2000; Jalowitzki et al., 2017, 2016; Mazzucchelli et al., 2016; Melchiorre et al., 2015, 2020; Mundl et al., 2015; Novais-Rodrigues et al., 2021; Ntaflos et al., 2007; Rivalenti et al., 2004; Schilling et al., 2005; Stern et al., 1999). Other symbols as in Fig. 1.

with NBS SRM-997 Tl standard prior to analysis with a $\text{Pb}/\text{Tl} \sim 4$ to correct for the instrumental mass fractionation using an exponential law with a $^{203}\text{Tl}/^{205}\text{Tl} = 0.418922$. $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ of samples are reported relative to NBS SRM-987 $^{87}\text{Sr}/^{86}\text{Sr} = 0.71024$, JNd-i Nd standard $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$ and JMC-475 Hf standard $^{176}\text{Hf}/^{177}\text{Hf} = 0.282160$ respectively. $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ are reported relative to the NBS 981 standard $^{206}\text{Pb}/^{204}\text{Pb} = 16.9356$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4891$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7006$. The external precision on the ratios over the course of two years is 30 ppm for Sr (2σ) and Nd (2σ), 40 ppm for Hf (2σ) and 80 ppm (2σ) for Pb. The Sr and Pb blanks were $< 50 \text{ pg}$, and Nd and Hf blanks were $< 30 \text{ pg}$. We have reanalyzed Sr, Nd and Pb isotopes for 18 out of 33 Chile Ridge glasses with previously published isotope data (Bach et al., 1996; Klein and Karsten, 1995; Sturm et al., 1999). Our new data is in good agreement with published results, giving us confidence that we can include the published information in our interpretation without significant laboratory bias (Table S2). Furthermore, a few samples that show minor deviation from the 1:1 line between the published and our data, in particularly the Pb-isotope ratios, are N-MORB from the northern Chile Ridge, and therefore, do not significantly impact our interpretation that is based on the four mantle components present in the southern segments of the Chile Ridge. The USGS reference material BHVO-1, BCR-2 and BIR-1 were processed during the sample analytical preparation and measured with the same instrument set up. The Sr, Nd, Hf and Pb isotope ratios for BHVO-1, BCR-1 and BIR-1 are well in agreement with the range of ratios reported by others (see Table S3).

3. Results

The Chile Ridge submarine glasses range from 6 to 10 wt.% MgO contents and define a large trace element compositional variability.

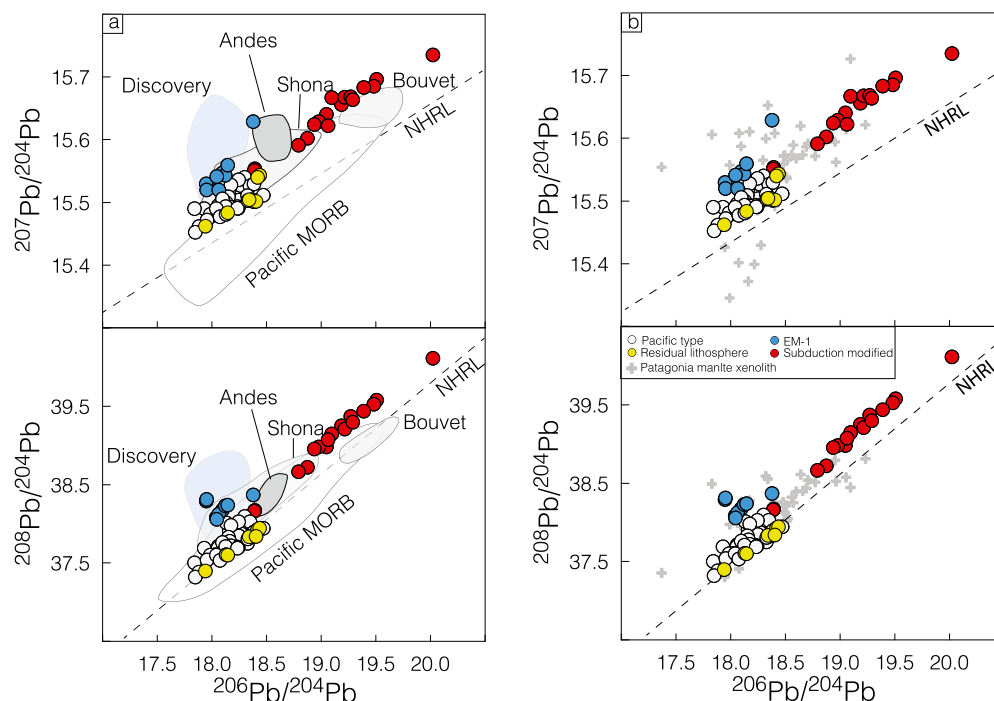


Fig. 4. Pb isotopic compositions of the Chile Ridge glasses. (a) The majority of the Chile Ridge glasses north of the Valdivia Fracture Zone overlaps with the Pacific MORB, whereas glasses located south of the Valdivia Fracture Zone overlap and extend the field for Andean Southern Volcanic Zone lavas towards the Discovery-Shona-Bouvet plume as well as the plume modified South Atlantic MORB composition. The EM-1 signature typical of the Discovery hotspot is characterized by elevated $(^{207,208}\text{Pb})/^{204}\text{Pb}$ at relatively low $^{206}\text{Pb}/^{204}\text{Pb}$. (b) Adjacent Southern Patagonia lithospheric mantle xenoliths show a remarkable similarity in Pb isotope space to the Chile Ridge lavas. Note that the mantle xenoliths analyzed at present do not extend to the extreme radiogenic Pb-isotopes measured for the Chile Ridge glasses with subduction signature. Symbols and references for the data as in Figs. 1 and 3.

ity from enriched MORB (E-MORB) with Th/La greater than 0.08, depleted MORB (D-MORB) with Th/La less than 0.03 and normal MORB (N-MORB) with Th/La between 0.03 and 0.08 values (Figs. 2 and S1). Essentially all the variations in trace element contents is captured by lavas with MgO content ≥ 7.5 wt.% suggesting that such variation is controlled by the combined effects of variations in source composition and extent of melting.

Based on trace element and radiogenic isotope ratios, the mantle source beneath the Chile Ridge requires four end-member components easily identified in Sr-, Nd-, Hf- and Pb isotope ratios diagrams (Figs. 3, 4, 5, 6, S2). We find D- and N-MORB having compositions typical of a “Pacific MORB mantle”; notably, in Hf-Nd isotope space these glasses plot below the mantle array, a distinguishing feature of the Pacific upper mantle (Fig. 5) (Salters et al., 2011). The second component, termed “Subduction Modified mantle”, is distinguished by E-MORB with high incompatible trace element ratios (Rb/Nb, Ba/Nb, U/Nb, Pb/Ce, Th/La) (Fig. 2) typical of basalts associated to subduction zones (Pearce and Peate, 1995). These glasses have isotopic compositions that extend beyond the range reported for the Andean Southern Volcanic Zone (SVZ) lavas (Jacques et al., 2013, 2014), from typical Pacific MORB mantle to more radiogenic Pb isotopes than those observed in South Atlantic MORB-Discovery-Shona-Bouvet lavas (Figs. 3, 4, 5). Moreover, the glasses with subduction signature define a relatively linear trend in Hf-Nd plot with a slope shallower ($\epsilon\text{Hf} = 0.92$ $\epsilon\text{Nd} + 6.05$, $R^2 = 0.96$) than that for the mantle array ($\epsilon\text{Hf} = 1.59$ $\epsilon\text{Nd} + 1.28$ (Chauvel et al., 2008)). To our knowledge this is the shallowest slope ever reported for MORB, consistent with the characteristic effect of recycled clay-rich sediments on subduction zones magmatism. The third mantle component is defined by E-MORB glasses with high $\Delta 7/4$ and $\Delta 8/4$ at a relatively unradiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ ratios indicative of an “EM-1 mantle component” as defined by Hart (1984). The Chile Ridge lavas with EM-1 signature are characterized by their enriched trace element compositions (Figs. 2 and

S3), and intermediate radiogenic Sr and unradiogenic Hf and Nd isotopes (Figs. 3, 4, 5, 6). The fourth component, is distinguished by a group of N-MORB having a more radiogenic Hf isotope ratio ($\epsilon\text{Hf} = 22.2$) for Sr, Nd and Pb isotope ratios within the values reported for the Pacific MORB mantle (Figs. 4, 5, 6). A Hf-Nd Depleted Mantle model age as old as 0.6–1.1 Ga of this component points to an ancient depletion (Table S4). We denominate this component as “Residual Lithosphere” akin to the component reported for the Atlantic and Indian MORB by Salters et al. (2011).

Despite the large compositional variation in trace element and isotope ratios of the Chile Ridge basalts, their volatiles contents display rather limited variability, ranging from average MORB concentrations to the lowest values reported for Pacific MORB (Fig. 7). The effect of shallow level processes (degassing and assimilation of hydrothermally altered material) must be evaluated before the volatile contents can be used to investigate the variation of primary volatile content of basalts and their mantle sources. Water, chlorine, sulfur and fluorine have sufficient solubility at sea-floor depths to allow an estimation of their initial concentrations in MORB. In contrast, the solubility of CO_2 is low, exsolving CO_2 -rich vapor, and as a result nearly all Chile Ridge glasses are saturated to over-saturated with a CO_2 - H_2O vapor phase at the pressure of eruption. After filtering out two samples for unusual enrichment of Cl content ($\text{Cl}/\text{K} = 0.20$ – 0.34) indicating possible assimilation of hydrothermally altered oceanic crust, the abundances of H_2O , Cl, F, S can be compared to refractory trace elements with similar incompatibility during mantle melting. The variations in the ratios of the volatile to refractory trace elements ($\text{H}_2\text{O}/\text{Ce} = 93$ – 391 , $\text{S}/\text{Dy} = 122$ – 290 , $\text{F}/\text{Nd} = 15$ – 27 , $\text{Cl}/\text{K} = 0.009$ – 0.087) range from average MORB to the lowest values reported for the Pacific MORB. Surprisingly, even the Chile Ridge glasses carrying the subduction signature have low volatile to refractory trace element ratios (e.g., $\text{H}_2\text{O}/\text{Ce}$ as low as 93 and $\text{Cl}/\text{F} = 0.01$ – 0.64) consistent with those measured in Pacific MORB.

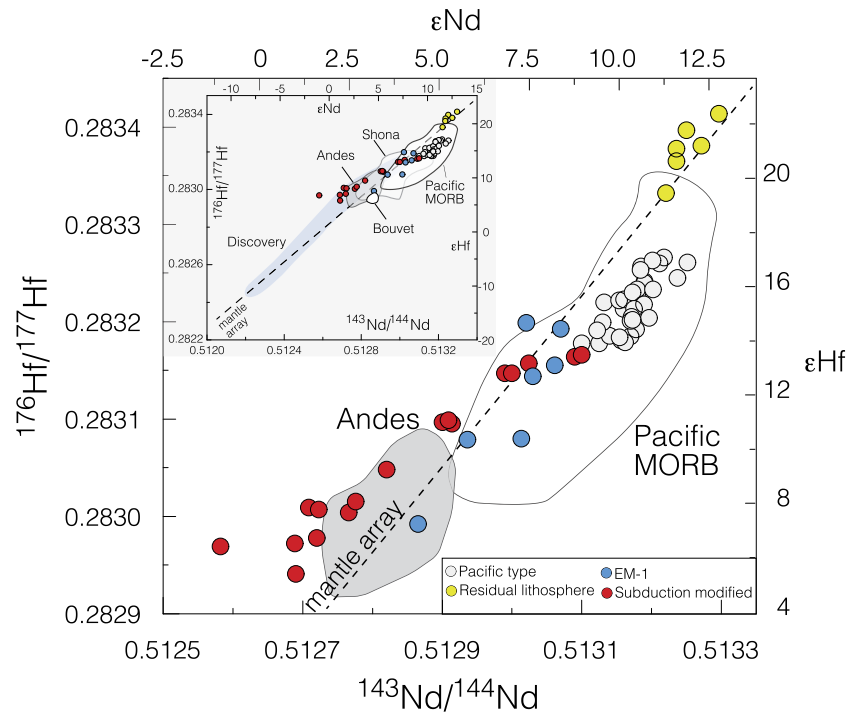


Fig. 5. Hf-Nd isotopic compositions of the Chile Ridge lavas. Also shown in the inset are the fields for the Pacific MORB, Discovery-Shona-Bouvet plume as well as the plume modified South Atlantic MORB mantle composition, and the Andean Southern Volcanic Zone lavas. Note that the Pacific MORB mantle plot below the mantle array (Chauvel et al., 2008) and that Chile Ridge lavas with subduction signature define a linear trend with a slope shallower than the mantle array, ranging to more unradiogenic Hf-Nd isotope composition. A group of Chile Ridge glasses with radiogenic Hf isotope ratios plot above the Pacific MORB field indicating the presence of a Residual Lithosphere component. Symbols and references for the data as in Figs. 1 and 3.

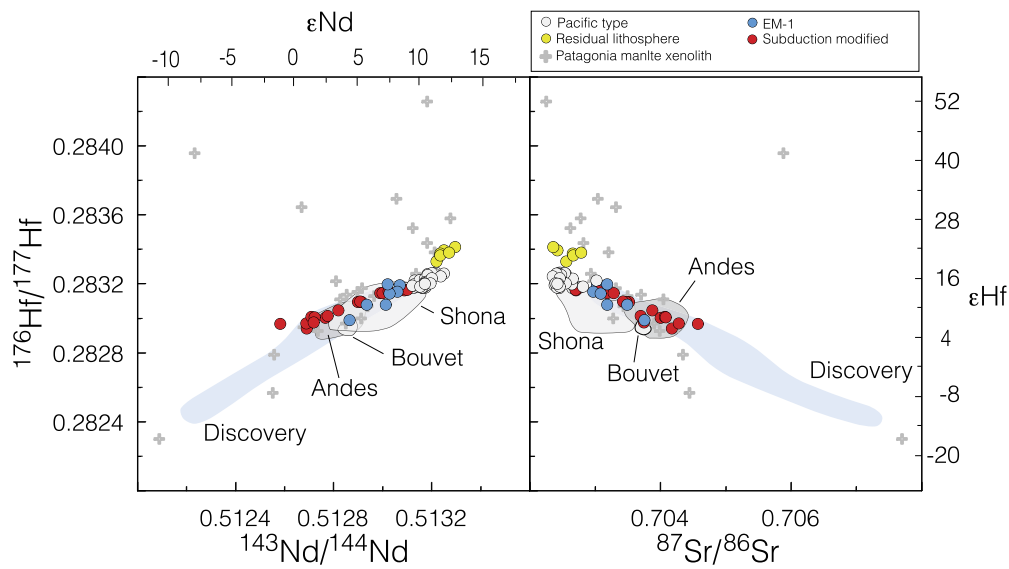


Fig. 6. $^{176}\text{Hf}/^{177}\text{Hf}$ versus $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the Chile Ridge glasses and Southern Patagonia mantle xenoliths. Existing Hf isotope analyses for the mantle xenoliths are only from clinopyroxene mineral separates. Note that the Southern Patagonia mantle xenoliths overlap with the different end-member components observed in the Chile Ridge lavas and extend to higher Hf at similar Nd and Sr isotopes. Symbols and data sources as in Figs. 1 and 3.

4. Discussion

Except for the Chile Ridge samples with Pacific MORB compositions, none of the other three compositional groups described for the Chile Ridge basalts are found erupted in any mid-ocean ridge lavas recovered from the Pacific basin. In contrast, the other three compositional groups are present to the East of the Andean subduction zone beneath Patagonia and the South Atlantic basin. Our examination of a compilation of published data for Pacific MORB (Gale et al., 2013; Mallick et al., 2019; Shimizu et al.,

2016; Stracke, 2012) shows no evidence in trace element and isotopic ratios pointing to the observed Subduction Modified, EM1 and Residual Lithosphere mantle components in the Chile Ridge basalts. The unique trace element and isotopic signatures of the E-MORB that characterize the Chile Ridge Subduction Modified mantle are nearly non-existent in the entire global MORB database except for a few samples from the Gakkel ridge in the Arctic basin (Yang et al., 2021). Moreover, although the EM1 isotopic composition is found in lavas from Pitcairn Island hotspot in the Pacific basin (Stracke, 2012), the Chile Ridge EM-1 component has higher

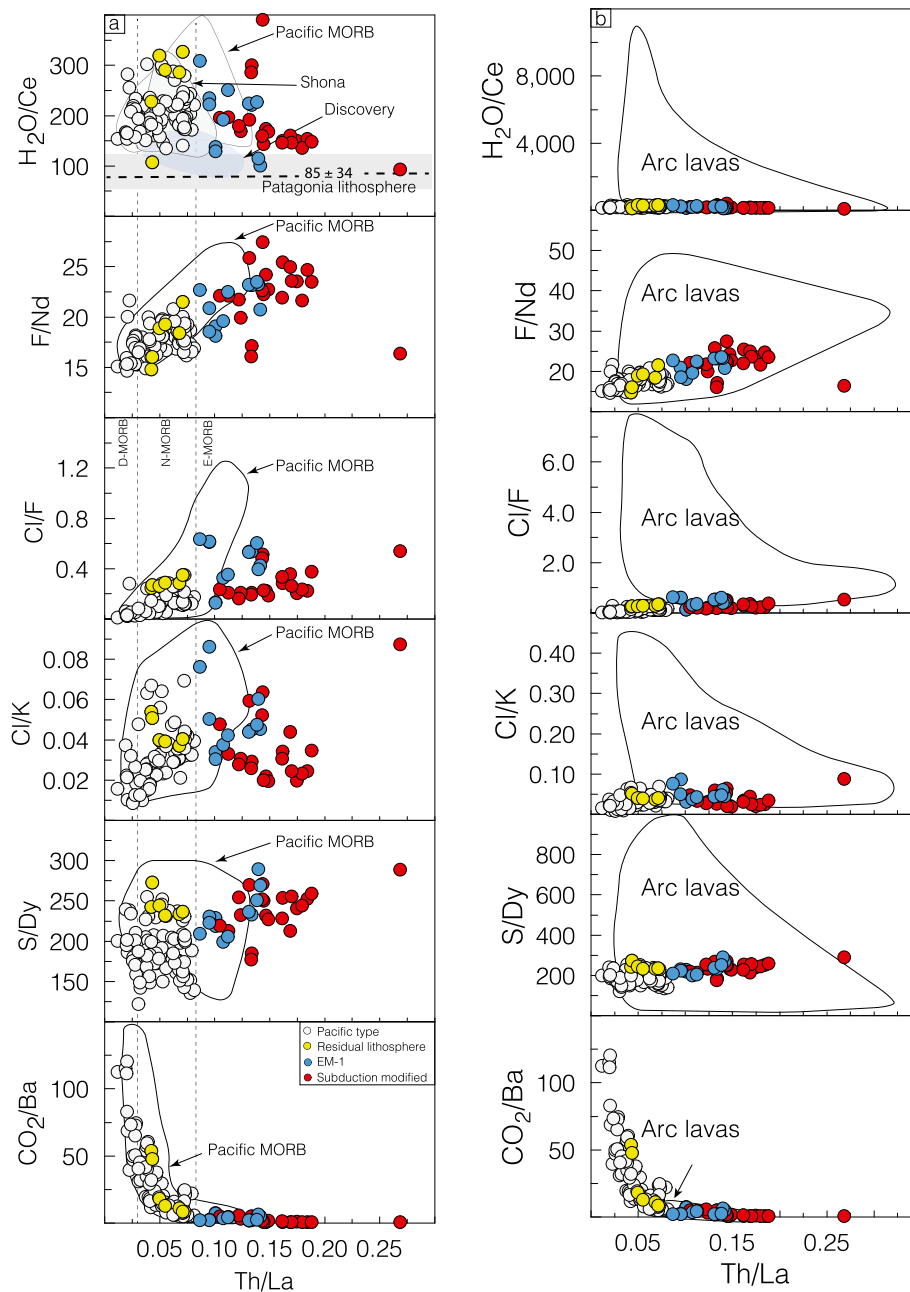


Fig. 7. Volatile-refractory incompatible element ratios versus Th/La. (a) Fields for Pacific N-MORB (Shimizu et al., 2016), Discovery and Shona (Dixon et al., 2002) are plotted for comparison. Estimate of the H₂O/Ce for the southern Patagonia lithospheric mantle ($85 \text{ ppm} \pm 34$) (Gibson et al., 2020) is shown by a horizontal black dash line. Excluding two samples that potentially had Cl contamination, all remaining Chile Ridge glasses ($\text{Cl/K} < 0.087$) have volatile-refractory element ratios ranging from average to the lowest values reported for the Pacific MORB despite the extreme variability in trace element and isotopic compositions. Even the Chile Ridge basalts with subduction signature extend to lower H₂O/Ce than Pacific MORB. Note that the Chile Ridge glasses with EM1 isotopic composition range to low H₂O/Ce consistent with Discovery-Shona Modified South Atlantic MORB. (b) Melt inclusions data for the Central American arc lavas (Lloyd et al., 2013; Sadofsky et al., 2008) are plotted for comparison. It is clear that none of the Chile Ridge glasses record any arc type volatile signature. Symbols as in Fig. 1.

$\Delta 7/4$ and lower $\Delta 8/4$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ in comparison to the Pitcairn EM-1 (Fig. S4) and therefore there is no match between the Pitcairn and Chile Ridge EM1 isotope ratios. In contrast, the isotopic compositions of the South Atlantic MORB affected by the Discovery-Shona hotspots do match that of the Chile Ridge EM1 basalts (Andres et al., 2002; Douglass et al., 1999; le Roux et al., 2002; Schwindrofska et al., 2016). Finally, the Chile Ridge lavas with isotopic compositions of the Residual Lithosphere component have more radiogenic Hf isotopes ($\epsilon_{\text{Hf}} = 22.2$) at similar Nd isotopes than the highest value reported for the Pacific MORB compilation ($\epsilon_{\text{Hf}} = 19.6$) (Fig. 5). Pacific MORB differ from Atlantic and Indian MORB in Hf-Nd isotope ratios, with low Hf at a given

Nd isotope ratio (Salters et al., 2011); and therefore, the composition of the Chile Ridge basalts points to affinities with lavas found in the Atlantic basin. In summary, we do not find in the Pacific mantle any evidence for the presence of three of the four mantle components identified beneath the Chile Ridge. In contrast, we find that the isotopic ratios of the Chile Ridge basalts have been observed in the Atlantic MORB – east of the Andean subduction zone – pointing to a possible connection to the mantle beneath Patagonia and the South Atlantic basin.

The evidence of a slab window beneath southern Patagonia produced by the subduction of the Chile Ridge (Breitsprecher and Thorkelson, 2009) raises the possibility that the asthenosphere un-

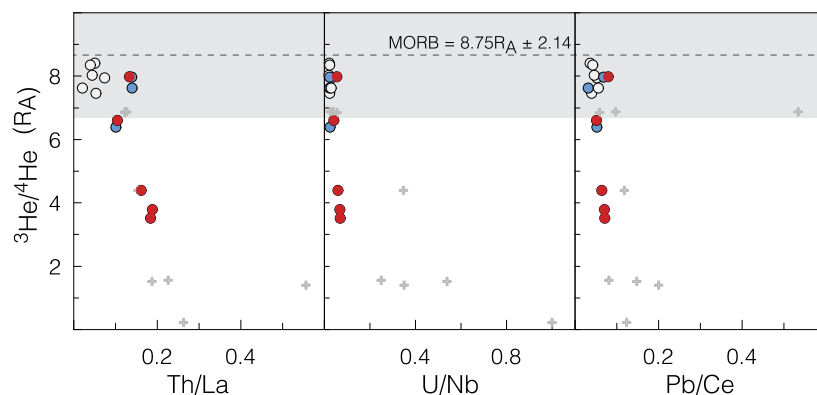


Fig. 8. $^3\text{He}/^4\text{He}$ isotopes versus trace element ratios indicating subduction signature (high Pb/Ce, U/Nb and Th/La) for the Chile Ridge glasses and southern Patagonia mantle xenoliths. The glasses (Niedermann and Bach, 1998; Sturm et al., 1999) range from MORB like $^3\text{He}/^4\text{He}$ value (8.75 ± 2.14 (Graham, 2002)) to low $^3\text{He}/^4\text{He}$ defining a compositional trend towards the Southern Patagonia mantle xenoliths with subduction signature (Gervasoni et al., 2012; Jalowitzki et al., 2016; Novais-Rodrigues et al., 2021). The plotted mantle xenoliths are whole rock data from Pali Aike and Coyhaique locations of the southern Patagonia. Gobernador Gregores location has $^3\text{He}/^4\text{He}$ ranging from 7.21–7.37 R_A , but these xenoliths do not have reported trace element data. Symbols as in Figs. 1 and 3.

derneath Patagonia might contribute to mantle melting at the Chile Ridge via the slab window. Mantle flow through the slab window of the present-day mantle beneath southern Patagonia, composed of South Atlantic mantle variably affected by the Andean subduction system (Chilson-Parks et al., 2022; Husson et al., 2012; Soager et al., 2021), may partially explain the composition of the Chile Ridge lavas, specifically the EM1 and Residual Lithosphere components of the Chile Ridge basalts also observed in lavas from the Atlantic basin. The presence of Discovery-Shona-Bouvet influenced South Atlantic MORB mantle has been well documented in the Patagonia back arc basalts, which have been linked to a westward flow of South Atlantic mantle beneath South America (Husson et al., 2012; Soager et al., 2021). Furthermore, the presence of an anciently depleted mantle “Residual Lithosphere” has been previously reported for the Atlantic basin (Salters et al., 2011). Therefore, it is possible that South Atlantic mantle might have moved westward across the slab window east of the Chile Ridge. Moreover, the subduction-modified trace element signature of the Chile Ridge lavas could also be explained by a westward flow of the mantle wedge modified by the Andean subduction processes. However, this process cannot reproduce the highly radiogenic Pb isotopes of the Chile Ridge glasses with the subduction signature (Fig. 4). Furthermore, these glasses have Cl/F ratios typical of MORB and $\text{H}_2\text{O}/\text{Ce}$ ratios (as low as 93) that are even lower than those reported for the Pacific MORB (140–384) (Shimizu et al., 2016) (Fig. 7). The low volatile contents and the larger range in radiogenic isotopes of the Chile Ridge lavas with subduction signatures argue against a direct involvement of the present Andean mantle wedge, with its high volatile contents and more limited isotopic range (Jacques et al., 2013, 2014; Robidoux et al., 2021; Weller and Stern, 2018).

A likely explanation for the identified mantle compositional range beneath the Chile Ridge is the presence of southern Patagonia sub-continental lithospheric mantle (SCLM) previously metasomatized by melts from the South Atlantic and subduction processes since the early Paleozoic (Conceicao et al., 2005; Gorrington and Kay, 2000; Jalowitzki et al., 2017, 2016; Mazzucchelli et al., 2016; Melchiorre et al., 2015, 2020; Mundl et al., 2015; Novais-Rodrigues et al., 2021; Ntafos et al., 2007; Rivalenti et al., 2004; Schilling et al., 2005; Stern et al., 1999). We find that metasomatized xenoliths from southern Patagonia (e.g., Gobernador Gregores) have higher K_2O and lower TiO_2 than the average depleted MORB mantle of Workman and Hart (2005) (Fig. S5) pointing to the southern Patagonia SCLM mantle as a suitable source for the Chile Ridge glasses with high K_2O and low TiO_2 at a given MgO content representing the Subduction Modified, EM1 and Residual

Lithosphere components (Fig. S1). More importantly, there is a remarkable similarity in Sr, Nd, Hf and Pb isotope ratios between the Chile Ridge lavas and SCLM xenoliths from the adjacent southern Patagonia (Figs. 3, 4, 6). There are 11 reported localities in this region where basalts hosting mantle xenoliths have erupted over the last 50 Ma (with the majority of them erupting over the last 0 to 5 Ma), providing a snapshot of the present-day isotopic composition of the sub-continental lithospheric mantle across the entire southern Patagonia (Melchiorre et al., 2020). Although there is a limited number of studies reporting radiogenic isotopes either in whole rock or mineral separates (clinopyroxene or phlogopite) (Table S5), the southern Patagonia SCLM xenolith data define the same isotopic end-member components observed in the Chile Ridge lavas (Figs. 3, 4, 6):

- 1) A “typical MORB mantle” composition (Salters and Stracke, 2004).
- 2) A highly radiogenic Hf component with a MORB-like Nd isotope ratios, similar to the “Residual Lithosphere” component of the Chile Ridge basalts. The Hf-Nd depleted mantle model ages of the Chile Ridge basalts with Residual Lithospheric component range from 0.6 to 1.1 Ga. This is consistent with the majority of the Hf-Nd model ages and the Re-depletion model ages of the Patagonia xenoliths, as well as with the zircon ages of the Patagonia crustal rocks (Mundl et al., 2015; Ramos, 2010; Schilling et al., 2017).
- 3) An “EM-1 mantle component” with Sr, Nd, Hf and Pb isotopes composition equivalent to that reported for the Chile Ridge basalts and the Discovery-Shona modified South Atlantic MORB (Andres et al., 2002; Douglass et al., 1999; le Roux et al., 2002; Schwindrofska et al., 2016). Moreover, the $\text{H}_2\text{O}/\text{Ce}$ values measured in the Chile Ridge lavas with the strongest EM1 isotopic composition are consistent with the low $\text{H}_2\text{O}/\text{Ce}$ ratios reported for the Discovery and Shona affected MORB (Dixon et al., 2002).
- 4) A “Subduction Modified mantle” with incompatible trace element ratios and Sr-Nd-Pb isotopes with subduction signature, similar to those observed in the Chile Ridge glasses with a subduction component (Figs. 3, 4, 6). Moreover, He isotope ratios provide additional evidence of the similarity between the Chile Ridge lavas with subduction signature and the southern Patagonia lithospheric mantle. Existing $^3\text{He}/^4\text{He}$ ratios reported for the Chile Ridge glasses (Niedermann and Bach, 1998; Sturm et al., 1999) have a range, mostly defined by those with subduction signature, from typical MORB values ($8.41 R_A$) to as low as $3.51 R_A$ (Graham, 2002) (Fig. 8).

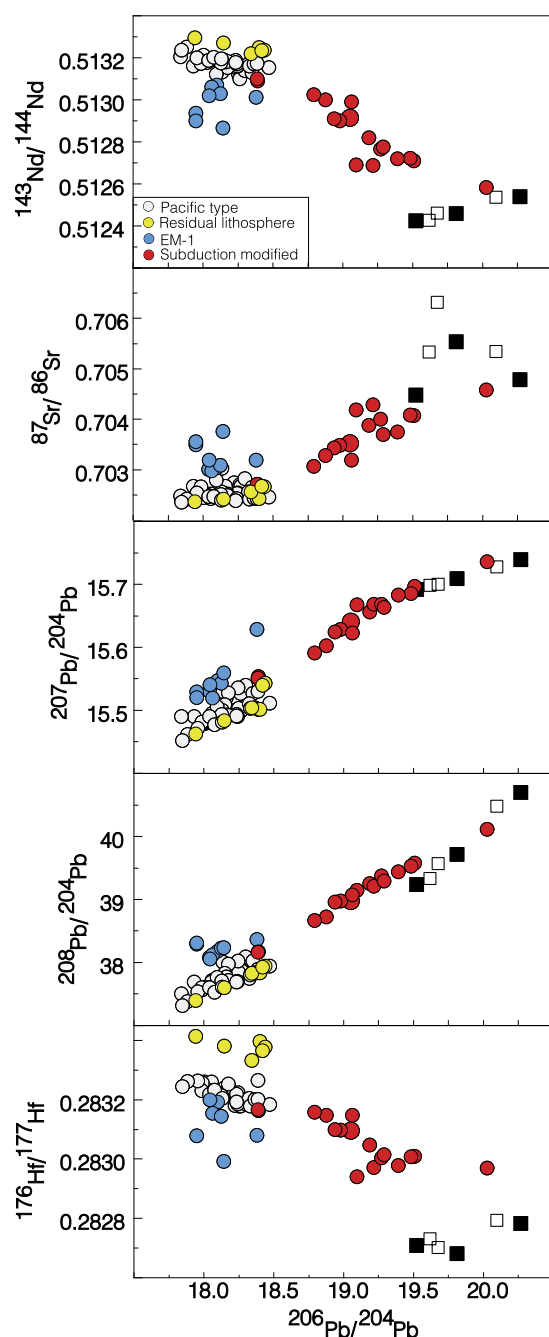


Fig. 9. The results of a simple model for the Patagonia SCLM refertilized during early to middle Paleozoic arc magmatism (470–400 Myr). This model can explain the most extreme radiogenic Pb isotopes of the Chile Ridge lavas with subduction signature as well as the Sr, Nd and Hf isotope signature of the subduction modified component. Three well characterized ~470 Ma Ordovician mafic lavas (Table S6) are used to constrain the isotopic compositions of the mantle source at 470 Myrs. We assumed the metasomatic melt have an average trace element composition of Andes back-arc lavas. Finally, we calculate the isotopic compositions for the present-day re-fertilized peridotite assuming that the parent-daughter ratios are the same as those of the metasomatic melt consistent with low incompatible trace element abundance of the residual lithospheric mantle. We did this calculation for both 470 Ma (black square) and 400 Ma (white square). Our modelling results match the end-member characteristics of the Chile Ridge lavas with a Subduction Modified component. Symbols as in Fig. 1.

Interestingly, $^3\text{He}/^4\text{He}$ ratios for a subset of southern Patagonia xenoliths range from MORB-like to much lower values (7.37–2.51 R_A) (Jalowitzki et al., 2016; Novais-Rodrigues et al., 2021), where the lowest He isotope values of the xenoliths are associated to trace element ratios indicating subduction signature. These results reinforce the genetic link between the southern Patagonia lithospheric mantle and the Chile Ridge lavas with subduction signature. Furthermore, the low volatiles contents measured on the Chile Ridge glasses with subduction signature provide further evidence of the genetic link between the Chile Ridge basalts and the southern Patagonia SCLM. The only available volatile data on xenoliths from the Patagonia SCLM xenoliths are from Pali Aike with an average H_2O content of 85 ppm (Demouchy et al., 2006; Gibson et al., 2020; Warren and Hauri, 2014), which is similar to the average H_2O estimate for other off-cratonic mantle peridotites (Peslier et al., 2010). More importantly, the recalculated water contents of whole-rock peridotites from a compilation of continental lithospheric mantle in the spinel stability field (10–110 ppm) are similar to those inferred for the source of MORB (50 to 200 ppm (Peslier et al., 2010), suggesting that the H_2O in the SCLM can be a viable candidate to explain the low $\text{H}_2\text{O}/\text{Ce}$ of the Chile Ridge lavas with subduction signature.

The only mis-match between the southern Patagonia SCLM xenoliths and the Chile Ridge lavas with subduction signatures is that the reported Pb isotope values of the xenoliths measured today do not extend to the most radiogenic Pb isotope ratios observed by the Chile Ridge basalts (Fig. 4). One possible explanation for the most radiogenic Pb isotope ratios in the Chile Ridge lavas with a subduction signature is that the Patagonia SCLM was affected by Paleozoic subduction processes. The Proterozoic lithospheric mantle of Patagonia has been under the influence of several episodes of subduction along the western margin of Gondwana during the Early to Mid-Paleozoic. Among them a major orogenic event along the proto-Andean margin is the Ordovician magmatic arc (~450–476 Ma, which is considered to extend into the Deseado Massif in southern Patagonia (Rapela et al., 2018). Based on the petrological, geochemical and tectonic reconstruction of Patagonia we present a simple geochemical model that attributes the most radiogenic isotopic composition of the Chile Ridge glasses with subduction signature to the Patagonia SCLM refertilized by lavas associated to the arc magmatism ~470 to 400 Ma. We utilized the measured parent-daughter and Sr, Nd, Hf and Pb isotopic compositions of mafic lavas from the Ordovician arc magmatism (samples provided by Professor Otamendi and analyzed in our lab, Table S6) to constrain the isotopic compositions of their mantle source at 470 and 400 Ma. We assume the melt carrying this isotopic compositions refertilized the overlying lithosphere 470 and 400 Ma, similar to the processes associated to the Andean lavas affecting the Patagonia lithospheric mantle today (Jalowitzki et al., 2017). We estimated an average trace element composition of the present-day Patagonia back-arc lava to assess the parent-daughter ratios of the refertilizing melt (e.g. (U, Th)/Pb, Rb/Sr, Sm/Nd, Lu/Hf ratios, Table S6). We use those ratios to calculate the isotopic compositions of the present-day lithospheric mantle refertilized ~470 and 400 Ma, since the refertilizing melt would dominate the incompatible trace elements and the Sr, Nd, Hf and Pb isotope budget of the lithospheric mantle. The results from our simple model can satisfactorily reproduce the extreme Sr, Nd, Hf and particularly Pb isotopes of the Chile Ridge lavas with subduction signature (Fig. 9) suggesting that Patagonia lithospheric mantle refertilized 470–400 Ma by arc magmatism could account for the origin of the most extreme isotopic values measured in the Chile Ridge basalts with the Subduction Modified component.

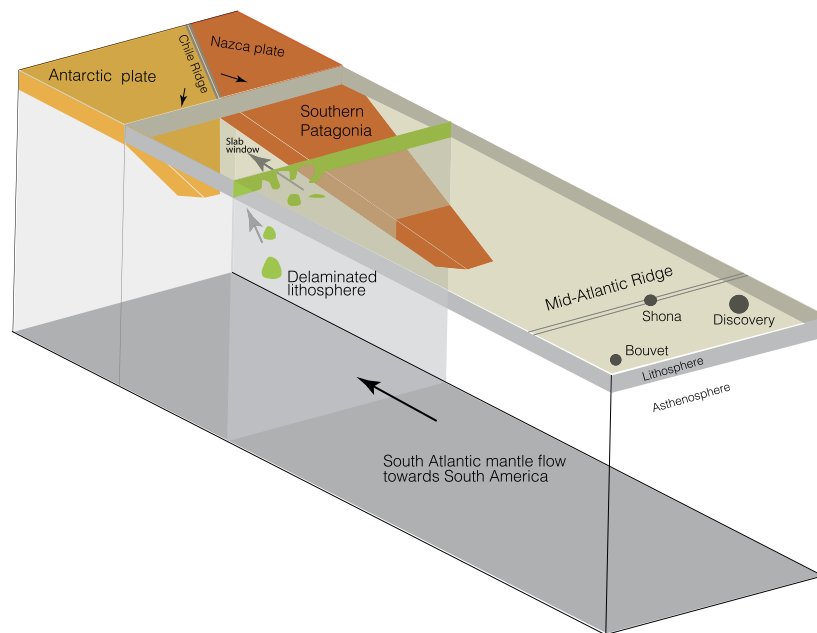


Fig. 10. A schematic cartoon showing the mantle flow westward to the Chile Ridge across the Patagonia slab window. The green blobs are the metasomatized southern Patagonia lithospheric mantle removed and incorporated into the asthenospheric mantle. The black arrow shows the South Atlantic mantle flow (Husson et al., 2012) carrying the Discovery-Shona-Bouvet geochemical signature beneath southern Patagonia. Our model points to a South Atlantic asthenospheric mantle carrying blobs of metasomatized southern Patagonia SCLM flowing westward towards the Chile Ridge mantle across the slab window.

Various geodynamic models have predicted the delamination, foundering or thermal erosion of the sub-continental lithospheric mantle during subduction processes (Beall et al., 2017; Conrad and Molnar, 1997). Regardless of the actual mechanism, the lithospheric mantle can effectively be removed into the asthenosphere within a relatively short time interval $\sim 10\text{--}40$ Ma (Beall et al., 2017). Petrological and seismological evidence such as sudden increase in mafic volcanism (Kay et al., 1994) and sub-crustal mantle with slow seismic velocity anomalies (Levander et al., 2011) have been used as evidence for the removal of sub-continental lithospheric mantle. Strong seismological evidence in support of the removal of the lithospheric mantle within the slab window area of southern Patagonia has been recently provided (Mark et al., 2022; Russo et al., 2022). Our hypothesis is also supported by the relatively high (≥ 4.69 Km/s) shear wave velocity of the mantle at 300 km depth beneath the Chile Ridge sampled from the S40RTS model suggesting a “colder/depleted” mantle beneath this ridge (Dalton et al., 2014).

Although the anciently depleted and subduction modified components beneath the Chile Ridge strongly suggest the migration of asthenospheric mantle with eroded southern Patagonia SCLM through the slab window, it is unclear whether the EM-1 component in Chile Ridge lavas is related only to a recently metasomatized southern Patagonia lithospheric mantle or it is also the result of the asthenosphere having a Discovery-Shona influenced South Atlantic MORB composition beneath southern Patagonia (Fig. 4). This is the case because the isotopic composition of the EM1 component in both the Patagonia mantle xenoliths and the South Atlantic MORB are essentially identical suggesting the metasomatism of the southern Patagonia lithospheric mantle is recent enough to have the same isotope ratios. Both possibilities have been previously proposed to explain the EM-1 compositions of some of the Patagonia back arc basalts and mantle xenoliths (Chilson-Parks et al., 2022; Gorrington and Kay, 2000; Melchiorre et al., 2020; Soager et al., 2021). However, the high K_2O and low TiO_2 of the EM1 glasses at equivalent MgO contents compared to typical MORB from the Chile Ridge (Fig. S5) suggest that most of the EM1 com-

ponent comes from recently metasomatized southern Patagonia lithospheric mantle.

5. Geodynamic implications and conclusions

We have shown that three of the four Chile Ridge mantle components are absent in the Pacific basin and are clearly linked to the mantle compositions located to the east of the Andean Subduction zone with the Patagonia sub-continental lithospheric mantle, variably metasomatized since the Early Paleozoic. We propose that the Patagonia sub-continental lithospheric mantle is eroded and incorporated into an asthenosphere with a Discovery-Shona influenced south Atlantic MORB mantle composition that is flowing westward across the slab window (Fig. 10). Assuming a rate of mantle flow of ~ 4 to 5 cm/yr (range from ~ 2 to ~ 6.5 cm/yr) for the South Atlantic spreading (Colli et al., 2014), it will take about 16 to 20 Myrs for a parcel of mantle located near the trench-ridge junction to cover the southern part of the Chile Ridge up to the Valdivian Fracture Zone. This is consistent with our finding that the three Chile Ridge mantle components that are absent from Pacific MORB are, in fact, restricted in the southern part of the Chile Ridge. We speculate that the opening of the Drake passage and Pacific mantle flow eastward into the South Atlantic basin for the last 30 Ma (Pearce et al., 2001) might have promoted a south Atlantic mantle counter flow westward across the slab window. Almost the entire southern Patagonia, south of the Chile Triple Junction, sits above the slab window (Breitsprecher and Thorkelson, 2009), providing a significant slab gap for the westward mantle flow. Most geodynamic models indicate eastward flow of mantle from beneath the slab across the slab window into the mantle wedge (Guillaume et al., 2010; MacDougall et al., 2014; Russo et al., 2010). In contrast, our geochemical data suggests that eroded Patagonia lithospheric mantle and possibly Discovery-Shona-influenced South Atlantic MORB mantle migrated westward through the slab window, introducing the unique mantle heterogeneity signature in the Chile Ridge MORB mantle.

CRediT authorship contribution statement

Soumen Mallick: Conceptualization, Investigation, Methodology, Writing – original draft, Writing – review & editing. **Sophie E. Kuhl:** Investigation, Methodology. **Alberto E. Saal:** Conceptualization, Investigation, Writing – review & editing. **Emily M. Klein:** Investigation, Writing – review & editing. **Wolfgang Bach:** Investigation, Writing – review & editing. **Brian D. Monteleone:** Methodology. **Joseph S. Boesenberg:** Methodology.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

I have shared the data in the supplementary material.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.epsl.2023.118320>.

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