

1 Forearc carbon sink reduces long-term volatile recycling into the mantle

2
3 P.H. Barry^{1,2,3*}, J. M. de Moor^{4,5}, ‡ D. Giovannelli^{6,7,8,9}, ‡ M. Schrenk¹⁰, D. Hummer¹¹, T.
4 Lopez¹², C.A. Pratt¹³, Y. Alpizar Segura¹⁴, A. Battaglia¹⁵, P. Beaudry¹⁶, G. Bini¹⁷, M.
5 Cascante⁴, G. d'Errico^{6,18}, M. di Carlo¹⁸, D. Fattorini^{18,19}, K. Fullerton²⁰, E. Gazel²¹, G.
6 González¹⁴, S. A. Halldórsson²², K. Iacovino^{23,24}, J.T. Kulongoski^{2,25}, E. Manini⁶, M.
7 Martínez⁴, H. Miller¹⁰, M. Nakagawa⁸, S. Ono¹⁶, S. Patwardhan⁷, C.J. Ramírez¹⁴, F.
8 Regoli^{18,19}, F. Smedile⁷, S. Turner²⁶, C. Vetriani⁷, M. Yücel²⁷, C.J. Ballentine¹, T.P. Fischer⁵,
9 D.R. Hilton²⁵, K.G. Lloyd^{20‡}

10
11 ¹Department of Earth Sciences, University of Oxford, UK

12 ²California Water Science Center, USGS, CA, USA

13 ³Now at: Marine Chemistry and Geochemistry Department, Woods Hole Oceanographic
14 Institution, Woods Hole, MA, USA

15 *Correspondence email: pbarry@whoi.edu

16 ⁴Observatorio Volcanológico y Sismológico de Costa Rica (OVSICORI), Universidad
17 Nacional, Costa Rica

18 ⁵Department of Earth and Planetary Sciences, University of New Mexico, NM, USA

19 ⁶Institute of Institute for Marine Biological and Biotechnological Resources, National
20 Research Council of Italy, (IRBIM-CNR), Ancona, Italy

21 ⁷Department of Marine and Coastal Science, Rutgers University, New Brunswick, NJ, USA

22 ⁸Earth-Life Science Institute, Tokyo Institute for Technology, Tokyo, Japan

23 ⁹Now at: Department of Biology, University of Naples "Federico II", Naples, Italy

24 ¹⁰Department of Earth and Environmental Sciences, Michigan State University, MI, USA

25 ¹¹Department of Geology, Southern Illinois University, IL, USA

26 ¹²Geophysical Institute, University of Alaska, Fairbanks, AK, USA

27 ¹³Graduate School of Oceanography, University of Rhode Island, RI, USA

28 ¹⁴Volcanes Sin Fronteras (VSF), Costa Rica

29 ¹⁵Department of Earth and Marine Sciences, Università degli Studi di Palermo, Palermo,
30 Italy

31 ¹⁶Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of
32 Technology, MA, USA

33 ¹⁷Department of Earth Sciences, University of Florence, Italy

34 ¹⁸Dipartimento di Scienze della Vita e dell’Ambiente (DISVA), Università Politecnica delle
35 Marche (UNIVPM), Italy

36 ¹⁹CoNISMa, Consorzio Nazionale Interuniversitario Scienze del Mare, Italy

37 ²⁰Department of Microbiology, University of Tennessee, TN, USA

38 ²¹Department of Earth and Atmospheric Sciences, Cornell University, NY, USA

39 ²²NordVulk, Institute of Earth Sciences, University of Iceland, Iceland

40 ²³School of Earth and Space Exploration, Arizona State University, AZ, USA

41 ²⁴Now at: Johnson Space Center, NASA, TX, USA

42 ²⁵Geosciences Research Division, Scripps Institution of Oceanography, University of
43 California, CA, USA

44 ²⁶Department of Earth and Planetary Sciences, Washington University in St Louis, St.
45 Louis, MO, USA

46 ²⁷Institute of Marine Sciences, Middle East Technical University, Erdemli, Turkey

47 ‡ Equally contributing authors

48

49 **Nature**

50 Number of Words in Summary= 150

51 Number of Words in Main Text = 3,114

52 Number of Figures = 4

53 Extended data Figures = 3

54 Number of Tables = 0

55 Number of Supplementary Tables = 4

56 Main Text References = 50

57 Methods References = 48

58

59 **Summary:**

60 Carbon and other volatiles are transported from Earth's surface into the
61 mantle at subduction margins. The efficiency of this transfer has profound
62 implications for the nature and scale of geochemical heterogeneities in Earth's deep
63 (mantle) and shallow (crustal) reservoirs, as well as Earth's oxidation state. However,
64 the proportion of volatiles released in the forearc and backarc are not well-
65 constrained compared to fluxes from the volcanic-front. Here, we use helium and
66 carbon isotope data from deeply-sourced springs along two cross-arc transects to
67 show that ~91% of carbon released from the slab/mantle beneath the Costa Rica
68 forearc is sequestered within the crust by calcite deposition, and an additional ~3% is
69 incorporated into biomass through microbial chemolithoautotrophy. We estimate
70 that $\sim 1.2 \times 10^8$ to 1.3×10^{10} mol CO₂/yr are released from the slab beneath the
71 forearc, resulting in up to ~19% less carbon being transferred to Earth's deep mantle
72 than previously estimated.

73

74 **Main Text:**

75 Terrestrial carbon traverses various reservoirs on Earth from the surface to the
76 mantle. It is subjected to a number of geological, geochemical, and biological cycles, each
77 of which operates on vastly different temporal and spatial scales. Perhaps the most
78 important physical process linking the deep and shallow carbon cycles is subduction,
79 which transports both oxidized and reduced forms of crustal carbon into the mantle.
80 During subduction, volatile-rich fluids are released from the downgoing slab (upper
81 mantle and crust). These fluids are thought to migrate through the overlying mantle-

82 wedge and crust, and are ultimately released across the forearc, volcanic arc-front and
83 backarc (i.e., behind the volcanic front). However, little is known about what effect
84 volatile fluxes through the forearc may have on the total volatile budget and estimates of
85 recycling efficiency¹. Much of the forearc subsurface is at low temperatures (<100°C) that
86 are conducive to microbial life as well as shallow water-rock interactions. Therefore,
87 microorganisms and/or abiotic chemical processes may alter the speciation, isotopic
88 composition, and presumed carbon budgets. Regional-scale effects of these shallow
89 processes on volatile fluxes in the forearc have not previously been quantified.

90

91 Carbon budgets for convergent margins typically assume negligible carbon
92 emissions from the area between the trench (i.e., where the downgoing slab subducts
93 beneath the overriding plate) and the degassing volcanic arc-front¹⁻³. It is not clear
94 whether the lack of obvious high emission sources reflects a lack of deep CO₂ input from
95 the slab-mantle mixture, or if secondary processes in the upper plate⁴⁻⁵ mask diffuse but
96 significant CO₂ release.

97

98 Carbon outputs at the Central American Volcanic Arc, which have been the focus
99 of several studies, are estimated to represent only 12% of the total subducted carbon
100 input along the middle American trench^{2,6-7}, whereas global arcs typically have carbon
101 outputs that approach their inputs, suggesting limited volatile delivery to the mantle¹.
102 However, recent work⁸ proposed a far higher volcanic carbon flux for Central America,
103 suggesting that this region may be more similar to other arc segments¹ than previously
104 thought^{2,6}. Our study focuses on the Nicoya Peninsula area of Costa Rica in part because it
105 is one of the few places on Earth with easy sampling access to an on-land forearc region
106 and thus presents an opportunity to study the fate of carbon across an entire arc. Few
107 carbon flux estimates have been made from the forearc region of any arc, despite the fact
108 that there is plentiful ancillary evidence for fluid venting in forearc regions (*e.g.*,
109 serpentinite diapirism in the Marianas⁹ and mud volcanism at various accretionary prisms
110 worldwide¹⁰), as well as ample geophysical evidence that shows fluid upwelling in the

111 forearc region from the downgoing slab¹¹. In Costa Rica, the only available forearc data
112 are from three submarine venting sites³, where the authors estimated that the carbon
113 output from the outer forearc represents less than 1% of the carbon input at the trench.
114 Taking into account the loss at the volcanic-front, they proposed two explanations: either
115 subducted carbon was largely transported into the deep mantle or significant quantities
116 of carbon were lost to the forearc or backarc regions. Independently, thermodynamic
117 models of subduction predict significant CO₂ loss (i.e., decarbonation) from the top of the
118 subducting slab beneath global forearc regions¹², as the slab penetrates to greater
119 temperature and pressure conditions.

120

121 The extensive occurrence of calcite veining throughout the Costa Rica forearc¹³⁻¹⁴
122 suggests that much of the CO₂ released from the slab beneath the forearc could be
123 sequestered into the crust as calcite, in which case direct measurements of diffuse
124 degassing in this region are not representative of deep mantle processes. Additional
125 mechanisms for masking CO₂ gas release in the upper plate include microbial biomass
126 production, conversion to CH₄, trapping in reservoirs beneath impermeable caps, and
127 abiotic organic matter synthesis. Calcite deposition results in a temperature dependent
128 isotope fractionation and may be microbially mediated¹⁵⁻¹⁶ in cation-rich alkaline waters
129 with high aqueous CO₂ concentrations. Additionally, in the absence of light for
130 photosynthesis, microorganisms in subsurface settings instead fix CO₂ into biomass
131 through chemolithoautotrophy¹⁷⁻¹⁹. Both calcite deposition and chemolithoautotrophy
132 occur mostly at temperatures below 100°C, which are the prevalent conditions in the
133 forearc subsurface²⁰. Biologically induced carbon fixation generally results in a kinetic
134 fractionation of carbon isotopes that preferentially removes ¹²C from CO₂²¹. The degree of
135 fractionation depends on the microorganism's physiology, as well as substrate limitations,
136 temperature, and pressure. Biological activity can also decrease the carbon isotopic
137 composition (δ¹³C) of CO₂, by adding ¹³C-depleted carbon through heterotrophic
138 respiration of organic matter or methane. This process is not associated with a large
139 carbon isotope fractionation²¹ relative to pure kinetic reactions driven solely by biological

140 processes. In addition, abiotic hydrocarbon production from dissolved CO₂ has been
141 demonstrated in laboratory experiments over 250°C²², a possible temperature regime in
142 hotter forearc regions.

143

144 **He and C Results:**

145 We collected samples from 23 sites in northern and central Costa Rica (Figure 1),
146 which traversed forearc (Nicoya Peninsula), arc and backarc regions. Springs likely to
147 represent deeply-sourced fluids (based on field data such as temperature, dissolved
148 oxygen, salinity) were targeted, and samples were taken by inserting tubes into outflow
149 vents to minimize fluid interaction with atmosphere and surface water. The sites were
150 classified into two groups: the northern transect samples, which were collected to the
151 north of the EPR-CNS on-land extension, and the Central transect samples, which were
152 collected to the south of this plate transition. The two groups, with the exception of
153 Santa Lucia, are separated by the on-land extension of a major transition in the
154 downgoing slab: the boundary between oceanic crust formed at the East Pacific Rise
155 (EPR) and the Cocos Nazca Spreading (CNS) zone. We measured ³He/⁴He vs. air,
156 expressed as (R/R_A), where R = ³He/⁴He_{sample} and R_A = ³He/⁴He_{air} = 1.39 × 10⁻⁶ for 17
157 geothermal fluid (i.e., spring water) samples and 17 free gas samples. In addition, we
158 measured δ¹³C vs. Vienna Pee Dee Belemnite (VPDB) in dissolved inorganic carbon (DIC)
159 in 31 geothermal fluid samples, dissolved organic carbon (DOC) in 16 fluid samples, and
160 CO₂ in 16 free gas samples (Supplementary Table 1). Sediments surrounding the surface
161 emanation of the springs were also sampled and total organic carbon (TOC) contents
162 and δ¹³C were measured. The relative abundances of He to CO₂ are also reported
163 (CO₂/³He; Extended Data Figure 1). The air-normalized ⁴He/²⁰Ne ratio is used to
164 calculate the X-value, (multiplied by the Bunsen solubility (1.23) at the assumed
165 recharge temperature of 15°C²³ for fluid samples), which is used to estimate the air-
166 corrected ³He/⁴He ratio (R_C) of the sample²⁴. As X-values are high (>5) for the majority of
167 samples of this study (Extended Data Figure 2), the correction factor is small and hence

168 there is typically little difference between measured (R/R_A) and corrected (R_C/R_A)
169 $^3\text{He}/^4\text{He}$ ratios (Supplementary Table 1).

170

171 The air-corrected $^3\text{He}/^4\text{He}$ (R_C/R_A) values range from 0.49 to 6.79 R_A
172 (Supplementary Table 1), with the highest values occurring in the volcanic arc and the
173 lowest occurring in the outer forearc. Arc values approach upper mantle values ($\sim 8 R_A$),
174 however, they exhibit evidence for a small but discernible addition of radiogenic helium
175 at all locations. In contrast, outer forearc and forearc values are predominantly
176 radiogenic, with a small but distinct mantle contribution, suggesting these fluids are an
177 admixture of crustal fluids and deeply sourced volatiles likely with some influence of
178 shallow water-rock interaction. He-isotope values are systematically higher (i.e., more
179 mantle-like) in both fluids and gases close to the volcanic arc-front and lower toward the
180 trench (i.e., in the forearc; Figure 2A), showing that slab/mantle outgassing is not limited
181 to the arc-front, and occurs throughout the entire forearc. However, free CO_2 gas
182 (bubbling springs) was only detected within $\sim 20\text{km}$ of the arc (Figure 2B). In the absence
183 of gas manifestations, we examined evidence for forearc carbon processing in dissolved
184 carbon from spring outflows.

185

186 The $\delta^{13}\text{C}$ and carbon content of DIC and DOC within spring fluids decrease
187 systematically trenchward across the entire arc (Figure 2B and Figure 3). Strikingly,
188 DIC values in northern and central Costa Rica follow distinct parallel trends (Figure 3),
189 which are not masked by site-dependent surface-derived organic material
190 heterogeneities, such as vegetation, degradation of photosynthetic organic matter
191 and/or surface water infiltration, indicating that the distribution of carbon in these
192 fluids results from deep subsurface phenomena. In contrast, TOC is heavily
193 influenced by surface detrital carbon and shows no apparent trend between
194 concentration and $\delta^{13}\text{C}$ in samples across the two transects. DIC and DOC define
195 Rayleigh distillation curves, with northern springs showing consistently higher $\delta^{13}\text{C}$
196 for both DIC and DOC at a given DIC content. The parallel trends of decreasing $\delta^{13}\text{C}$

197 with decreasing DIC are consistent with isothermal (~65°C) precipitation of
198 isotopically heavy calcite from forearc fluids (see methods for details), with generally
199 higher degrees of calcite precipitation observed closer to the trench. This model is
200 supported by water chemistry data; PhreeqC was used to show that all outer forearc
201 samples are strongly saturated with respect to calcite and thus would be predicted to
202 readily precipitate calcite (Supplementary Table 3). We present a model for calcite
203 precipitation that closely fits the observed data distribution (Figure 3), but requires a
204 more positive $\delta^{13}\text{C}$ value of the deep total dissolved carbon (DC = DIC+DOC) source
205 fluid (+5.0‰) released from the slab in northern Costa Rica than in central Costa Rica
206 (+0.5‰). Volcanic gases, which are presumed to represent the primary magmatic
207 fluid, show isotopically more negative values than dissolved carbon in the calculated
208 DIC endmember fluids, due to the additional isotopic fractionation associated with
209 dissolution of CO_2 gas into an aqueous fluid²⁵ (Figure 3). Importantly, the modeled
210 initial dissolved carbon values thus reflect both the isotopic composition of the
211 subduction fluids and a fractionation effect derived from CO_2 dissolution from source
212 gases²⁶⁻²⁷ (Figure 3). Our data suggest that surface carbon expressions across the
213 forearc are ultimately inherited from slab/mantle fluids, which are intricately linked
214 to the tectonics of the region, and modified by broadly coherent shallow processes.

215

216 **Origin of fluids:**

217 The observation that northern and central Costa Rica samples have markedly
218 different source fluid compositions suggests a relationship to the character of the
219 subducting slab. The northern EPR crust has a higher density of seamounts and is
220 more permeable than the CNS crust²⁸. The higher resulting fluid flow through sub-
221 seafloor basalts at the EPR cools, hydrates, and chemically weathers the plate²⁹.
222 Building on previous models³⁰, we hypothesize that the higher fluid flow from this
223 water-rich downgoing slab flushes more carbon from the slab upward into the
224 overriding plate at shallower depths beneath the forearc, accounting for the greater
225 contributions of relatively ^{13}C -enriched carbonates in our northern sample set.

226 Additionally, enhanced fluid circulation in the EPR crust likely promotes calcite
227 veining in the downgoing plate, potentially providing an additional source of heavy
228 carbon³¹ in northern Costa Rica. Thus, the composition of the subducting slab is
229 expressed in surface-manifestations across the forearc. Our model predicts that
230 source fluids from northern Costa Rica are more ¹³C-enriched than in central Costa
231 Rica (Figure 3). Both volcanic arc CO₂ and dissolved forearc carbon reflect a larger
232 carbonate contribution in northern Costa Rica, which is consistent with previous
233 observations in the volcanic arc which show an increased carbonate signal in
234 northern Costa Rica, which extends into Nicaragua^{30, 32-36}.

235

236 Importantly, the carbon isotope compositions of forearc springs can be used to
237 calculate the fraction of carbon lost through calcite deposition (see Figure 3 and
238 methods for details). Using the average $\delta^{13}\text{C}$ of the DC ($\delta^{13}\text{C}_{\text{DC}}$) of all the forearc springs
239 for each transect (northern = -8.8‰, central = -14.3‰) we find that 88% and 89% of the
240 total carbon released in the forearc is precipitated as calcite, respectively. Using the
241 average $\delta^{13}\text{C}_{\text{DC}}$ of the outer forearc springs (i.e., Nicoya Peninsula only; northern = -
242 14.4‰, central = -16.5‰) yields 95% and 92% of the total carbon precipitated as calcite,
243 for the northern and central transects, respectively. The close agreement between the
244 calculated fractions of total carbon lost to calcite is due to the fact that the Rayleigh
245 fractionation curves are steep at low $\delta^{13}\text{C}$ values (Figure 3). Thus, a large range in $\delta^{13}\text{C}$
246 observed in the forearc corresponds to a relatively narrow range of calculated
247 fractionation (F) values (i.e., fraction of carbon remaining; Figure 3). We conclude that
248 $91 \pm 4\%$ of forearc carbon is lost through calcite precipitation.

249

250 Measured DOC $\delta^{13}\text{C}$ values varied widely from -0.65 to -25.48‰ vs. VPDB,
251 with a mean value of -12.00‰. Like DIC, the lowest values were observed in the
252 outer forearc and the highest values were observed in the forearc, where values are
253 highly variable (Figure 2B and 2C). However, with the exception of one site in the
254 central region (Santa Lucia), DOC carbon isotope compositions and concentrations

255 strongly correlate with those of DIC (Figure 3), suggesting that DOC is produced from
256 deeply sourced fluids. Considering this, we propose a two-stage model whereby $91 \pm$
257 4% of the carbon released from the slab/mantle is consumed by calcite precipitation
258 and the remaining dissolved carbon is further fractionated by biological consumption.
259 Our model assumes a steady-state flux of deep (slab/mantle) fluids, which imparts
260 the carbon isotope signature of the slab into the upper plate where carbon is
261 partitioned into CO_2 gas, calcite, DIC, and DOC. DOC is potentially a mixture of deep
262 thermogenic DOC, deep microbial chemolithoautotrophy, and shallow
263 photosynthetic DOC. The outlier DOC sample, Santa Lucia, is likely dominated by
264 deep thermogenic DOC, due to the fact that it has an anomalously high DOC
265 concentration (5.69mmolC/L), $\delta^{13}\text{C}$ value (-0.65‰), and polycyclic aromatic
266 hydrocarbon concentrations (Supplementary Table 2), accompanied by a pronounced
267 visible oily sheen on the surface fluids. In all other sampling sites, DOC is likely
268 synthesized from DIC at physiologically feasible temperatures in the subsurface
269 rather than being a mixture of exogenous sources, since its concentrations and $\delta^{13}\text{C}$
270 values correlate tightly with DIC.

271

272 DIC and DOC carbon isotopes are offset from each other by $10.9 \pm 1.6\text{‰}$ in
273 the north, and $5.8 \pm 2.2\text{‰}$ in the central region (Figure 3); these $\Delta^{13}\text{C}_{\text{DIC-DOC}}$ values are
274 within the expected range for the reverse tricarboxylic cycle, which is a common
275 microbial carbon fixation pathway in the subsurface^{17,37}. The $\Delta^{13}\text{C}_{\text{DIC-DOC}}$ values are
276 also consistent with isotopic fractionation of hydrocarbons synthesized abiotically
277 from DIC at 250°C ²². However, calcite precipitation occurs at $\sim 65^\circ\text{C}$, and DOC
278 synthesis must occur after calcite precipitation for DOC carbon isotope compositions
279 to correlate with the post-precipitation DIC values. Therefore most of the DOC
280 appears to be derived from subsurface chemolithoautotrophy at $<65^\circ\text{C}$. This is
281 further supported by the detection of microbial cells in all hot spring fluids except Las
282 Hornillas. We conclude that DOC at the remaining sites is primarily synthesized from
283 chemolithoautotrophy within the deep subsurface environment and that

284 slab/mantle-derived carbon is used by microorganisms to build biomass. By using cell
285 abundance values for the sampled subsurface fluids, we estimate that up to 2.8×10^9
286 moles of additional carbon could be locked into biomass in the Costa Rican forearc,
287 potentially contributing significantly to the overall carbon sink.

288

289 These findings have major implications for the global carbon mass balance of
290 subduction zones. We calculate a CO_2 flux from the forearc (Supplementary Table 4) by
291 combining the average DIC concentration in forearc waters of 4.24 mmol/L CO_2 with
292 measured flow rates, which ranged between 1-10 L/s and an estimated 50-500 springs³⁸
293 throughout the forearc region. We further consider that 5-50 of these springs have a
294 separate gas phase, with measured CO_2 fluxes of $201 \text{ mol} \times \text{m}^{-2} \times \text{d}^{-1}$ to $655 \text{ mol} \times \text{m}^{-2} \times$
295 d^{-1} , and bubbling areas that typically cover 1 m^2 to 10 m^2 based on our field
296 observations. Using these broad criteria, the steady-state CO_2 flux is constrained to $7.1 \times$
297 10^6 to $7.9 \times 10^8 \text{ mol/yr}$ (mean = 4.0×10^8), which is two orders-of-magnitude smaller
298 than the volcanic-arc flux ($1.3\text{-}6.1 \times 10^{10} \text{ mol/yr}$)^{2,8}. As argued above, carbon isotopes
299 indicate that forearc calcite deposition and chemolithoautotrophy together remove
300 ~94% of the total carbon inputs. This increases the flux range that we calculate to $1.2 \times$
301 10^8 to $1.3 \times 10^{10} \text{ mol/yr}$, which is significantly larger than the previous outer forearc
302 estimate of $2.1 \times 10^7 \text{ mol/yr}$, determined using a smaller number of submarine seeps³.
303 This represents up to 36% of the total volcanic-arc flux ($= 3.7 \times 10^{10} \pm 66\% \text{ mol/yr}$; taken
304 as the mean of previous CO_2 flux estimates from references^{2,8}; Figure 4; Supplementary
305 Table 4), which would result in a ~19% reduction in the amount of total carbon
306 transported to the deep mantle. Similarly, dissolved CH_4 concentrations and CH_4/CO_2 in
307 sampled fluids are used to constrain the CH_4 flux from 5.1×10^3 to $1.0 \times 10^6 \text{ mol/yr}$.
308 Thus, CH_4 emissions contribute negligibly to the total forearc C budget.

309

310 **Implications for evolution of Earth Reservoirs:**

311 Our results suggest that significantly less carbon is transported into Earth's
312 mantle than previous estimates suggest¹, due to the previously unrecognized calcite

313 forearc carbon sink. This observation has wide ranging implications for the volatile
314 inventory of the mantle and the temporal evolution of Earth reservoirs, which controls
315 the planet's redox balance³⁹⁻⁴¹. For example, the nature (reduced vs. oxidized carbon)
316 and extent of carbon reaching the mantle is intricately linked to volatile recycling, and
317 impacts the net oxidation state of Earth's surface and deep interior. Furthermore, we
318 propose that carbon sequestration in the forearc may be directly related to plate
319 subduction angle, which dictates the extent of forearc. Globally, flat subduction zones
320 represent only about 10% of total subduction zones⁴², which would indicate that
321 approximately 2% less carbon than previously estimated is currently delivered to the
322 deep mantle. However, such a carbon sink may have been enhanced during the late
323 Archean, when oceanic crust was subducted at an anomalously low-angle⁴³. Notably,
324 evidence for the so-called Archean flat-subduction is preserved in most late Archean
325 (3.0–2.5 Ga) terrains, but is lacking in the early Archean (>3.3 Ga). If carbon was stored
326 overwhelmingly on continental (or island arc) margins, then continental collisions and
327 continental arc flare-ups would be the most important regulator of atmospheric CO₂
328 through time. During the Proterozoic, subduction zones were dominated by high dip
329 angles and smaller forearcs⁴⁴, enabling volatiles to be more efficiently transferred into
330 deep mantle, as the forearc carbon sink would likely be less significant and transfer to
331 the mantle would be more efficient. A more efficient transfer of reduced carbon to the
332 mantle could then lead to enhanced accumulation of oxygen in the atmosphere over
333 time. Thus, this work provides potential forcing mechanisms on the great oxygenation
334 event, which was certainly controlled in part by subduction efficiency and plate
335 tectonics⁴⁵⁻⁴⁷. In addition, these findings also have implications for the modern
336 atmosphere, as better constraints on the long-term volcanic carbon budget and how it
337 may be buffered by chemical and biological processes is critical for evaluating natural
338 and anthropogenic climate forcings.

339

340 **Main Text References:**

341

- 342 1. Kelemen, P. B., & Manning, C. E. Reevaluating carbon fluxes in subduction
343 zones, what goes down, mostly comes up. *Proceedings of the National*
344 *Academy of Sciences*, 112(30), E3997-E4006. (2015).
- 345
- 346 2. Shaw, A. M., Hilton, D. R., Fischer, T. P., Walker, J. A., & Alvarado, G. E.
347 Contrasting He–C relationships in Nicaragua and Costa Rica: insights into C
348 cycling through subduction zones. *Earth and Planetary Science Letters*,
349 214(3-4), 499-513. (2003).
- 350
- 351 3. Füre, E., Hilton, D. R., Tryon, M. D., Brown, K. M., McMurtry, G. M.,
352 Brückmann, W., & Wheat, C. G. Carbon release from submarine seeps at
353 the Costa Rica fore arc: Implications for the volatile cycle at the Central
354 America convergent margin. *Geochemistry, Geophysics, Geosystems*,
355 11(4). (2010).
- 356
- 357 4. Schwarzenbach, E.M., Früh-Green, G.L., Bernasconi, S.M., Alt, J.C. and
358 Plas, A. Serpentinization and carbon sequestration: A study of two ancient
359 peridotite-hosted hydrothermal systems. *Chemical Geology*, 351, pp.115-
360 133. (2013).
- 361
- 362 5. McCollom, T. M., & Seewald, J. S. Serpentinites, hydrogen, and life.
363 *Elements*, 9(2), 129-134. (2013).
- 364
- 365 6. Hilton, D. R., Fischer, T. P., & Marty, B. Noble gases and volatile recycling
366 at subduction zones. *Reviews in mineralogy and geochemistry*, 47(1), 319-
367 370. (2002).
- 368
- 369 7. de Leeuw, G.A.M., Hilton, D.R., Fischer, T.P. and Walker J.A., The He-CO₂
370 isotope and relative abundance characteristics of geothermal fluids in El
371 Salvador and Honduras: New constraints on volatile mass balance of the

- 372 Central American Volcanic Arc, *Earth and Planetary Science Letters*, 258(1–
373 2), 132–146. (2007).
- 374
- 375 8. de Moor, J.M., Kern, C., Avar, G., Muller, C., Aiuppa, A., Saballos, A.,
376 Ibarra, M., LaFemina, P., Protti, M. and Fischer, T.P.. A new sulfur and
377 carbon degassing inventory for the Southern Central American Volcanic
378 Arc: The importance of accurate time-series data sets and possible
379 tectonic processes responsible for temporal variations in arc-scale volatile
380 emissions. *Geochemistry, Geophysics, Geosystems*, 18(12), pp.4437-4468.
381 (2017).
- 382
- 383 9. Fryer, P., Ambos, E. L., & Hussong, D. M. Origin and emplacement of
384 Mariana forearc seamounts. *Geology*, 13(11), 774-777. (1985).
- 385
- 386 10. Brown, K. M. The nature and hydrogeologic significance of mud diapirs
387 and diatremes for accretionary systems. *Journal of Geophysical Research:*
388 *Solid Earth*, 95(B6), 8969-8982. . (1990).
- 389
- 390 11. Naif, S., Key, K., Constable, S., & Evans, R. L. Water-rich bending faults at
391 the Middle America Trench. *Geochemistry, Geophysics, Geosystems*, 16(8),
392 2582-2597. (2015).
- 393
- 394 12. Gorman, P. J., Kerrick, D. M., & Connolly, J. A. D. Modeling open system
395 metamorphic decarbonation of subducting slabs. *Geochemistry,*
396 *Geophysics, Geosystems*, 7(4). (2006).
- 397
- 398 13. Vaca, L., Alvarado, A., & Corrales, R. Calcite deposition at Miravalles
399 geothermal field Costa Rica. *Geothermics*, 18(1-2), 305-312. (1989).
- 400

401 14. Corrigan, J., Mann, P., & Ingle Jr, J. C. Forearc response to subduction of
402 the Cocos ridge, Panama-Costa Rica. *Geological Society of America*
403 *Bulletin*, 102(5), 628-652. (1990).
404

405 15. Pacton, M., Wacey, D., Corinaldesi, C., Tangherlini, M., Kilburn, M.R.,
406 Gorin, G.E., Danovaro, R. and Vasconcelos, C. Viruses as new agents of
407 organomineralization in the geological record. *Nature communications*, 5,
408 p.4298. (2014).
409

410 16. Zhu, T. & Dittrich, M. Carbonate precipitation through microbial activities
411 in natural environment, and their potential in biotechnology: A review.
412 *Frontiers in Bioengineering and Biotechnology*, 4:4. (2016).
413

414 17. Berg, I. A. Ecological aspects of the distribution of different autotrophic CO₂
415 Fixation Pathways. *Appl. Environ. Microbiol.* 77, 1925–1936. (2011).
416

417 18. Colwell, F. S., D’Hondt, S. Nature and extent of the deep biosphere.
418 *Reviews in Mineralogy and Geochemistry*, 75, 547-574. (2013).
419

420 19. Emerson, J. B., Thomas, B. C., Alvarez, W., & Banfield, J. F. Metagenomic
421 analysis of a high carbon dioxide subsurface microbial community
422 populated by chemolithoautotrophs and bacteria and archaea from
423 candidate phyla. *Environmental Microbiology*, 18(6), 1686-1703. (2016).
424

425 20. Harris, R. N., & Wang, K. Thermal models of the middle America trench at
426 the Nicoya Peninsula, Costa Rica. *Geophysical Research Letters*, 29(21), 6-
427 1. (2002).
428

- 429 21. Whiticar, M. J. Carbon and hydrogen isotope systematics of bacterial
430 formation and oxidation of methane. *Chemical Geology*, 161(1-3), 291-
431 314. (1999).
432
- 433 22. McCollom, T. M., & Seewald, J. S. Abiotic synthesis of organic compounds
434 in deep-sea hydrothermal environments. *Chemical Reviews*, 107(2), 382-
435 401. (2007).
436
- 437 23. Ozima, M., & Podosek, F. A. Noble gas geochemistry. *Cambridge*
438 *University Press*. (2002).
439
- 440 24. Hilton, D. R. The helium and carbon isotope systematics of a continental
441 geothermal system: results from monitoring studies at Long Valley caldera
442 (California, USA). *Chemical Geology*, 127(4), 269-295. (1996).
443
- 444 25. Mook, W.G., Bommerson, J.C., Stavermann, W.H. Carbon isotope
445 fractionation between dissolved bicarbonate and gaseous carbon dioxide.
446 *Earth and Planetary Science Letters* 22, 169 (1974).
447
- 448 26. Vogel, J. C., Grootes, P. M., & Mook, W. G. Isotopic fractionation between
449 gaseous and dissolved carbon dioxide. *Zeitschrift für Physik A Hadrons and*
450 *nuclei*, 230(3), 225-238. (1970).
451
- 452 27. Barry, P. H., Hilton, D. R., Fischer, T. P., De Moor, J. M., Mangasini, F., &
453 Ramirez, C. Helium and carbon isotope systematics of cold “mazuku” CO₂
454 vents and hydrothermal gases and fluids from Rungwe Volcanic Province,
455 southern Tanzania. *Chemical Geology*, 339, 141-156. (2013).
456

- 457 28. Audet, P., & Schwartz, S. Y. Hydrologic control of forearc strength and
458 seismicity in the Costa Rican subduction zone. *Nature Geoscience*, 6(10),
459 852. (2013).
460
- 461 29. Wheat, C. G., & Fisher, A. T. Massive, low-temperature hydrothermal flow
462 from a basaltic outcrop on 23 Ma seafloor of the Cocos Plate: Chemical
463 constraints and implications. *Geochemistry, Geophysics, Geosystems*,
464 9(12). (2008).
465
- 466 30. Aiuppa, A., Robidoux, P., Tamburello, G., Conde, V., Galle, B., Avard, G.,
467 Bagnato, E., de Moor, J.M., Martinez, M., Muñoz, A. Gas measurements
468 from the Costa Rica-Nicaragua volcanic segment suggest possible along-
469 arc variations in volcanic gas chemistry. *Earth and Planetary Science*
470 *Letters*, 407, 134-147. (2014).
471
- 472 31. Alt J. C., Laverne C., Coggon R. M., Teagle D. A., Banerjee N. R., Morgan S.,
473 Smith-Duque C. E., Harris M., & Galli L. Subsurface structure of a
474 submarine hydrothermal system in ocean crust formed at the East Pacific
475 Rise, ODP/IODP Site 1256. *Geochemistry, Geophysics, Geosystems*, 11(10).
476 (2010).
477
- 478 32. Carr, M. J., Feigenson, M. D., & Bennett, E. A. Incompatible element and
479 isotopic evidence for tectonic control of source mixing and melt extraction
480 along the Central American arc. *Contributions to Mineralogy and*
481 *Petrology*, 105(4), 369-380. (1990).
482
- 483 33. Leeman, W. P., Carr, M. J., & Morris, J. D. Boron geochemistry of the
484 Central American volcanic arc: constraints on the genesis of subduction-

- 485 related magmas. *Geochimica et Cosmochimica Acta*, 58(1), 149-168.
486 (1994).
487
- 488 34. Zimmer, M. M., Fischer, T. P., Hilton, D. R., Alvarado, G. E., Sharp, Z. D., &
489 Walker, J. A. Nitrogen systematics and gas fluxes of subduction zones:
490 insights from Costa Rica arc volatiles. *Geochemistry, Geophysics,*
491 *Geosystems*, 5(5). (2004).
492
- 493 35. Hilton, D. R., Ramirez, C. J., Mora-Amador, R., Fischer, T. P., Füre, E., Barry,
494 P. H., & Shaw, A. M. Monitoring of temporal and spatial variations in
495 fumarole helium and carbon dioxide characteristics at Poás and Turrialba
496 volcanoes, Costa Rica (2001-2009). *Geochemical Journal*, 44(5), 431-440.
497 (2010).
498
- 499 36. Lee, H., Fischer, T. P., de Moor, J. M., Sharp, Z. D., Takahata, N., & Sano, Y.
500 Nitrogen recycling at the Costa Rican subduction zone: The role of
501 incoming plate structure. *Scientific Reports*, 7(1), 13933. (2017).
502
- 503 37. House, C. H., Schopf, J. W., & Stetter, K. O. Carbon isotopic fractionation
504 by Archaeans and other thermophilic prokaryotes. *Organic Geochemistry*,
505 34(3), 345-356. (2003).
506
- 507 38. Alvarado, G.E. & Vargas, A.G., History of discovery and exploitation of
508 thermal water in Costa Rica. *Revista Geológica de América Central*, (57),
509 pp.55-84 (2017).
510
- 511 39. Marty, B., & Dauphas, N. The nitrogen record of crust–mantle interaction
512 and mantle convection from Archean to present. *Earth and Planetary*
513 *Science Letters*, 206(3), 397-410. (2003).

- 514
515 40. Hirschmann, M. M., & Dasgupta, R. The H/C ratios of Earth's near-surface
516 and deep reservoirs, and consequences for deep Earth volatile cycles.
517 *Chemical Geology*, 262(1-2), 4-16. (2009).
518
- 519 41. Jelen, B. I., Giovannelli, D., and Falkowski, P. G. The Role of Microbial Electron
520 Transfer in the Coevolution of the Biosphere and Geosphere. *Annual Review*
521 *of Microbiology* 70, 45–62. (2016).
522
- 523 42. Li, Z.H., Xu, Z.Q., Gerya, T.V. Flat versus steep subduction: Contrasting
524 modes for the formation and exhumation of high- to ultrahigh-pressure
525 rocks in continental collision zones. *Earth and Planetary Science Letters*,
526 301 (1-2), 65-77 (2011).
527
- 528 43. Smithies, R. H., Champion, D. C., & Cassidy, K. F. Formation of Earth's early
529 Archean continental crust. *Precambrian Research*, 127(1-3), 89-101.
530 (2003).
531
- 532 44. Abbott, D., Drury, R., & Smith, W. H. Flat to steep transition in subduction
533 style. *Geology*, 22(10), 937-940. (1994).
534
- 535 45. Holland, H. D. Volcanic gases, black smokers, and the Great Oxidation
536 Event. *Geochimica et Cosmochimica Acta*, 66(21), 3811-3826. (2002).
537
- 538 46. Kump, L. R., Kasting, J. F., & Barley, M. E. Rise of atmospheric oxygen and
539 the “upside-down” Archean mantle. *Geochemistry, Geophysics,*
540 *Geosystems*, 2(1). (2001).
541

- 542 47. Och, L. M., & Shields-Zhou, G. A. The Neoproterozoic oxygenation event:
543 Environmental perturbations and biogeochemical cycling. *Earth-Science*
544 *Reviews*, 110(1-4), 26-57. (2012).
- 545
- 546 48. Bird, P. "An updated digital model of plate boundaries." *Geochemistry,*
547 *Geophysics, Geosystems* 4.3 (2003).
- 548
- 549 49. Protti, M., Gu, F., & McNally, K. The geometry of the Wadati-Benioff zone
550 under southern Central America and its tectonic significance: Results from
551 a high-resolution local seismographic network. *Physics of the Earth and*
552 *Planetary Interiors*, 84(1-4), 271-287. (1994).
- 553
- 554 50. Ryan, W.B.F., Carbotte, S.M. Coplan, J.O. O'Hara, S. Melkonian, A. Arko, R.
555 Weissel, R.A. Ferrini, V. Goodwillie, A. Nitsche, F. Bonczkowski, J. & Zemsky R.
556 Global Multi-Resolution Topography synthesis, *Geochem. Geophys. Geosyst.*,
557 10, Q03014. (2009).
- 558

559 **Acknowledgments:**

560 This project was inspired by the late Dave Hilton, who was a great mentor and friend
561 to several of the coauthors. This work was principally supported by a grant (G-2016-
562 7206) from the Alfred P. Sloan Foundation and the Deep Carbon Observatory to
563 P.H.B., K.G.L., D.G., K.P., T.L., J.M.dM. and D.H. In addition, P.H.B. was supported by
564 NSF grant 1144559 during a portion of this project. D.G. was supported by an NSF
565 grant (MCB 15–17567) and an ELSI Origins Network (EON) research Fellowship, which
566 is supported by a grant from the John Templeton Foundation. The opinions expressed
567 in this publication are those of the authors and do not necessarily reflect the views of
568 the John Templeton Foundation. This work was further supported in party by JSPS
569 KAKENHI grants (JP17K14412, JP17H06105, JP17H02989) awarded to M.N., NSF OCE-
570 1431598 and NASA Exobiology NNX16AL59G awarded to K.G.L., NSF grants 0206113,

571 0711533 and 1049713 awarded to T.P.F., and NSF grants 0003628 and 1049748 to
572 D.R.H. M.Y. was supported by a DEKOSIM grant (BAP-08-11-DPT.2012K120880),
573 financed by the Ministry of Development of Turkey. M.N. produced most data, and
574 we thank her for her significant contributions. We thank Patricia Barcala Dominguez
575 for assistance with figure illustration. We thank Bruce Deck, Marten Wahlen and
576 Keith Blackmon for analytical assistance at SIO. We thank Bernard Marty, Guillermo
577 Alvarado, Michael Broadly, David Byrne, David Bekaert, Jabrane Libidi and Jon Wade
578 for discussions about the project.

579

580 **Author contributions:**

581 P.H.B. originally conceived the idea for the project, was lead-PI on the Sloan (Deep
582 Carbon Observatory) grant that supported the work, and prepared the first draft of
583 the manuscript. J.M.dM., D.G., and K.G.L. were all co-PIs on the grant and
584 contributed immensely (and equally) to modeling these data and to the writing
585 process. M.S. contributed significantly to modeling and writing, although he was not
586 a co-PI on the Sloan grant. D.H., T.L. and C.A.P. were co-PIs on the Sloan grant and
587 contributed to the writing process. Noble gas analysis was conducted in the
588 laboratory of C.J.B. at Oxford. T.P.F. and D.R.H. are senior PIs who first brought P.H.B.
589 and J.M.dM. to Costa Rica as PhD students, and were instrumental in the conception
590 of this project. In addition, a portion of the data reported in this contribution was
591 generated from those early expeditions. All other authors (listed alphabetically)
592 provided comments on the manuscript and either assisted in sample collection (as
593 part of the Biology Meets Subduction team or on previous expeditions) and/or
594 analyzed samples in their respective laboratories.

595

596 **Author information:**

597 The authors declare no competing interests. Reprints and permissions information is
598 available at www.nature.com/reprints. Correspondence and requests for materials
599 should be addressed to pbarry@whoi.edu.

600

601 **Figure 1** – Map of the northwest coast of Costa Rica. Northern sites (blue) and central
602 sites (orange) as well as the plate boundary between the East Pacific Rise (EPR) crust
603 and Cocos Nazca spreading center (CNS) crust, and the Quesada Sharp Contortion (QSC)
604 are shown. Sample distances to trench (Supplementary Table 1) were calculated as the
605 distance of a line segment extending from the sample location, along the angle of
606 convergence, to the plate boundary⁴⁸. Red-tipped triangles are volcanoes Orosí, Rincón
607 dela Vieja, Miravalles, Tenorio, Arenal, Platanar, Poás, Barva, Turrialba, and Irazú, from
608 north to south. Thin lines are depth to slab in 20km intervals⁴⁹. Background data from
609 GeoMapApp (<http://www.geomapapp.org>)⁵⁰.

610

611 **Figure 2A** – Helium isotopes ($^3\text{He}/^4\text{He}$) vs. distance from trench. The plot shows a
612 decrease in $^3\text{He}/^4\text{He}$ trenchward, suggesting that there is pervasive deep slab/mantle
613 degassing occurring across the entire arc, even though free CO_2 gas is absent. **2B** –
614 carbon concentrations (as indicated by circle size) and $\delta^{13}\text{C}$ of CO_2 gas, dissolved
615 inorganic carbon (DIC), dissolved organic carbon (DOC), and total organic carbon in
616 sediments surrounding the surface emanation of the springs (sTOC) are shown vs.
617 distance from trench and subduction zone section (C) in order to show the full range
618 in data. These “bubble plots” show that there is a corresponding decrease in carbon
619 concentrations and $\delta^{13}\text{C}$ values of DIC and DOC trenchward, and no change in
620 concentrations and $\delta^{13}\text{C}$ values of TOC.

621

622 **Figure 3** – Carbon isotopes as a function of DIC concentrations for northern (blue)
623 and central (orange) DIC (filled symbols), along with isotope fractionation model in
624 solid lines. DOC $\delta^{13}\text{C}$ values (open markers) as well as DOC concentrations (inset)
625 correlate with those of DIC. For clarity, Santa Lucia (5.69 mmol/L DOC) is not included
626 in inset. Values for arc gases ($T \geq$ boiling; plotted at 0% C sequestered as calcite)
627 represent an endpoint of CO_2 concentration and $\delta^{13}\text{C}$, offset from DIC by the
628 fractionation from gas to aqueous phase.

629

630 **Figure 4A**– Box model showing the carbon inputs⁸ in the Costa Rica Forearc.

631 Estimated inputs are from sediments, altered oceanic crust and serpentized mantle
632 via subduction. Estimated outputs are shown for the forearc (this study) and the arc^{2,8},
633 as well as predicted transport to the deep mantle (inputs minus outputs). **4B** – Inset
634 box model showing endmember carbon isotopic values into the forearc following
635 release from the slab/mantle. The model shows fluid pathways and associated
636 fractionation as calcite forms, with approximately 91% of total carbon released in the
637 forearc sequestered as calcite. The remaining dissolved carbon (DC) is isotopically
638 depleted and partitioned into dissolved inorganic carbon (DIC) and dissolved organic
639 carbon (DOC).

640

641 **Methods:**

642 **Sample collection and analysis:**

643 In 2017, fluid and gas samples were collected across two transects of the
644 Costa Rican Arc (Figure 1), with pH ranging from 0.9-10.0 and temperatures ranging
645 from 23-89°C. Fluid and gas samples were collected in evacuated glass flasks and Cu-
646 tubes using standard collection procedures⁵¹, whereby precautions were taken to
647 minimize any possible air contamination²⁷. Gas and fluids samples (n=24) from 2017
648 are accompanied by addition (n=17) samples collected during reconnaissance field
649 campaigns in 2008, 2010 and 2012. He and C isotope data from the initial
650 reconnaissance field campaigns were produced in the Fluids and Volatiles Laboratory
651 at Scripps Institution of Oceanography (SIO), whereas data from 2017 are from
652 Oxford (He-isotopes) and Tokyo Institute for Technology (C-isotopes).

653

654 Samples were collected over several field campaigns; however, all samples
655 were collected during the dry season in an effort to minimize seasonal effects
656 (Supplementary Table 1). Considering this, the data from the various labs are in good
657 agreement. For example, fluids were collected at the Sabana Grande site in 2008,

658 2010 and again in 2017; C-isotope values of -12.69‰ (2017; Japan) agree well with -
659 12.75‰ (2008; SIO), -12.79‰ (2008; SIO) and -13.43‰ (2012; SIO). He-isotope
660 values for this site were $2.66 \pm 0.13 R_A$ (2017; Oxford), $0.60 \pm 0.03 R_A$ (2008; SIO) and
661 $1.04 \pm 0.11 R_A$ (2012; SIO), all indicate an admixture of radiogenic and mantle derived
662 gases. Notably, there is not thought to be a discernable cosmogenic component in
663 subduction-related fluids, as ^3He outputs greatly exceed input parameters⁶. Also,
664 much too little interplanetary dust particles is available to sustain the flux required.
665 See Trull 1994. Also, high diffusivity of He in most low-T minerals is important. When
666 considering the reproducibility of He isotope measurements, it is essential to
667 consider the amount of air contamination in a given sample, which is estimated using
668 the relative amount of He and Ne, expressed as the X-value ($^4\text{He}/^{20}\text{Ne}$ normalized to
669 air). At Sabana Grande, the most pristine sample (highest X-value) yielded the highest
670 He isotope value of $2.66 R_A$ (Extended Data Figure 2). Helium isotopes were also
671 measured in samples collected at the Pueblo Antiguo site in 2010 (SIO), 2012 (SIO)
672 and 2017 (Oxford), and in the two samples with high X-values (>5), the He isotopes
673 measured at different laboratories are within analytical error (Oxford, 2017 = $4.34 \pm$
674 $0.22 R_A$ and SIO, 2010 = $4.51 \pm 0.11 R_A$).

675

676 Gas and water samples from the 2008, 2010 and 2012 campaigns were analyzed
677 at SIO for helium and carbon isotopes using instrumentation and protocols described
678 previously^{2,7,52}. All samples were extracted on a dedicated preparation line with a
679 fraction of the non-condensable gas (containing He and Ne) captured in a 1720-glass
680 breakseal. All CO_2 was condensed into a Pyrex breakseal following separation from
681 water vapor, non-inert gases (N_2 , CO , CH_4) and heavy noble gases (Ar, Kr and Xe).

682

683 Helium and neon analyses were carried out on a MAP-215 noble gas mass
684 spectrometer SIO. First, the gas was released from the breakseal and prepared for
685 analysis using a series of traps, held at liquid nitrogen temperature, and active-gas
686 getters. Helium was separated from neon using a helium-cooled refrigeration stage

687 interfaced to a trap lined with activated charcoal. All sample $^3\text{He}/^4\text{He}$ ratios were
688 normalized to standard aliquots of air processed and analyzed under identical
689 conditions.

690

691 Carbon dioxide was purified at SIO on a dedicated line using a variable
692 temperature trap designed to separate CO_2 from sulfur-bearing species. Following
693 cleanup, the amount of CO_2 was measured using a capacitance gauge manometer in a
694 calibrated volume, prior to freezing an aliquot of the CO_2 in a Pyrex breakseal. For
695 isotope analysis, the CO_2 aliquot was inlet into a Thermo-Finnigan Delta XP^{Plus} Isotope
696 Ratio Mass Spectrometer (IRMS). Carbon isotopes on gas samples from the 2017
697 campaign were analyzed at Universidad Nacional on a Picarro G2201-I by acidification of
698 NaOH solutions extracted from Giggenbach bottle samples. $\delta^{13}\text{C}_{\text{PDB}}$ values were
699 calibrated against a set of 8 standards with values ranging from + 2.42 ‰ to -37.21‰,
700 including internationally accepted standards NBS19 and Carrara Marble. Reported delta
701 values have uncertainties of <0.1 ‰ based on repeat analyses of standards and samples.

702

703 Noble gas analysis was also conducted in the Noble Laboratory at the University
704 of Oxford (2017 samples), using a dual mass spectrometer setup, interfaced to a
705 dedicated extraction and purification system⁵³. Gases were collected in Cu-tubes, and
706 then transferred to the extraction and purification line where reactive gases were
707 removed by exposing gases to a titanium sponge held at 950 °C. The titanium sponge
708 was cooled for 15 minutes to room temperature before gases were expanded to a dual
709 hot (SAES GP-50) and cold (SAES NP-10) getter system, held at 250 °C and room
710 temperature, respectively. A small aliquot of gases was segregated for preliminary
711 analysis on a Hiden Analytical HAL-200 quadrupole mass spectrometer. All noble gases
712 were then concentrated using a series of cryogenic traps; heavy noble gases (Ar-Kr-Xe)
713 were frozen down at 15 K on an all SS finger and the He and Ne were frozen down at 19
714 K on a cold finger filled with charcoal. The temperature on the charcoal finger was then
715 raised to 34 K to release only He, which was inlet into a Helix SFT mass spectrometer.

716 Following He analysis, the temperature on the charcoal cryogenic trap was raised to 90
717 K to release Ne, which was inlet into an ARGUS VI mass spectrometer.

718

719 Water samples for carbon isotope analysis (2017 samples) of dissolved inorganic
720 carbon (DIC), dissolved organic carbon (DOC) were collected by 50-mL syringes and
721 filtered by connecting membrane syringe filters with a pore size of 0.20 μm (DISMIC–
722 25AS; Advantec Toyo Kaisha, Tokyo, Japan) and syringe needle. Then filtered water was
723 directly injected to the pre-vacuumed 50-mL serum bottle sealed with butyl rubber
724 septa and an aluminum crimp. The subsampled water (10 mL) for DIC measurement
725 from each water sample of 50-mL sealed vials by nitrogen gas and transferred to a pre-
726 vacuumed 30-mL glass vial sealed with butyl rubber septa and an aluminum crimp. DIC
727 concentrations and their $\delta^{13}\text{C}$ values were measured using CO_2 in the headspace of glass
728 vials after a 1-h reaction with injected 0.5 mL H_3PO_4 . DOC were also measured CO_2 in the
729 headspace after the reaction of carbonate-free residue with 0.2 g sodium persulfate.
730 The amount of CO_2 and the isotopic values were measured using a Agilent 6890N gas
731 chromatograph attached to a Thermo-Finnigan Delta XP^{Plus}. Two international standards
732 ($\delta^{13}\text{C} = -13.90\text{‰}$ and 2.52‰) were used for standardization, and the standard
733 deviations were shown by over 3 times measurement.

734

735 The sediments surrounding the surface emanations of the springs were collected
736 for measuring TOC content and carbon isotopic compositions. The sediment samples
737 were kept at 4°C until transporting to the laboratory. Glass vial samples were then
738 stored at -80°C until further treatment. Firstly, the sediment samples were freeze-dried
739 and then crushed into fine grains using a mortar to remove large leaves and roots. 50–
740 100 mg of sediment samples were weighed and reacted with 1 M HCl solution until
741 effervescence stopped, followed by a rinse with distilled water until the pH neutralized.
742 The TOC sediment samples were analyzed using an elemental analyzer (EA-1110;
743 Thermo Fisher Scientific) coupled to a Thermo Fisher Scientific MAT 252 isotope ratio
744 mass spectrometer (IRMS).

745

746 Samples for cell counts were taken in 2017 as close to the source spring as
747 possible, usually in an outflow from a rock outcrop or a small surface pool that was
748 rapidly being refilled by the source. We placed 1 ml fluids into a 2 ml plastic tube with a
749 rubber o-ring screwcap (to prevent evaporation) containing 500 μ l 3%
750 paraformaldehyde solution in phosphate-buffered-saline (PBS). Cell count samples fixed
751 with 3% paraformaldehyde in the field were kept at room temperature during return to
752 the University of Tennessee and were weighed upon returning to the lab. Cell counts
753 were determined on a Guava Easy Cyte 6HT-2L (Millipore) flow cytometer. Triplicate
754 aliquots of each sample (200 μ L) were stained with 5 \times SybrGreen prior to analysis. We
755 estimated contributions of cell biomass with total cell counts, and average carbon
756 content of subsurface microbes⁵⁴, by multiplying the average number of cells in our fluid
757 samples by the volume of hosting rocks (from the trench to the arc – assuming a log
758 increase of the isotherms moving toward the arc) up to 2 km depths, and using an
759 average rock porosity (to obtain possible fluid amounts)⁵⁵, and found that they did
760 represent a significantly large carbon reservoir.

761

762 Aliphatic hydrocarbons (C10-C40) and polycyclic aromatic hydrocarbons
763 (PAHs) were analyzed using conventional procedures based on gas chromatography
764 with a flame ionization detector (FID) and HPLC with diode array and fluorimetric
765 detection⁵⁶. Briefly, aliphatic hydrocarbons (C10-C40) were extracted with
766 hexane:acetone (2:1) in a microwave (110°C for 25 min, 800 Watt) (Mars CEM, CEM
767 Corporation, Matthews NC). After centrifugation at 3.000 \times g for 10 min, the
768 supernatants were purified with solid-phase extraction (Phenomenex Strata-X, 500
769 mg \times 6 mL plus Phenomenex Strata-FL, 1000 mg \times 6 mL) and then concentrated using
770 a SpeedVac (RC1009; grade n-hexane and analyzed with a PerkinElmer gas
771 chromatograph) equipped with an Elite-5 capillary column (30 mm \times 0.32 mm ID \times
772 0.25 μ m-df) and a FID. For quantitative determination, the system was calibrated
773 with an unsaturated pair n-alkane standard mixture according to ENISO 9377-3 (Fluka

774 68281). For the analysis of PAHs, sediment samples were extracted using 0.5 M
775 potassium hydroxide in methanol with microwave at 55°C for 20 min (800 Watt)
776 (CEM, Mars System). After centrifugation at 3.000 × g for 10 min, the methanol
777 extracts were concentrated using a SpeedVac and purified with solid-phase
778 extraction (Octadecyl C18, 500 mg × 6 mL, Bakerbond). A final volume of 1 mL was
779 recovered with pure, analytical HPLC gradient grade acetonitrile; HPLC analyses were
780 carried out in a water-acetonitrile gradient by fluorimetric and diode array detection.
781 The PAHs were identified according to the retention times of an appropriate pure
782 standards solution (EPA 610 Polynuclear Aromatic Hydrocarbons Mix), and classified
783 as low molecular weight (LMW: naphthalene, acenaphthylene, 1-methyl
784 naphthalene, 2-methyl naphthalene, acenaphthene, fluorene, phenanthrene,
785 anthracene) or high molecular weight (HMW: fluoranthene, pyrene,
786 benzo(a)anthracene, chrysene, 7,12-dimethyl-benzo(a)anthracene,
787 benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene,
788 dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene). Accuracy
789 and precision were checked analyzing both pure standard solutions and reference
790 materials (NIST 1944) and the obtained concentrations were always within the 95%
791 confidence intervals of certified values. Aliquots of all the samples were dried in a
792 oven at 60°C for at least 8 h, up to obtain a constant weight, in order to quantify the
793 interstitial water content, allowing to express all the analyzed chemicals as a function
794 of the dry weight (d.w.) of the sediments.

795

796 **Isotope fractionation modeling:**

797 He-C studies in volcanic arc settings^{2,57-60} have coupled helium and carbon
798 isotopes to distinguish carbon from different provenances using a three-component
799 mixing model (Extended Data Figure 1). In such acidic settings, volcanic activity has been
800 suggested to release previously sequestered CO₂⁶¹⁻⁶⁴, which mixes with slab/mantle
801 carbon and results in the characteristic signatures. Samples from this study were
802 collected from a range of lithologies from ophiolites in Nicoya⁶⁵⁻⁷⁰ to andesitic and

803 basaltic volcanic rocks in the arc and forearc. The volcanic front in Costa Rica developed
804 on the western edge of the Caribbean Plateau, an oceanic plate basement without any
805 preexisting continental or arc material⁷¹⁻⁷³. The Santa Elena ophiolite is part of a series
806 of exotic, arc-related terranes that make the basement of the volcanic front in southern
807 Nicaragua and does not extend south of the Hess Escarpment-Santa Elena suture⁷⁴⁻⁷⁵.
808 However, these carbon isotope data are consistent with a model that requires for a
809 homogenous C isotope input flux. This indicates that degassing of the downgoing
810 slab/mantle drives the ¹³C-isotope inputs, rather than the over-riding crust, but in some
811 cases, this signal is subsequently obfuscated by low temperature precipitation of
812 isotopically heavy calcite, which effectively fractionates the carbon isotopes. Here we
813 provide additional details on the fractionation modeling used to construct the calcite
814 fractionation curves in Figure 3 (main text).

815

816 In summary, carbon is released from the slab/mantle and reacts with shallow
817 groundwater forming an initial pool of dissolved carbon (DC). An isotopic fractionation
818 factor between dissolved carbon and calcite (see details below) is calculated based on
819 best fit to the observed data by varying temperature iteratively. The starting $\delta^{13}\text{C}$ of DC
820 is determined to be different from the northern (5.0‰) and central (0.5‰) transect,
821 presumably controlled by different slab inputs. Notably, the presumed slab inputs are
822 consistent with positive isotope values measured in carbonate sediments off the coast
823 of Nicoya⁷⁶. Starting $\delta^{13}\text{C}$ input conditions are assumed to be the same for forearc,
824 backarc and arc. As the Rayleigh fractionation progresses, calcite is precipitated and the
825 isotope composition of residual DC reflects open system (Rayleigh) fractionation
826 processes. Rayleigh distillation curves were iteratively fitted to the data using:

827

828 eq. 1.

$$829 \delta^{13}C_{DCf} \cong (\delta^{13}C_{DCi} + 1000)(F^{\alpha_{DC-calcite}} - 1) - 1000$$

830

831 after⁷⁷, where F is the fraction of dissolved carbon (DC) remaining in the fluid, $\delta^{13}C_{DCf}$
832 is the carbon isotope composition of DC at F, $\delta^{13}C_{DCi}$ is the initial isotope composition
833 of the DC, and $\alpha_{DC-calcite}$ is the fractionation factor between DC and calcite at a given
834 temperature. The fractionation factor between DC and calcite was calculated from⁷⁸:
835
836 eq. 2.

$$838 \quad 1000 \ln \alpha_{DC-calcite} = -8.91 \times 10^8 T^{-3} + 8.557 \times 10^6 T^{-2} - 1.881 \times 10^4 T^{-1} + 8.27$$

839

840 where T is the temperature in Kelvin.

841
842 Model curves were fit to the data from each transect by iteratively varying the
843 values of $\delta^{13}C_{DCi}$ and the temperature of calcite formation. Best-fit results were
844 obtained with $\delta^{13}C_{DCi} = +5.0\text{‰}$ and T = 67 °C (R² = 0.91) for the northern transect and
845 $\delta^{13}C_{DCi} = +0.5\text{‰}$ and T = 63 °C (R² = 0.86) for the central transect.

846
847 Total dissolved carbon (DC) values used in the model are calculated from the
848 sum of measured DIC and DOC concentrations (Supplementary Table 4), and $\delta^{13}C_{DC}$ is
849 the average of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$, weighted by their respective DIC and DOC
850 concentrations. DIC dominates total DC contents, typically accounting for ~80% of DC
851 on a sample by sample basis. DOC data are not available for 12 of our 30 samples, as
852 several samples were collected on previous reconnaissance field campaigns.
853 However, the strong correlation between DC and DIC (Extended Data Figure 3) allows
854 us to confidently predict the DC concentration and $\delta^{13}C_{DC}$ of the samples for which
855 DOC is not available. The predicted DC and $\delta^{13}C_{DC}$ are thus used for the 12 samples
856 for which DOC data are not available in Figure 3 (main text). The slope of the linear
857 regressions in Figures S2a and S2c is used to calculate the fraction of DOC in the
858 northern and central transects (5.4 % and 4.7 %, respectively).

859

860 **Carbon budget calculations:**

861 The carbon isotope fractionation model allows calculation of the fraction of
862 carbon in various forearc reservoirs. Based on the average $\delta^{13}\text{C}_{\text{DC}}$ values at the forearc
863 sites (here defined as located at <155 km from the trench), the fraction (F) of carbon
864 remaining in the fluid can be calculated (expressed as "% carbon sequestered as calcite"
865 in Figure 3, which is equal to $100(1 - F)$). The average $\delta^{13}\text{C}_{\text{DC}}$ values at forearc sites are
866 further used to calculate the total DC concentration in mmol/L based on the Rayleigh
867 curves. Because the curves are steep at low F values, the $\delta^{13}\text{C}_{\text{DC}}$ values represent a more
868 robust and sensitive parameter than DC concentrations, which are more susceptible to
869 dilution and analytical uncertainty at low concentrations. The average DIC concentration
870 for forearc fluid is then calculated from dissolved carbon concentrations from the
871 relationship between DC and DIC expressed in Figures S2a and S2c. In this model, DOC
872 is then the residual carbon once DIC and calcite concentrations are accounted for. The
873 results of these calculations indicate that 91.3% of the total forearc carbon is
874 sequestered as calcite, 6.0% is released at the surface as DIC, and 2.7% is consumed by
875 microbiological processes to form DOC.

876

877 Our flux estimates for the Costa Rican forearc (see main text) show that between
878 7.1×10^6 and 7.9×10^8 mol CO_2/yr are released to the surface by spring outflow as DIC
879 and CO_2 gas. Based on the above-described model, we argue that this represents the
880 residual carbon left over after pervasive calcite deposition. The total flux (i.e., subducted
881 slab and mantle fluid) through the forearc, including both calcite deposition and
882 microbial consumption, ranges from 1.2×10^8 to 1.3×10^{10} mol/yr (Figure 4).

883

884 **Previous Mass Balance calculations:**

885 To put our forearc flux estimate into context, we must consider previous flux
886 estimates, which to date, have focused mostly on high temperature regions¹¹⁻¹³, where
887 there is a distinct point-source for carbon emissions. However, little work has been
888 conducted in the forearc of Costa Rica³ even though thermodynamic modeling of the

889 Costa Rica convergent margin predicts efficient CO₂ release from the top of the
890 subducting slab beneath forearcs, at depths of 65-80 km¹².

891

892 Past budget approaches⁵⁸ coupled He and C isotopes to tease apart C sourced
893 from different provenances using a three-component mixing model (Fig. S1). Subducted
894 slab carbon is presumed to derive from carbonate rocks and have a value of ~0 VPDB,
895 mantle values are assumed to be approximately $-6.5 \pm 2.0\%$ and isotopically low
896 carbon isotope values are attributed to contributions from organic sediments (-30‰).
897 Here we argue that in the forearc environment these values do not result from mixing,
898 but instead from low temperature calcite precipitation and biological consumption.

899

900 Arc fluxes are typically only measured along a relatively narrow transect source:
901 the volcanic front. In contrast, springs occur over a large stretch of the forearc, so this is
902 a much larger area to integrate. Quantitative assessment of gas fluxes from the forearc,
903 backarc, fault-related sites, hydrothermal volcanic systems (e.g., Tenorio, Miravalles,
904 Irazú, Rincón de la Vieja flank sites), and concurrent diffuse degassing are lacking. Here
905 we place better constraints on forearc fluxes, which complement recent constraints on
906 magmatic C fluxes⁸. We estimate a flux between of 1.2×10^8 and 1.3×10^{10} to mol CO₂
907 per year, which represents as much as ~36% of the total arc flux. , and could reduce the
908 amount transferred into the deep mantle by up to ~19%.

909

910 Previous studies have utilized helium and carbon isotopes (³He/⁴He, δ¹³C) and
911 relative abundances ratios (CO₂/³He) of fumarole sites at arc settings. Two approaches
912 were taken in these areas in order to determine CO₂ fluxes: 1) combining measured
913 CO₂/³He data with known ³He fluxes and 2) to combine measured CO₂/SO₂ data with
914 known SO₂ fluxes. Previous work was conducted throughout Costa Rica^{3,6,8} El Salvador
915 Honduras⁷ and Nicaragua².

916

917 In typical subduction zones, the vast majority of carbon is thought to be recycled
918 back into the lithosphere, hydrosphere, and atmosphere¹, and what remains is
919 transported into the deep mantle. In stark contrast, mass balance considerations from
920 the Costa Rica convergent margin suggest the majority of subducted C (more than 85%)
921 is ultimately transferred into the deep mantle^{2,3,6}. Importantly, this estimation assumes
922 that the forearc and backarc fluxes are negligible, which we have shown in this
923 contribution to be untrue. Prior work⁶ estimated the subducting CO₂ input flux for ~310
924 km Arc of Costa Rica to be 8.2×10^{10} mol/yr⁶, assuming “1% organic CO₂” in sediments
925 based on data from a single IODP site (1039) and a “global average” altered crustal
926 composition of 0.2% CO₂, extrapolated over the entire slab thickness. Published carbon
927 degassing (output) flux estimates vary between 1.2×10^{10} mol/yr to 1.5×10^{10} mol/yr,
928 with an average value of 1.26×10^{10} mol/yr. Importantly, these estimates are
929 determined to be >90% sediment and marine carbonate derived, based on C-isotope
930 data². However, more recent studies^{8,61,79} use a more complete assessment of volcanic
931 degassing from the arc to show that the current volcanic CO₂ flux from Costa Rica is
932 significantly higher (6.10×10^{10} mol/yr). The 2017 study⁸ is based on new data for 11
933 volcanoes in Costa Rica and Nicaragua showing that the CO₂ flux from the arc is
934 underestimated in previous studies. Their finding suggests that the Central American
935 subduction margin may be more similar to other arc segments¹ than previously
936 thought^{2,6}. The 2017 findings⁸ suggest the 2014-2015 CO₂ flux from the Costa Rican arc
937 is an order of magnitude greater than previous estimates^{2,6}. However, the Costa Rican-
938 Nicaraguan margin has displayed an increase in arc-wide volcanic activity in recent
939 years⁸. Thus, arc systems probably show significant variation in gas output over time. If
940 the older estimates^{2,6} of CO₂ flux are taken to be more representative of the time-
941 integrated CO₂ flux, then there is still a considerable missing flux in the forearc or arc. In
942 Figure 4 we take the average value from references 2 and 8 to determine an average
943 CO₂ flux of $3.7 \text{ mol/yr} \pm 66\%$.

944

945 **Geologic Background:**

946 The Central American subduction zone is characterized by rapid (70–90 mm/year)
947 convergence of young (15–25 Ma) oceanic lithosphere⁸⁰⁻⁸², whereas the downgoing Cocos
948 plate is composed of a thin sedimentary layer (~428m). The upper section of the column
949 (177 m) consists of Quaternary to upper Miocene hemipelagic diatomaceous mud and
950 middle Miocene brown abyssal clay and the lower section consists of middle–lower
951 Miocene chalky carbonate ooze and manganiferous chalk and chert⁸³⁻⁸⁴. The composition
952 of subducted sediments and carboniferous material is microbiologically altered, due to
953 the fact that anaerobic respiration and fermentation determine sediment redox
954 conditions, alkalinity, and carbon isotope pools⁸⁵⁻⁸⁶. The entire column of incoming
955 sediments under-thrusts the toe of the Caribbean Plate. However, the absence of
956 significant off-scraping or sediment accretion suggests the Costa Rica convergent margin
957 is either non-accretionary, or underplated further landward^{79,87}. Under-thrusting leads to
958 rapid compaction of the upper hemipelagic sediments and dewatering of pore fluids
959 within the first few kilometers of subduction⁸⁸, resulting in the release of carbon dioxide
960 and methane at relatively shallow depths into the overlying forearc³. Fluids released
961 during dehydration reactions ascend through the overriding plate along deep-penetrating
962 faults, producing numerous fluid venting sites in the forearc of Costa Rica⁸⁹. A significant
963 portion of the forearc is subaerial (Nicoya and Osa peninsulas), providing unique sampling
964 opportunities not found at the majority of arc systems. In addition to mechanically
965 induced shallow dewatering near the toe of the overriding plate, deeply-sourced (i.e.,
966 abiotic) fluids are released by mineral dehydration reactions and phase transformations at
967 depths of approximately 10-15 km (between 60-140°C)^{88,90}, which are pressure and
968 temperature ranges that are within the range of theoretically habitable environments for
969 microorganisms⁹¹⁻⁹². Volcanoes in Costa Rica form a part of the southern segment of the
970 Central American Volcanic Arc. The volcanic arc in Costa Rica extends from the north to
971 the center of Costa Rica, immediately to the east of the Nicoya Peninsula. We collected
972 samples for this study in the forearc, arc and backarc of this region.

973

974 **Microbiological Background:**

975 ¹³C-depleted carbon dioxide in fluids released in the submarine portion of the
976 outer forearc indicate a $\delta^{13}\text{C}$ depleted source and may imply biological production
977 through anaerobic respiration of sulfate, which is an abundant oxidant in seawater
978 (Füri et al. 2010). The level of ¹³C-depletion can be moderate (-10 to -15‰),
979 suggesting electron donors from organic matter, or extreme (-60 to -70‰),
980 suggesting electron donors from methane. Methanotrophy can occur anaerobically
981 through sulfate reduction⁹³, or aerobically when oxygenated seawater mixes with
982 methane-rich fluids⁹⁴. The methane itself may be methanogenic products mobilized
983 from the >12 km source fluids⁹⁵, or shallower methanogenesis⁹⁶, but this has yet to
984 be resolved with isotopic analysis.

985

986 Methane in the subaerial section of the margin has been found to have a
987 significant biogenic component, with $\delta^{13}\text{C}$ of -35 to -45‰, and presence of
988 methanogenic archaea⁹⁷⁻⁹⁸. However, no large-scale survey of the effects of
989 microbiology on degassing across a convergent margin have been performed. The
990 few microbiological studies that have been performed in convergent margins have
991 focused on a single site at a time, preventing any region-scale exploration of how
992 microbes interact with these deep geological processes.

993

994 **Methods References:**

995 51. Giggenbach, W.F., Goguel, R.L. Methods for the collection and analysis of
996 geothermal and volcanic water and gas samples, Rep. CD 2387, Chem.
997 Div., Dept. of Sci. and Ind. Res., Petone, N. Z., p. 53. (1989).

998

999 52. Kulongoski, J. T., & Hilton, D. R. A quadrupole-based mass spectrometric
1000 system for the determination of noble gas abundances in fluids.
1001 *Geochemistry, Geophysics, Geosystems*, 3(6), 1-10. (2002).

1002

- 1003 53. Barry, P. H., Lawson, M., Meurer, W. P., Warr, O., Mabry, J. C., Byrne, D. J.,
1004 & Ballentine, C. J. Noble gases solubility models of hydrocarbon charge
1005 mechanism in the Sleipner Vest gas field. *Geochimica et Cosmochimica*
1006 *Acta*, 194, 291-309. (2016).
1007
- 1008 54. Braun, S., Morono, Y., Becker, K.W., Hinrichs, K.U., Kjeldsen, K.U.,
1009 Jørgensen, B.B. and Lomstein, B.A. Cellular content of biomolecules in sub-
1010 seafloor microbial communities. *Geochimica et Cosmochimica Acta*, 188,
1011 pp.330-351. (2016).
1012
- 1013 55. Giovannelli, D., d'Errico, G., Fiorentino, F., Fattorini, D., Regoli, F.,
1014 Angeletti, L., et al. Diversity and Distribution of Prokaryotes within a
1015 Shallow-Water Pockmark Field. *Front. Microbiol.* 7. (2016).
1016
- 1017 56. McMahon, S., & Parnell, J. Weighing the deep continental biosphere.
1018 *FEMS Microbiology Ecology*, 87(1), 113-120. (2014).
1019
- 1020 57. Sano, Y., & Marty, B. Origin of carbon in fumarolic gas from island arcs.
1021 *Chemical Geology*, 119(1-4), 265-274. (1995).
1022
- 1023 58. Snyder, G., Poreda, R., Hunt, A., & Fehn, U. Regional variations in volatile
1024 composition: Isotopic evidence for carbonate recycling in the Central
1025 American volcanic arc. *Geochemistry, Geophysics, Geosystems*, 2(10).
1026 (2001).
1027
- 1028 59. Snyder, G., Poreda, R., Fehn, U., & Hunt, A. The geothermal fields of
1029 Central America: influence of the subduction process on its volatile
1030 composition. *Geological Magazine of Central America* , (30). (2004).
1031

- 1032 60. Wehrmann, H., Hoernle, K., Portnyagin, M., Wiedenbeck, M., & Heydolph,
1033 K. Volcanic CO₂ output at the Central American subduction zone inferred
1034 from melt inclusions in olivine crystals from mafic tephras. *Geochemistry,*
1035 *Geophysics, Geosystems*, 12(6). (2011).
1036
- 1037 61. de Moor, J. M., Aiuppa, A., Avard, G., Wehrmann, H., Dunbar, N., Muller,
1038 C., Tamburello, G., Giudice, G., Liuzzo, M., Moretti, R. & Conde, V. Turmoil
1039 at Turrialba Volcano (Costa Rica): Degassing and eruptive processes
1040 inferred from high-frequency gas monitoring. *Journal of Geophysical*
1041 *Research: Solid Earth*, 121(8), 5761-5775. (2016).
1042
- 1043 62. Dawson, P., Chouet, B., & Pitt, A. Tomographic image of a seismically
1044 active volcano: Mammoth Mountain, California. *Journal of Geophysical*
1045 *Research: Solid Earth*, 121(1), 114-133. (2016).
1046
- 1047 63. Mason, E., Edmonds, M., & Turchyn, A. V. Remobilization of crustal carbon
1048 may dominate volcanic arc emissions. *Science*, 357(6348), 290-294.
1049 (2017).
1050
- 1051 64. Chiodini, G., Pappalardo, L., Aiuppa, A., & Caliro, S. The geological CO₂
1052 degassing history of a long-lived caldera. *Geology*, 43(9), 767-770. (2015).
1053
- 1054 65. Berrange, J. P., & Thorpe, R. S. The geology, geochemistry and
1055 emplacement of the Cretaceous—Tertiary ophiolitic Nicoya Complex of
1056 the Osa Peninsula, southern Costa Rica. *Tectonophysics*, 147(3-4), 193-
1057 220. (1988).
1058
- 1059 66. Giggenbach, W. F. Relative importance of thermodynamic and kinetic
1060 processes in governing the chemical and isotopic composition of carbon

- 1061 gases in high-heatflow sedimentary basins. *Geochimica et Cosmochimica*
1062 *Acta*, 61(17), 3763-3785. (1997).
- 1063
- 1064 67. Kuijpers, E. P. The geologic history of the Nicoya Ophiolite Complex, Costa
1065 Rica, and its geotectonic significance. *Tectonophysics*, 68(3-4), 233-255.
1066 (1980).
- 1067
- 1068 68. Schwarzenbach, E. M., Lang, S. Q., Früh-Green, G. L., Lilley, M. D.,
1069 Bernasconi, S. M., & Méhay, S. Sources and cycling of carbon in
1070 continental, serpentinite-hosted alkaline springs in the Voltri Massif,
1071 Italy. *Lithos*, 177, 226-244. (2013).
- 1072
- 1073 69. Torgersen, T. Terrestrial helium degassing fluxes and the atmospheric
1074 helium budget: Implications with respect to the degassing processes of
1075 continental crust. *Chemical Geology: Isotope Geoscience Section*, 79(1), 1-
1076 14. (1989).
- 1077
- 1078 70. Walther, C. H. E., Flueh, E. R., Ranero, C. R., Von Huene, R., & Strauch, W.
1079 Crustal structure across the Pacific margin of Nicaragua: Evidence for
1080 ophiolitic basement and a shallow mantle sliver. *Geophysical Journal*
1081 *International*, 141(3), 759-777. (2000).
- 1082
- 1083 71. Gazel, E., Denyer, P., & Baumgartner, P. O. Magmatic and geotectonic
1084 significance of santa elena peninsula, costa rica. *Geologica Acta*, 4(1-2),
1085 0193-202. (2006).
- 1086
- 1087 72. Gazel, E., Hoernle, K., Carr, M. J., Herzberg, C., Saginor, I., Van den
1088 Bogaard, P., Hauff, F., Feigenson, M., & Swisher, C. Plume–subduction
1089 interaction in southern Central America: Mantle upwelling and slab
1090 melting. *Lithos*, 121(1), 117-134. (2011).

1091
1092 73. Gazel, E., Hayes, J. L., Hoernle, K., Kelemen, P., Everson, E., Holbrook, W.S.,
1093 Hauff, F., Van Den Bogaard, P., Vance, E.A., Chu, S., & Calvert, A. J.
1094 Continental crust generated in oceanic arcs. *Nature Geoscience*, 8(4), 321.
1095 (2015).

1096
1097 74. Madrigal, P., Gazel, E., Denyer, P., Smith, I., Jicha, B., Flores, K.E., Coleman,
1098 D. & Snow, J. A melt-focusing zone in the lithospheric mantle preserved in
1099 the Santa Elena Ophiolite, Costa Rica. *Lithos*, 230, 189-205. (2015).

1100
1101 75. Madrigal, P., Gazel, E., Flores, K. E., Bizimis, M., & Jicha, B. Record of
1102 massive upwellings from the Pacific large low shear velocity province:
1103 Nature Communications, v. 7, p. 13309. (2016).

1104
1105 76. Li, L., & Bebout, G. E. Carbon and nitrogen geochemistry of sediments in
1106 the Central American convergent margin: Insights regarding subduction
1107 input fluxes, diagenesis, and paleoproductivity. *Journal of Geophysical*
1108 *Research: Solid Earth*, 110(B11). (2005).

1109
1110 77. Holloway, J. R., & Blank, J. G. Application of experimental results to COH
1111 species in natural melts. *Reviews in mineralogy*, 30, 187-187. (1994).

1112
1113 78. Ohmoto, H., & Rye, R. O. Isotopes of sulfur and carbon. *Geochemistry of*
1114 *Hydrothermal Ore Deposits (Barnes, HL, ed.)*, 509-567. (1979).

1115
1116 79. de Moor, J. M., Aiuppa, A., Pacheco, J., Avard, G., Kern, C., Liuzzo, M.,
1117 Martinez, M., Giudice, G., & Fischer, T. P. Short-period volcanic gas
1118 precursors to phreatic eruptions: Insights from Poás Volcano, Costa
1119 Rica. *Earth and Planetary Science Letters*, 442, 218-227. (2016).

1120

- 1121 80. Kimura, G., et al. (Eds.) Proceedings of the Ocean Drilling Program, *Initial*
1122 *Reports, vol. 170, Ocean Drill. Program*, College Station, Tex. (1997).
1123
- 1124 81. Barckhausen, U., Ranero, C. R., Huene, R. V., Cande, S. C., & Roeser, H. A.
1125 Revised tectonic boundaries in the Cocos Plate off Costa Rica: Implications
1126 for the segmentation of the convergent margin and for plate tectonic
1127 models. *Journal of Geophysical Research: Solid Earth*, 106(B9), 19207-
1128 19220. (2001).
1129
- 1130 82. DeMets, C. A new estimate for present day Cocos Caribbean plate motion:
1131 Implications for slip along the Central American volcanic arc. *Geophysical*
1132 *Research Letters*, 28(21), 4043-4046. (2001).
1133
- 1134 83. Patino, L. C., Carr, M. J., & Feigenson, M. D. Local and regional variations in
1135 Central American arc lavas controlled by variations in subducted sediment
1136 input. *Contributions to Mineralogy and Petrology*, 138(3), 265-283. (2000).
1137
- 1138 84. von Huene, R., Langseth, M., Nasu, N., & Okada, H. A summary of
1139 Cenozoic tectonic history along the IPOD Japan Trench transect.
1140 *Geological Society of America Bulletin*, 93(9), 829-846. (1982).
1141
- 1142 85. Parkes, R. J., Cragg, B. A., Fry, J. C., Herbert, R. A., & Wimpenny, J. W. T.
1143 Bacterial biomass and activity in deep sediment layers from the Peru
1144 margin. *Phil. Trans. R. Soc. Lond. A*, 331(1616), 139-153. (1990).
1145
- 1146 86. Biddle, J.F., Lipp, J.S., Lever, M.A., Lloyd, K.G., Sørensen, K.B., Anderson, R.,
1147 Fredricks, H.F., Elvert, M., Kelly, T.J., Schrag, D.P. and Sogin, M.L.
1148 Heterotrophic Archaea dominate sedimentary subsurface ecosystems off
1149 Peru. *Proceedings of the National Academy of Sciences*, 103(10), 3846-
1150 3851. (2006).

- 1151
- 1152 87. Vannucchi, P., and Tobin, H. Deformation structures and implications for
1153 fluid flow at the Costa Rica convergent margin, ODP Sites 1040 and 1043,
1154 Leg 170, *Journal of Structural Geology*, 22(8), 1087–1103. (2000).
- 1155
- 1156 88. Spinelli, G. A., and Underwood, M. B. Character of sediments entering the
1157 Costa Rica subduction zone: Implications for partitioning of water along the
1158 plate interface, *Isl. Arc*, 13(3), 432–451. (2004).
- 1159
- 1160 89. Ranero, C.R., Grevemeyer, I., Sahling, H., Barckhausen, U., Hensen, C.,
1161 Wallmann, K., Weinrebe, W., Vannucchi, P., Von Huene, R. and McIntosh, K.
1162 Hydrogeological system of erosional convergent margins and its influence on
1163 tectonics and interplate seismogenesis. *Geochemistry, Geophysics,*
1164 *Geosystems*, 9(3). (2008).
- 1165
- 1166 90. Spinelli, G. A., and Saffer, D. M. Along-strike variations in underthrust
1167 sediment dewatering on the Nicoya margin, Costa Rica related to the updip
1168 limit of seismicity, *Geophysical Research Letters*, 31, L04613. (2004).
- 1169
- 1170 91. Lloyd, K. G., Edgcomb, V. P., Molyneaux, S. J., Boer, S., Wirsén, C. O.,
1171 Atkins, M. S., & Teske, A. Effects of dissolved sulfide, pH, and temperature
1172 on growth and survival of marine hyperthermophilic archaea. *Applied and*
1173 *Environmental Microbiology*, 71: 6383-6387. (2005).
- 1174
- 1175 92. Edgcomb, V.P., Molyneaux, S.J., Böer, S., Wirsén, C.O., Saito, M., Atkins,
1176 M.S., Lloyd, K. and Teske, A. Survival and growth of two heterotrophic
1177 hydrothermal vent archaea, *Pyrococcus* strain GB-D and *Thermococcus*
1178 *fumicolans*, under low pH and high sulfide concentrations in combination

1179 with high temperature and pressure regimes. *Extremophiles*, 11(2), 329-
1180 342. (2007).

1181
1182 93. Marlow, J. J., Steele, J. A., Ziebis, W., Thurber, A. R., Levin, L. A., & Orphan,
1183 V. J. Carbonate-hosted methanotrophy represents an unrecognized
1184 methane sink in the deep sea. *Nature Communications*, 5, 5094. (2014).

1185
1186 94. Boetius, A., & Wenzhöfer, F. Seafloor oxygen consumption fuelled by
1187 methane from cold seeps. *Nature Geoscience*, 6(9), 725. (2013).

1188
1189 95. Hensen, C., Wallmann, K., Schmidt, M., Ranero, C. R., & Suess, E. Fluid
1190 expulsion related to mud extrusion off Costa Rica—a window to the
1191 subducting slab. *Geology*, 32(3), 201-204. (2004).

1192
1193 96. Colwell, F. S., Boyd, S., Delwiche, M. E., Reed, D. W., Phelps, T. J., &
1194 Newby, D. T. Estimates of biogenic methane production rates in deep
1195 marine sediments at Hydrate Ridge, Cascadia Margin. *Applied and
1196 environmental microbiology*, 74(11), 3444-3452. (2008).

1197
1198 97. Sánchez-Murillo, R., Gazel, E., Schwarzenbach, E. M., Crespo-Medina, M.,
1199 Schrenk, M. O., Boll, J., & Gill, B. C. Geochemical evidence for active
1200 tropical serpentinization in the Santa Elena Ophiolite, Costa Rica: An
1201 analog of a humid early Earth?. *Geochemistry, Geophysics, Geosystems*,
1202 15(5), 1783-1800. (2014).

1203
1204 98. Crespo-Medina, M., Twing, K. I., Kubo, M. D., Hoehler, T. M., Cardace, D.,
1205 McCollom, T., & Schrenk, M. O. Insights into environmental controls on
1206 microbial communities in a continental serpentinite aquifer using a
1207 microcosm-based approach. *Frontiers in microbiology*, 5, 604. (2014).

1208
1209

1210 **Data Availability Statement (DAS):**

1211 All raw data needed to make the plots are available in Supplementary Tables 1 and 2
1212 as well as in the Source Data file provided. All data is archived through EarthChem
1213 (DOI: 10.1594/IEDA/111271).

1214

1215

1216

1217 **Extended Data Figure 1** – CO₂/³He vs. δ¹³C for all samples collected, together with
1218 endmember mixing lines between mantle, organic sediment and carbonate
1219 endmembers. We argue that such mixing relationships cannot easily explain the water
1220 data, and instead carbon isotope fractionation associated with calcite precipitation and
1221 chemolithoautotrophy introduces the observed δ¹³C variations.

1222

1223 **Extended Data Figure 2** – Helium isotopes (³He/⁴He) vs. X-values (air-normalized
1224 ⁴He/²⁰Ne; considering solubility in water for fluid samples²³). The majority of samples
1225 have high (>5) X-values, indicating minimal air-contributions to samples.

1226

1227 **Extended Data Figure 3** – Relationship between DC and DIC concentrations and δ¹³C.
1228 Values for northern Costa Rica (panels A and B) are shown with blue symbols and
1229 central Costa Rica (panels c and d), with red symbols. Strong correlations allow
1230 prediction of DC concentrations and δ¹³C values for the sites for which DIC compositions
1231 are lacking. The slope of the concentration plots is used to calculate the fraction of DIC
1232 and DOC in the sample suites.