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# Compositional variability in mafic arc magmas over short spatial and temporal scales: Evidence for the signature of mantle reactive melt channels



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#### ABSTRACT

Understanding arc magma genesis is critical to deciphering the construction of continental crust, understanding the relationship between plutonic and volcanic rocks, and for assessing volcanic hazards. Arc magma genesis is complex. Interpreting the underlying causes of major and trace element diversity in erupted magmas is challenging and often non-unique. To navigate this complexity mafic magma diversity is investigated using sample suites that span short temporal and spatial scales. These constraints allow us to evaluate models of arc magma genesis and their geochemical implications based on physical arguments and recent model results. Young volcanic deposits (\$\leq 18 \text{ kyr}) are analysed from the Southern Volcanic Zone (SVZ), Chile, in particular suites of scoria cones on the flanks of arc stratovolcanoes that have erupted relatively primitive magmas of diverse compositions. Our study is centred on the high-resolution post-glacial tephrochronological record for Mocho-Choshuenco volcano where tight age constraints and a high density of scoria cones provide a spatially well-resolved mafic magma dataset. Two compositional trends emerge from the data. Firstly, magmas from cones on the flanks of the main edifice become more mafic with distance from the central vent. This is attributed to fractional crystallisation processes within the crust, with distal cones sampling less differentiated magmas. Secondly, there is a set of cones with distinct major and trace element compositions that are more primitive but enriched in incompatible elements relative to the central system and other 'normal SVZ' magmas. This distinct signature - termed the 'Kangechi' signature - is observed at three further clusters of cones within the SVZ. This is attributed to greater preservation of the enriched melt signature arising from reactive melt transport within the mantle wedge. Our model has important implications for arc magma genesis in general, and in particular for the spatial and temporal scales over which compositional variations are preserved in erupted magmas. © 2016 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

# 1. Introduction

Mafic magmas are critically important for our understanding of arc magma genesis. In arc settings it is widely agreed that mantle melting is dominated by flux melting due to the release of volatile-rich fluids and/or melts from the subducting slab (e.g., Elliott et al., 1997; Grove et al., 2012; Spandler and Pirard, 2013). These melts differentiate and interact with the mantle and crust as they ascend to the surface. Major volcanic centres have a characteristic spacing of order 10–100 km along-arc. As there

is no particular reason why this pattern should reflect the locus of primary melt production along the slab or within the mantle wedge, it has long been assumed that some melt transport processes must be responsible for focussing melt into these major crustal processing systems (Spiegelman and McKenzie, 1987; Wilson et al., 2014). All the processes that occur between the slab and surface affect the geochemical signature of the magma; however, their respective roles and relative importance in causing the chemical diversity observed in erupted magmas remain largely unresolved.

Ideas regarding the origins of the chemical diversity in mafic arc magmas can be broadly grouped into three sets of hypotheses. These are that diversity in magma composition (i) is gener-

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ated during ascent, degassing and differentiation (e.g., Hildreth and Moorbath, 1988; Annen et al., 2006), (ii) is inherited from compositional variations in mantle source occurring either in space or time, for example changes in slab inputs (e.g., Plank and Langmuir, 1988; Watt et al., 2013; Turner and Langmuir, 2015a, 2015b), and/or (iii) emerges as a consequence of channelised melt transport in the mantle wedge (e.g., Kelemen et al., 1997; Reiners, 1998).

Hypotheses (i) and (ii) are well-established in the literature (e.g., McCulloch and Gamble, 1991; Peacock et al., 1994; Plank and Langmuir, 1988; Wallace and Carmichael, 1999; Elliott, 2003; Grove et al., 2006). Hypothesis (iii) has mainly been discussed in the context of decompression melting at mid ocean ridges (e.g., McKenzie, 1985; Kelemen et al., 1995, 1997; Spiegelman and Kelemen, 2003; Katz et al., 2004; Keller and Katz, 2016). Hence, there is some uncertainty in applying this concept to arc settings. Recent models of magma/mantle dynamics (e.g., Spiegelman and Kelemen, 2003; Hewitt, 2010; Katz and Weatherley, 2012; Keller and Katz, 2016) suggest that geochemical consequences of channelised melt transport in the mantle wedge may be more important than previously understood.

The physical mode of melt transport significantly influences the way melts are generated and how they physically and chemically interact with the mantle. These dynamic processes can thus control both the type of compositional variations emerging in a magmatic system as well as the distances over which such variations are preserved. Recent work has shown that volatile-flux melting may cause strongly channelised melt transport in an upwelling mantle column (Keller and Katz, 2016). Flux of a volatile-rich liguid enhances partial melting of peridotite. Melt produced by such flux melting increases the local mantle permeability, thus facilitating faster rates of volatile-flux, which cause even more melting. This reaction-transport feedback known as the Reactive Infiltration Instability (see references in Keller and Katz, 2016) leads to channelised melt transport in the mantle wedge. Such reactive channelling causes significant lateral variability in melt composition, with low-degree incompatible-enriched melts arising in the centre, and high-degree depleted melts on the periphery of channels (Spiegelman and Kelemen, 2003). This process has particular relevance in arc settings, where water-flux melting from slab dehydration is a dominant source of magma generation in the mantle wedge.

Magmas erupted at arc volcanoes are chemically and isotopically diverse across a range of temporal and spatial scales (e.g., Carr et al., 1990; Stern, 2004; Ramos and Kay, 1992; Druitt et al., 1999; Gertisser and Keller, 2003; Ripepe et al., 2005; Singer et al., 2008; Watt et al., 2013; Jacques et al., 2014; Turner and Langmuir, 2015a, 2015b; Rawson et al., 2016). Interpretations of the origin of this diversity are often non-unique when using solely geochemical arguments. However, if samples of materials on appropriate spatial and temporal scales are used physical arguments can be additionally applied. For example, investigating along-arc or across-arc variations using samples erupted over short timescales (e.g., less than tens of millennia) removes some potential drivers which operate on much longer timescales, such as changing regional stress fields or long-term variations in slab parameters. However, many prior studies of arc-scale or global trends have used limited datasets that have poorly constrained chronology and spatial relationships (e.g., Hildreth and Moorbath, 1988; Plank and Langmuir, 1988; Jacques et al., 2014). This can lead to potential biases in the data, including underestimating the full magma diversity at a single volcanic centre; over-emphasising the volumetric significance of geochemical variability; and confusing spatial trends for temporal trends.

Here, we focus on a region where mafic magma diversity is seen over short temporal ( $\sim$ 1 kyr) and spatial (1–10 km)

scales. Our particular focus is on the mafic products of post-glacial ( $\lesssim$ 18 kyr) eruptions from the Mocho-Choshuenco Volcanic Complex ( $40^{\circ}$ S,  $72^{\circ}$ W), in the Southern Volcanic Zone of Chile ( $33.3^{\circ}$ S- $46^{\circ}$ S; SVZ: Fig. 1). Mocho-Choshuenco is a large, late Quaternary (<350 kyr) stratovolcano that has erupted melts of basaltic-andesite to rhyolite composition in post-glacial times (Rawson et al., 2015). The central part of the SVZ ( $37^{\circ}$ S- $45^{\circ}$ S) is an ideal case study since the regional tectonics and arc inputs are relatively invariant along strike and typical for an arc setting. The subduction angle (20- $30^{\circ}$ ), dip (25- $35^{\circ}$ ), convergence rate (7-9 cm/yr), sediment thickness, sediment lithology and crustal thicknesses ( $\sim$ 35 km) are all spatially quasi-uniform (e.g. Stern, 2004; Syracuse and Abers, 2006; Lucassen et al., 2010). This setting allows us to reduce the number of potential physical and chemical variables that could control observed mafic magma diversity.

Mocho-Choshuenco has a high number and density of mafic cones ( $\sim$ 40 scoria cones, situated up to  $\sim$ 15 km from the central vent), which have erupted relatively primitive but compositionally diverse magmas. This spatially well-resolved sample set has the potential to reveal km-scale melt compositional variability – a signal that is otherwise easily overlooked. A high-resolution post-glacial tephrochronological record for Mocho-Choshuenco additionally provides tight age constraints for the deposits, all of which have erupted within the last 18 kyr (Rawson et al., 2015).

### 2. Methods and samples

Whole-rock major and trace element analyses were carried out on a suite of 120 post-glacial tephra samples from Mocho-Choshuenco, including 44 scoria cone samples. Major elements were analysed by X-ray fluorescence spectrometry (XRF) at the Department of Geology, University of Leicester, and trace elements by Inductively Coupled Plasma-Mass Spectrometry on a Thermo Finnigan Element 2 Sector-Field instrument at the Department of Earth Sciences, University of Oxford. See Supplementary Material for the detailed methodology and full set of analyses.

To capture the compositional range of the broader SVZ we compiled whole-rock data from the literature, and augmented this by analysing 109 additional samples (method as above) from Llaima, the Caburgua-Huelemolle Small Eruptive Centers (CHSEC), Villarrica, Quetrupillan, Puyehue-Cordón Caulle, Casablanca, Osorno and Huanguihue. We only compiled/analysed samples known to have erupted in post-glacial times (\$18 kyr) and from volcanic centres between 37°S and 45°S. Volcanoes within the Northern and Transitional segments of the SVZ (33.3°S to 37°S) are excluded due to the thicker continental crust in that part of the arc, which may impart a stronger crustal signature to the magmas (e.g., Hildreth and Moorbath, 1988). Volcanoes south of 45°S are excluded because of the potential influence of the Chile Rise, an oceanic ridge that marks the boundary between the Nazca and Antarctic Plates (e.g., Gutiérrez et al., 2005). We refer to this filtered dataset as 'SVZ' hereafter.

Within this SVZ dataset we distinguish deposits within three volcanic groups for further discussion: the Puyuhuapi volcanic group; the CHSEC ca. 20–35 km north-east of Villarrica and the peripheral cones within the Carrán-Los Venados volcanic field (Fig. 1). The Puyuhuapi volcanic group is a chain of Holocene basaltic cinder cones (44°18′S, 72°32′W; about 500 km south of Mocho-Choshuenco). These cones were constructed on two NE-SW trending fissures, each with four associated cones (e.g., Lahsen et al., 1994). The CHSEC (~39°30′S, 71°50′W; 60 km north of Mocho-Choshuenco) field comprises small scoria cones and associated flows of probable post-glacial age (Fontijn et al., 2016 described an event from CHSEC at 10.38 ± 0.04 cal ka BP). The cones are grouped into five clusters and three individual centres: Huelemolle, Cordillera Cañi, Caburgua, La Barda and Relicura and the

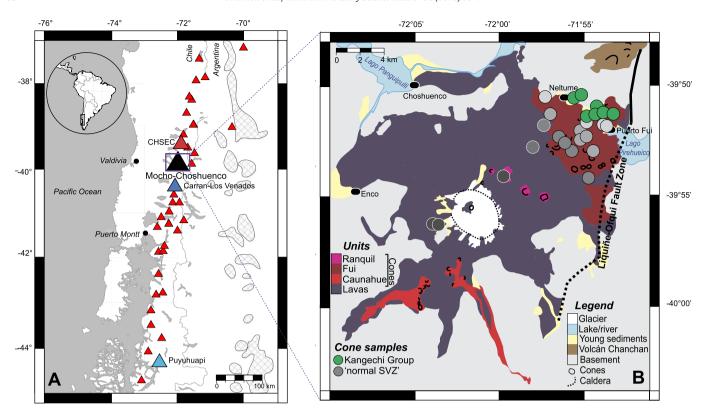


Fig. 1. A: Map of the Southern Volcanic Zone (SVZ). Volcanoes that have been active during the Holocene are marked with red triangles. Mocho-Choshuenco is marked with a black triangle, Puyuhuapi with a blue triangle, Carrán-Los Venados with a dark blue triangle, Caburgua-Huelemolle Small Eruptive Centers (CHSEC) with a larger red triangle; these are the volcanic centers where the unusual melt composition (Kangechi) is observed. Back-arc activity is shaded with cross-hatching and adapted from Kay et al. (2013). B: Simplified geological map of Mocho-Choshuenco adapted from Moreno and Lara (2007). Cone samples are marked with a circle. These are shaded by distance from the central vent; dark grey samples are closer to the central vent. The Kangechi cones are shaded in green. Previous work subdivided the cones into three geographical groups, which are marked on the figure: Fui (burgundy, ca. 20 cones to the north-east and east of the edifice), Caunahue (red, ca. 13 cones on the south-west flank) and Ranquil (pink, 4 cones on the north-east flank) (Moreno and Lara, 2007). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

single cones of Cañi, Redondo and San Jorge (Hickey-Vargas et al., 1989, 2016; Morgado et al., 2015). All of these cones, except San Jorge, are distinguished for further discussion. Carrán-Los Venados is a cluster of 65 scoria cones and maars. Within this volcanic field one cluster of three cones, called Medialuna, is distinguished; these cones are situated on the eastern edge of the field and are thought to have formed at  $0.61 \pm 0.03$  cal ka BP (Bucchi et al., 2015). To assess how crustal contamination may influence magma composition we also compiled unpublished whole rock data on basement samples taken in the region around Mocho-Choshuenco (Echegaray, 2004). Although the precise location of these samples is not available they are considered representative of the major upper crustal basement lithologies found within  $\sim$ 20 km of the volcanic complex (Moreno and Lara, 2007).

### 3. Results

Fig. 2 shows selected major and trace element compositional variation diagrams of SVZ samples. On these diagrams there is a distinct cluster of samples that, despite their wide spatial separation, share similarities with each other. They are enriched in incompatible elements and have elevated Ce/Pb, La/Yb, Dy/Yb, P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O and lower U/Th and Zr/Nb compared to other SVZ samples. Hereafter, we refer to deposits with these signatures as 'Kangechi' (a Mapuche word, meaning in 'another way' or 'of a different form') and volcanic centres without these signatures as 'normal SVZ'. In Fig. 2 we distinguish seven groups: the compiled SVZ data (between 37°S and 45°S); deposits from the Mocho-Choshuenco central vent; Mocho-Choshuenco scoria

cones in general; one chemically-distinct cluster of scoria cones at Mocho-Choshuenco; the Puyuhuapi Volcanic Group; the CHSEC cones (not including San Jorge) and the Medialuna cones within the Carrán-Los Venados volcanic field. The latter four groups have the defined 'Kangechi' signature, described above which is distinct from the normal SVZ trend. Products with a similar Kangechi signature have been recognised at the Tatara-San Pedro Complex, Chile, (36°S) within the basaltic-andesite lavas of the Lower Volcán Tatara episode (Dungan et al., 2001). However, these deposits are not considered in this study as they are both older (~130–60 kyr; Dungan et al., 2001) and outside our study area.

### 3.1. Mocho-Choshuenco case study

As discussed above young mafic magmas with the distinctive Kangechi signature are found along the SVZ. At the Mocho-Choshuenco Volcanic Complex (40°S) both normal SVZ and Kangechi signatures are observed in close proximity (<1 km between cones and <15 km from the central vent: Fig. 1). The tephrostratigraphic record implies that eruptions of normal SVZ compositions have occurred on average every ~220 yr in postglacial times at Mocho-Choshuenco ( $\lesssim$ 18 kyr; from both the central vent and flank cones). At Mocho-Choshuenco, tephra deposits with the Kangechi signature are recognised in the post-glacial records from 13.5 cal. ka BP to 1.7–1.2 cal. ka BP, and are interbedded with tephra of normal SVZ composition (Rawson et al., 2015), implying that these chemically distinct magmas were erupted effectively contemporaneously (i.e., within 500 yrs).

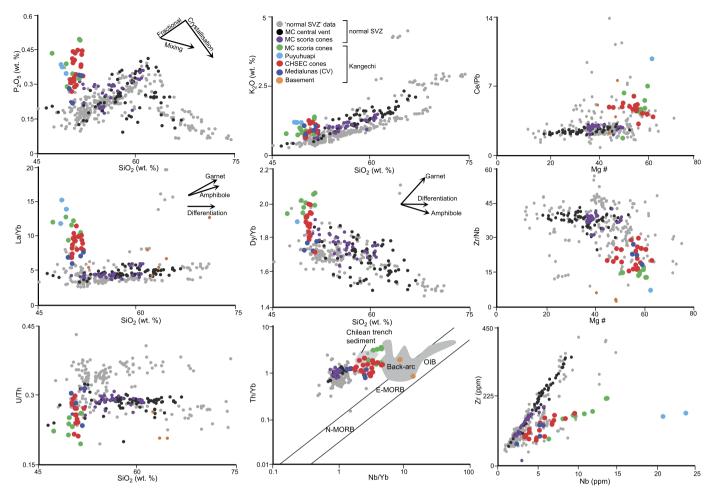


Fig. 2. Whole rock major and trace element compositions of Mocho-Choshuenco deposits compared to other volcanoes within the SVZ (López-Escobar and Moreno, 1981; Hickey-Vargas et al., 1989; López-Escobar et al., 1993, 1995; Naranjo and Stern, 2004; Witter et al., 2004; Echegaray, 2004; Singer et al., 2008; Costantini et al., 2011; Reubi et al., 2011; Watt et al., 2011; De Maisonneuve et al., 2012; Lohmar et al., 2012; Jacques et al., 2014; Schindlbeck et al., 2014; Bucchi et al., 2015; Morgado et al., 2015). Graphs illustrate how the normal SVZ cones (purple) and central vent (black) deposits from Mocho-Choshuenco plot in the same field as most samples from other volcanoes within the SVZ. The Kangechi composition at Mocho-Choshuenco (green) is different to the main SVZ trend and is similar to the composition of the Puyuhuapi cones (blues), Caburgua-Huelemolle Small Eruptive Centers (CHSEC; red) and Medialuna cones from the Carrán-Los Venados field (dark blue; locations marked in Fig. 1). Country rock samples (orange; Echegaray, 2004) are also included. On the Th/Yb vs. Nb/Yb plot (after Pearce, 2008), the back-arc and Chilean trench sediments are defined from Jacques et al. (2014) and Lucassen et al. (2010). Crystallisation vectors emerge from the most primitive normal SVZ samples. Trace element errors are approximately 10% of the measurement. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The 40 scoria cones at Mocho-Choshuenco form chains that are aligned predominantly northeast–southwest (Fig. 1B) with the Liquiñe-Ofqui Fault Zone (LOFZ) marking the north-east limit of the cones. Scoria cones have basal diameters of up to 1250 m, heights of 150–250 m, crater diameters of 200–750 m and comprise black–red scoria of fine-lapilli to bombs that are up to 2 m across. Both the Kangechi and normal SVZ ejecta have rare phenocrysts of plagioclase, olivine  $\pm$  orthopyroxene  $\pm$  clinopyroxene  $\pm$  Fe–Ti oxides. The groundmass is very rich in microlites, with the same crystal phases as the phenocrysts, and only small areas (<5  $\mu$ m) of fresh glass (Fig. 3). Microlites and phenocrysts are rarely euhedral, and the Fe–Ti oxides have highly irregular edges. Zoning is rare and only observed in some olivine phenocrysts and pyroxene microlites, which preserve a thin, but distinct rim.

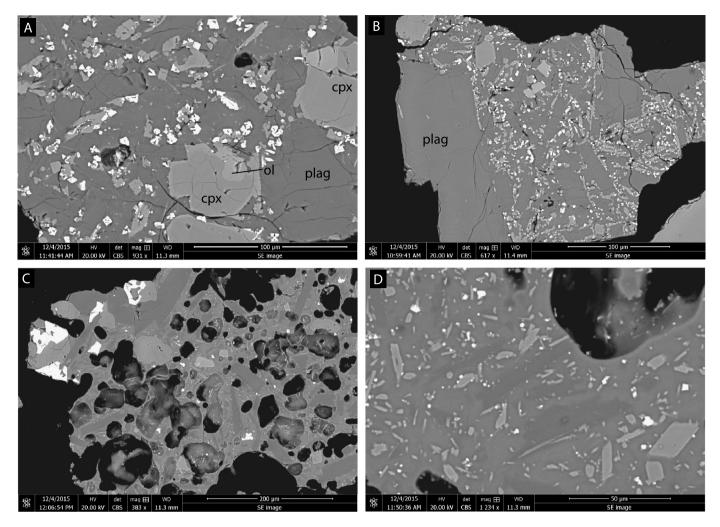
### 3.1.1. Spatial variations

Cones with chemical signatures that overlap the normal SVZ trend (Fig. 1) plot in the same major and trace element fields as deposits from the central vent and the normal SVZ trend (Fig. 2). Figs. 4 and 5 illustrate how major and trace element compositions vary with distance from the central vent. The cones show a general trend to more mafic compositions, with slightly higher MgO, lower SiO<sub>2</sub> and lower incompatible elemental contents (e.g., LREE

and Nb), with distance from the central vent (Figs. 4, 5). Trace element ratios of mafic magmas that are considered to be unaffected by crustal processes (U/Th, Zr/Nb and Ce/Pb: e.g., McCulloch and Gamble, 1991; Lee and Bachmann, 2014) plot within the central vent range and show no significant spatial variation (Fig. 5).

# 3.1.2. Kangechi signature

The Mocho-Choshuenco cones with the Kangechi signature form a cluster near the town of Puerto Fui (Fig. 1). They occur <1 km from other normal SVZ cones and <15 km from the central vent (Figs. 1, 5). These cones are the most mafic samples analysed from Mocho-Choshuenco; their Mg#s (= 100 \* Mg/[Mg+Fe<sup>T</sup>]; 51–61) are higher (normal SVZ composition cones ~Mg# < 51) and SiO<sub>2</sub> contents slightly lower (47–52 wt.%) than at other cones (51–61 wt.%; Figs. 2, 5). The Kangechi cones are more enriched in incompatible elements, with higher LREE, and Nb, and lower Zr concentrations relative to the other cones (Figs. 2, 4, 5). Kangechi cones also have a distinct REE profile, and both La/Yb (LREE/HREE) and Dy/Yb (MREE/HREE; Figs. 2, 4) ratios are elevated compared to the normal SVZ trend (Fig. 2). U/Th, Ce/Pb and Zr/Nb signatures of Kangechi cones also differ significantly from the normal SVZ trend (Figs. 2, 4).



**Fig. 3.** Backscatter secondary electron images of cone samples from Mocho-Choshuenco. **A, B:** Kangechi sample with clinopyroxene (cpx), olivine (ol) and plagioclase (plag). **C:** mafic (55 wt.% SiO<sub>2</sub>) normal SVZ cone sample comprising olivine, plagioclase and clinopyroxene. **D:** a more evolved (61 wt.% SiO<sub>2</sub>) normal SVZ cone sample with plagioclase, clinopyroxene and orthopyroxene.

### 4. Discussion

Our observations in the SVZ show two distinct geochemical groups of mafic magma composition; the 'normal SVZ' and the 'Kangechi' signature. As introduced above, hypotheses to explain the origins of chemical diversity in mafic arc magmas fall broadly into three groups. These are that magma compositional diversity observed upon eruption arises from (i) crystal fractionation and assimilation during crustal ascent, (ii) variations in the slab or mantle source composition, or (iii) dynamic melt transport processes. Previous studies have addressed the possible origins of the Kangechi signature. U/Th and Ce/Pb are traditional slab and mantle geochemical tracers (e.g., McCulloch and Gamble, 1991). An elevated Ce/Pb and lowered U/Th ratio (as seen in the Kangechi signature) are often attributed to a smaller slab fluid component being sampled by the magmas. Previous observations of this signature have attributed it to variations in the mantle source composition due to variable subducting slab inputs (hypothesis ii) (e.g., Hickey-Vargas et al., 1989, 2002; Lahsen et al., 1994; Morgado et al., 2015). Hickey-Vargas et al. (2002) proposed that the subducted component sampled by the CHSEC cones (Kangechi signature) was both older and poorer in fluid-mobile elements (e.g., Ba, B, U) than the subducted component sampled by the magma erupted from Villarrica stratovolcano and the San Jorge cone (normal SVZ). They suggested that the CHSEC cones sampled a metasomatised mantle source generated by either slab-derived melts formed in a hotter subduction zone, or by fluid expulsion following solidification in the wedge. Alternatively Lahsen et al. (1994) and López-Escobar et al. (1995) suggested the signature could be caused by a lower hydrous influx from the subducted oceanic crust, inducing a smaller degree of melting. Although these hypotheses may account for the geochemical differences, neither offers a physical mechanism to explain why both the Kangechi and nearby cones would simultaneously tap distinct magmatic sources.

Although the Kangechi signature is seen at a number of volcanic centres within the SVZ we focus our discussion on the new observations from Mocho-Choshuenco Volcano. Here, a plausible model must explain the generation and preservation of mafic magmas with distinct geochemical compositions despite close spatial and temporal association. In the following sections we explore the extent to which the three sets of hypotheses might provide an appropriate explanation for the mafic magma diversity that is both physically and geochemically consistent. We firstly consider the possible origins of the Kangechi signature and secondly the processes that could lead to its preservation upon eruption for each of the above hypotheses in turn.

# 4.1. Assimilation and crystal fractionation (hypothesis i)

Assimilation and crystal fractionation are clearly important in the evolution of Mocho-Choshuenco magmas (McMillan et al., 1989; Rawson et al., 2015, 2016). In post-glacial times, Mocho-

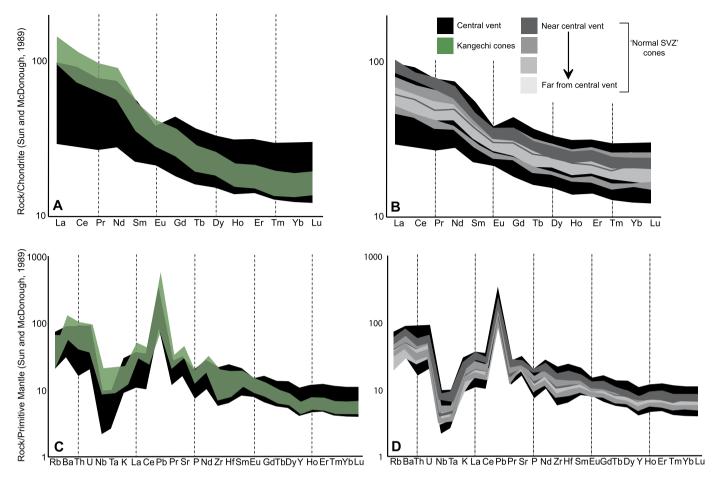


Fig. 4. Whole rock chondrite-normalised REE and mantle normalised trace element compositions of normal SVZ cones, Kangechi cones and mafic central vent deposits from Mocho-Choshuenco. A: the Kangechi cones (green) have elevated LREE abundances and a steeper REE profile compared to the central vent (black). B: The normal SVZ cones (grey) fall in the same REE range as samples from the central vent (black). There is a slight trend to elevated REE concentrations for cones closer to the central vent. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Choshuenco has erupted a wide range of magma compositions (basalt to dacite; Fig. 2). From whole rock and glass major elemental signatures (e.g., P<sub>2</sub>O<sub>5</sub> vs. SiO<sub>2</sub>; Fig. 2) we infer that the normal SVZ chemical trend at Mocho-Choshuenco is primarily driven by fractional crystallisation (Rawson et al., 2015, 2016); the non-linear systematics of P2O5 versus SiO2 suggests that mixing between ascending mafic melts and evolved magmas within the crust is not a dominant process (e.g., Lee and Bachmann, 2014). Within the normal SVZ Mocho-Choshuenco cones there is a slight trend towards more mafic magmas, with lower concentrations of incompatible elements (e.g., LREE) with increasing distance from the central vent. This is consistent with decreasing extents of crystal fractionation for magmas with increasing distance from the main edifice. The trend to higher La/Yb (i.e. LREE/HREE) and lower Dy/Yb (i.e., MREE/HREE) with increasing SiO<sub>2</sub> (Fig. 2) is consistent with (cryptic) amphibole fractionation within the crust (Davidson et al., 2007). We suggest that spatial variations within the Mocho-Choshuenco normal SVZ magmas reflect the compositional evolution of magma in the main crustal processing system. As these cones plot in the same major and trace element fields, and follow the same evolutionary trends as deposits from the central vent, these cones are likely to be parasitic to the main crustal processing system. These magmas are thus derived from the same primitive melt source, but sampled in various states of differentiation. This has been observed and modelled at other volcanoes (e.g., Pinel and Jaupart, 2004; Karlstrom et al., 2015).

The Kangechi magmas have elevated La/Yb and Dy/Yb compared to normal SVZ magma compositions (Fig. 2). The only crystal phase that could account for the elevated LREE/HREE and MREE/HREE through fractional crystallisation is garnet. Garnet, however, is not a known phenocryst phase in any of these magmas. The thickness of the crust beneath Mocho-Choshuenco (35 km estimated by Lowrie and Hey, 1981 using seismic data) is at the lower limit of the estimated garnet stability field (e.g., Hacker et al., 2008). Therefore any garnet fractionation would likely take place below the crust; however thermal conditions generally become less conducive to fractional crystallisation with depth. Also, partition coefficients are sensitive to many variables (including pressure, temperature, fugacity, mineral composition etc.). Thus, although garnet fractionation cannot be ruled out as a cause of REE trends in the Kangechi signature the amount, depth or nature of it cannot be independently quantified from current constraints.

In addition to fractional crystallisation, crustal contamination may influence the evolution of continental arc magmas. This is a complex process to unravel, as there is potentially a wide range of crustal lithologies, few of which are exposed at the surface. Quantifying the amounts of crustal assimilation usually requires isotopic data (e.g., McMillan et al., 1989; Reubi et al., 2011) and prior work at Mocho-Choshuenco suggests that andesitic and dacitic magma at Mocho-Choshuenco assimilated  $\sim$ 5% and  $\sim$ 15% crustal rocks, respectively (McMillan et al., 1989). However, major and trace element compositional trends can be used to qualitatively assess whether or not crustal assimilation might have significantly af-

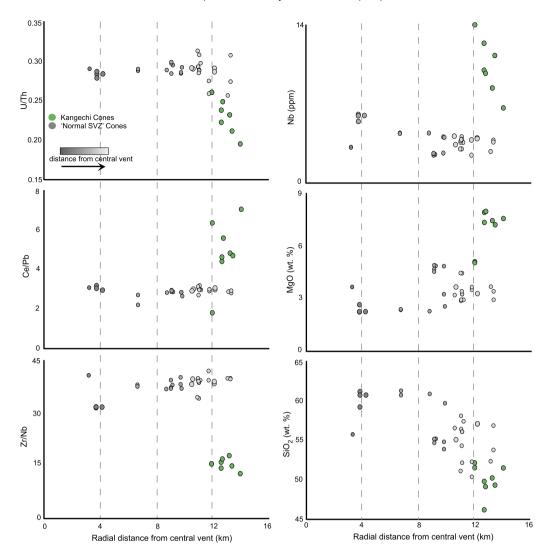


Fig. 5. Whole rock compositions of samples of the cones on the flanks of Mocho-Choshuenco, plotted against radial distance from the central vent. Normal SVZ cones are shaded in grey with darker shading for cones closer to the central vent. The Kangechi cones are indicated in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fected compositional diversity. Using the known compositions of available basement samples we show in Fig. 6 that shallow crustal assimilation cannot in itself account for the differences in composition between Kangechi and the most mafic (MgO  $\geq 4$  wt.%) normal SVZ magmas from Mocho-Choshuenco. However, since the composition of the lower crust is poorly constrained it is again not possible to independently quantify how crustal assimilation would account for the Kangechi signature.

### 4.2. Source composition (hypothesis ii)

The source composition of arc magmas beneath a continental arc is affected by the subducting slab and flow within the mantle wedge. As the subducting slab descends, it heats up, causing the release of fluids and melts into the overlying mantle. Changes in the rate, angle and dip of the subducting slab as well as the nature, age and thickness of the sediment and oceanic crust can all affect the flux and composition of the fluids and melts released, which in turn can affect the magma chemistry (e.g., Carr et al., 1990; Peacock et al., 1994; Stern and Kilian, 1996; Plank et al., 2002; van Keken et al., 2011). Further, these fluids and melts from the subducting slab may fail to reach the surface and instead metasomatise or refertilise the mantle (e.g., Hickey-Vargas et al., 2002). Mantle xenolith and ophiolite studies have shown that although

the mantle is dominated by a lherzolite composition it is heterogeneous on a variety of length scales (e.g., metasomatised and/or refertilised veins and lenses) (e.g., Hirschmann and Stolper, 1996; Kelemen et al., 1997). Therefore the slab and mantle source compositions may be both spatially and temporally variable. As prior studies have argued, the Kangechi signature could arise from a source metasomatised by slab melts (e.g. Hickey-Vargas et al., 2002) or by a lower hydrous influx from the slab inducing a smaller degree of melting (e.g., Lahsen et al., 1994). Spatially the latter argument is consistent with the location of the Kangechi deposits. They are all found on the eastern edge of the magmatic arc; therefore it is expected that these magmas have sampled more distal parts of the mantle wedge where less slab fluids are present and the mantle melts to a lower degree than closer to the trench. However, this hypothesis does not yet explain how this distinct signature is preserved during melt extraction through the mantle wedge and crust within the tight spatial and temporal constraints posed by the eruptive record.

## 4.3. Melt transport (hypothesis iii)

The important effects of melt transport on magma chemistry are not often considered. The physical mode of melt transport significantly influences the way melts form and chemically interact

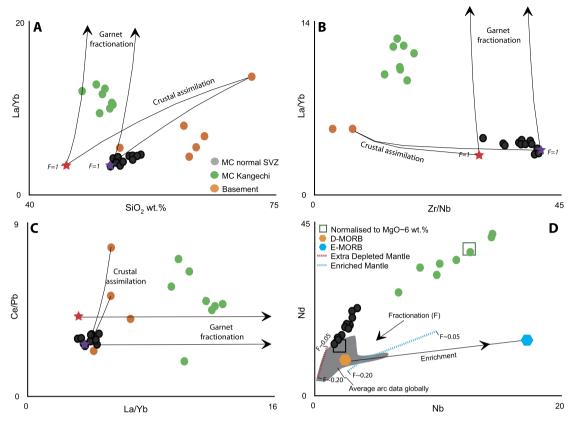
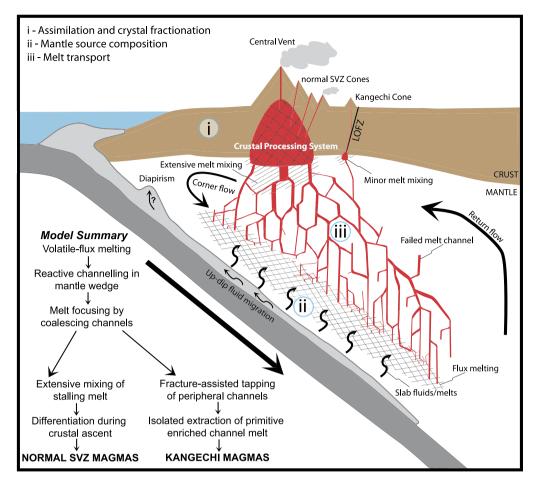


Fig. 6. Whole rock major and trace element compositions for Mocho-Choshuenco deposits with a MgO ≥4 wt.%. A, B, C: Curves indicate expected garnet fractionation effects and crustal assimilation. Garnet fractionation is calculated using the experimentally determined partition coefficients from Johnson (1998). Crustal assimilation is estimated by mixing between the most evolved basement sample (Echegaray, 2004) and an assumed primary melt. The two primary melts used for modelling are the most mafic deposit from Mocho-Choshuenco (purple star) and the most mafic sample from the SVZ (red star). A two-step process of both garnet fractionation and crustal assimilation could potentially account for the divergence B: To reproduce the Kangechi La/Yb vs. Zr/Nb signature from the most primitive Mocho-Choshuenco analysis would require garnet fractionation and crustal assimilation. C: To reproduce the Kangechi (Ce/Pb vs. La/Yb signature from the most primitive Mocho-Choshuenco analysis would require garnet fractionation and crustal assimilation. D: Dashed curves indicate fractionation trends when starting from an extra depleted mantle source (red; calculated by removing 0.5% melt from D-MORB) and an enriched mantle source (D-MORB +2% E-MORB; blue). These modelled curves and source compositions are taken from Turner and Langmuir (2015a). Average arc compositions globally (shaded in grey) are normalised to a constant MgO  $\sim$ 6 wt.% and calculated by Turner and Langmuir (2015b). For better comparison to the global range and to remove the effects of fractional crystallisation we also normalise the Kangechi (green square) and normal SVZ (black square) compositions to MgO 6.0 wt.% (determined by the intercept of the regression line through the data as in Plank and Langmuir, 1988). F is the amount of crystal fractionation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with the mantle. The nature of these processes can affect both the magma composition, and the distances and timescales over which geochemical variations are preserved throughout a magmatic system (Spiegelman and Kelemen, 2003; Liang et al., 2011).

As introduced above reactive channels are likely to emerge in the mantle wedge as a consequence of slab-derived volatile-flux melting. Reactive channels form when fluid or melt ascends along pressure- or temperature-dependent solubility gradients of various mineral phases. As a result, melt can become under-saturated in some phases, causing dissolution of minerals along the melt extraction path, and hence changes in the melt composition. As such reactions produce additional melt, the increased porosity and permeability will promote a higher melt flux. This positive feedback leads to reactive channelisation (e.g., Kelemen et al., 1995). Dynamic models suggest that reactive channelling produces orders of magnitude of variations in the concentrations of incompatible elements along the cross-section of each reactive channel (Spiegelman and Kelemen, 2003). The models predict that more incompatible elements will have a greater variation in concentration between the centre and edge of the channel. For example, the LREEs are expected to vary more than HREEs across a single channel. It is the balance between rates of melt advection and melting reactions that governs the evolution of magma chemistry (e.g. Keller and Katz, 2016). Despite the higher melting rates at the centre of the channel this balance is tipped in favour of advection in reaction channels. Melt transported on the inside of a channel thus carries the signature of an enriched melt formed by low-degree melting of an undepleted source. In contrast, melt on the edges of a channel has a more depleted signature, which resembles a melt formed by high-degree melting of a more depleted source (Spiegelman and Kelemen, 2003). In this case it is not a spatial or temporal variability in the mantle source, but the dynamics of reactive melt transport that produce magma compositional variability. Indeed, Keller and Katz (2016) found that models seeded with different types and amplitudes of chemical heterogeneity in the mantle all resulted in the same type of reactive channels with the same systematic variability in melt chemistry. These findings suggest that reactive channelling can, under some circumstances, overprint chemical diversity inherited from compositional variations in the melt source.

So far, this effect has only been demonstrated for decompression melting in upwelling column models. However, this reaction-transport feedback is fundamentally an expression of flux melting – the dominant source of magmatism in the mantle wedge. As dynamics in the mantle wedge are more complex closer to the trench (higher fluid flux, lower mantle temperatures, possible sediment diapirism, strong corner flow), we argue that well expressed reactive channels are more likely to emerge in the distal parts of the mantle wedge (lower fluid flux, higher mantle temperatures, possibly some upwelling return flow). It is in such an environment that



**Fig. 7.** Schematic diagram of a subduction zone illustrating the different hypotheses. The three hypothesis are that (i) diversity is inherited during ascent and differentiation, (ii) is inherited from compositional variations in mantle source occurring either in space or time and/or (iii) emerges as a consequence of channelisation melt transport in the mantle wedge. With distance from the central vent the normal SVZ cones become more mafic. This is attributed to fractional crystallisation processes within the crust and it is suggested that the spatial trend arises from more distal cones tapping a more primitive melt reservoir (i.e., hypothesis i). The Kangechi cones have a major and trace element composition distinct from the normal SVZ. This is proposed to arise from varying degrees of preservation of a type of enriched melt signature arising from the process of reactive melt channelling in the mantle (i.e., hypothesis iii). Beneath the main volcanic arc there is an extensive melt network produced by the focussing and coalescing of numerous melt channels. As melt channels coalesce during melt focusing the increased melt flux in a focusing centre will heat the rock matrix. As a result, the rock viscosity is lowered, rock failure becomes prohibited, and thus melt extraction is retarded. This thermal feedback leads to stalling of melts, which promotes mixing between melts from various slab and mantle environments, and enables equilibration with the host rock over longer spatial and temporal scales. If reactive channelling is present in the mantle, any related geochemical signature, in particular the more enriched signature expressed in the centre of melt channels, would be diluted. Additionally, conductive heat transfer to the cooler surrounding lithosphere and crust would cause differentiation by fractional crystallisation and crustal assimilation. In contrast, reactive channels at the periphery of a focused channel network are likely to retain their enriched melt signature. We propose Kangechi magmas tap thes

the geochemical signature formed within a reactive melt channel will most likely be formed and preserved. We therefore propose that the primitive yet enriched Kangechi signature arises from the likely presence of volatile-flux-induced reactive channels, at least in the back-arc facing parts of the mantle wedge.

### 4.4. Preservation of the Kangechi signature

As we have seen, all three hypotheses *could* plausibly account for the differences between normal SVZ and Kangechi magma compositions. We now proceed to evaluate the explanatory power of each hypothesis regarding the observed spatial and temporal patterns of mafic magma diversity: can the Kangechi and normal SVZ magma compositions be generated nearly simultaneously and preserved over the short distances (<1 km between cones and <15 km from the central vent: Fig. 1) observed at Mocho-Choshuenco?

As discussed in section 4.1 assimilation and garnet fractionation are in principle plausible hypotheses to account for the observed mafic magma diversity. However, there are large uncertainties associated with geochemical modelling of garnet fractionation. In the

absence of independent constraints on the garnet-bearing mineral assemblage being fractionated here, this hypothesis is susceptible to proposing a model that incidentally matches the Kangechi signature. We think it must therefore be regarded as a geochemically trivial solution. Similarly, the absence of independent constraints on crustal basement compositions across all Kangechi localities leaves crustal assimilation as a model for the Kangechi signature an incidental fit as well. Therefore, we will not further discuss these two options.

We return instead to general physical considerations related to recent models of melt transport. Keller and Katz (2016) suggest that volatile-flux melting gives rise to strongly channelised melt transport, thus establishing fast and chemically isolated pathways of melt extraction. The spacing of reactive channels is controlled by the compaction length ( $\delta_c$ ), which here is best understood as the lateral distance over which melt is collected into melt channels. The compaction length depends on the mantle permeability ( $k_0$ ), and viscosity ( $\eta$ ), the melt viscosity ( $\mu$ ) and porosity ( $\varphi$ ). This means that the spacing of melt channels is expected to increase as the mantle viscosity stiffens from the hot

centre of the mantle wedge towards the cooler base of the lithosphere and crust. Thus, melt channels originating in the mantle wedge would coalesce into more widely spaced, larger channels as they propagate upwards toward the crust (Fig. 7). Using conservative estimates for upper mantle properties (e.g. McKenzie, 1984; Bürgmann and Dresen, 2008) the compaction length is estimated to increase by order of 1 to 100 km from the mantle wedge towards the base of the crust.

These physical arguments suggest that melt is focussed into the base of the arc crustal magma processing systems by coalescing channel networks. This is supported by the observation that overlying stratovolcanoes exhibit a typical spacing of order 10–100 km, and process large volumes of magma (100–200 km³; e.g., Völker et al., 2011) over long periods of time (often 100's of kyrs). During focusing, melts originating across a wide range of channelling environments are collected, pooled and mixed together (Fig. 7). Consequently, this suggests that melt mixing in a coalescing channel network overprints geochemical variations on scales smaller than the compaction length. Given these arguments on melt focusing into the arc crust it is unlikely that source-related variations in melt chemistry (hypothesis ii) can be preserved on a scale smaller than the spacing of melt channels (i.e., within one volcanic complex).

The final preservation of a mantle-derived geochemical signature relies on fast and chemically isolated melt extraction pathways through the crust to eruption. The most likely physical mechanism providing such pathways is tensile failure, or dyke propagation. However, this mechanism is only viable in relatively cool rock of viscosity of order 10<sup>22</sup> or higher (e.g. Keller et al., 2013). As melt channels coalesce during melt focusing at the base of the crust the increased melt flux in a focusing centre will heat the rock matrix. As a result, the rock viscosity is lowered, rock failure becomes prohibited, and thus melt extraction is retarded. This thermal feedback should lead to stalling of melts within a hot zone protruding into the upper lithosphere and lower crust. Melt stalling promotes mixing between melts from various slab and mantle environments, and enables equilibration with the host rock over longer spatial and temporal scales. If reactive channelling is present in the mantle, any related geochemical signature, in particular the more enriched signature expressed in the centre of melt channels, would be diluted. Additionally, conductive heat transfer to the cooler surrounding lithosphere and crust would cause differentiation by fractional crystallisation and crustal assimilation. In contrast, reactive channels at the periphery of a focused channel network are likely to retain their enriched melt signature as melt fluxes are lower and melts are less likely to stall.

We use this conceptual model to explain the difference between the normal SVZ and Kangechi geochemical trends. We propose that Kangechi magmas tap melts directly from reactive channels at the periphery of a coalescing channel network. The channel network focuses melt into the crustal processing system feeding the central stratovolcano and its parasitic cones. Melt mixing during focusing along with differentiation produces the range of observed normal SVZ magmas (Fig. 7; hypothesis iii). This proposed scenario is physically plausible and consistent with the temporal and spatial constraints at Mocho-Choshuenco.

However, this scenario still requires an extraction pathway for Kangechi magmas that is separate from the central magma processing system through which normal SVZ magmas are extracted. The observed proximity of the cones erupting Kangechi magmas to a major crustal fracture zone suggests that tectonic fracture-assisted melt extraction may provide just such a direct and separate melt extraction pathway. This hypothesis is supported by the location of the other Kangechi cones in the SVZ. As discussed above (section 3), the Kangechi signature is observed in deposits at the Puyuhuapi Volcanic Group, the CHSEC cones (excluding San

Jorge) and the Medialuna cones within Carrán-Los Venados volcanic field. Spatially, all of these samples lie to the east of the main volcanic arc front and – as at Mocho-Choshuenco – in close proximity (order 1 km) to the trace of the LOFZ (or the presumed trace in regions where it is not well constrained, see Fig. 1). The LOFZ is a major dextral transform fault thought to propagate through the entire crust (e.g., Cembrano et al., 1996). We therefore propose that Kangechi-type magmas are sourced from the eastern periphery of a coalescing network of reactive channels; and that their separate extraction is controlled by regional crustal tectonics.

### 5. Conclusions

The analysis of major and trace element compositions for a large number of mafic samples from Mocho-Choshuenco volcano in the SVZ, Chile, yields important new insights into the geochemical evolution of arc magmas. Two main compositional trends were identified. Firstly, the composition of the magmas erupted from the cones on Mocho-Choshuenco's flanks becomes more mafic with distance from the central vent. This is attributed to fractional crystallisation processes within the crust, with the more distal cones erupting less differentiated magmas. Secondly, there is a set of mafic cones that have distinct major and trace element compositions: they are more primitive but are enriched in incompatible elements and have elevated La/Yb, Dy/Yb, Ce/Pb, Nb/Yb and depleted Zr/Nb and U/Th ratios relative to the central vent. We call this the Kangechi signature. This distinct geochemical signature contrasts with that of normal SVZ samples, and is observed at three further clusters of small eruptive centres within the SVZ. All of these Kangechi samples lie to the east of the main volcanic arc front, and in close proximity to the trace of the Liquiñe-Ofqui Fault Zone (LOFZ). Kangechi magmas are found to have co-erupted with normal SVZ magmas in close spatial and temporal proximity.

Interpretations of the origin of this distinct Kangechi geochemical signature are non-unique: the signature could in theory be inherited from assimilation and crystal fractionation within the crust, variations in the mantle source or melt transport processes. However, based on physical arguments and results of melt transport models we propose that the mafic compositional diversity can be plausibly explained by the varying preservation of the enriched primitive melts arising from melt transport, specifically reactive melt channelling. We suggest that melts from various melt transport environments are mixed when channels coalesce during melt focusing into the base of the crustal magma processing system beneath a major volcanic centre. As a consequence, the distinct enriched primitive signature arising inside reactive channels would be diluted in normal SVZ magmas. We propose that the Kangechi magmas instead directly tap melts from channels at the periphery of such a melt focusing network. The separate extraction away from the main crustal processing system is explained by the regional crustal tectonics associated with the LOFZ.

Although we cannot use available constraints to fully eliminate assimilation and crystal fractionation during melt ascent as an explanation for the Kangechi signature, the challenge remains to provide a plausible scenario, which produces this distinct signature in four separate localities along the SVZ. Further, from the findings of Keller and Katz (2016), variation in the mantle source on scales smaller than the spacing of melt focusing into the arc crust are unlikely to be expressed at the surface. Therefore any hypothesis invoking mantle source variation as the drive of magma diversity needs to account for how melt compositional variability could be preserved at distances smaller than the compaction length rather than being overprinted by melt transport processes. Although we argue that the observed magma diversity is unlikely to be driven by mantle source variability (e.g., variations in the fluids/melts released from the down-going slab) we do acknowledge

that it is likely to still contribute to the geochemical budget and the initiation of melting within the mantle wedge.

The proposed model has the potential to explain the origin of both the normal SVZ and the primitive yet enriched Kangechi signature found in our data, while satisfying spatial and temporal constraints given by the eruptive record. The model incorporates some general physical principles of magma dynamics theory along with specific results from recent models of melt transport. Many of the processes involved in our conceptual model are not yet fully understood. Yet, if our arguments are borne out by future data and improved models, there are important implications for interpreting compositional diversity in mafic arc magmas, which could yield significant new insights into magma genesis at subduction zones.

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# Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2016.09.056.

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