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Contrasting He–C relationships in Nicaragua and Costa Rica: insights into C cycling through subduction zones[☆]

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Abstract

We report ^{3}He/^{4}He ratios, relative He, Ne, and CO_2 abundances as well as $\delta^{13}C$ values for volatiles from the volcanic output along the Costa Rica and Nicaragua segments of the Central American arc utilising fumaroles, geothermal wells, water springs and bubbling hot springs. CO_2/^{3}He ratios are relatively constant throughout Costa Rica (av. 2.1×10^{10}) and Nicaragua (av. 2.5×10^{10}) and similar to arcs worldwide ($\sim1.5\times10^{10}$). $\delta^{13}C$ values range from -6.8‰ (MORB-like) to -0.1‰ (similar to marine carbonate (0‰)). ^{3}He/^{4}He ratios are essentially MORB-like ($8\pm1~R_A$) with some samples showing evidence of crustal He additions – water spring samples are particularly susceptible to modification. The He–CO_2 relationships are consistent with an enhanced input of slab-derived C to magma sources in Nicaragua ((L+S)/M = 16; where L, M and S represent the fraction of CO_2 derived from limestone and/or marine carbonate (L), the mantle (M) and sedimentary organic C (S) sources) relative to Costa Rica ((L+S)/M = 10). This is consistent with prior studies showing a higher sedimentary flux to the arc volcanics in Nicaragua (as traced by Ba/La, ^{10}Be and La/Yb). Possible explanations include: (1) offscraping of the uppermost sediments in the Costa Rica forearc, and (2) a cooler thermal regime in the Nicaragua subduction zone, preserving a higher proportion of melt-inducing fluids to subarc depths, leading to a higher degree of sediment transfer to the subarc mantle. The absolute flux of CO_2 from the Central American arc as determined by correlation spectrometry methods (5.8×10^{10} mol/yr) and CO_2/^{3}He ratios (7.1×10^{10} mol/yr) represents approximately 14–18% of the amount of CO_2 input at the trench from the various slab contributors (carbonate sediments, organic C, and altered oceanic crust). Although the absolute flux is comparable to other arcs, the efficiency of CO_2 recycling through the Central American arc is surprisingly low (14–18% vs. a global average of $\sim50\%$). This may be attributed to either significant C loss in the forearc region, or incomplete decarbonation of carbonate sediments at subarc depths. The implication of the latter

case is that a large fraction of C (up to 86%) may be transferred to the deep mantle (depths beyond the source of arc magmas).

1. Introduction

Understanding how physical features of subduction zones influence the chemistry of arc magmas is a fundamental issue in subduction-related studies. Prior studies have focused on the Central American volcanic arc because it is characterised by dramatic variations in the angle of subduction, the thickness of the arc crust through which magmas erupt and the faulting style of the subducting plate [1–3]. Several geochemical parameters, including Ba/La, ^{10}Be, B, La/Yb and $\delta^{15}N$, have been shown to effectively track changes along the arc due to variations in these subduction forcing functions [1,4–8]. Of particular interest is the Nicaragua–Costa Rica section of the arc, since the volcanic outputs in these adjacent segments show remarkable geochemical differences. For example, particularly low ^{10}Be and B concentrations are observed in the volcanic output in Costa Rica versus extremely high values measured in Nicaraguan volcanics [7–9]. These geochemical data provide evidence for a high slab flux and recycling of sediments beneath Nicaragua, but with a minimal slab contribution to the volcanic output in Costa Rica, despite similar sedimentary inputs at the trench. Therefore, a major aim of this study is to assess how regional differences in subduction style affect the volatile systematics – particularly He–C isotopes and relative abundances – of the arc output in Nicaragua and Costa Rica.

The Central American arc also presents a unique opportunity to consider C cycling through subduction zones since the subducting sedimentary sequence on the incoming Cocos plate is especially carbonate-rich (26.55 wt% CO_2 [10]), resulting in an extremely high influx of carbon into the subduction zone. Determining whether this manifests itself in an enhanced volcanic CO_2 flux along the arc relative to other arcs worldwide is an important objective of this study. A related goal is to assess whether a balance exists between CO_2 input at the trench and CO_2 emanating from Central American volcanoes – as has been postulated for N_2 [6].

A final aim is to consider the nature of the volcanic output of carbon in relation to its provenance on the subducting slab. By coupling CO_2 and He measurements (isotopes and relative abundances), we can identify and quantitatively assess the various contributors to the magmatic output from the various subduction zone reservoirs: (a) the mantle wedge, (b) the overlying arc crust through which the magmas erupt and (c) the subducting slab – both the oceanic basement and sedimentary veneer of the slab. Helium isotopes are sensitive indicators of mantle derivation and crustal influences, whereas $\delta^{13}C$ values can be used to identify mantle (M), marine carbonate/limestone (L) and organic sedimentary (S) components [11]. A previous study investigating He–C relationships in the North Fiji back-arc basin [12] suggested that significant fractionation of L and S components occurs during the subduction process. Since the sedimentary input on the Cocos plate is well characterised in terms of L and S components, our study of the He–C relationships along the volcanic front in Central America will be able to test this conclusion.

2. Geologic setting and background

Volcanoes in Costa Rica and Nicaragua form the southern segment of the Central American volcanic arc which extends from central Costa Rica to western Guatemala (see Fig. 1). Volcanism along this active margin is the consequence of Cocos plate subduction beneath the Caribbean plate. This region has been the focus of numerous geochemical studies (e.g. [1,6,9,13,14]) since there are striking changes in subduction forcing param-

eters (e.g. faulting style of incoming plate, slab dip, crustal thickness) whose influence can be assessed at a relatively fine scale given the narrow spacing of volcanoes (~ 25 km) compared with that found in other arc settings (40–70 km) [1].

Despite comparable subduction rates (~ 8–9 cm/yr) and incoming sediment compositions (inferred from similar lithologies in Ocean Drilling Project (ODP) site 1039 and Deep Sea Drilling Project (DSDP) site 495 offshore Costa Rica and Guatemala, respectively), remarkable geochemical differences are observed in the volcanic output in Nicaragua and Costa Rica. For example, Morris et al. [7] measured exceptionally high [10]Be enrichments in lavas from Nicaragua ([10]Be/Be up to 59.9×10^{-11}) while anomalously low values were found in neighbouring Costa Rica ([10]Be/Be = 1.4×10^{-11}). [10]Be is a short-lived ($t_{1/2} \sim 1.5$ Myr) cosmogenic radionuclide that becomes concentrated in the uppermost oceanic sediments. Because postulated mantle [10]Be contents are low, any enrichments observed in erupted arc lavas are indicative of contributions from recently subducted sediment. Likewise, Ba/La ratios, often used to trace a slab-derived fluid phase, are high in Nicaragua and low in Costa Rica [4,5]. Additionally, low La/Yb ratios, generally attributed to high degrees of partial melting, are found in Nicaragua [4]. It has been suggested that a higher slab flux could be responsible for enhanced melting of the wedge beneath Nicaragua [4]. The results of these findings suggest that Nicaraguan volcanics are more strongly influenced by a slab-sediment signal than volcanoes in Costa Rica.

The contrasting geochemical characteristics observed along the arc have been attributed to variations in physical subduction parameters such as: (1) crustal thickness, (2) angle of dip, (3) sediment underplating, (4) faulting style and (5) subduction erosion [1,3–5,7,9,15]. Relatively thinner crust (32 km) and a higher angle of slab dip (65–75° below the volcanic front) in Nicaragua afford a geometry conducive to a high flux of slab fluids being transferred to a relatively small volume of asthenosphere, leading to a high degree of melting [1,4]. Although Costa Rica is characterised by shallower dips (35–65°) and slightly thicker crust (40 km), the virtual absence of a [10]Be signal in

these lavas has been attributed to either sediment underplating, whereby sediments are effectively scraped off the down-going plate before reaching the zone of magma generation [15], or subduction erosion [9,16,17]. In the former case, the process of sediment underplating may be related to faulting style. A recent study [3] looking at the relationship between outer rise faulting and geochemical variability along the arc showed how large offsets in reactivated trench-parallel faults on the plate subducting beneath Nicaragua could protect sediment from offscraping, resulting in a high sediment flux being transferred into the zone of magma generation. In contrast, the relatively small displacement of faults (new) in the slab subducting beneath Costa Rica would favour offscraping and thus limit the sediment flux in the volcanic output, as observed. An alternative explanation for the discrepancy in [10]Be and other slab signals is the idea of subduction erosion, where any slab signature is essentially diluted by material eroded from the underside of the upper plate during subduction [9,16,17]. Seismic evidence reveals that as seamounts are subducted, they can efficiently erode the upper plate by a process referred to as seamount tunnelling [17]. Seamounts associated with the Galapagos hotspot are common features observed on the Cocos plate subducting beneath Costa Rica, but they are virtually non-existent on the downgoing plate in Nicaragua. The reason why subduction erosion is enhanced in Costa Rica relative to Nicaragua may be related to the difference in seafloor morphology on the subducting plate [16–18].

3. Analytical techniques

Geothermal fluid samples were collected from fumaroles, bubbling hot springs, water springs and geothermal wells using evacuated AR-glass flasks and/or copper tubes (see [19] for further details on collection procedures). Samples were extracted on a vacuum line using a series of traps at liquid nitrogen and acetone/dry ice temperatures to isolate any water vapour and to separate the condensable gas fraction (mainly CO_2) from the non-condensable fraction. The condensable

Fig. 1. Regional map of Central America showing the location of the major volcanic centres in Costa Rica and Nicaragua. The Cocos plate is presently subducting beneath the Caribbean plate at a rate of 82–88 mm/yr [2]. Deep-sea drill site 1039 from ODP leg 67 [33] is shown for reference.

fraction was frozen into a Pyrex® breakseal, whereas the non-condensable fraction was purified using a hot Ti getter and activated charcoal traps. A calibrated split of this gas was aliquoted into an AR-glass breakseal. Helium and neon abundance measurements, as well as the ^{3}He/^{4}He ratios, were measured on a MAP 215 noble gas mass spectrometer. The CO_2 fraction of the condensable gas was further purified using a variable temperature trap, and abundances were measured manometrically. The $\delta^{13}C$ values were measured from an aliquot of the CO_2 gas using a VG Prism stable isotope mass spectrometer.

4. Results

We report ^{3}He/^{4}He ratios, $CO_2/^3$He ratios, He abundances (for water spring samples) and C isotope results for samples in Tables 1[1] (Costa Rica)

and 2[1] (Nicaragua). Sample locations are given in Fig. 1, and the complete data set is plotted as a function of latitude in Fig. 2.

4.1. ^{3}He/^{4}He ratios

All measured ^{3}He/^{4}He ratios (reported as (R_m/R_A) where R_m = measured ^{3}He/^{4}He of sample and $R_A = {}^3$He/^{4}He of air) have been corrected for the effects of atmospheric contamination (to R_C/R_A). Agreement between air-corrected duplicate samples generally falls within 0.2 R_A with the exception of samples from Poás and San Jacinto where duplicates vary by 0.38 and 0.36 R_A, respectively.

Air-corrected ^{3}He/^{4}He ratios span a wide range in values (from 0.74 R_A to 8.1 R_A) indicating the influence of both crustal (^{3}He/^{4}He ≈ 0.05 R_A) and

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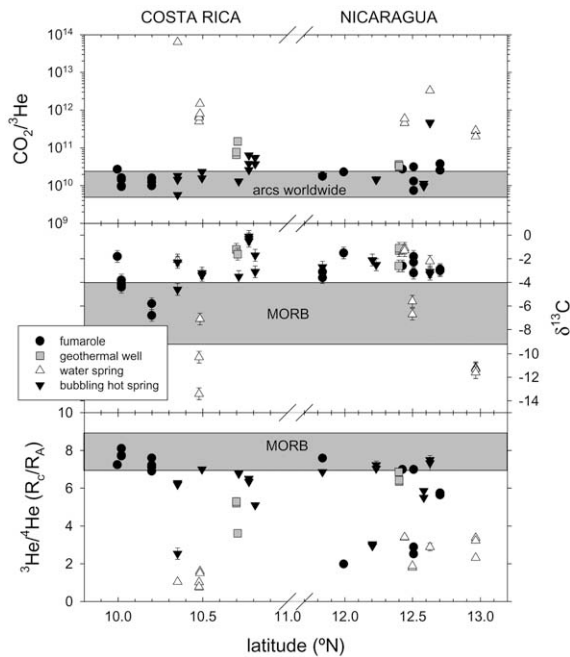[1] See Tables 1 and 2 in the online version of this paper.

Fig. 2. Along-arc variations in $CO_2/^3He$, $\delta^{13}C$ (CO_2), and $^3He/^4He$ results for geothermal fluids from Costa Rica and Nicaragua. The shaded boxes show: (1) the $CO_2/^3He$ range for arcs worldwide: $1.5 \pm 1.1 \times 10^{10}$ [27], (2) the MORB range of $\delta^{13}C$ values: $-6.5 \pm 2.5\permil$ [11], and (3) the $^3He/^4He$ range for MORB: 8 ± 1 R_A [19].

(upper) mantle (8 ± 1 R_A) contributions [19] to Central American volcanism. Although other studies (see [20,21]) have argued for a plume-like mantle beneath Costa Rica (associated with the Galapagos hotspot), we find no indication of plume-like He isotope values anywhere along the arc. MORB (mid-ocean ridge basalt)-like and predominantly radiogenic $^3He/^4He$ ratios are found in both Costa Rica and Nicaragua. In addition, there is no evidence for systematic variations in He isotopes along the strike of the arc (Fig. 2), despite a decrease in crustal thickness towards the north. Based on our observations, we note that much of the observed variation is related to the type of geothermal media sampled (i.e. fumaroles, bubbling hot springs, water springs and geothermal wells).

The highest $^3He/^4He$ values are found in fumarole samples from both segments of the arc – at

Turrialba (8.1 R_A), Poás (7.6 R_A) in Costa Rica and at Mombacho (7.6 R_A) in Nicaragua. Indeed, most of fumarole samples, irrespective of location, lie within the typical MORB range (8 ± 1 R_A), consistent with values observed at other arcs worldwide (e.g. [19,22,23]). The principal exception to this observation is a flank fumarole sample from Masaya, where air contamination is a major problem (the measured He/Ne is exceptionally low). The lowest $^3He/^4He$ values (0.7–3.4 R_A) are found in water spring samples, and point to a significant radiogenic He contribution. Based on prior arguments against He being subducted into the mantle [24], the presence of radiogenic He likely reflects contamination processes in the uppermost crust (see also Section 5.1). The bubbling hot spring and geothermal well samples show varying degrees of crustal interaction with $^3He/^4He$ ratios ranging from 2 R_A to MORB-like values.

4.2. $\delta^{13}C$ (CO_2)

The $\delta^{13}C$ (CO_2) values of most samples (Fig. 2) are $> -4\permil$, or higher than the nominal range found in MORB ($-6.5 \pm 2.5\permil$ [11]). This includes all sample types (fumaroles, geothermal wells, spring waters and bubbling hot springs) from both Nicaragua and Costa Rica sections of the arc. The highest value observed in this study is $-0.1\permil$ at Rincón de la Vieja in northern Costa Rica. $\delta^{13}C$ (CO_2) values lower than $-4\permil$ are observed in fumaroles from Poás ($-6.8\permil$), and in various spring water samples from both Costa Rica and Nicaragua. The lowest $\delta^{13}C$ (CO_2) values ($-13.4\permil$) were found in water samples from Arenal (Costa Rica). The significance of the large range in $\delta^{13}C$ (CO_2), in terms of crust versus slab/mantle wedge inputs to the carbon inventory, is considered in Section 5.1.

4.3. $CO_2/^3He$

The $CO_2/^3He$ ratio can be used as a sensitive indicator of carbon provenance since the Earth's various reservoirs (crust/mantle/atmosphere) have diagnostic values [25,26]. In addition, it is an important parameter to constrain in order to calcu-
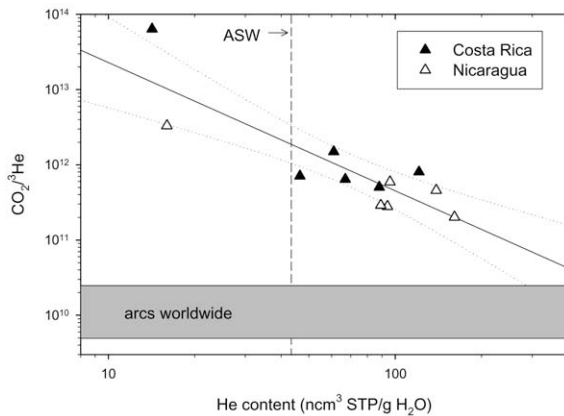
Fig. 3. Water spring $CO_2/^3He$ ratios plotted as a function of dissolved He contents. Note the consistent trend of increasing $CO_2/^3He$ ratios with decreasing He contents. Samples from Recreo Verde and Telica have He contents significantly lower that the air-saturated water (ASW) value of 44.1 ncm^3 STP/g H_2O (shown with a dashed line). Two samples from San Francisco Libre are not plotted since they have exceptionally high He contents: they also have low $^3He/^4He$ values indicating severe crustal contamination. The solid line, bounded by the dotted lines representing the 95% confidence limits, is a linear regression through all water spring samples except those mentioned above. The shaded region represents the worldwide average $CO_2/^3He$ ratio for arc-related geothermal fluids.

late volcanic CO_2 fluxes [27]. The $CO_2/^3He$ ratios of all samples (with the exception of samples from Tipitapa (N-32, N-33) and San Francisco Libre (N-15, I-118)) are significantly higher than values found at mid-ocean ridges ($CO_2/^3He = 2 \times 10^9$ [27]), presumably due to the addition of either slab-derived or crustal carbon (see Fig. 2). We find that most samples have $CO_2/^3He$ ratios that lie within the range found at arcs worldwide ($1.5 \pm 1.1 \times 10^{10}$ [28]). We note, however, that all water spring samples have particularly high values ($CO_2/^3He$ up to 6×10^{13}). In addition, bubbling hot spring samples from Telica and geothermal well samples at Miravalles show ratios which are elevated with respect to average arc values.

4.4. Dissolved He contents in water spring samples

We observe a wide range in He concentrations from 14.2 to 3230 ncm^3 He/g H_2O. In Fig. 3 we plot $CO_2/^3He$ ratios as a function of dissolved He concentration for all water spring samples (except for samples from San Francisco Libre (N-15, I-118) – discussed below). Most samples are enriched in He relative to air-saturated water (i.e. 44.1 ncm^3 He/g H_2O at 25°C [29]). However, thermal waters from Telica and Recreo Verde have exceptionally low values, 16.0 and 14.2 ncm^3 He/g H_2O respectively. These low values represent highly degassed samples, where He loss has likely occurred during formation of a vapour phase. The trend of increasing $CO_2/^3He$ ratios with decreasing He contents for other samples can also be explained by the preferential partitioning of He into a vapour phase and subsequent loss since its solubility in water is much lower than that of CO_2.

Duplicate samples from San Francisco Libre show particularly high He concentrations (2970 and 3230 ncm^3 He/g H_2O), and exceptionally low $CO_2/^3He$ values (2.2×10^8 and 3.6×10^8). This locality, however, is relatively far (> 20 km) from the volcanic centre of Momotombo and thus the observed He–C characteristics may be dominated by crustal influences. This is consistent with the low $^3He/^4He$ ratios (1.79 and 1.88 R_A), indicating addition of radiogenic He.

5. Discussion

In order to evaluate the integrity of our results, we must first determine which samples may have been affected by crustal contamination and/or near-surface processes. Once compromised samples have been identified and removed from further consideration, we can use combined CO_2–He systematics to determine the provenance of the C [11]. In this way, we can determine the relative contributions from the various C reservoirs (mantle, sediments, slab) and evaluate whether subduction of the carbonate-rich Cocos plate sediments results in an enhanced C output along the Central American arc, as compared with subduction zones dominated by siliceous sedimentary inputs. By identifying the source of volatiles, we aim to estimate the amount of C which is recycled via the subduction zone factory.
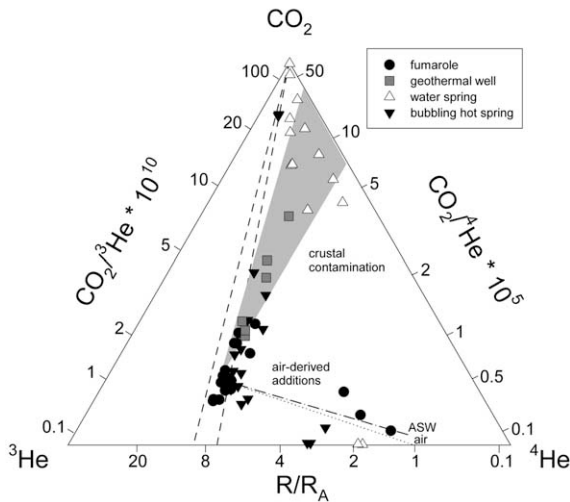
Fig. 4. Ternary CO_2–^4He–^3He plot of all geothermal samples illustrating the effects of air and crustal contamination. Dashed lines bound the upper mantle range of $^3He/^4He$ ratios (8 ± 1 R_A). Samples influenced by crustal contamination plot within the shaded region of the diagram, bounded by calculated mixing lines between typical arc ($CO_2/^3He = 1.5 \pm 0.6 \times 10^9$, $^3He/^4He = 8 \pm 1$ R_A) and crustal endmembers ($CO_2/^3He = 5–50 \times 10^{12}$, $^3He/^4He = 0.05$ R_A). We note that all water spring samples (open triangles) show significant crustal contamination. Some samples show contamination from an air-derived component and plot close to mixing lines between an arc endmember and air (dotted line) or air-saturated water (ASW; dash-dotted line). The N_2/Ar ratios of samples in this region of the diagram (with the exception of La Marina) confirm the presence of an air-derived contaminant ($N_2/Ar = 52–96$, where $N_2/Ar_{air} \approx 80$ and $N_2/Ar_{ASW} \approx 40$). The $CO_2/^3He$ ratio of air is calculated using [He] = 5.24 ppm, $^3He/^4He = 1.4 \times 10^{-6}$ [48] and $[CO_2] = 370.9$ ppm [49]. The $CO_2/^3He$ of air-saturated water is calculated using air concentrations and Ostwald coefficients at 15°C (He = 0.009325, $CO_2 = 1.071$ [50]).

5.1. Integrity of results

In Fig. 4 we plot samples on a CO_2–^4He–^3He ternary diagram to identify the effects of crustal contamination. There are a number of criteria which may be used to recognise contaminated samples, i.e. samples deemed unrepresentative of the underlying magma source: (1) low $^3He/^4He$ values, (2) high $CO_2/^3He$ ratios and (3) low X values (where X = air-normalised He/Ne ratio; see Table 1 caption). Helium isotopes are highly sensitive indicators of crustal influences since crustal production values are low ($^3He/^4He \sim 0.05$ R_A) relative to mantle values (8 ± 1 R_A). A compilation of arc-related volcanic and geothermal fluids at arcs worldwide yields an average $^3He/^4He$ value of 5.37 ± 1.87 R_A [19]; however, it is important to note that this database includes samples which have been affected by crustal additions ($^3He/^4He$ as low as 0.01 R_A). In the subsequent sections, we will only consider samples with air-corrected $^3He/^4He$ values higher than 5.4 R_A, thereby avoiding samples influenced by significant crustal inputs.

In the case of $CO_2/^3He$ ratios, values in crustal material can vary widely depending on rock lithology; however, given the virtual absence of primordial ^3He in all types of crust, $CO_2/^3He$ ratios are predominantly high (10^{11}–10^{13}) [26]. In Fig. 4 we note that water spring samples along with some of the geothermal well samples trend towards a high $CO_2/^3He$ (and $CO_2/^4He$) crustal endmember.

In addition to crustal contamination, atmospheric gases can infiltrate magmatic systems via air-saturated recharge waters, thereby masking source characteristics. Samples which have low X values have suffered significant air contamination and as such are unreliable tracers of mantle processes. Samples N-7, N-6, N-14 and CR-14 have particularly low X values (2.5–3.1) and their He–C systematics are overwhelmed by an air component (see Fig. 4). Although samples from Tipitapa and San Francisco Libre plot near the air-contaminated samples, they have high X values (112.9–240.1) and thus have been influenced by a low $CO_2/^3He$ crustal component rather than atmospheric gases.

Given the variety of sample types collected during this study, the present data set allows for a realistic evaluation of the integrity of different sampling media for tracing mantle processes. A clear conclusion is that all water spring samples show evidence of crustal contamination: low $^3He/^4He$ values, low X values, extreme $\delta^{13}C$ values (-13.4 to -1‰) and generally high $CO_2/^3He$ ratios. Such samples are thus considered highly susceptible to near-surface fractionating processes, which have modified C isotopes to extreme values (see [14] for further details).

It has been argued that geothermal well sam-

ples are the most pristine samples since they originate from deep reservoirs (1–2 km depth) and are less prone to near-surface boiling and degassing [14]. To test this hypothesis we sampled at two different geothermal well sites on the flanks of active volcanoes – Momotombo and Miravalles – and compared the results to other sampling media (fumaroles in Momotombo's crater and bubbling hot spring gas on Miravalles' flank). Results are given in Table 3. At Momotombo volcano, we sampled two different wells (OM-53 and MT-43) and found that a 2-month-old well (sample N-16) yielded results which were essentially indistinguishable from the summit fumarole samples (N-11, N-31); however, an older well that had been in production for over 2 years showed evidence of crustal contamination (lower ^{3}He/^{4}He, slightly lower X values and higher δ^{13}C values – see Table 2). Likewise, geothermal well samples from the power plant at Miravalles (CR-10, CR-20 and CR-21) showed significantly lower ^{3}He/^{4}He ratios than bubbling hot spring samples on Miravalles' flank (CRT-9). A possible explanation is that air-derived volatiles may be introduced into geothermal wells either by injection wells or

by infiltration of surrounding groundwaters into the geothermal system. Based on our observations at two sites, we conclude that although young geothermal wells can be exploited for volcanic gases, results from older wells should be treated with caution.

5.2. Sources of CO_2

One approach used to assess carbon provenance at subduction zones is the three-component mixing model of Sano and Marty [11]. Based on He–C characteristics, samples can be described in terms of carbon mixtures derived from three endmembers: limestone and/or marine carbonate (L), the mantle (M) and sedimentary organic C (S). Using the following equations, the relative contributions (expressed as fractions, f) from the various sources can be determined:

$$(^{13}C/^{12}C)_{obs} =$$

$$f_M(^{13}C/^{12}C)_M + f_L(^{13}C/^{12}C)_L + f_S(^{13}C/^{12}C)_S$$

$$1/(^{12}C/^{3}He)_{obs} =$$

$$f_M/(^{12}C/^{3}He)_M + f_L/(^{12}C/^{3}He)_L + f_S/(^{12}C/^{3}He)_S$$

$$f_M + f_L + f_S = 1$$

Endmember compositions used in prior studies [11,28] are M: $\delta^{13}C = -6.5$‰, C/^{3}He $= 1.5 \times 10^9$; L: $\delta^{13}C = 0$‰, C/^{3}He $= 10^{13}$; S: $\delta^{13}C = -30$‰, C/^{3}He $= 10^{13}$.

There are two potential problems with this approach [19,22]: (1) the effect of crustal volatiles is not considered and (2) the δ^{13}C value of organic matter (-30‰) may be unrepresentative since it may be fractionated to heavier values upon subduction (see [30–32]). To circumvent these problems, we have removed samples showing crustal influences from our dataset (Section 5.1) and calculated L, M and S fractions using an extreme estimate of the equilibrium δ^{13}C value of organic matter, $\delta^{13}C = -12$‰ (see [30]), in addition to the above endmembers (for comparison). The results of these calculations are shown in Table 4.

An important parameter used to compare output fluxes in different arcs is the L/S ratio (i.e. the

Table 3
Comparison of geothermal well gas samples to other sampling media at Momotombo and Miravalles volcanoes

Site Medium	R_C/R_A	$CO_2/^3$He	δ^{13}C (‰)
Momotombo volcano (Nicaragua)			
fumarole	7.0	2.7×10^{10}	-2.6
fumarole *dup* [a]	–	–	-2.6
well MT-43[b]	6.4	3.1×10^{10}	-1.3
well MT-43 *dup*	6.4	3.3×10^{10}	-1.1
new well OM-53[c]	6.9	3.6×10^{10}	-2.6
Miravalles volcano (Costa Rica)			
bubbling hot spring	6.8	1.3×10^{10}	-3.5
well PTM-45	5.2	6.6×10^{10}	-1.2
well PTM-45 *dup*	5.3	7.8×10^{10}	-1.2
well PGM-8	3.6	14.8×10^{10}	-1.6

All errors are given in Tables 1 and 2.
[a] Samples indicated with a *dup* represent duplicates of preceding sample.
[b] MT-43 was sampled 22 months earlier by Snyder et al. [14], yielding a ^{3}He/^{4}He of 6.7 R_A; thus we note a drop in the isotopic composition since then (to 6.4 R_A) possibly due to dilution by re-injection wells – see text for discussion.
[c] Geothermal well OM-53 was 2 months old at the time of sampling, whereas site MT-43 was over 2 years old.

fraction of C derived from a limestone or marine carbonate source to that from a sedimentary organic component). The worldwide average arc L/S value (from [28]) is 6.0 ± 3.8 (calculated assuming $S = -30‰$) whereas the mean values calculated for Costa Rica and Nicaragua are 9.6 ± 4.3 and 11.1 ± 2.1, respectively (Table 4). Such high values presumably reflect the carbonate-rich nature of the sedimentary sequences being subducted. Deep-sea drill sites off Guatemala (DSDP 495) and Costa Rica (ODP 1039) show little variation in sedimentary composition, consisting of ~ 250 m of pelagic carbonates overlain by ~ 175 m of hemipelagic diatom-rich mud [33,34]. Since there is no difference in the subducting lithologies in Costa Rica and Nicaragua, it may not be surprising that their L/S ratios are similar. However, prior studies have emphasised striking differences in the geochemical characteristics (Be, B, La/Yb, Ba/La, etc.) of lavas from Costa Rica and Nicaragua, so we would have anticipated a higher proportion of sedimentary-derived C in Nicaragua (a lower L/S). For example, assuming that the hemipelagic portion of the sediment column in Costa

Table 4
L-M-S calculations for Costa Rica and Nicaragua geothermal fluids

Volcano locality	Sample ID	Type	L[a]	M[a]	S[a]	L/S[a]	L/S$_{mod}$ [b]
Costa Rica							
Turrialba	CR-3	FC	78.1	10.5	11.4	6.9	2.1
	CR2-1	FC	73.4	15.3	11.4	6.5	2.0
	CR2-2	FC	74.8	15.9	9.2	8.1	2.6
	CR3-2	FC	78.8	9.3	11.9	6.6	2.0
Irazú	CR-5	FC	88.0	5.5	6.4	13.6	4.8
Poás	CR2-14	FC	65.8	15.1	19.0	3.5	0.8
	CR3-17	FC	73.1	9.8	17.1	4.3	1.1
Poco Sol	CRT-2	BF	84.1	10.5	5.4	15.6	5.6
Quebrada Naranja	CRT-5	BF	83.7	6.4	9.9	8.4	2.8
	CRT-6	BF	81.9	9.5	8.6	9.5	3.2
Miravalles	CRT-9	BF	79.3	11.5	9.2	8.6	2.9
Rincón de la Vieja	CRT-10	BF	97.2	2.3	0.5	197.4	78.4
	CR2-9	BF	95.2	3.9	0.8	116.9	46.2
Average[c]			82.3	9.1	8.6	9.6	3.3
Nicaragua							
Mombacho	N-35	FC	81.4	8.4	10.2	8.0	2.6
	N-20	MF	84.6	8.2	7.2	11.7	4.1
Xiloa	N-12	BF	83.7	10.1	6.1	13.6	4.9
	N-13	BF	83.3	10.6	6.0	13.8	4.9
Momotombo	N-11	FC	87.1	5.5	7.5	11.6	4.1
	N-16	GF	88.1	4.1	7.8	11.3	3.9
	N-34	GF	91.9	4.8	3.3	27.9	10.6
	N-17	GF	92.8	4.5	2.7	34.5	13.2
Cerro Negro	N-4	FC	88.6	4.8	6.6	13.4	4.7
Telica	N-8	BF	89.4	0.3	10.3	8.7	2.9
	N-9	BF	88.8	0.3	10.9	8.1	2.6
San Cristobal	N-2	FC	87.2	4.0	8.8	9.9	3.4
	N-5	FC	85.4	5.9	8.7	9.8	3.3
Average[c]			86.4	5.6	8.1	11.1	3.8
Worldwide average[d]			74.6	12.8	12.5	6.0	

[a] L, M and S proportions (in %) are calculated using the same endmembers as in [11].
[b] L/S$_{mod}$ is calculated using a sedimentary organic endmember of $\delta^{13}C = -12‰$ (as opposed to $-30‰$).
[c] Averages for Nicaragua and Costa Rica are calculated using an average value for each locality (in cases where there is more than one sample at a given locality). Four samples are excluded from average calculations: CRT-10 and CR2-9 (possible outliers), as well as N-34 and N-17 (crustal contamination).
[d] Calculated from [11] considering only samples with $^3He/^4He$ ratios = ≥ 5.4 R_A.

Rica (containing a higher proportion of sedimentary organic C) is being underplated before reaching the zone of magma generation, as invoked by Valentine et al. [15], we would expect a lower S contribution (i.e. a higher L/S) in the volcanic output in Costa Rica. However, we note that the L/S ratios are virtually indistinguishable irrespective of whether $-30‰$ or $-12‰$ is selected as the $\delta^{13}C_S$ endmember (Table 4, L/S and L/S$_{mod}$). In the subsequent sections we select a $\delta^{13}C_S$ endmember value of $S = -30‰$ in order to be consistent with prior studies, allowing direct comparisons to be made.

The first-order implication of uniform L/S ratios would be that there is no significant difference between the composition of sediment-derived C that makes it into the magma generation zone in Costa Rica versus Nicaragua. One possible explanation is that the uniformly high values reflect loss of organic C by thermal decomposition in the forearc (see [35]). This would be consistent with the occurrence of methane-rich seeps, offshore mud volcanoes and methane hydrate zones in the forearc region of the Central American arc, as well as at arcs worldwide [36]. An argument against this possibility is that subduction-zone metamorphic rock studies have shown that significant loss of organic C at temperatures below $\sim500°C$ does not occur [32]. These studies even suggest that $>75\%$ of subducted organic C is retained to great depths. An alternative explanation for the constant L/S ratios may lie in the fact that sedimentary carbon is found not only in the shallow hemipelagic muds but also in the lower carbonate sequences. ODP drilling has revealed that underlying carbonates bear carbonaceous organic matter at a level up to $\sim1\%$ (as opposed to $\sim3\%$ for the muds) [33,34]). Whereas offscraping and underplating of the hemipelagic sediments off Costa Rica may account for the low ^{10}Be signal (see below), a striking difference in L/S ratios along the arc may not necessarily be anticipated since both sedimentary units contain organic C.

Although there are no discernible along-strike variations in the L/S ratio, there is a marked difference in the relative slab contribution (L+S) vs. mantle contributions between Costa Rica and Nicaragua. In Fig. 5 we plot (L+S)/M vs. latitude
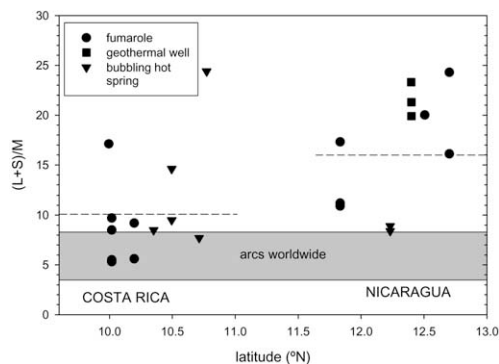

Fig. 5. Variations in (L+S)/M as a function of latitude. The average value for Nicaragua (16) is higher than Costa Rica's average (10) and we note a general increase in relative slab contributions to the north. Average values (dashed lines) are shown relative to the worldwide average for arcs (shaded area) $= 6.0 \pm 2.4$ (calculated from [11], considering only samples with $^3He/^4He$ ratios ≥ 5.4 R_A).

and we note that the average ratio in Nicaragua is 16.0 versus a mean of 10.0 in Costa Rica. Such an enhanced slab contribution to the volcanic output in Nicaragua agrees with prior findings (i.e. ^{10}Be [7], B/La [8], Ba/La [4,5], etc.). There are two possible explanations for this observation: (1) offscraping of sediments in Costa Rica [15] and (2) a warmer thermal regime in Costa Rica possibly associated with subduction of the Cocos ridge (a hotspot-related oceanic plateau) and/or the trace of the Galapagos hotspot [20].

The idea of offscraping of sediments was put forth by Valentine et al. [15] to explain low ^{10}Be contents of lavas in Costa Rican arc volcanics. If the water-rich upper hemipelagic portion of the sediment column was lost, then only the older (^{10}Be-poor due to decay) and more refractory sediments would be available to contribute to the volcanic output. In this way, loss of the hemipelagic sediments in Costa Rica could lead to lower (L+S)/M ratios. Isotopically light N isotopes in geothermal fluids from Costa Rica [6] confirm minimal sedimentary-derived N contributions to the volcanic output.

Alternatively, the enhanced slab contribution observed in Nicaragua may be related to the thermal structure of the subduction zones in Costa Rica and Nicaragua. Crucial parameters control-

ling the release and transfer of sediments to the mantle wedge are the thermal conditions at subarc depths and the availability of melt inducing fluids [37]. The contrasting plate geometries of the subduction zones in Costa Rica and Nicaragua could have important consequences for their thermal structures. Steep subduction in Nicaragua implies a much cooler slab at subarc depths, which would not dehydrate until greater depths. The warmer, shallower subduction along the arc in Costa Rica could promote significant fluid loss from the slab (along with fluid mobile elements) prior to reaching the magma generation zone (i.e. in the forearc region). Such a model was invoked to explain variations in B (and ^{10}Be) concentrations along the strike of the arc [20]. The lower slab temperatures associated with subduction in Nicaragua would result in deeper initiation of dehydration reactions, enhancing the transfer of fluids to subarc depths which would trigger melting. The occurrence of low La/Yb values (generally indicative of high degrees of partial melting) in Nicaraguan arc volcanics is consistent with this model [4]. We suggest that higher degrees of melting in the Nicaraguan subarc (relative to Costa Rica) could reflect enhanced sediment transfer to the volcanic output in Nicaragua, resulting in higher (L+S)/M values.

5.3. Absolute flux calculations

We use two different techniques to calculate the flux of CO_2 from volcanoes along the strike of the Central America arc. In the first case, we use measured $CO_2/^3He$ ratios, along with an assumed ^3He flux (scaled to length of arc) to derive a CO_2 flux estimate. Secondly, we use correlation spectrometer (COSPEC) measurements of SO_2 fluxes at individual volcanoes, coupled with measurements of CO_2/SO_2 ratios to calculate a CO_2 flux for the entire Central American arc.

Average $CO_2/^3He$ ratios for Nicaragua and Costa Rica are $2.5 \pm 0.4 \times 10^{10}$ ($n=9$) and $2.1 \pm 0.4 \times 10^{10}$ ($n=13$), respectively (from Tables 1 and 2; excluding samples which show crustal contamination – see Section 5.1). If we assume an average $CO_2/^3He$ ratio of 2.3×10^{10} for the entire Central American arc (based on this data

set) and a global ^3He arc flux of 92.4 mol/yr [19] scaled to the length of the Central American arc (using a trench length of 1450 km [38], relative to the global trench length of 43 400 km [39]), we derive a CO_2 flux of 7.1×10^{10} mol/yr for the Central American arc.

An alternative method to derive CO_2 fluxes for a particular volcano is to use COSPEC measurements of SO_2 fluxes in conjunction with measured CO_2/SO_2 values. Since COSPEC measurements can only be obtained for large flux volcanoes (those with a plume), it is necessary to account for the smaller flux volcanoes to estimate a total CO_2 flux for the Central American arc. One approach assumes that the distribution of volcanic emissions for any arc segment follows a power law [40] and using this relationship a total flux can be calculated. Hilton et al. [19] used this method to estimate a total CO_2 flux of 5.8×10^{10} mol/yr for the Central American arc. Despite potential caveats such as the large variation in measured CO_2/SO_2 ratios for a given arc and the error associated with individual COSPEC measurements (estimated at 10–40% [41]), this value agrees remarkably well with the estimate derived using $CO_2/^3He$ relationships (7.1×10^{10} mol CO_2/yr).

If we consider that global subaerial CO_2 fluxes are estimated at 2.5×10^{12} mol/yr (see [42] and references therein), then the Central American flux represents 2.3–2.8% of the entire CO_2 output from subaerial volcanoes (both along arcs and at hotspots). However, most of the global CO_2 flux is attributed to only two volcanoes: Mt. Etna ($\sim 23\%$) and Popocatepetl (13.6%) [42]. The global CO_2 flux along arcs is estimated at 1.6×10^{12} mol/yr [19]. Using this value, we calculate a global average (including Central America) output flux of 3.7×10^7 mol CO_2/yr per km of arc (or trench), as compared to the average for Central America ($4.0-4.7 \times 10^7$ mol/yr/km). Despite the potentially large errors associated with these calculations, we note that the Central American output flux is surprisingly low (only slightly higher than the average) given the high influx of CO_2-bearing sediments on the down-going plate relative to other arcs. For example, the Central American margin has an annual sedimentary input flux of 176 mol

CO_2/km arc, more than five times the average of 31 mol CO_2/km arc subducted at arcs worldwide (calculations based on sedimentary CO_2 fluxes in [19]). In Section 5.4, we consider the total C mass balance along the Central American margin to evaluate the efficiency of C recycling through the subduction zone factory.

5.4. Mass balance at subduction zones

In order to assess how much C is cycled through the Central American subduction zone versus the amount which is ultimately transferred to the deep mantle, we must quantitatively determine the C inputs from the various sources: (1) subducting carbonate sediments, (2) organic matter and (3) altered oceanic crust. A critical assumption in any mass balance calculation is that the present-day input at the trench is representative of the material that is producing the arc magmas today. Sediments on the subducting Cocos plate underwent a major transition from carbonate-rich sediments to hemipelagic muds due to the so-called carbonate crash 10 Ma associated with a major change in ocean circulation patterns (see [43]). Since then, however, sediment compositions have remained relatively homogeneous and thus the assumption that present-day sediment compositions at the trench are representative is reasonable.

The flux of sedimentary material into the Central American subduction zone can be estimated from the subduction rate (77 mm/yr), sediment thickness (425 m), trench length (1450 km) and the bulk density (1.62 g/cm^3) [38]. Taking bulk sediment water content (48.69%) and the dry weight CO_2 concentration (26.55 wt%) into account, we calculate a carbonate-derived CO_2 input of 2.38×10^5 Mmol/yr (as in [19]).

The organic component can be estimated in two ways: (1) assuming an average of 1 wt% organic CO_2 [32] to yield 1.75×10^4 Mmol CO_2/yr (as in [19]) or (2) using a calculated average of 0.98 wt% C for the upper hemipelagic portion, and 0.26 wt% C for the lower carbonate sequence, based on drill report measurements [33], resulting in an organic CO_2 input flux of 3.56×10^4 Mmol/yr. The latter value is deemed more representative

since it is based on core measurements (ODP site 1039) in this region and is consistent with the notion that carbonate sediments have poorer preservation of organic matter than hemipelagic muds [43].

Oceanic crustal basement is also a potentially significant source of C since carbonate veining and/or calcite precipitation associated with hydrothermal alteration affects seafloor crust progressively with age [44]. We have calculated the oceanic crustal C contribution using two methods: (1) an average altered crust value of 0.214 wt% CO_2 for 7 km thick crust [44] and (2) a value of 2.95 wt% CO_2 for the upper 500 m, where most of the alteration is concentrated [45]. In both cases we assume a crustal density of 2.89 g/cm^3. In the first case we calculate a CO_2 input of 1.10×10^5 Mmol/yr, which is essentially indistinguishable from a value of 1.08×10^5 Mmol/yr calculated in the second case. Since the age of the subducting crust is 23 ± 5 Myr and precipitation of carbonates within the crust may persist for up to 100 Myr [44], these estimates represent maximum values.

Based on the above calculations, the relative proportion of limestone and marine carbonate C to sedimentary organic C being input at the arc from both sediments and oceanic crust is 10:1. This value is remarkably similar to the L/S values observed in the volcanic output (Costa Rica average L/S = 9.6 and Nicaragua average L/S = 11.1). The implication of this finding is that organic carbon is not significantly fractionated from carbonate during the subduction and magma generation processes. This is in contrast to results reported in a study on submarine basalt glasses in the North Fiji back-arc basin [12], where considerable fractionation of the L/S ratio was calculated. The proportion of L to S measured in the volatile output in the back-arc (L:S = 7:3) was significantly different from proportions being input at the trench (L:S = 20:1). The most reasonable explanation for the discrepancy between our results and those of Nishio et al. is that they did not consider C losses from the arc front, which are likely to be significant (based on this work and observations of high CO_2/^{3}He ratios in arcs worldwide [28]). In addition, a back-arc setting would have a different

thermal regime and availability of fluids, potentially resulting in less efficient carbonate devolatilisation (see discussion below).

Considering the CO_2 contributions from the slab components (crust+sediments), the total CO_2 input along the Central American margin is of the order of 3.8×10^{11} mol/yr, as compared to a volcanic output of $5.8–7.1 \times 10^{10}$ mol/yr. If we subtract the mantle C contribution to the volcanic output (9.1% in Costa Rica and 5.6% in Nicaragua), we can determine the percentage of material which is recycled through the arc (i.e. $[(L+S)_{out}/(L+S)_{in}] \times 100$). Based on these calculations, we find that 14–18% of the material input at the arc is lost via arc volcanism. Consequently, as much as 86% of the CO_2 input along the arc could be transferred to the deeper mantle. Note, however, that it is likely that some fraction is lost in the forearc. The percentage of CO_2 emitted via the Central American arc is exceptionally low relative to global estimates of the output/input, ~ 0.50 (calculated from global flux estimates in [46] and [19]). Kerrick and Connelly [46] attributed low CO_2 arc emissions along arcs to two processes: (1) strong devolatilisation of clay-rich marls in the forearc region, provided the geotherm is sufficiently high, and (2) retention of CO_2 in carbonate-bearing marine sediments to depths greater than subarc depths. It is possible that both of these processes occur in the Central American subduction zone to limit CO_2 loss via arc volcanism. In addition, given the carbonate-rich nature of the lower sediments, it is possible that there are insufficient fluids available at subarc depths to promote efficient decarbonation of the carbonate sediments [47]. H_2O-rich fluid availability is potentially the limiting factor controlling whether marine carbonates will devolatilise at subarc depths or be transferred to the deep mantle (e.g. wet solidus versus dry solidus). As discussed, the warmer subduction in Costa Rica would likely initiate fluid loss in the forearc, resulting in limited availability of H_2O-rich fluids necessary to trigger devolatilisation at subarc depths. Likewise, in Nicaragua, despite a greater transfer of slab C to the arc, it is possible that insufficient melt-inducing fluids are available to accommodate the overwhelmingly high influx of

slab C (relative to other arcs), resulting in the low efficiency (14–18%) of C cycling.

6. Conclusions

1. Most geothermal fluids from Costa Rica and Nicaragua have MORB-like $^3He/^4He$ ratios, $\delta^{13}C$ values ranging from -6.8 to $-0.1‰$, and elevated $CO_2/^3He$ values relative to MORB (2.1×10^{10} and 2.5×10^{10}, for Costa Rica and Nicaragua respectively), consistent with prior studies of arc-related domains (e.g. [27]).

2. Water springs and old geothermal wells show evidence for crustal additions (variable $\delta^{13}C$, low $^3He/^4He$ and high $CO_2/^3He$ ratios) and are considered unreliable tracers of mantle processes.

3. Using the approach of Sano and Marty [11], we find that the geothermal fluid volcanic output is dominated by a limestone/marine carbonate component (82–86%), with relatively low sedimentary organic and mantle C contributions.

4. The L/S ratios observed in the volcanic output in Costa Rica (9.6) and Nicaragua (11.1) are high relative to arcs worldwide (6.0). This likely reflects the carbonate-rich nature of the sediments on the downgoing Cocos plate. The L/S input ratio is 10, implying that significant fractionation of organic matter C from carbonate C does not occur during subduction and magma generation.

5. The (L+S)/M ratios in Costa Rica ($= 10$) and Nicaragua ($= 16$) support the suggestion of an enhanced slab flux to the volcanic output in Nicaragua, consistent with prior findings [1,4,5,7,8,13].

6. Similar fluxes of CO_2 for the entire Central American arc are derived using COSPEC methods (5.8×10^{10} mol/yr) and measured $CO_2/^3He$ ratios combined with global ^3He fluxes scaled to arc length (7.1×10^{10} mol/yr). These values, however, are low (14–18%) relative to the amount of CO_2 being input at the trench. This imbalance can be attributed to three processes: (i) C losses in the forearc re-

gion, (ii) incomplete decarbonation of lime-stone/marine carbonate and (iii) limited availability of melt-inducing fluids to accommodate the influx of slab C.

7. Up to 86% of CO_2 input at the trench is potentially subducted back into the mantle – however, the forearc may be a significant reservoir to consider; constraining this flux should be the focus of future studies.

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