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Insights from trace element geochemistry as to the roles of subduction zone geometry and subduction input on the chemistry of arc magmas

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Abstract Subduction zones of continental, transitional, and oceanic settings, relative to the nature of the overriding plate, are compared in terms of trace element compositions of mafic to intermediate arc rocks, in order to evaluate the relationship between subduction parameters and the presence of subduction fluids. The continental Chilean Southern Volcanic Zone (SVZ) and the transitional to oceanic Central American Volcanic Arc (CAVA) show increasing degrees of melting with increasing involvement of slab fluids, as is typical for hydrous flux melting beneath arc volcanoes. At the SVZ, the central segment with the thinnest continental crust/lithosphere erupted the highestdegree melts from the most depleted sources, similar to the oceanic-like Nicaraguan segment of the CAVA. The northern part of the SVZ, located on the thickest continental crust/lithosphere, exhibits features more similar to Costa Rica situated on the Caribbean Large Igneous Province, with lower degrees of melting from more enriched source materials. The composition of the slab fluids is characteristic for each arc system, with a particularly

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pronounced enrichment in Pb at the SVZ and in Ba at the CAVA. A direct compositional relationship between the arc rocks and the corresponding marine sediments that are subducted at the trenches clearly shows that the compositional signature of the lavas erupted in the different arcs carries an inherited signal from the subducted sediments.

Keywords Subduction zones - Trace element geochemistry - Hydrous flux melting - Marine sediment input - Chilean Southern Volcanic Zone - Central American Volcanic Arc

Introduction

Fluids from the subducting slab play a fundamental role in driving arc volcanism. They promote mantle melting at depth and evoke explosive eruptions near the surface. The presence and behaviour of subduction fluids and related magma compositions are a function of a number of factors: they firstly depend on the composition of the subduction input materials, i.e. the variably hydrated subducting slab (igneous crust and serpentinised uppermost mantle), the overlying sediments, and possibly material eroded from the overriding plate in the forearc by subduction erosion (e.g. Kay and Kay [1993;](#page-14-0) Kay and Mpodozis [2002](#page-14-0); von Huene and Scholl [1991](#page-15-0); and references therein), or from the slabmetasomatised forearc mantle wedge through frictional stresses (Tatsumi [1986](#page-15-0); Savov et al. [2007\)](#page-15-0). The mantle wedge beneath the arc may show compositional differences, ranging from mid-ocean ridge basalt (MORB)- to enriched (E-)MORB-sourced mantle, possibly including ocean island basalt (OIB) components. Subduction parameters, e.g. slab ages, convergence rates, and geometric properties such as slab dip angles, thickness of the

mantle wedge and of the overriding plate, will affect the thermal conditions in the system, thus governing mineral dehydration reactions (e.g. Syracuse and Abers [2006](#page-15-0); Hacker [2008;](#page-14-0) Syracuse et al. [2010;](#page-15-0) John et al. [2011](#page-14-0); and references therein) and subsequently the extent of fluid transfer at depth. The addition of fluids to the asthenospheric wedge will in turn influence the degree of melting beneath the arc. During ascent, melts may assimilate material from the overriding plate, consisting of continental, transitional (e.g. accreted ophiolitic terranes and oceanic plateaux/large igneous provinces), oceanic lithosphere, or young to zero-age plutonic rocks and crystal mushes of immediately prior magmatism. The thickness of the overriding plate may affect magma migration rates, storage times, degree of magma differentiation, and amount of assimilation.

To understand better the relevance of any of the factors influencing the erupted melt compositions, we compare the following different subduction systems in this paper: the Chilean Southern Volcanic Zone (SVZ) and the Central American Volcanic Arc (CAVA). These arcs show salient differences in a number of parameters, such that the SVZ accommodates a continental end member with regard to crustal thickness of the upper plate (reaching >60 km beneath the northern part of the SVZ), while the CAVA is a transitional arc, extending from an oceanic plateau beneath Costa Rica through accreted mafic terranes in Nicaragua to El Salvador and then to thickening continental crust in Guatemala. Compositions of input materials (the igneous crust, i.e. MORB or a subducted hotspot track, and the marine sediments) and overall subduction geometries vary strongly between the arcs. Nevertheless, each arc system comprises segments with properties comparable to some segments in the other arc. By considering both the differing and the similar subduction parameters, the comparison of the arc output from the different subduction systems permits to filter the relative importance of the parameters influencing the compositions of the erupted arc rocks, thus allowing us to address the question of whether the nature of the overriding plate or the subduction input plays a more important role.

A variety of previous studies have characterised the major and trace element compositions of arc rocks of the SVZ (e.g. Hildreth and Moorbath [1988](#page-14-0); Hickey et al. [1984](#page-14-0); López-Escobar et al. [1992](#page-14-0)) and of the CAVA (e.g. Carr et al. [2007;](#page-13-0) Sadofsky et al. [2008](#page-15-0); Hoernle et al. [2008;](#page-14-0) Gazel et al. [2009;](#page-13-0) Heydolph et al. [2012](#page-14-0); and references therein). In this paper, we integrate geochemical data from Sadofsky et al. ([2008\)](#page-15-0), Hoernle et al. ([2008\)](#page-14-0), Heydolph et al. [\(2012](#page-14-0)), Wehrmann et al. (in review), and Jacques et al. ([2013](#page-14-0)) with new data sets from the SVZ and from subducting marine sediments. The major goal of this study is to gain a better insight into the parameters controlling the geochemistry of subduction zone volcanic rocks through a comparison of different end-member type arc systems, concerning input, slab geometries, and the nature and thickness of the overriding plate (crust and mantle).

Geologic setting

The Chilean Southern Volcanic Zone

The SVZ (Fig. [1](#page-2-0)a) encompasses more than 60 large volcanic centres, in addition to numerous small cones and satellite vents between latitudes 33° S and 46° S, located along the western margin of South America. The volcanic activity results from the subduction of the Nazca Plate beneath the South American Plate with convergence rates ranging from 70 to 90 mm/year (Stern [2004](#page-15-0)). The dip of the subducting plate decreases northwards from 39° to 28° from latitude 42° S to 35°S, and then to less than 24° into a region of flat subduction north of 33° S, where volcanism ceases. The SVZ comprises a continental end member in arc systems with thicknesses of the overriding continental crust reaching up to 60 km in its northern part. Details of subduction geometry are provided in Fig. [2](#page-3-0)a.

Subduction input materials, consisting of MORB-type oceanic crust and overlying marine sediments, have been described as relatively homogeneous in composition along the SVZ (Hildreth and Moorbath [1988;](#page-14-0) Melnick and Echtler [2006](#page-14-0)). The age of the incoming plate subducting beneath the active arc ranges from \sim 15 Ma in the south at 43°S to \sim 32 Ma in the north at 33°N. Several fracture zones are situated on the Nazca Plate (the Mocha, Valdivia, Chiloe´, and Guafo Fracture Zones; Fig. [1](#page-2-0)a). These fracture zones might be sites of increased input of water and altered oceanic crust into the subduction zone (Dzierma et al. [2012](#page-13-0)). In southern and central Chile, glaciation has had a major control on the sediment supply to the trench, and hence, climate variability may have modulated the balance between accretionary and erosional processes along the mid- and southern latitudes of the margin through time (e.g. Bangs and Cande [1997](#page-13-0)). At present, the forearc along the SVZ is accretionary.

We here subdivide the SVZ according to a segmentation given by Hildreth and Moorbath [\(1988\)](#page-14-0) and Dungan et al. [\(2001](#page-13-0)), with a slight modification as also used by Wehrmann et al. (in review), into a Northern SVZ (NSVZ; $33-34.5^\circ$ S), a Transitional SVZ (TSVZ; 34.5-38 $^\circ$ S; the previously used southern boundary at 37° S is shifted to 38°S), a Central SVZ (CSVZ; 38–42.5°S), and a Southern SVZ (SSVZ, here represented by small volcanic centres at Volcán Michinmávida/Chaitén at 43°S). The boundaries are illustrated in Fig. [1](#page-2-0)a.

Fig. 1 Location map of a the Chilean Southern Volcanic Zone (SVZ) (red triangles depict studied volcanoes, yellow triangles indicate other young volcanic centres), b the Central American Volcanic Arc (CAVA) (red triangles indicate the volcanoes for which data have been evaluated in this study). Images of courtesy SRTM Team NASA/JPL/NIMA, modified

The Central American Volcanic Arc

The geologic setting of the CAVA (Fig. 1b) has been described in many previous studies (e.g. Carr [1984;](#page-13-0) Carr et al. [2007](#page-13-0); Patino et al. [2000](#page-14-0); Sadofsky et al. [2008](#page-15-0); Wehrmann et al. [2011;](#page-15-0) and references therein). Volcanism at the CAVA extends over a distance of 1,100 km from north-western Guatemala to Central Costa Rica (CCR),

produced by north-eastward subduction of the Cocos Plate beneath the Caribbean Plate at convergence rates of \sim 74–84 mm/year (DeMets [2001\)](#page-13-0). It comprises dozens of major volcanic centres, including complex stratovolcanoes and caldera systems, in addition to numerous peripheral vents and small cinder cones. The overriding plate is of oceanic nature in the south-western arc segments. In Costa Rica, it consists of the Caribbean Large Igneous Province, in Nicaragua and part of El Salvador, and the crust is made up of oceanic plateaux and accreted mafic terranes. A transition to continental crust of the overriding plate occurs in El Salvador, becoming progressively thicker towards Guatemala. Subduction geometry, illustrating the differences in upper-plate thickness, melting column lengths, and angles of the downgoing slab, is shown in the along-arc profile in Fig. [2b](#page-3-0).

Materials transported into the subduction zone vary greatly between the incoming plate outboard of Costa Rica and the incoming plate outboard of Nicaragua to Guatemala. Approximately 15–20 Ma old crust formed at the Cocos-Nazca Spreading Centre and the Galapagos Spreading Centre, which also contains parts of the zoned Galapagos Hotspot Tracks (Cocos Ridge and Seamount Province to the north-west of the ridge), subducts beneath Costa Rica and western Panama (Werner et al. [1999](#page-15-0), [2003](#page-15-0); Hoernle et al. [2000](#page-14-0), [2002](#page-14-0), [2008](#page-14-0); Sadofsky et al. [2008](#page-15-0)). Offshore Nicaragua to Guatemala, subducting sediments on the incoming plate, as defined from Deep Sea Drilling Project (DSDP) Site 495, consist of a basal unit with \sim 250 m of carbonate ooze and a second overlying unit of \sim 200 m of organic carbon-rich hemipelagic clay (Aubouin and von Huene [1982\)](#page-13-0). This input of carbonate-bearing lithologies is at a global maximum (Tera et al. [1986](#page-15-0); Carr et al. [1990](#page-13-0); Plank et al. [2002\)](#page-14-0). The subducting slab outboard north-western Central America was formed \sim 20–25 Ma ago at the East Pacific Rise and has normal (N-)MORB-type composition, which was inferred from ocean crust samples from Site 1256 (Sadofsky et al. [2009](#page-15-0)), from a faulted seamount outboard of Nicaragua (Werner et al. [2003\)](#page-15-0), and from Sites 499 and 500 off Guatemala (Geldmacher et al. [2008](#page-13-0)). It has been shown that the uppermost mantle of the incoming plate outboard of Nicaragua has been hydrated and converted to serpentinite at the outer rise due to extensive bend-faulting down to mantle depths (Ranero et al. [2003](#page-14-0); Grevemeyer et al. [2007](#page-14-0); Ivandic et al. [2007](#page-14-0)).

The greatest, or most focused, fluid release is believed to occur beneath Nicaragua, constrained by various geophysical means including seismic imaging (e.g. Peacock et al. [2005](#page-14-0); Abers et al. [2006](#page-13-0); Rychert et al. [2008;](#page-15-0) and references therein), by low δ^{18} O compositions of the erupted rocks (Eiler et al. [2005\)](#page-13-0), and by studies of volatiles in olivine-hosted melt inclusions (e.g. Sadofsky et al. [2008](#page-15-0); Wehrmann et al. 2011 ; and references therein).

Fig. 2 Generalised along-arc profile of a the Chilean SVZ and b the CAVA, both extending \sim 1,100 km, illustrating variations in slab depth, crustal thickness, and melting column length. Arc volcanoes are also shown. SVZ geometry modified from Völker et al. [\(2011](#page-15-0)) based on models of Tassara et al. ([2006\)](#page-15-0). CAVA geometry modified

Samples and data

For the large-scale geochemical coverage of the volcanic arcs, young mafic to intermediate tephra and lava samples were collected during a number of field campaigns along the volcanic fronts of Central America and southern Chile between 2002 and 2011. The major and trace element data presented here are compiled for the CAVA from Hoernle et al. ([2008\)](#page-14-0), Sadofsky et al. [\(2008](#page-15-0)), and Heydolph et al. [\(2012](#page-14-0)). For the SVZ, 96 new rock samples were analysed (Online Resource 1) and incorporated with 31 samples from Jacques et al. ([2013\)](#page-14-0), 20 samples from Wehrmann et al. (in review) (Online Resource 2), and one analysis from Volcán Huequi from Watt et al. [\(2011](#page-15-0)). All major and trace element data presented in the figures except for the one from Huequi were generated by the same procedures and the same instruments, giving analytical consistency and therefore comparability.

To characterise subduction input materials, several sea floor samples are included in this study. For the CAVA, geochemical data were obtained for sediments and altered ocean crust from ocean drilling project (ODP) Site 1256 (Sadofsky et al. [2009;](#page-15-0) Geldmacher et al. [2013\)](#page-13-0), from DSDP Sites 495, 499, and 500 (Online Resource 1 and Table [1,](#page-4-0)

from Wehrmann et al. ([2011\)](#page-15-0) using slab depths (generalised) and Guatemalan crustal thickness from Syracuse and Abers [\(2006](#page-15-0)), crustal thicknesses of Nicaragua and Costa Rica from MacKenzie et al. [\(2008\)](#page-14-0)

this study, and Heydolph et al. [2012](#page-14-0)), and averaged sediment compositions were provided by Patino et al. [\(2000](#page-14-0)). Off the coast of the Chilean SVZ, a number of marine sediment samples were obtained from the sea floor during the RV Sonne Cruise 210. Sediment compositions on these samples were determined by Jacques et al. [\(2013](#page-14-0)). Our Chilean marine sediment data set is complemented by data from Lucassen et al. [\(2010](#page-14-0)).

Methods

The tephra and lava samples were hand-picked for fresh, juvenile material, and powdered. Sediment samples were powdered as bulk material. Whole-rock major element analyses of the volcanic samples were carried out with a Philips X'Unique PW 1480 XRF instrument at GEOMAR, Kiel, and the sediments were analysed on a MagixPro PW 2540 XRF at the University of Hamburg. For the trace element analyses, conventional table-top digests were made in PFA vials at 160° C with HF-aqua regia-perchloric acid following the multi-step procedure established by Garbe-Schönberg ([1993\)](#page-13-0). Sediment samples were stored in high-pressure, high-temperature bombs for 4 days prior

Table 1 continued

to digestion to ensure complete digestion of zircons. Trace element compositions of the bulk rocks were determined with an Agilent 7500cs ICP-MS instrument at the Institute of Geosciences, University of Kiel in Germany. The results were confirmed to be analytically repeatable, reproducible, and true by several means: (1) every tenth sample was digested in duplicate; (2) the same digest solutions of several randomly chosen samples were repeatedly measured (3–5 times) within each analytical run to ensure consistency of the ICP-MS instrument, (3) a subset of approximately 100 digests was re-analysed in a single run with a dedicated washout protocol, and (4) external reproducibility/trueness was verified by means of a set of reference materials: BHVO-1, BHVO-2, AGV-1, JA-2, BIR-1, and JB-1a (Online Resource 3). Both laboratory blanks and instrumental background were monitored with different blank types included in each analytical run.

Results

Rickwood [\(1989](#page-15-0))), the CSVZ rock array has the lowest K_2O . The TSVZ samples fall largely in the medium- K_2O , calc-alkaline field, similar to samples from Guatemala (GU), El Salvador (ES), and Nicaragua (Nic). Rocks from the NSVZ and the more evolved samples from Northern Costa Rica (NCR) reach into the high-K, calc-alkaline field, while the highest-K array is formed by samples from Central Costa Rica (CCR). Trace elements form typical subduction zone/island arc patterns in MORB-normalised multi-element diagrams (Fig. [4](#page-6-0)a–c), with pronounced troughs (relative depletion) at Nb and Ta, and peaks (relative enrichment) at highly fluid-mobile elements such as Ba, U, Pb, and Sr. Rocks from CCR show the least pronounced Nb and Ta negative and Pb-positive anomalies and overall show a more Galapagos-like ocean island basalt (OIB) signature, as was already described in previous studies (e.g. Reagan and Gill [1989](#page-15-0); Benjamin et al. [2007](#page-13-0); Sadofsky et al. [2008](#page-15-0); Hoernle et al. [2008;](#page-14-0) Gazel et al. [2009](#page-13-0)). The incoming marine sediments (Fig. [4](#page-6-0)d) show enrichment of elements that become fluid-mobile during subduction. The carbonate sediments outboard the CAVA display the highest relative Ba and Sr, and lowest Rb, Pb, Th, and U contents. Averaged compositions of the SVZ

Fig. 3 K_2O versus SiO_2 of the SVZ (CSVZ purple, TSVZ red, and NSVZ yellow–red diamonds) in comparison to the CAVA (Guatemala (GU) and El Salvador (ES) yellow, Nicaragua (Nic) green, and northern (NCR) and Central Costa Rica (CCR) light blue fields)

and hemipelagic CAVA sediments have middle and heavy rare earth elements (REE) similar to MORB, while the carbonate sediments at the CAVA show strong relative depletion in REE. In terms of variations in trace element ratios along the arcs (Fig. [5a](#page-7-0)–h), both the SVZ and the CAVA involve segments with strongly elevated ratios of highly fluid-mobile to less fluid-mobile incompatible trace elements. There is an obvious geographic distinction in particular incompatible trace element ratios between the two arc systems. The Nicaraguan segment of the CAVA exhibits very high Ba/Th, Ba/Nb, U/Th, and Sr/Ce values, whereas the SVZ, in particular the CSVZ, displays strongly elevated Pb/Ce and Pb/U values. La/Yb and Nb/Y values peak in Costa Rica, while being low in the central to northwestern CAVA. They are also low in the CSVZ, but show a gradual increase over the TSVZ towards the NSVZ.

Discussion

In the following, we use several trace elements as proxies for subduction processes and material involvement. Elements such as Ba, U, Pb, and Sr are termed "highly fluidmobile'', since they are readily scavenged by subduction fluids even at low temperatures (Kessel et al. [2005\)](#page-14-0). ''Less fluid-mobile'' refers to Th and light REE, which are progressively released from the slab as the temperature increases, while middle and heavy REE are considered relatively fluid-immobile.

Fig. 4 N-MORB-normalised multi-element variation diagram [normalising values from Sun and McDonough ([1989\)](#page-15-0)] comparing a the CSVZ (purple field with solid line) with Nicaragua (green field with dashed line), **b** the TSVZ (red field with solid line) with Guatemala (pale yellow field with long dashed line) and El Salvador (pale orange field with short dashed line), c the NSVZ (yellow field with solid line) with Northern (blue field with short dashed line) and Central (pale blue field with *long dashed line*) Costa Rica, and **d** input marine sediment compositions also comparing the SVZ (red field with solid line) with the CAVA (carbonate sediments brown-yellowish-green, dashed; hemipelagic sediments green, dashed), whereby the thick lines reflect the bulk sediment compositions as estimated by Patino et al. [\(2000\)](#page-14-0) for the CAVA

Compositional variation along the arcs

Strongly elevated values of canonical slab proxies in subduction systems, such as Ba/Th, Ba/Nb, U/Th, or Sr/Ce, occur within the Nicaraguan sample set, and decline towards both the north-western and south-eastern CAVA,

Fig. 5 Variation of trace element ratios along the Chilean SVZ (left, red diamonds) and the CAVA (right, yellow, green, and blue symbols). a Ba/La, **b** Ba/Nb, c U/Th, and d Sr/Ce ratios, despite their internal variability (Wehrmann et al., in review), are relatively uniform and low at the SVZ. At the CAVA, these ratios extend to higher values, reaching a maximum at Nicaragua. e Pb/Ce and f Pb/U

and are also considerably lower in the SVZ (Fig. 5a–d). Several previous studies also employed Ba/La, which displays a similar regional variation, but because of the differing partition coefficients of the two elements, the ratio

reach the highest values at the SVZ, the latter in particular in the CSVZ. For g La/Yb and h Nb/Y, the highest values occur at the NSVZ of the SVZ and at the Costa Rican segment of the CAVA. The shaded blue bars indicate location and composition of the subducting seamount province of the Galapagos hot spot track [data from Hoernle et al. (2000) (2000)]

can be affected both by slab and by mantle processes. The origin of this along-arc pattern of the CAVA is still subject of debate. It has been ascribed to the most channelised fluid

Fig. 6 a U/Th and b Sr/Ce versus Sm/Lu for the SVZ and the CAVA arc rocks, showing a typical pattern of hydrous flux melting with increasing U/Th and Sr/Ce at decreasing Sm/Lu, with exceptionally

(Carr et al. [1990](#page-13-0)), or to highly variable fluid flow beneath different parts of the arc (e.g. Benjamin et al. [2007;](#page-13-0) Sadofsky et al. [2008](#page-15-0)). Other authors suggest variable involvement of sediments of different compositions (Plank and Langmuir [1993](#page-14-0); Patino et al. [2000;](#page-14-0) Jicha et al. [2010](#page-14-0)). For the Ba/La ratio, it has also been proposed that the primary control is variation in La (Carr et al. [2007\)](#page-13-0), which may reflect variations in the degree of melting of the mantle wedge (Sadofsky et al. [2008\)](#page-15-0) and/or contribution from the melting of volcanic rocks in/on the downgoing slab (e.g. Hoernle et al. [2008](#page-14-0); Gazel et al. [2009](#page-13-0)). At the SVZ, in contrast, these trace element ratios are comparatively uniform and low (in spite of their internal variability described by Wehrmann et al. in review) (Fig. [5](#page-7-0)a–d). Nb/U ratios are uniformly low in all CAVA and SVZ segments ($\lt 10$; not shown) compared to the value of 47 ± 10 for oceanic basalts (MORB and OIB) from Hofman et al. [\(1986](#page-14-0)), reflecting enrichment of U relative to Nb by hydrous subduction fluids and melts.

A different pattern is observed for Pb/Ce and Pb/U ratios, which are highest at the southern-central SVZ, slightly lower in Guatemala, and gradually decreasing to El Salvador, Honduras, Nicaragua, and Costa Rica (Fig. [5](#page-7-0)e, f). The low values at Costa Rica and Nicaragua are considered to primarily reflect addition of melts from the subducting Galapagos hot spot track to the mantle wedge beneath CCR, and subsequent flow of this material northward as far as north-west Nicaragua (Hoernle et al. [2008](#page-14-0); Gazel et al. [2009](#page-13-0)).

Assimilation of continental plutonic basement can also affect the highly fluid-mobile to less fluid-mobile element ratios, when long-term subduction recycling has concentrated highly fluid-mobile elements in the crust of the

high values at the Nicaraguan segment of the CAVA. Symbols and colours as in Figs. [3](#page-6-0) and [5](#page-7-0)

overriding plate by intrusion of highly fluid-mobile element-rich melts. In particular at the SVZ, many authors indeed favour a scenario of increasing interaction of the melts with progressively thickening crust towards the north (e.g. Hildreth and Moorbath [1988](#page-14-0); Davidson et al. [1987](#page-13-0); Ferguson et al. [1992\)](#page-13-0). Based on U-series disequilibria, Reubi et al. ([2011\)](#page-15-0) concluded that assimilation of plutonic rocks in the volcano basement can be significant. Oxygen and Pb isotopes, however, show that crustal contamination is not the major factor controlling along-arc changes in the geochemistry of the SVZ arc lavas unless ancient Proterozoic lower crust is present beneath the NSVZ (Jacques et al. [2013](#page-14-0) and G. Jacques, unpublished data).

These ratios of highly fluid-mobile to less fluid-mobile or fluid-immobile trace elements (Ba/Th, Ba/Nb, U/Th, Sr/Ce, Pb/Ce, and Pb/U) are commonly believed to serve as proxies for the delivery of fluids from the subducting slab to the mantle wedge. With regard to the issues raised above, the observed strong variation in these trace element ratios cannot directly be translated into different absolute amounts of fluids in the individual arc segments in a straightforward manner. Rather than simply representing varying amounts of fluids, the observed trace element patterns more likely point to differences in the fluid/melt compositions, in response to different subduction input materials and slab processes.

Lavas from CCR and the NSVZ have the highest La/Yb and Nb/Y ratios, which can be related to differing degrees of melting and/or an enriched mantle wedge component (Figs. [5](#page-7-0)g). In Costa Rica, this has been attributed to the addition of low-degree melts from the Galapagos hotspot track with high La/Sm, La/Yb, and Nb/Y to the mantle wedge (Hoernle et al. [2008](#page-14-0); Gazel et al. [2009](#page-13-0)). The NSVZ

also shows high La/Yb, La/Sm, and Nb/Y but low Ba/Nb, U/Th, Sr/Ce, and Pb/U, which might, similar to the situation in Costa Rica, indicate that an enriched source component was involved in magma genesis beneath the NSVZ.

Hydrous flux melting

Typically, hydrous flux melting in subduction zones is associated with two characteristics: (a) high values of highly fluid-mobile to less fluid-mobile elements (e.g. U/Th, Sr/Ce, Ba/Th, Ba/Nb, and U/La), serving as proxies for high fluid flux, and (b) low ratios of more incompatible to less incompatible elements of relatively low fluidmobility (e.g. La/Yb, Sm/Lu, Nb/Y, and Nb/Zr), reflecting high degrees of melting (e.g. Carr et al. [1990](#page-13-0)). We here use Sm/Lu as an indicator for the degree of melting instead of the widely employed La/Yb, because the latter suffers ambiguity arising from the mobilisation of La by subduction fluids at high temperatures and by possible addition from enriched source materials as described above. Sr/Ce, besides acting as an indicator for subduction fluids, is also affected by fractionation of plagioclase during magma evolution such that Sr is incorporated into the plagioclase, and the Sr/Ce ratio decreases when plagioclase precipitates from the melt. In the presence of fluids, however, the fractionation of plagioclase is suppressed (e.g. Grove and Baker [1984](#page-14-0); Sisson and Grove [1993](#page-15-0)). Therefore, high Sr/Ce values likely reflect high fluid contents interrelated with limited plagioclase fractionation, while low Sr/Ce points to less fluids and accordingly Sr removal by plagioclase.

Serpentinite, if present in the crust and uppermost mantle for the incoming plate, is predicted to be a major source of fluids released from the slab beneath the arc (e.g. Ulmer and Trommsdorff [1999\)](#page-15-0). Additionally, water may be contributed by dehydration of other mineral phases such as talc or chlorite (Spandler et al. [2008](#page-15-0)). Water release through deserpentinisation of the slab during subduction is a pressure–temperature-dependent reaction, whereby the temperature conditions play a key role (e.g. Hacker [2008](#page-14-0); van Keken et al. [2011](#page-15-0); Cooper et al. [2012\)](#page-13-0). The slab temperature is generally a function of slab age, decreasing with increasing age of the slab, and it gradually increases as the slab proceeds to greater depths.

The inverse arrays formed between Sm/Lu with both U/Th and Sr/Ce (Fig. [6](#page-8-0)a, b) are consistent with high fluid fluxes into the mantle wedge, particularly beneath the CSVZ, Nicaragua, and El Salvador, resulting in the largest degrees of melting. Each of these areas is associated with the slab surface being more than 120 km beneath the mantle wedge, where the pressure–temperature conditions allow serpentine to break down and dehydrate. At the CAVA, there is clear evidence that serpentinite forms in the uppermost mantle of the incoming plate through bendfaulting at the outer rise of the subduction zone (Ranero et al. [2003;](#page-14-0) Grevemeyer et al. [2007;](#page-14-0) Ivandic et al. [2007\)](#page-14-0). It is likely to play a key role also in the water transfer of the CSVZ via the incoming fracture zones. Subducting fracture zones are predicted to require lower temperatures to dehydrate at subarc depths (Hacker [2008\)](#page-14-0). Moreover, although no detailed thermal modelling has to date been performed along the SVZ, the northward age progression of the incoming plate expectably produces higher temperatures beneath the CSVZ than beneath the TSVZ and the NSVZ, promoting a larger fluid contribution to the mantle wedge beneath the CSVZ. This peak fluid flow coincides with a peak in magma extrusion rate in the CSVZ in an along-SVZ consideration (Völker et al. [2011](#page-15-0)). This latter correlation does, however, not apply to all arc segments considered here. In Nicaragua, magma extrusion rates are low despite the high degrees of melting (Sadofsky et al. [2008](#page-15-0)). It has been proposed, however, that Nicaragua experiences large magma intrusion in a scenario of a positive feedback mechanism of upper plate extension because of structure weakening through magma intrusion and subsequent decompression melting because of crustal extension (Phipps-Morgan et al. [2008](#page-14-0)).

The TSVZ and Guatemala have intermediate Sm/Lu, U/Th, and Sr/Ce, whereas CCR and the NSVZ have low U/Th and Sr/Ce and extend to the highest Sm/Lu. Although the slab beneath the TSVZ is sufficiently warm at the depth it reached beneath the arc to allow serpentine to dehydrate, the incoming plate beneath the TSVZ was possibly not serpentinised to the same degree as beneath the CSVZ. This might be due to the near-absence of fracture zones in this area (Hoernle et al. [2010](#page-14-0)). Only the Mocha Fracture Zone, not nearly as prominent a feature as the Valdivia Fracture Zone further to the south (Dzierma et al. [2012](#page-13-0)), is present outboard the TSVZ. A strong, but localised fluid signal at Volcán Nevado de Longaví, however, has been attributed to the Mocha Fracture Zone (Sellés et al. [2004](#page-15-0); Sellés [2006\)](#page-15-0), but in an arc-scale context, this is not a major fracture zone compared to those outboard the CSVZ. The fluid signal at the SSVZ is low, likely related to only incipient serpentinisation of the incoming plate, which is young and therefore warmer in this section of the arc than farther north (Völker et al. [2011\)](#page-15-0).

Guatemala, CCR, and the NSVZ are characterised by shallow slabs subducting at relatively low angles and thick crust/lithosphere of the overriding plate resulting in short melting columns. Modelling results of Syracuse et al. [\(2010](#page-15-0)) leave ambiguity for the possibility of deserpentinisation beneath these arc segments. The estimated temperatures the slabs have reached at the respective depths beneath the arc partly coincide and partly do not coincide with the serpentine stability field, depending on the underlying model of Syracuse et al. ([2010](#page-15-0)) and the different constraints on subduction geometry by Tassara et al. [\(2006](#page-15-0)) (Fig. [2\)](#page-3-0) versus that of Syracuse and Abers [\(2006](#page-15-0)) for the SVZ, and the data revision of Syracuse et al. [\(2010](#page-15-0)) for the CAVA compared to their earlier results. While the temperature regime might be high enough for deserpentinisation to occur beneath Guatemala, the shallow depth and corresponding lower temperature of the subducting slab beneath the volcanic front of the NSVZ and Costa Rica may limit serpentine dehydration (even if it was present in the uppermost mantle of the incoming plate). This would be consistent with a lower fluid flux and the low U/Th and Sr/Ce we observe in the arc output of the NSVZ and Costa Rica. For the more evolved melts erupted at the NSVZ, the Sr/Ce values might also have experienced a lowering through plagioclase fractionation, which is also evident from the negative Eu anomalies in Fig. [4.](#page-6-0) Although the depth of the subducting slab and the thickness of the overlying crust/lithosphere beneath Guatemala and CCR are very similar, the Sm/Lu ratios in the Costa Rica lavas extend to significantly higher values than in Guatemala. Combined with the Galapagos-type isotopic compositions of the CCR arc lavas, this is likely to reflect the contribution of melts from the incoming Galapagos hot spot track (seamount domain) (Hoernle et al. [2008](#page-14-0)) with elevated Sm/Lu. Therefore, high Sm/Lu (and other more to less incompatible element ratios of limited fluid-mobility, such as La/Yb or Nb/Y) can also reflect the presence or addition of enriched components to the mantle wedge. The higher Sm/Lu of the NSVZ as compared to the TSVZ could reflect lower degrees of melting due to a lower fluid flux, but it could also reflect the presence/addition of enriched material in the mantle wedge beneath the NSVZ. Such scenario is consistent with the enriched Sr–Nd–Hf isotopic composition of the NSVZ, since the Pb and O isotope ratios argue against assimilation of all known crustal material from this area (G. Jacques, unpublished data). Finally, the greater degree of differentiation of the NSVZ could also have contributed to the higher Sm/Lu compared to the TSVZ. Sm/Lu forms, however, no clear differentiation trend when compared to $SiO₂$ or Mg-number (Online Resource 4a), suggesting that magma evolution was of minor importance for the variation in Sm/Lu. In conclusion, the high ratios of more incompatible to less incompatible elements, coupled with low ratios of highly fluidmobile to less fluid-mobile elements may either reflect lower degrees of melting due to low fluid flux beneath the volcanic front underlain by a shallow subducting slab, or be related to subducting slabs where the lower oceanic crust/ upper mantle has not been substantially hydrated. Furthermore, an involvement of enriched OIB-type components, either on the subducting plate or within the mantle wedge, could generate such a combination of incompatible element ratios.

Source depletion versus source enrichment and the depth of melting

Ratios of Th, Ta, Nb, and $TiO₂$ to Yb are used to derive information about the composition of the source and the depth of melting (Pearce [1983](#page-14-0), [2008\)](#page-14-0). Caution must be applied when rocks that have been generated by variable degrees of melting and differentiation are compared. In these cases, the initial ratio will be shifted to higher values, because the more incompatible element (Th, Ta, Nb, and Ti) will be enriched relative to Yb, both by relatively lower degrees of melting at depth and by magma differentiation.

Plots of Th/Yb versus Nb/Yb or Ta/Yb can be used to identify depleted versus enriched mantle sources and to evaluate the role of sediment-derived supercritical fluids/ melts (Pearce [1983,](#page-14-0) [2008](#page-14-0)) (Fig. [7\)](#page-11-0). At all the SVZ and the CAVA, Th/Yb correlates positively with Nb/Yb, and the Th/Yb values are generally elevated compared to MORB and intra-plate basalts at a given Nb/Yb (or Ta/Yb) ratio. While the entire SVZ shows a strong arc signature, plotting in an array distant from the MORB-OIB field, a few Nicaraguan samples from small monogenetic centres at Nejapa and near Mombacho have compositions similar to E-MORB with respect to this classification.

At the SVZ, CSVZ samples display the lowest values, indicating that they are derived from the most depleted mantle sources. The TSVZ samples have intermediate and the NSVZ samples have the highest values, pointing to increasing source enrichment towards the north. No differentiation trend, however, is observable within the NSVZ sample suite when comparing these ratios with, e.g., $SiO₂$, Mg-number, or incompatible, fluid-immobile trace elements, and more differentiated rocks from the TSVZ do not exceed the NSVZ with regard to Th/Yb and Nb/Yb (Online Resource 4b). Samples from Nicaragua and El Salvador carry signatures of the most depleted sources amongst the CAVA rocks, while samples from Guatemala are elevated compared to an intermediately enriched mantle source and reach the most arc-like composition with the greatest enrichment of Th/Yb relative to the MORB and the intraplate array. Rocks from Costa Rica, especially from CCR, overlap with the NSVZ. The high Costa Rican Th/Yb and Nb/Yb values (Fig. [7](#page-11-0)) reflect the derivation of OIB material through melting of the subducting Galapagos hot spot track beneath Costa Rica (Hoernle et al. [2008](#page-14-0)).

 $TiO₂/Yb$ versus Nb/Yb relationships can be instructive to constrain the depth of melting (Fig. [8](#page-11-0)) in relation to the temperature regime. In addition, a distinction can be made between enriched versus normal MORB-like source components, and possible crustal assimilation (Pearce [2008](#page-14-0)). Since $TiO₂$ is particularly prone to be affected by magma differentiation through fractionation of Fe–Ti-oxides, the data sets were filtered such that only samples with

Fig. 7 Th/Yb versus Nb/Yb for the SVZ compared to the CAVA (symbols and colours as in Figs. [3](#page-6-0) and [5](#page-7-0)), after Pearce ([2008\)](#page-14-0). The SVZ rocks form a positive correlation with elevated Th/Yb compared to the MORB-OIB array. Of the SVZ, the CSVZ shows the lowest Nb/Yb and Th/Yb, indicating their derivation from the most depleted mantle source, and the TSVZ has intermediate and the NSVZ has highest values, pointing to increasing source enrichment. Nicaraguan rocks partly overlap with the CSVZ, plotting in the most depleted field, including rocks with the least arc-like compositions. Compositions of input marine sediments are also shown (asterisks, yellow on red SVZ, Jacques et al. ([2013\)](#page-14-0), red on yellow: SVZ, from Lucassen et al. [\(2010](#page-14-0)), green CAVA, this study and from Heydolph et al. [2012](#page-14-0)), and they fall into the volcanic arc array. Data for the seamount province subducting beneath Costa Rica (blue stars) from Hoernle et al. ([2000\)](#page-14-0)

 $MgO \geq 4$ and $SiO₂ \leq 54.5$ wt% are presented in Fig. 8. In the SVZ, the CSVZ samples have the most N-MORB-like composition, while the TSVZ samples have both higher Nb/Yb and TiO₂/Yb, plotting into the MORB and OIBarrays. SSVZ samples show shallow derivation from E-MORB composition. This points to deeper melting beneath the TSVZ than in the CSVZ and SSVZ, which would be in agreement with the subduction geometry (Fig. [2](#page-3-0)a; Völker et al. [2011](#page-15-0) after Tassara et al. [2006](#page-15-0)). CAVA rocks span a wide range in the $TiO₂/Yb$ versus Nb/Yb diagram. The Nicaraguan and Costa Rican samples cover the entire MORB (shallow melting) array and extend into the OIB (deep melting) array. The large range and peak $TiO₂/Yb$ ratios in the Nicaraguan samples likely respond to the great depth reached by the subducting slab and the long melting column (Fig. [2](#page-3-0)b). The high $TiO₂/Yb$ of one Costa Rican sample from Barva volcano likely also reflects addition of melts from the seamount province of the subducting Galapagos hot spot track, of which several samples are characterised by high $TiO₂/Yb$.

Fig. 8 $TiO₂/Yb$ versus Nb/Yb for the SVZ compared to the CAVA (symbols and colours as in Figs. [3](#page-6-0) and [5\)](#page-7-0), after Pearce ([2008\)](#page-14-0). Since the $TiO₂/Yb$ ratio is affected by oxide crystallisation, data filtering was applied: only samples for which we determined $MgO \geq 4$ and $SiO₂ \le 54.5$ wt% are contained in this diagram, whereby the NSVZ becomes excluded. The TSVZ shows the deepest melting compared to the CSVZ, possibly in response to the greatest slab depth in this arc segment. At the CAVA, the Costa Rican arc segment trends towards and partly overlaps with the subducting seamount province (blue stars), showing the most enriched compositions. Data for the seamount province subducting beneath Costa Rica from Hoernle et al. [\(2000\)](#page-14-0)

The composition of subducted sediments and subduction fluids

Sediment subduction appears to play a key role in producing the variable compositions of the erupted materials at both arc systems. Outboard the CAVA from Nicaragua to Guatemala, the subducting sediment package consists of $a \sim 430$ m thick layer of sediments (Coulbourn et al. [1982](#page-13-0)). The lower layer (\sim 250 m thick) consists primarily of Middle Miocene chalky carbonate ooze, whereas the upper layer (\sim 180 m thick) consists of Middle Miocene abyssal clay and Upper Miocene to Quaternary hemipelagic diatomaceous mud (Patino et al. [2000](#page-14-0)).

With respect to Th/Yb versus Nb/Yb (Fig. 7), both the carbonate and the hemipelagic sediments plot into the volcanic arc array, and arc rocks from Nicaragua and El Salvador have compositions between the two. High Ba, Ba/La, Ba/Th, Ba/Nb, and U/Th are the characteristic for both the carbonate and the hemipelagic sediments. The carbonate sediments also have high Sr, Sr/Th, Sr/Yb, Sr/Ce, and low Nb and REE, while the hemipelagic sediments show high Cs, Th, U, Nb, and U/La (Table [1](#page-4-0); Fig. [4](#page-6-0)d). Rocks from the volcanic front at the CAVA, in particular in Nicaragua, carry a pronounced signature of

subducted sediments (Patino et al. [2000](#page-14-0)). Since elements such as Ba and Sr are strongly enriched in particular in the marine carbonates and scavenged by subduction fluids, the erupted rocks show markedly elevated Ba and Sr concentrations compared to elements of a relatively lower fluidmobility such as Th, Nb, and REE, resulting in high ratios of Ba/(LREE, Nb, Ta, Th), U/Th, and Sr/LREE (Figs. [5,](#page-7-0) [6](#page-8-0)a, b).

In contrast, marine sediments subducted at the Chile trench are dominated by high Pb, Cs, U, Nb, and Rb concentrations, while being comparatively depleted in Sr (Table [1](#page-4-0); Fig. [4d](#page-6-0)). Ba is relatively depleted in the sediment samples outboard the central part of the SVZ (\sim 36–40°S) (data from Jacques et al. [2013](#page-14-0), Lucassen et al. [2010](#page-14-0)), whereas concentrations reach $2,250 \mu g/g$ Ba offshore the NSVZ and TSVZ (\sim 33–36.5°S), similar to the Nicaraguan carbonate sediments (Table [1](#page-4-0)). The sediments on the incoming plate show some minor differences to those on the continental slope of the overriding plate, with the incoming plate sediments having slightly higher Ba/Th and Pb/Ce. For the interpretation of the erupted rocks with regard to their source components, a complication arises from the fact that several elements cannot be unambiguously ascribed to a unique source material (e.g. subducting sediments versus altered oceanic crust). Thorium and REE concentrations higher than in MORB are considered to be derived from subducting sediments, for they do not become enriched during hydrothermal alteration of the incoming oceanic crust. In the Th/Yb versus Nb/Yb diagram (Fig. [7](#page-11-0)), the Chilean marine sediments entirely overlap with the TSVZ. For Pb, the picture is not as straightforward, since Pb can be derived either from the basaltic layer of the downgoing plate (Plank [2005](#page-14-0); Goss and Kay [2006](#page-14-0)) or by arc-cannibalism from Pb-rich continentally-derived volcaniclastic sediments, such as the Chilean marine sediments, or a combination of both.

In summary, the subducting sediments offshore Chile and Central America can be clearly distinguished from each other by their trace element composition, in particular with respect to Pb and Ba (Fig. 9). The arc rocks mirror the compositional differences of the sediments, with the SVZ rocks having high Pb, Pb/Ce, and Pb/Yb, while the CAVA rocks extend towards high Ba, Ba/Th, Ba/Nb, U/Th, and Sr/Ce (Figs. [5,](#page-7-0) 9). Fluids released from a dehydrating serpentinised slab have the capacity to transport the sediment signal to the arc magmas (e.g. Halama et al. [2011](#page-14-0)). Within this association, the trends formed by the arc rocks are somewhat shifted towards a Pb–Ba ratio slightly higher than that of the corresponding sediments (Fig. 9), which most likely originates from a Pb addition from the subducting ocean floor basalt. The direct compositional relationship between the subducting sediments and erupted volcanic rocks underscores the imprint of the sedimentary

Fig. 9 Pb versus Ba for the SVZ and the CAVA, illustrating the distinct enrichment of individual fluid-mobile elements at the different arcs (symbols and *colours* as in Figs. [3](#page-6-0) and [5\)](#page-7-0). The SVZ is dominated by the fluid-mobile element Pb, in line with the high Pbconcentration in the marine sediments offshore southern Chile (asterisks, yellow on red Jacques et al. [\(2013](#page-14-0)), red on yellow Lucassen et al. [2010\)](#page-14-0). The CAVA, in contrast, shows strongly elevated concentrations of the fluid-mobile element Ba, resulting from the Ba-enrichment of the incoming marine carbonate sediments (brown-green asterisks, this study and Heydolph et al. [2012\)](#page-14-0). Data for the arrow to depleted morb mantle (DMM) and altered oceanic crust (AOC) from Salters and Stracke ([2004\)](#page-15-0) and Sadofsky et al. [\(2009](#page-15-0)), respectively

input into the subduction zone on the composition of the erupted arc rocks.

Conclusion

In this paper, we have compared two different arc systems, the continental Chilean Southern Volcanic Zone and the transitional to oceanic Central American Volcanic Arc, which display a number of different features regarding subduction geometry and geochemistry of the involved materials. The CAVA lavas, in particular those from Nicaragua, extend to very high Ba/Th, Ba/Nb, U/Th, and Sr/Ce ratios, while the Central and Southern SVZ show high Pb/Ce and Pb/U ratios. An inverse correlation exists between highly fluid-mobile to less fluid-mobile element ratios and proxies for degree of melting (e.g. Sm/Lu) whereby the CSVZ in Chile is most similar to the oceaniclike Nicaragua/El Salvador at the CAVA, showing the highest degrees of melting and/or derivation from the most depleted mantle sources. Costa Rica and the NSVZ have the highest Sm/Lu and La/Yb, which most likely reflects a Combination of the incoming marine can be a state of the same of the same of the same of melting and derivation of individual fluid mobile elements of melting and colours is in Fig. 3 and 5). The SVZ of different arcs (sy

The type of fluid signal is fundamentally different between the SVZ and the CAVA such that arc rocks at the SVZ show high Pb, while the CAVA is characterised by strongly elevated Ba. The same compositional difference is displayed by the subducting marine sediments with high Pb offshore the SVZ, and high Ba outboard the CAVA, pointing to a clear compositional relationship between the subducted sediments and the subduction fluids/hydrous melts they release. This geochemical signal is preserved during infiltration of the fluids into the mantle wedge and formation of arc magmas, and likely recycled back into the system by deposition of arc volcanic ejecta onto the ocean floor. In conclusion, the sedimentary input into the subduction system appears to have the greatest effect on the composition of fluid-mobile elements in the arc rocks, with high concentrations in the sediments and ratios of highly fluid-mobile to less fluid-mobile elements (e.g. Ba/Th, Ba/Nb, U/Th, Sr/Ce, Pb/Ce, and Pb/U), whereas the composition of the mantle wedge (enriched versus depleted) and the depth and degrees of melting appear to control the variations in the ratios highly incompatible to less incompatible, relatively immobile elements (e.g. Nb/Yb, Ta/Yb, La/Yb, Sm/Lu, and Nb/Y).

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