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\(^{11}\)B-rich fluids in subduction zones: the role of antigorite dehydration in subducting slabs and boron isotope heterogeneity in the mantle

Jason Harvey\(^*\)\(^1\), Carlos Garrido\(^2\), Ivan Savov\(^1\), Samuele Agostini\(^3\), José Alberto Padrón-Navarta\(^4,5\), Claudio Marchesi\(^2\), Vicente López Sánchez-Vizcaíno\(^6\), María Teresa Gómez-Pugnaire\(^2\)

\(^1\)School of Earth and Environment, University of Leeds, UK.
\(^2\)Instituto Andaluz de Ciencias de la Tierra (IACT), CSIC & UGR, 18100 Armilla (Granada), Spain.
\(^3\)Istituto di Geoscienze e Georisorse-CNR, Via Moruzzi 1, 56124 Pisa, Italy.
\(^4\)Géosciences Montpellier, Univ. Montpellier 2 & CNRS, 34095 Montpellier, France.
\(^5\)Research School of Earth Sciences, The Australian National University, Canberra 0200, ACT, Australia
\(^6\)Departamento de Geología (Unidad Asociada al IACT-Granada), Escuela Politécnica Superior, Universidad de Jaén, 23700 Linares, Spain.

\(^*\) Corresponding author. Telephone: +44 (0)113 343 6769. Fax: +44 113 343 5259. Email: feejh@leeds.ac.uk (J. Harvey).

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Abstract

Serpentinites form by hydration of mantle peridotite and constitute the largest potential reservoir of fluid-mobile elements entering subduction zones. Isotope ratios of one such element, boron, distinguish fluid contributions from crustal versus serpentinite sources. Despite 85% of boron hosted within abyssal peridotite being lost at the onset of subduction at the lizardite-to-antigorite transition, a sufficient cargo of boron to account for the composition of island arc magma is retained (c. 7 μg g⁻¹, with a δ¹¹B of +22 ‰) until the down-going slab reaches the antigorite-out isograd. At this point a ¹¹B-rich fluid, capable of providing the distinctive δ¹¹B signature of island arc basalts, is released. Beyond the uniquely preserved antigorite-out isograd in serpentinites from Cerro del Almirez, Betic Cordillera, Spain, the prograde lithologies (antigorite-chlorite-orthopyroxene-olivine serpentinite, granofels-texture chlorite-harzburgite and spinifex-texture chlorite-harzburgite) have very different boron isotope signatures (δ¹¹B = -3 to +6 ‰), but with no significant difference in boron concentration compared to the antigorite-serpentinite on the low P-T side of the isograd. ¹¹B-rich fluid, which at least partly equilibrated with pelagic sediments, is implicated in the composition of these prograde lithologies, which dehydrated under open-system conditions. Serpentinite-hosted boron lost during the early stages of dehydration is readily incorporated into forearc peridotite. This, in turn, may be dragged to sub-arc depths as a result of subduction erosion and incorporated in a mélange comprising forearc serpentinite, altered oceanic crust and pelagic sediment. At the antigorite-out isograd it dehydrates, thus potentially providing an additional source of ¹¹B-rich fluids.
1. Introduction

Nominally anhydrous, melt-depleted upper oceanic mantle accommodates very low abundances of highly incompatible elements and volatiles (Salters and Stracke, 2004). Serpentinization of refractory ultramafic lithologies hydrates peridotite (Seyfried and Dibble, 1980) and dramatically increases its cargo of fluid-mobile elements (As, Sb, B, Cs, Li, Pb, U, Ba; e.g. Thompson and Melson, 1970; Bonatti et al., 1984; Benton et al., 2001; Savov et al., 2005, 2007; Deschamps et al., 2011). For example, boron is easily incorporated into serpentine phyllosilicates during serpentinization (Pabst et al., 2011) with boron concentrations increasing by up to four orders of magnitude compared to anhydrous peridotite (cf. Chaussidon and Jambon, 1994; Vils et al., 2008). Ultimately, serpentinites may be subducted at convergent margins, potentially transporting their fluid-mobile element-, halogen-, and noble gas-rich contents to sub-arc depths and beyond, hence introducing volatile-rich fluid into arc magma sources upon dehydration and potentially generating chemical and isotopic heterogeneity in the deeper convecting mantle (Scambelluri et al., 1995; Benton et al., 2001; Savov et al., 2005, 2007; Sumino et al., 2010; Kendrick et al., 2011, 2012).

Progressive dehydration of serpentinite, altered oceanic crust and pelagic sediment, caused by compaction of pore space and low temperature dehydration reactions, releases large volumes of pore fluid and structurally-bound water. An example of the consequences of this early slab-fluid out-flux can be seen in the serpentinite mud volcanoes of the modern Izu-Bonin-Mariana forearc (Fryer et al., 1985; Mottl, 1992; Fryer, 2011). Subduction-related volcanism is controlled by deeper dehydration reactions which trigger and contribute to flux-related melt generation in the overlying mantle wedge (e.g., Arculus and Powell, 1986; Hattori and Guillot, 2003). Although this melting may be initiated by the introduction of slab-
derived fluids released by high P-T metamorphic devolatilization reactions (Schmidt and
Poli, 1998), there is increasing evidence for fluid being generated by forearc serpentinite
dragged down to sub-arc depths during subduction erosion (Savov et al., 2005; Tonarini et
al., 2011; Marschall and Schumacher, 2012). Similarly, it is presently unclear whether the
fluid is released continuously over a discrete interval (Schmidt and Poli, 1998; Kerrick and
Connolly, 2001) or if it is released spasmodically in a series of pulses (Padrón-Navarta et al.,
2010, 2011; John et al., 2012; Dragovic et al., 2012; Baxter and Caddick, 2013).

Irrespective of the mechanism governing the release of fluid, or its rate of release
during dehydration, boron abundances and isotopes have been established as an excellent
tracer for processes that involve flux-related melting at convergent margins (e.g. Bebout et
al., 1993; Ryan and Langmuir, 1993; Tonarini et al., 2001). During dehydration reactions
boron preferentially partitions into the fluid phase (Seyfried et al., 1984). Because of prior
seawater-pelagic sediment interactions, boron is abundant in all of the lithologies that enter
the trenches at subduction zones. However, how pelagic sediment, altered oceanic crust, and
serpentinized peridotite (serpentinites) interact to produce the heterogeneous and somewhat
\(^{11}\)B-rich isotope signatures of arc volcanics remains equivocal. This \(^{11}\)B-rich isotope signature
of island arc volcanics, which extends to \(\delta^{11}\)B = +18 \(^\circ\) (where \(\delta^{11}\)B refers to parts per
thousand deviation in \(^{11}\)B/\(^{10}\)B from NIST951 boric acid; Cantanzano et al., 1970) (Palmer,
1991; Ishikawa and Nakamura, 1994; Ishikawa et al., 2001; Tonarini et al., 2007, 2011),
cannot be accounted for by fluid released from pelagic sediments (\(\delta^{11}\)B of <0 \(^\circ\); [B] > 100
ppm; Ishikawa and Nakamura, 1993) or altered oceanic crust (mean \(\delta^{11}\)B ±3.4 ±1 \(^\circ\); mean
[B] = 15 ppm; Smith et al., 1995). Although fluid-mineral fractionation releases fluids with
\(^{11}\)B-rich isotope signatures from these reservoirs at very shallow depths, deeper dehydration
will only yield fluids with \(^{11}\)B-poor isotope ratios (i.e. \(\delta^{11}\)B <0 \(^\circ\); You et al., 1995; Peacock
and Hervig, 1999; Benton et al., 2001; Marschall et al., 2006). Straub and Layne (2003)
suggest that a combination of altered oceanic crust and sediments is unlikely to produce a fluid, at sub-arc depths, with $\delta^{11}B$ of $> +1\%$. This is supported by the observation that not only is $^{11}B$-rich fluid released by serpentinites in the forearc (Mottl, 1992; Savov et al. 2005, 2007), but also that a distinctly $^{11}B$-poor signature remains in residual slab-hosted phengite, amphibole and epidote (Pabst et al., 2012). Seawater has a distinctive, $^{11}B$-rich isotope signature ($\delta^{11}B = +39.61 \pm 0.04 \%$; Foster et al, 2010) which is at least partially transferred to oceanic peridotite during the process of serpentinization at mid-ocean ridges (Boschi et al., 2008; Vils et al., 2009; Harvey et al., 2014), through fluid infiltration during slab bending at the outer rise of convergent margins (Ranero and Morgan, 2003; Ranero and Sallares, 2004; Faccenda et al., 2009), or through the hydration of forearc mantle overlying a slab undergoing subduction. This forearc serpentinite may be subsequently transported to sub-arc depths by subduction erosion (Hyndman and Peacock, 2003; Hattori and Guillot, 2007; Savov et al., 2007; Scambelluri and Tonarini, 2012). Even accounting for fluid-mineral fractionation under varying conditions of serpentinization, a range of $^{11}B$-rich isotope ratios are preserved in serpentinized abyssal peridotite ($\delta^{11}B = +11.4$ to $+40.7 \%$; Boschi et al., 2008; Vils et al., 2009; Harvey et al., 2014), which potentially constitutes the largest component of the boron feedstock to the subduction factory.

All island arc volcanics are enriched in boron compared to the primitive mantle (cf. Chaussidon and Jambon, 1994; Ryan and Langmuir, 1993), but the evidence for how sufficient boron with a $^{11}B$-rich signature is delivered to sub-arc depths to generate arc volcanics with $\delta^{11}B$ of up to $+18 \%$ (Tonarini et al., 2007 and references therein) is not conclusive. This is because the series of hydration-dehydration reactions en route to the deep mantle suggests that much of the boron transported by slabs should be lost before sub-arc depths are attained (e.g. Kodolányi and Pettke, 2011). The aim of this study is to examine the boron elemental and isotopic signatures of natural samples that preserve a unique antigorite-
serpentinite to prograde chlorite-harzburgite isograd in the Cerro del Almirez, southern Spain (Trommsdorff et al., 1998; Garrido et al., 2005; Padrón-Navarta et al., 2011). This unique locality makes it an excellent natural laboratory for the examination of serpentinite dehydration reactions at near sub-arc depths (680 to 710 °C and 1.6 to 1.9 GPa; Padrón-Navarta et al., 2010). This study explores the significance of dehydration reactions in down-going slabs at convergent margins and, specifically, evaluates the contribution these reactions may (or may not) make to the production of \(^{11}\)B-rich fluids implicated in arc-related volcanism. In addition, we comment on the fate of boron retained within the prograde lithologies and the likelihood that this boron may be implicated in the distinctive boron systematics observed in ocean island basalts.

2. Geological setting and sampling

The Cerro del Almirez massif is one of several lenses of ultramafic material within the upper sequences of the Nevado-Filábride Complex (Betic Cordillera Internal Zones, Southern Spain; Figure 1). It comprises c. 2-3 km\(^2\) of antigorite-serpentinite and chlorite-harzburgite separated by a narrow (c.1 metre) zone of transitional lithologies (chlorite-serpentinite and antigorite-chlorite-orthopyroxene-olivine serpentinite). The Nevado-Filábride Complex experienced extensive metamorphism as a result of the Alpine orogeny (Gómez-Pugnaire and Franz, 1988; Bakker et al., 1989; Puga et al., 1999), which peaked with the subduction of serpentinites to eclogite-facies conditions during the Middle Miocene (López Sánchez-Vizcaíno et al., 2001). The prograde transformation of antigorite-serpentinite to chlorite-harzburgite occurred between 680 to 710 °C and 1.6 to 1.9 GPa (Trommsdorff et al., 1998; Padrón-Navarta et al., 2010), where antigorite ceases to be a stable phase and dehydration results in the formation of chlorite-bearing harzburgite. The
preserved P-T conditions are therefore consistent with eclogite-facies metamorphism at a
depth of c. 50-60 km (Gerya and Yuen, 2003; Hacker et al., 2003). At Cerro del Almirez the
chlorite-bearing harzburgite can be further subdivided according to texture, i.e. (a) granofels-
texture chlorite-harzburgite with anhedral olivine and prismatic orthopyroxene (Padrón-
Navarta et al. 2011) and (b) spinifex-texture chlorite-harzburgite with arborescent olivine and
acicular orthopyroxene (e.g. Trommsdorff et al., 1998). Therefore, four distinctive Cerro del
Almirez lithologies were sampled in order to investigate the effects of dehydration associated
with eclogite-facies, subduction-related metamorphism; (i) antigorite-serpentinite, (ii) the
"transitional lithologies" (in particular, antigorite-chlorite-orthopyroxene-olivine
serpentinite), (iii) granofels-texture chlorite-harzburgite, and (iv) spinifex-texture chlorite-
harzburgite. Representative samples of each of these lithologies are illustrated in e.g. Garrido
et al. (2005), and Padrón-Navarta et al. (2011).

3. Analytical methods

Boron abundances and isotopic compositions were measured at IGG (CNR-Pisa, Italy) using a VG Isomass 54E positive ion thermal ionization mass spectrometer following
boron extraction and purification procedures described by Tonarini et al. (1997, 2003).
Briefly, following a K₂CO₃ alkali fusion, boron is extracted in ultra-pure water and purified
using standard column chemistry. Boron is loaded onto Ta filaments as caesium borate prior
to analysis by thermal ionisation mass spectrometry, where masses 309 and 310 represent ¹⁰B
and ¹¹B respectively. The ¹¹B/¹⁰B isotopic ratio is reported in standard delta notation as per
mil (‰) deviation from the mean value for the SRM951 boric acid standard (Cantanzaro et
al., 1970) routinely passed through the same chemistry as the samples. Precision and
accuracy are estimated conservatively as ± 0.64 ‰, based on replicate measurements of
reference material JB-2 (δ^{11}B = +7.25 ± 0.64 %e (2 σ), n=33 analyses with independent chemistry).

Samples analysed for bulk rock Sr isotopes and Sr abundance were spiked using a highly enriched $^{84}$Sr solution before complete dissolution in Romil UpA HNO$_3$ and UpA HF, prior to a final dissolution stage in 6M Romil UpA HCl. Strontium was extracted using Sr-Spec resin in dilute UpA HNO$_3$, before drying prior to analysis by thermal ionisation mass spectrometry (TIMS) at the University of Leeds on a Thermo Scientific Triton running in static mode. The instrumental mass fractionation was corrected for by normalizing results to $^{86}$Sr/$^{88}$Sr = 0.1194. The total Sr blank was negligible (< 100 pg) compared to the amount of material processed (typically several hundred ng Sr). The analysis of SRM 987 standard solution during the course of the measurements gave an average $^{87}$Sr/$^{86}$Sr = 0.710248 ± 4 (2σ; n=11).

4. Results

Boron and strontium isotope ratios and elemental abundances were measured in representative samples of each major lithological division (Table 1). Boron abundances range from 7 to 12 μg g$^{-1}$, significantly higher than in primitive mantle estimates (0.25 μg g$^{-1}$; Chaussidon and Jambon, 1994), but much lower than in bulk-rock serpentinites from mid-ocean ridge settings (mean [B] = 49 μg g$^{-1}$; Boschi et al., 2008; Vils et al., 2009), and mantle wedge serpentinites (mean [B] c. 20 μg g$^{-1}$; Benton et al., 2001; Savov et al., 2007; Scambelluri and Tonarini, 2012). Antigorite-serpentinite and granofels-texture chlorite-harzburgite contain the lowest boron abundances (7.03 and 7.15 μg g$^{-1}$ respectively; Figure 2), while the transitional lithologies contain the most boron (11.78 μg g$^{-1}$). Two measurements of [B] in spinifex-texture chlorite-harzburgite gave abundances of 7.59 and
Boron isotope ratios are also highly variable ($\delta^{11}B = +25.07 \pm 1.68 \text{ }^\circLambda to -3.46 \pm 0.27 \text{ }^\circLambda$). With a range of $\delta^{11}B$ from +21.61 to +25.07 $\text{ }^\circLambda$, antigorite-serpentinite is indistinguishable from $\delta^{11}B$ of serpentinites recovered from the Mid-Atlantic Ridge (Boschi et al., 2008; Vils et al., 2009; Harvey et al., 2014), and convergent margins (Benton et al., 2001; Tonarini et al., 2007; Scambelluri and Tonarini, 2012). In particular, $\delta^{11}B$ in the Cerro del Almirez serpentinites falls between the values of abyssal serpentinites from the Atlantis Massif ($\delta^{11}B = +11.38$ to +15.15 $\text{ }^\circLambda$, Boschi et al., 2008) and ODP Leg 209 (15° 20’ Fracture Zone, Mid Atlantic Ridge; $\delta^{11}B = +29.72$ to +40.66 $\text{ }^\circLambda$, Vils et al., 2009). All other lithologies have significantly lower $\delta^{11}B$ (< +6.2 $\text{ }^\circLambda$), with spinifex-texture chlorite-harzburgite ranging from +2.68 ± 0.35 $\text{ }^\circLambda$ to +6.22 ± 0.76 $\text{ }^\circLambda$, transitional lithologies having $\delta^{11}B$ of +3.38 ± 0.35 $\text{ }^\circLambda$, and granofels-texture chlorite-antigorite $\delta^{11}B$ values of -3.3 ± 0.27 $\text{ }^\circLambda$.

Strontium elemental abundance is consistently <10 $\mu$g g$^{-1}$, while $^{87}Sr/^{86}Sr$ ranges from 0.70752 ± 1 to 0.70871 ± 2, i.e. significantly more radiogenic than depleted MORB-source mantle (e.g. Pacific MORB glass mean $^{87}Sr/^{86}Sr = 0.7026$, n= 602; http://www.petdb.org; Lehnert et al., 2000) and approaching the value for modern-day seawater ($^{87}Sr/^{86}Sr = 0.70916$; Palmer and Edmond, 1989). In general, the Sr isotope ratios of the antigorite-serpentinite, the antigorite-chlorite-orthopyroxene-olivine transitional lithology, and the granofels-texture chlorite harzburgite are remarkably similar ($^{87}Sr/^{86}Sr = 0.70819 ± 1$ to 0.70871 ± 2), with this entire range being found within the antigorite-serpentinite alone. In contrast, Sr elemental abundance is variable across these lithologies. The antigorite-chlorite-orthopyroxene-olivine transitional lithology has a higher [Sr] (4.33 $\mu$g g$^{-1}$) than both the antigorite-serpentinite ([Sr] = 0.33 to 2.29 $\mu$g g$^{-1}$) and the prograde granofels-texture chlorite-harzburgite ([Sr] = 1.23 $\mu$g g$^{-1}$). Curiously, the highest [Sr] of all the lithologies is found in the prograde spinifex-texture chlorite-harzburgite ([Sr] = 5.57 to 9.50 $\mu$g g$^{-1}$) which is accompanied by a much less radiogenic Sr isotope ratio ($^{87}Sr/^{86}Sr = 0.70752 ± 1$ to 0.70763 ±
1). All of the Cerro del Almirez lithologies are significantly more radiogenic than similar serpentinites reported by e.g. Scambelluri and Tonarini (2012), where $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from 0.704584 to 0.706520, and more closely resemble Mid-Atlantic Ridge serpentinites whose $^{87}\text{Sr}/^{86}\text{Sr}$ ranges from 0.707318 to 0.70921 for both leached and unleached serpentinites (Boschi et al., 2008; Vils et al., 2009; Harvey et al., 2014). The $^{87}\text{Sr}/^{86}\text{Sr}$ of the Cerro del Almirez samples are also indistinguishable from modern day vent fluids recovered from the Logatchev hydrothermal field ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70394$ to 0.70914; Amini et al., 2008).

5. Discussion

Elements which preferentially partition into a fluid phase during dehydration will become strongly depleted in the prograde assemblage (Bebout et al., 1993) and, in the case of boron in particular, the potential exists for a strong fractionation of boron isotopes given favourable temperature and pH conditions. The drastic shift in $\delta^{11}\text{B}$ observed at Cerro del Almirez during the transformation of antigorite-serpentinite, first to the transitional lithologies, and subsequently to the chlorite-bearing harzburgites, is consistent with this prediction and the production of $^{11}\text{B}$-rich fluids. However, both boron and strontium abundances in the prograde lithologies are difficult to reconcile with a simple dehydration reaction that results in a loss of boron and strontium while fractionating boron isotope ratios. This is compounded by an unusually low loss of fluid at the antigorite-out isograd, based upon loss on ignition (LOI) values for the Cerro del Almirez lithologies (Figure 2; cf. Scambelluri et al., 2001, 2004). These observations suggest that a completely closed-system transformation from antigorite-serpentinite to chlorite-harzburgite may not have occurred. As such, it is necessary to (i) examine the nature of the protolith and (ii) confirm that the Cerro del Almirez represents an isograd in the field, i.e. ensure that the observed field relations are
not consistent with a tectonic contact, (iii) examine the degree to which the Cerro del Almirez antigorite-serpentinite to chlorite-harzburgite transition remained isochemical, i.e. a closed system during metamorphism, and (iv) quantify the effects of boron release from the downgoing antigorite-serpentinite.

5.1. The formation and composition of the antigorite-serpentinite protolith

Serpentinization of a nominally anhydrous ultramafic precursor, either at a mid-ocean ridge (e.g. Bach et al., 2004), or as a result of flexure when a lithospheric plate enters a subduction zone (e.g. Ranero et al., 2003), has the effect of transforming an olivine-pyroxene-dominated lithology into lizardite (and/or chrysotile) phyllosilicates which contain c. 12 wt. % H$_2$O (“serpentinization sensu stricto”; e.g., Miyashiro et al., 1969; Wicks and Whittaker, 1977; Komor et al., 1985; Janecky and Seyfried, 1986; O’Hanley, 1996) and develop fluid-mobile element abundances orders of magnitude higher than their anhydrous precursor. Although it can be challenging to distinguish between serpentinites derived from mantle wedge and those originating from subducted oceanic lithosphere (e.g. Hattori and Guillot, 2007; Deschamps et al., 2013), the ultramafic lithologies of Cerro del Almirez have been identified as being the result of seafloor serpentinization. This origin is supported by the ratio of SO$_4$ to total sulphur and S-D-H-O isotope signatures (Alt et al., 2012). In addition, a comparison of the trace element abundances and, in particular, the high abundances of relatively immobile heavy rare earth elements of Cerro del Almirez antigorite-serpentinites compared to subducted serpentinites (cf. Marchesi et al., 2013; Deschamps et al., 2013) illustrates that the latter is the most likely precursor lithology.

Soon after the onset of subduction, lizardite is no longer stable and will be transformed to the high(er) temperature serpentine variant, antigorite, at 200-400 °C; (Evans
et al., 1976; Ribeiro da Costa et al., 2008; Kodolányi and Pettke, 2011; Schwartz et al., 2013).

Critically, this is expected to be accompanied by B depletion (84 ± 5 %; Scambelluri et al., 2004; Savov et al., 2007; Deschamps et al., 2010; Kodolányi and Pettke, 2011; Vils et al., 2011) and a significant loss of Sr (50 ± 40 %; Kodolányi and Pettke, 2011). The Cerro del Almirez antigorite-serpentinite is indeed depleted in Sr compared to lizardite-rich abyssal peridotites, containing only around 15 % of the Sr budget of lower P-T serpentinites (Marchesi et al., 2013). Boron is also significantly depleted in the Cerro del Almirez antigorite-serpentinite. Compared to abyssal serpentinites with a mean boron concentration of 45 μg g⁻¹ (Deschamps et al., 2013) the antigorite-serpentinites of this study ([B] = 7 μg g⁻¹) have lost approximately 85 % of their B budget at the onset of subduction (Figure 3).

Abundances of Cs, U and Rb are also moderately depleted in Cerro del Almirez antigorite-serpentinites compared to mantle wedge and abyssal serpentinites (Figure 3), as suggested by their mobility in subduction zone fluids elsewhere (Savov et al., 2007).

The ⁷⁷B-rich signature of Cerro del Almirez antigorite-serpentinite (δ⁷⁷B = +22 to +25 ± 2 %o) falls within the reported range of abyssal serpentinites (δ⁷⁷B = +11.4 to +40.7; Boschi et al., 2008; Vils et al., 2009; Harvey et al., 2014). This suggests that the loss of B, during the shallow lizardite to antigorite transition, may not have been accompanied by significant fluid-mineral fractionation of B isotopes, although small amounts of fractionation are difficult to recognize, given the large range of δ⁷⁷B in abyssal serpentinites. Therefore, the δ⁷⁷B of the abyssal serpentinite protolith prior to subduction was probably retained with the formation of antigorite. This hypothesis is supported by the observation that early metamorphism during subduction occurs in the presence of a high pH fluid, which does not fractionate isotopes of boron during fluid-assisted metamorphism at c. 300 °C (Mottl et al., 1992; Savov et al., 2005, 2007; Foustoukos et al., 2008).
5.2 Metamorphic isograd versus tectonic contact

The dramatic change in $\delta^{11}$B coupled with little or no loss of boron (and even an increase in [B]) across the antigorite-out isograd isograd could be explained if the boundaries between the lithologies at Cerro del Almirez were faulted contacts rather than the result of continuous dehydration of antigorite-serpentinite (Figure 2). However, there is no field evidence to support this hypothesis, i.e. evidence for truncated structures, mylonites or cataclasis is lacking (Morten and Puga, 1984; Trommsdorff et al., 1998; Padrón-Navarta et al., 2011). In addition, the sequence of reactions and progressive changes in mineralogy observed in the field during the transition from antigorite-serpentinite, through chlorite-serpentinite and antigorite-chlorite-orthopyroxene-olivine-bearing assemblages (the transitional lithologies), to chlorite-harzburgites are consistent with the results of piston cylinder experiments designed to mimic the effects of progressive fluid loss during the dehydration of a cold slab (Padrón-Navarta et al., 2010). Increasing P-T conditions replicated the mineralogical assemblages observed on the high P-T side of the isograd using an antigorite-serpentinite starting assemblage (Padrón-Navarta et al., 2010).

Moreover, textural relationships, mineral compositions and chemographic phase relations indicate that the prograde breakdown of antigorite-serpentinite to chlorite-harzburgite occurred through a series of continuous metamorphic reactions forming the intervening transitional lithologies of the Cerro del Almirez (Padrón-Navarta et al., 2011). Although the earlier study of Trommsdorff et al. (1998) did not recognize transitional lithologies and reported a sharp contact between antigorite-serpentinite and chlorite-harzburgite (the "antigorite-out" isograd), this earlier work also came to the conclusion that the change in mineralogy observed is consistent with dehydration of an antigorite-rich precursor rather than the contrasting lithologies being juxtaposed as a result of tectonism. The
more recent observations of Padrón-Navarta et al. (2011), coupled with experimental
evidence determining the nature of the transitional lithologies, overlooked in previous studies
(Trommsdorff et al., 1998; Hürlimann, 1999; Schönbächler, 1999; Garrido et al., 2005), only
strengthens this hypothesis. Critically, the antigorite-serpentinite to chlorite-serpentinite
lithological transition is oblique to and overprints the penetrative foliation of the antigorite-
serpentinite (see Figure 4a and b in Padrón-Navarta et al., 2011). This indicates that chlorite-
serpentinite formed at the expense of a foliated antigorite-serpentinite protolith similar to
those overlying the transitional lithologies.

5.3 Open versus closed system dehydration

Major element compositions do not radically alter during dehydration (Padrón-
Navarta et al., 2011; Marchesi et al., 2013; Figure 4) and the bulk composition of the
protolith is largely preserved. However, changes in trace element abundances during the
metamorphic sequence suggest that the transformation of antigorite-serpentinite to chlorite-
harzburgite cannot have occurred as part of a closed system (Figure 5; Garrido et al., 2005;
Marchesi et al., 2013) and that the non-isochemical transformations may shed some light on
the $\delta^{11}$B systematics and boron abundances that are otherwise difficult to interpret. A large
change in $\delta^{11}$B, from $+22$ % to $+3$ %, occurs as antigorite-serpentinite transforms to the
transitional lithologies. Fluid-mineral fractionation of boron isotopes, controlled by the
temperature and the $p$H of the fluid involved is common (e.g. Boschi et al., 2008; Harvey et
al., 2014). Since the transition between these two lithologies constitutes a dehydration
reaction, it is not surprising that a sharp change in boron isotope ratios is observed between
the antigorite-serpentinite and the transitional lithologies. Indeed the release of a fluid
enriched in $^{11}$B is required to account for the $\delta^{11}$B of arc volcanics, which extend to values of
\[ \delta^{11}\text{B} \sim +18 \% \] (Tonarini et al., 2011). However, despite the likelihood of the release of a \(^{11}\text{B}\)-rich fluid, simple dehydration and the loss of a \(^{11}\text{B}\)-bearing fluid cannot account for the observed composition of the prograde lithologies.

For example, the transitional lithologies are richer in both B and Sr than the antigorite-serpentinite and differ in terms of bound H\textsubscript{2}O, represented by loss on ignition, by less than 0.5 wt %. In fact the transitional lithologies are richer in many of the incompatible trace elements compared to the antigorite-serpentinite pre-cursor (Figure 5). It is difficult to account for the shift in observed isotope ratios with little net change in the boron elemental budget and the relatively high Sr abundances observed in the transitional lithologies. Given that the transitional lithologies are relatively enriched not only in fluid-mobile elements (B, Cs, Ba, Rb, Sr), but also some high field strength elements (Nb, Ta) (Figure 3), externally derived fluids, i.e. not associated with the dehydration of antigorite-serpentinite, may have metasomatized the prograde lithologies. In other words, the B and Sr isotope signature of the prograde lithologies is unlikely to solely reflect the process of dehydration at the antigorite-out isograd. Indeed, Marchesi et al. (2013) calculated that up to 40 m\textsuperscript{3} of external fluids equilibrated with crustal sources fluxed through each cubic metre of dehydrated chlorite-harzburgite. Although elevated to levels significantly above those of other similar serpentinites (cf. Scambelluri and Tonarini, 2012), the Nb/B ratios from Cerro del Almirez are remarkably similar to those of arc lavas in general (Figure 6).

Partial equilibration with a crustally derived, Sr-rich fluid may have not only added Sr (and Nb) to a protolith that originally resembled Mid-Atlantic Ridge serpentinite (typically < 2ppm Sr, \(^{87}\text{Sr}/^{86}\text{Sr} \text{ up to 0.70921; Paulick et al., 2006; Harvey et al., 2014} \) but also affected its Sr isotope ratio. Whether or not the serpentinites of Scambelluri and Tonarini (2012) preserve \(^{87}\text{Sr}/^{86}\text{Sr} \text{ that is typical of subducted serpentinites (}^{87}\text{Sr}/^{86}\text{Sr = 0.704584 to 0.706520)} \text{ is difficult to assess, given the wide range of Sr isotope ratios preserved both at mid-ocean
ridges and in subducted serpentinites. What is clear from the study of Logatchev hydrothermal fluid by Amini et al. (2008) is that local variations in Sr isotope ratio through interaction with an externally derived fluid can vary enormously ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70394$ to $0.70914$). Furthermore, at least some of the Sr isotope signature of oceanic serpentinites is derived from an easily leachable component (Harvey et al., 2014), making the significance of the Sr isotope ratios of this study difficult to interpret in the context of closed system dehydration. An alternative explanation for the remarkable differences in incompatible trace element abundances of the prograde lithologies is that they did not share a common protolith.

However, as outlined in section 5.2 above, and explored in detail in Padon-Navarta et al. (2010) and Marchesi et al. (2013), the mineralogical changes observed in the prograde lithologies are consistent with the Cerro del Almirez antigorite serpentinite being the protolith of all of the prograde lithologies.

Given the enrichment of the prograde lithologies in high field strength elements and some of the fluid-mobile elements, and the relative loss of rare earth elements, a non-isochronal evolution to the chlorite-harzburgite lithologies also seems likely (Marchesi et al., 2013; Figures 3, 4 and 5). Moreover, the compositions of the two chlorite-harzburgite lithologies are difficult to explain through interaction with a single fluid external to the dehydration process. For example, the $^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ of the two chlorite-harzburgites differ significantly (Table 1). The granofels textured chlorite-harzburgite ($^{11}\text{B} = -3.4 \permil$; $^{87}\text{Sr}/^{86}\text{Sr} = 0.70820$) has a less $^{11}\text{B}$-rich and more radiogenic Sr isotope signature than the spinifex-texture chlorite-harzburgite ($^{11}\text{B} = +2.7$ to $+6.2 \permil$; $^{87}\text{Sr}/^{86}\text{Sr} = c. 0.7076$). The latter lithology also contains by far the most Sr of all of the lithologies analysed ([Sr] = 5.57 to 9.50 $\mu$g g$^{-1}$), which is difficult to reconcile with the observation elsewhere that Sr is lost as a result of subduction-related dehydration (e.g. Kodolányi and Pettke, 2011). This is, however, consistent with the observation of Savov et al. (2005) where changes in Sr
systematics of arc volcanics can be related to changes in fluid composition beneath the arc. The favoured models of Padrón-Navarta et al. (2011) for the formation of the different prograde lithologies (spinifex- versus granofels-texture chlorite-harzburgite) involve the pulsed release of fluids to account for their mineralogical and chemical composition, not unlike the hypothesis of Fryer et al. (2006) to account for the distribution of serpentinite muds in the modern-day Izu-Bonin-Marianas arc. The association of spinifex-texture chlorite-harzburgite with Sr and B isotope systematics that differ from the granofels-texture chlorite-harzburgite suggests that two fluids with different compositions were present. This is supported by the observations that fluids that had equilibrated with sediments (< -5 ‰; Ishikawa and Nakamura, 1993), as suggested by Marchesi et al. (2013), would possess a particularly low δ^{11}B (Tonarini et al., 2011). Indeed, more than one fluid is also required to account for the composition of modern-day Izu-Bonin-Mariana arc volcanics (Ishikawa and Tera, 1999). In summary, it would appear that while there is strong chemical and isotopic evidence for the antigorite-serpentinite retaining the characteristics of a hydrated serpentinite that passed through the lizardite-to-antigorite transition beneath the forearc, it is difficult to reconcile the B and Sr elemental and isotopic characteristics of the prograde lithologies with subduction-related dehydration alone. Either they lost the majority of their boron during metamorphism and acquired a subsequent metasomatic overprint from a fluid unrelated to subduction or, more likely, the influx of a fluid not related to antigorite breakdown was involved during fluid-assisted dehydration of antigorite-serpentinite (Ishikawa and Tera, 1999; Kodolányi and Pettke, 2011).

5.4 Slab serpentinite versus entrained forearc serpentinite as a source of the δ^{11}B signature of arc volcanics
Notwithstanding the uncertainty of the source of the B and Sr elemental and isotopic signatures of the prograde lithologies at Cerro del Almirez, the composition of the antigorite-serpentinite prior to subduction-related dehydration provides valuable information regarding the cargo of fluid mobile elements going into the dehydration reaction and, critically, their capacity for contributing to the distinctive signature of arc volcanics. However, portions of serpentinized forearc wedge can also be transported to similar depths as the Cerro del Almirez antigorite-serpentinites through subduction erosion (e.g. Tonarini et al., 2011; Marschall and Schumacher, 2012; Scambelluri and Tonarini, 2012), and this forearc wedge has the capacity to carry a large cargo of B with a high and variable $\delta^{11}$B, acquired during the addition of fluid mobile elements in the forearc (Benton et al., 2001; Savov et al. 2005, 2007; Pabst et al., 2011; Kodolányi and Pettke, 2011). Thus, instead of its derivation from the dehydration of a subducting slab, an alternative means for the delivery of $^{11}$B-rich fluid to the sub-arc portion of the mantle wedge may come from forearc serpentinites entrained during subduction erosion. If $85 \pm 5 \%$ of the original boron cargo of a portion of subducted serpentinite is lost during the transition from lizardite- to antigorite-serpentinite (Savov et al., 2007; Kodolányi and Pettke, 2011; this study), the vast majority of boron available for transfer at depth into the source region of arc volcanics has already been lost from the slab and most likely transferred into this shallow part of the overlying mantle wedge.

The recent comprehensive review of subducted serpentinites by Deschamps et al. (2013) demonstrates that there is a large degree of scatter in the available data from individual tectonic settings. However, despite these limitations, the boron abundance and isotopic characteristics of Cerro del Almirez lithologies (Scambelluri et al., 2004; this study) represent those of the only known antigorite-serpentinite at the cusp of dehydration, i.e. immediately adjacent to the antigorite-out isograd. Its categorization as a portion of subducted slab (Alt et al., 2012; Marchesi et al., 2013) places it beneath the subduction
channel (Gerya et al., 2002; King et al., 2003) during active subduction. On the other hand, 
serpentinite mud and clasts recovered during Ocean Drilling Program Legs 125 and 195 from 
the modern Izu-Bonin-Mariana forearc (Benton et al., 2001) represent modern day forearc 
serpentinites, hydrated during the early dehydration of abyssal peridotites, altered oceanic 
crust and pelagic sediments, which have been entrained by the down-going slab and 
subsequently exhumed along the subduction channel (e.g. Savov et al., 2005, 2007, Pabst et 
al., 2012). Using these end-members a quantitative assessment of the relative contribution to 
the boron budget of arc volcanoes from the slab versus fore-arc serpentinite can be attempted. 

Island arc basalts have a wide range of boron isotope values ($^{11}$B up to +18 %) and 
boron abundances ([B] up to 90 µg g$^{-1}$, but more typically c. 15 µg g$^{-1}$; Ryan and Langmuir, 
1993; Tonarini et al., 2007, 2011). A mantle wedge domain that melts to produce island arc 
basalt must have similar isotopic characteristics to the melt it produces, since isotope ratios 
are barely fractionated at magmatic temperatures. Transfer of boron to the mantle wedge as a 
result of dehydration, followed by a simple batch melting calculation can be employed to 
ascertain whether the boron budget of the Cerro del Almirez antigorite-serpentinite is capable 
of providing an adequate feedstock of fluid-mobile boron into the overlying mantle wedge, 
that will subsequently be incorporated into island arc basalts. The boron abundance of the 
antigorite-serpentinite in this study is 7 µg g$^{-1}$, and using the experimentally determined fluid 
/residue partition coefficient of Tenthorey and Herman (2004), i.e. D = 4, it can be assumed 
that 80 % of the boron content of the antigorite-serpentinite will be lost during dehydration; 
the remaining 20 % being retained in the down-going prograde assemblage. Fluid loss as a 
result of the production of the transitional lithologies and prograde assemblages at the 
expense of antigorite-serpentinite is between 2.8 and 3.3 weight % (Marchesi et al., 2013). 
The fluid produced has a B/H$\text{O}_2$ ratio of $2.5 \times 10^{-5}$ to $4.2 \times 10^{-5}$. As boron and water are 
almost perfectly incompatible during partial melting of the mantle (Brenan et al., 1998) this
ratio is expected to be preserved when the mantle wedge undergoes partial melting (assuming that both its boron and water contents were negligible to start with). Using \( C_1 = C_0/[D-F(1-D)] \), where \( C_1 \) is the [B] in the melt produced, \( C_0 \) is the [B] lost from Cerro del Almirez antigorite-serpentinite during dehydration i.e., 5.6 \( \mu \)g g\(^{-1}\) (80 % of the 7 \( \mu \)g g\(^{-1}\) abundance measured in the antigorite-serpentinite) and provides the boron feedstock for any subsequent melting, \( D \) is the bulk rock partition coefficient during partial melting (\( D_B^{\text{bulk rock/melt}} = 0.003 \) to 0.02; Brenan et al., 1998) and \( F \) is the fraction of partial melting (15 to 30 % melt production in arc settings; Pearce and Parkinson, 1993) will yield [B] in island arc volcanics of 18 to 37 \( \mu \)g g\(^{-1}\), i.e. well within the range of [B] observed at actual island arc settings. However, several assumptions need to be made for this calculation to be valid. First of all, the mantle wedge protolith (i.e. pre-hydration) has a composition resembling asthenospheric mantle \( (\delta^{11}B = -10 \%); \) Chaussidon & Marty, 1995; [B] 0.25 \( \mu \)g g\(^{-1}\); Chaussidon & Jambon, 1994), i.e. a composition that is instantly overprinted by the first influx of boron-rich fluid with a high \( ^{11}B \) content. Secondly, this assumes that all of the boron lost from antigorite-serpentinite at the antigorite-out isograd is transferred to the overlying mantle wedge. This is difficult to assess quantitatively as the prograde lithologies from this study are assumed to have metamorphosed under open-system conditions, i.e. it is not possible to determine what proportion, if any, of the original boron budget was actually retained at the isograd and what was added under open-system conditions, although the use of the experimentally determined fluid / residue partition coefficient of Tenthorey and Hermann (2004) does allow this to be at least partially constrained. Finally, it assumes that there is a constant-rate loss of boron from the mantle wedge through the production of melt (constant volcanic output at arc fronts) and steady-state supply of boron to the mantle wedge (constant rate of subduction of uniformly serpentinized material), i.e. there is no opportunity for boron either to be completely exhausted from the mantle wedge undergoing partial melting, or to accumulate to such
extents that boron concentrations can become particularly enhanced during a period of magmatic quiescence.

While some of these assumptions are not critical to the overall result of the calculation, others do have an effect on the range of compositions of arc magmas. The transfer of the boron cargo from Cerro del Almirez antigorite-serpentinite to arc basalts, first by dehydration and then by melting does not replicate the entire range of [B] observed in arc volcanics. However, mean subducted serpentinite (Deschamps et al., 2013) has a [B] of c. 23 μg g⁻¹, and using this value in the simple batch melting calculation produces a range of B concentrations of 59 to 121 μg g⁻¹, which easily encompasses the upper range of [B] observed at island arcs. The almost perfect incompatibility of boron during fractional crystallization will also ensure that magmatic differentiation further concentrates B in the remaining melt (Tonarini et al., 2011). Moreover, B/H₂O remains invariant during the partial melting of hydrated mantle wedge. This is supported by the observation that the calculated B/H₂O ratios for fluid released from Cerro del Almirez are indistinguishable from the composition of island arc-derived melt inclusions (modified MORB source melt inclusions, Bouvier et al., 2008). Finally, binary mixing of serpentine-derived fluid with fluid in equilibrium with marine sediments (mean δ¹¹B = -4 ‰, mean [B] = 115 μg g⁻¹; Ishikawa and Nakamura, 1993), would be able to account for the full compositional range of island arc volcanics presented in previous studies (e.g. Ryan and Langmuir, 1993; Tonarini et al., 2007, 2011; Scambelluri and Tonarini, 2012) and is also consistent with the hypothesis of Ishikawa and Tera (1999) that requires two distinctly different fluids to account for many island arc compositions.

However, fluid produced by dehydration in the slab must cross the subduction channel (Gerya et al., 2002; King et al., 2003) before it reaches the overlying mantle wedge. An alternative hypothesis for the source of fluid delivered to the arc magma source region is
serpentinite / altered oceanic crust / marine sediment mélanges dragged to comparable depths to the antigorite-out isograd through subduction erosion, along the subduction channel, directly above the subducting slab (Savov et al., 2007; Marschall and Schumacher, 2012). The combination of this mélange and abundant chlorite ± actinolite-schist (Ukar, 2012; Ukar et al., 2012), produced from the intimate association of ultramafic and mafic lithologies, contains as much fluid as the down-going slab itself (Spandler et al., 2008; Pabst et al., 2012; Marschall and Schumacher, 2012). This assemblage is also likely to be boron-rich; Deschamps et al. (2013) report [B] for mantle wedge serpentinites of 22 to 72 μg g⁻¹. Moreover, a mélange contains all of the hydrated lithologies required to fulfil the requirements of the two-fluid hypothesis of Ishikawa and Tera (1999). As demonstrated by the calculations above, the supply of all of the fluid from both the dehydrating slab and the overlying mélange is not required to account for the composition of island arc basalts. There is sufficient availability and mobility of B in either reservoir for the reproduction of the typical range of compositions measured in arc basalts. Accordingly, the basalts may result from either dehydration of mélange overlying the down-going slab, the down-going slab itself, or a combination of the two. Given that the slab is separated from the mantle wedge by the mélange and strongly foliated chlorite-schist that bounds the subduction channel (Marschall and Schumacher, 2012), the passage of slab-derived fluid may be impeded, but the exact provenance of the fluid responsible for enriching mantle wedge, i.e. the source of island arc fluid-mobile element budgets, remains equivocal.

5.5 The fate of boron in prograde lithologies – asthenospheric heterogeneity?

Irrespective of the exact mechanism of antigorite-serpentinite dehydration, i.e. open-versus closed-system, the overall result of the antigorite-serpentinite to chlorite-harzburgite
transition is incomplete dehydration, i.e. 5 to 6 wt. % of H₂O remains in the prograde lithologies at Cerro del Almirez (Padrón-Navarta et al., 2011). This means that the potential exists for the delivery of volatiles (Kendrick et al., 2011), boron and other fluid-mobile elements (and a wide range of other variably mobile elements; Morris and Ryan, 2003) to much greater depths than those associated with flux melting of sub-arc mantle wedge. While hydrous chlorite may be abundant (exceptionally, up to 20 modal %) in the Cerro del Almirez prograde assemblage (Alt et al., 2012), the contribution to the boron budget from chlorite is low compared to other phases (chlorite mean [B] = 5 μg g⁻¹, Scambelluri et al., 2004; Pabst et al., 2012; Figure 7), e.g. prograde olivine, present as at least 40 modal % in harzburgite, by definition (mean prograde olivine [B] = 38 μg g⁻¹, Scambelluri et al., 2004; Figure 7). Brine-rich fluid inclusions, abundant in brown and colourless prograde olivine (Scambelluri et al., 2004; Padrón-Navarta et al., 2011), are the dominant hosts of B in the prograde assemblage, with B abundances up to two orders of magnitude greater than that of chlorite (Figure 7). If the prograde lithologies sampled at Cerro del Almirez survive further dehydration beneath and beyond the arc - prograde olivine is an anhydrous phase (notwithstanding its fluid-inclusion content) - it is possible that peridotite that is significantly enriched in boron, and with a heterogeneous δ¹¹B may be returned to the convecting mantle. This in turn may have implications for the generation of the wide range of compositions observed in ocean island basalts.

6. Concluding remarks

The prograde lithologies on the high P-T side of the antigorite-out isograd at Cerro del Almirez are complex and likely preserve evidence not only for the dehydration of antigorite-serpentinite but also the flux of fluids partially equilibrated with pelagic sediment.
Notwithstanding the complexities of the prograde lithologies, the antigorite-serpentinite on the low P-T side of the antigorite-out isograd appears to preserve the composition of subducted serpentinite prior to dehydration at pressures and temperatures of 1.6 to 1.9 GPa and 680 to 710 °C. This allows a quantitative assessment of the possibility that slab-hosted antigorite-serpentinite is a significant source of fluid-mobile elements delivered to the overlying mantle wedge, which are subsequently incorporated in island arc volcanics. Assuming the removal of 80% of the boron from the antigorite-serpentinite at the antigorite-out isograd, and its transfer into the overlying mantle wedge, subsequent partial melting of this boron-enriched reservoir is capable of producing the range of boron abundances observed in island arcs. With the influence of pelagic sediments, or fluids derived from them, the full range of isotopic and elemental characteristics of island arc basalts can be produced with simple batch melting and mixing calculations. However, the dehydrating slab is separated from the overlying wedge by the subduction channel and possibly mélange, comprising serpentinite eroded from the fore-arc (dragged to the antigorite-out isograd during subduction erosion), altered oceanic crust, and pelagic sediment. The boron elemental flux and isotopic signature of such a mélange should not differ significantly from that of slab derived fluids and, as such, may also constitute a source of fluids which hydrate the overlying mantle wedge and form the source for island arc basalts. Distinguishing between these two sources of fluids (slab versus mélange) remains problematic.

The prograde lithologies on the high P-T side of the antigorite-out isograd have much lower δ^{11}B signatures but still contain a comparable cargo of boron to antigorite-serpentinite. This is because they have at least partly equilibrated with pelagic sediment-derived fluids. The preservation, in the prograde lithologies, of boron in olivine-hosted fluid inclusions allows the transport of boron, with a higher δ^{11}B than primitive mantle, to depths below that of the source of island arc magmatism. Thus, the prograde lithologies possibly provide a
component, enriched in boron by at least an order of magnitude relative to primitive mantle, capable of contributing to the observed boron isotope heterogeneity in ocean island basalts.

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**Figure captions**

Figure 1. (a) Simplified geological map showing the main tectono-metamorphic domains of the Betic Cordillera. (b) Main tectonic and lithological units of the Nevado–Filábride Complex and location of the Cerro del Almirez (inset) together with other smaller ultramafic bodies cropping out in this complex. (c) Geological map of the Cerro del Almirez (modified from Padrón-Navarta et al., 2011).

Figure 2. Field relationships between antigorite-serpentinite, transitional lithologies, and chlorite-harzburgite, and their modal variations (modified after Padrón-Navarta et al., 2011). Boron and strontium abundances ([B]) expressed in µg g⁻¹. $\delta^{11}B = \{[(^{11}B/^{10}B_{\text{sample}}) / (^{11}B/^{10}B_{\text{NIST-SRM951}}) - 1] \times 1000\}$. Loss on ignition (LOI) expressed in weight % H₂O.

Figure 3. Mean fluid-mobile and high field-strength element abundances in Cerro del Almirez antigorite-serpentinite (data from Marchesi et al., 2013 with the exception of boron abundances) normalized to mean abyssal serpentinite and mean mantle wedge serpentinite (Deschamps et al., 2013).
Figure 4. Relative major element abundances in prograde lithologies from Cerro del Almirez, normalized to Cerro del Almirez antigorite-serpentinite (major element abundances from Marchesi et al., 2013).

Figure 5. Relative mean trace element abundances in prograde lithologies from Cerro del Almirez, normalized to Cerro del Almirez antigorite-serpentinite (trace element abundances from Marchesi et al., 2013).

Figure 6. $\delta^{11}$B versus Nb/B for Cerro del Almirez lithologies (unless stated symbols are the same as previous Figures). Elevated Nb/B at Cerro del Almirez are comparable to the ratios seen in arc lavas in general (diagonal shaded field). The antigorite-serpentinite however (white square) appears to have $\delta^{11}$B and Nb/B that closely resembles the values obtained for arc magmas of the South Sandwich Arc (dotted field; Tonarini et al., 2011). Redrawn after Scambelluri et al. (2012).

Figure 7. (a) Boron isotope ratios and (b) boron elemental abundances of Cerro del Almirez serpentinites and harzburgites compared to common mafic / ultramafic lithologies and their constituent minerals (Literature values from Palmer, 1991; Ishikawa and Nakamura, 1994; Ishikawa and Tera, 1997, 1999; Benton et al., 2001; Ishikawa et al 2001; Tonarini et al., 2001, 2007, 2011; Leeman et al., 2004; Scambelluri et al., 2004 (which includes representative prograde lithologies from Cerro del Almirez); Agranier et al., 2007; Vils et al., 2008, 2009; Boschi et al., 2008; Deschamps et al., 2010, 2012; Pabst et al., 2011; Scambelluri and Tonarini, 2012).
Figure

Neogene Cover

Upper metamorphic complexes
Malague complex
Alpujarride complex

Nevado-Filábride complex
Mulhacén unit
Marble
Marble and calcschist
Atg-serpentinite
Chl-harzburgite
Tahal schist
Montenegro dark schist

Veleta unit
Quartzite
Dark schist

Cerro del Almirez
Cerro del Almirez antigorite-serpentinite normalized to global mean serpentinite lithologies
Figure
Figure 2.
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<th>$^{87}$Sr/$^{86}$Sr</th>
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Table 1. Boron and strontium elemental abundance and isotope ratios of ultramafic rocks from the Cerro del Almirez. * = duplicate analysis, # triplicate analysis. $\delta^{11}$B expressed in %, elemental abundances expressed in $\mu g\ g^{-1}$. Sample localities for AL95-24, AL95-29 and AL96-17-1 can
be found in Figure 1A of Garrido et al. (2005). Location of samples ALO8-14 and ALO8-16 are 308 507457 4104646 and 308 507639 410481 respectively, using the ED50 co-ordinate system (European datum 1950), UTM.