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1 **A re-assessment of the nitrogen geochemical behavior in**
2 **upper oceanic crust from Hole 504B:**
3 **Implications for subduction budget**
4 **in Central America**

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33 **Abstract**

34

35 The geochemical behavior of N during seawater-oceanic crust alteration remains poorly
36 constrained. Yet, it is a central parameter to assess the flux of N to subduction zones. Most
37 studies proposed that hydrothermally altered basaltic rocks are enriched in N relative to fresh
38 basalts. However, published data from DSDP/ODP Hole 504B, a reference site for the
39 composition of the oceanic crust, suggest that seawater alteration leads to the N depletion of
40 the upper ocean crust. To better address this issue, we analyzed N concentration and isotope
41 composition of 21 altered basalts from the lavas and sheeted dikes sampled by Hole 504B.
42 These new analyses show significant N enrichment (up to 14.1 ppm) relative to fresh
43 degassed MORB (~1 ppm). The differences observed between earlier and modern data are
44 interpreted as resulting from analytical artifact due to the earlier use of a molybdenum
45 crucible for N extraction. Furthermore, our new data show a progressive decrease of N
46 concentration with depth, from 14.1 to 1.4 ppm. Nitrogen isotope compositions display a large
47 range, with $\delta^{15}\text{N}$ values from -0.9 to +7.3‰, and most likely reflect multiple stages of
48 alteration with fluids of various compositions. In contrast to N concentration, $\delta^{15}\text{N}$ values do
49 not show a global depth trend but oscillate around a mean value of 3.0 ± 2.2 ‰ (1SD). The N
50 concentration shows a positive correlation with bulk rock $\delta^{18}\text{O}$ values, suggesting that N
51 behavior during alteration process is mainly controlled by temperature. We propose that N
52 speciation in the hydrothermal fluid is dominated by NH_3/NH_4 at low temperature (<200°C)
53 but is transformed to N_2 , associated with H_2 , at higher temperature (>200°C). These new data
54 are used to re-evaluate the global flux of N input into Central American subduction zone,
55 showing that the upper basaltic crust represent about 20% of the total N buried in subduction
56 zone. A comparison with previous results obtained on N degassed in volcanic arc illustrates
57 that, in “warm” subduction zone like Central America, up to 50% of the subducted N may be
58 transferred to the deep mantle. This contrasts with “cold” subduction environments, where
59 >80% of the N inputs escape sub-arc slab devolatilization and supports that the geothermal
60 gradient plays a major role in determining the N fate in subduction zones.

61

62 **1. Introduction**

63

64 Hydrothermal circulation systems associated with mid-ocean ridges profoundly influence the
65 chemistry of the oceanic crust (*e.g.* Alt, 1995; Alt and Teagle, 2000). Understanding these
66 systems is crucial to unravel the chemical evolution of the ocean, the oceanic crust and
67 ultimately the mantle, which is affected by inputs from subducting-slabs. It is well accepted
68 that the upper oceanic crust acts as a significant sink for elements such as K, Mg, Rb, Cs, B,
69 Li, U, CO₂ and H₂O, while it is a source for Ca and Si (*e.g.* Alt, 1995; Alt et al., 1996a, 1996b;
70 Laverne et al., 2001; Staudigel, 2003; Bach et al., 2003). Some elements like N, for which
71 analysis is technically challenging, still have uncertain geochemical behavior.

72 Only few studies have focused on the N exchanges during fluid-induced alteration of basalts
73 (Hall, 1989; Erzinger and Bach, 1996; Busigny et al., 2005a; Li et al., 2007; Bebout et al.,
74 2018). In an early contribution, Hall (1989) estimated the N content of spilitized basalts from
75 the Cornubian massif (Southwest England) and suggested that N was enriched in rocks during
76 alteration processes. However, whether spilitic alteration of Cornubian basalts could be
77 considered as representative of oceanic crust processes in general remains uncertain. Nitrogen
78 content determination in subsequent studies of oceanic basalts from several DSDP/ODP Sites
79 (Busigny et al., 2005a; Li et al., 2007) and from Mesozoic ophiolites (Bebout et al., 2018)
80 supported the interpretation of N enrichment but showed smaller magnitude than basalts from
81 Cornubian massif. The analysis of altered basalts from DSDP/ODP Hole 504B contrasted
82 with these results, and pointed to a loss of N from rock to fluid (Erzinger and Bach, 1996).
83 The different results obtained on samples from DSDP/ODP sites were suggested to originate
84 either from different types of alteration processes or analytical discrepancies between the
85 various studies (Busigny et al., 2005a). In their study of Hole 504B basalts, Erzinger and Bach
86 (1996) extracted N using a pyrolysis technique, heating the samples in a molybdenum
87 crucible. However, later experiments demonstrated that N is strongly adsorbed by
88 molybdenum even at high temperature (Yokochi et al., 2006). The low N concentration

89 measured in Hole 504B altered basalts may thus result from incomplete recovery of N rather
90 than a specific type of alteration.

91 In the present contribution, we conducted new analyses of altered basalts and dolerites from
92 Hole 504B to evaluate the behavior of N during hydrothermal alteration and evaluate potential
93 analytical artifacts in previously published results. Nitrogen contents and isotopic
94 compositions were measured for 21 samples recovered at various depths, from 317.2 to
95 1830.4 meters below seafloor (mbsf) of the upper oceanic crust. These new results confirm
96 the general N enrichment during oceanic crust alteration. Additionally, the combination of
97 these new N data with major and trace element concentrations and bulk O isotope
98 compositions is used to better constrain N geochemical behavior during alteration of the upper
99 crust. A global mass balance approach is presented to evaluate the contribution of upper
100 oceanic crust to the subducted N in Central America.

101

102 **2. Geological background and sample description**

103

104 Hole 504B has been extensively studied within the last 40 years and is generally considered as
105 a reference site for the structure, petrology and composition of upper oceanic crust. It is
106 located in the eastern equatorial Pacific in the Panama basin, 200 km south of the intermediate
107 spreading rate Costa Rica Rift (Fig. 1). It lies on ~ 6 Ma oceanic lithosphere under 3474 m of
108 water. The drilled section is the deepest within oceanic crust and reaches 2111 meters below
109 seafloor (mbsf). The lithostratigraphy of Hole 504B (Fig. 2) is characterized by (i) 274.5 m of
110 sediments (siliceous oozes, chert, limestone and chalk), (ii) a 571.5 m-thick volcanic section
111 including pillow lavas, massive flows, and breccias with local dikes in the lower half of the
112 section, (iii) a 209 m-thick transition zone of lavas and dikes, underlain by (iv) 1056 m of
113 sheeted dike complex (Alt et al., 1986a, 1986b, 1996a). The section collected at Hole 504B
114 has been further divided into five hydrothermal alteration zones based on secondary mineral
115 assemblages and bulk-rock chemical compositions (see review in Alt et al, 1996a). These five
116 zones, from top to bottom, are:

117 (1) The Upper Pillow Alteration Zone (UPAZ), from 274 to 594 mbsf, exhibits three types of
118 alteration (Honnorez et al., 1983; Alt et al., 1996b). The first type corresponds to the slightly
119 altered background dark grey rocks that occur throughout the volcanic section with smectite
120 (Mg-saponite) as the dominant secondary mineral. These rocks are interpreted to result from
121 low temperature seawater/basalt exchanges at low water/rock ratio. The other two styles of
122 alteration occur as halos adjacent to veins and include (i) “black halos”, characterized by the
123 presence of celadonite, a K-bearing mica, and (ii) “brown oxidized halos” which can exhibit
124 various shades of brown, red and orange, due to the presence of iron-oxyhydroxides reflecting
125 the effect of a low temperature (<110°C) oxidative alteration process (Alt et al., 1996a).

126 (2) The Lower Pillow Alteration Zone (LPAZ) extends from 594 to 846 mbsf. In this zone,
127 basalts contain no alteration halos adjacent to veins. They display a uniform dark grey color,
128 with smectite and pyrite representing the dominant secondary minerals. The alteration
129 conditions are interpreted as non-oxidative with more restricted fluid circulation and
130 temperatures up to 150°C.

131 (3) The Mineralized Zone (MZ), from 846 to 1055 mbsf, contains highly fractured, brecciated
132 pillows and dikes. This zone records the transition from low-temperature alteration (<150°C)
133 and higher temperature hydrothermal alteration (> 250°C) with the appearance and then
134 increasing abundance with depth of greenschist facies minerals. Four successive stages of
135 alteration have been deduced from secondary minerals relationships in veins and crosscutting
136 veins (following Alt et al., 1986b): (1) chlorite, actinolite, albite-oligoclase and titanite
137 formed at 200°C to >300°C from reaction with seawater-derived hydrothermal fluids; (2)
138 quartz, epidote and sulfides at 250°C-380°C from highly reacted, evolved hydrothermal
139 fluids; (3) anhydrite, resulting from the recharge of hydrothermal system by seawater; and (4)
140 zeolites, prehnite and calcite, formed at temperature <250°C by evolved hydrothermal fluids.
141 A Cu-rich mineralized stockwork zone occurs at 910-918 mbsf (Honnorez et al., 1985).

142 (4) The Upper Dikes (UD) extend from 1055 to 1500 mbsf, and are characterized by
143 secondary minerals and alteration sequence similar to those of the Mineralized Zone (MZ).
144 The intensities of hydrothermal alteration and recrystallization of the UD are highly variable
145 and depend on the fracturing and permeability of the rocks.

146 (5) The Lower Dikes (LD) range from 1500 to 2111 mbsf. They generally show the same
147 alteration stages than the Mineralized Zone (MZ) and Upper Dikes (UD), except an early
148 high-temperature alteration stage ($>400^{\circ}\text{C}$) that preceded the stages described in the UD. This
149 stage is characterized the presence of secondary calcic plagioclase and Mg-hornblende
150 (Vanko and Laverne, 1998). It is interpreted as resulting from calcium-enriched hydrothermal
151 fluids present in the reaction zone, between the hydrothermal system and the magmatic
152 chamber at the bottom of the dike section.

153 Overall, the various rocks from Hole 504B thus record a complex multi-stage alteration
154 history (*e.g.* Alt et al., 1996a). They are characterized by increasing alteration temperatures
155 and decreasing water/rock ratios with depth (Friedrichsen et al., 1985; Alt et al., 1986a;
156 Kawahata et al., 1987; Kusakabe et al., 1989; Agrinier et al., 1995; Teagle et al., 1998a, b,
157 2003). In the present work, twenty-one samples were selected to represent the various mafic
158 lithologies and alteration types (Table 1): 3 samples are from the UPAZ, 5 from the LPAZ, 6
159 from the MZ, 4 from the UD, and 3 from the LD. All of them are background alteration
160 samples, while veins and alteration halos were avoided.

161

162 **3. Analytical techniques**

163

164 For N analyses, between 40 to 70 mg of fine, homogeneous sample powder was embedded in
165 platinum foil and loaded in quartz tubes prepared with pre-purified reactants (Cu, CuO and
166 CaO). The samples were pre-heated at 300°C under vacuum during one night and then
167 saturated with O_2 pressure generated with CuO heated to 900°C . These steps allow removing
168 any organic contamination and/or atmospheric N_2 adsorbed on the powder surface. The tubes
169 were then sealed under vacuum and N was extracted by a combustion step at temperature of
170 950 or 1050°C during 6 h (Busigny et al., 2005b). A comparison of the combustion at 950 and
171 1050°C for 6 samples shows identical N concentration and isotope composition, suggesting
172 that N was fully extracted at temperature $> 950^{\circ}\text{C}$ (see also results part, below). Nitrogen was
173 purified and separated from other volatiles (mainly H_2O and CO_2) using Cu, CuO and CaO
174 (Kendall and Grim, 1990). It was then quantified as dinitrogen N_2 by capacitance manometry

175 in ultra-high vacuum line and its isotope analysis was performed on a triple-collector static
176 vacuum mass spectrometer, allowing the measurement of nanomole quantities of N₂. Nitrogen
177 isotopic composition was expressed in the usual δ notation as, $\delta^{15}\text{N}_{\text{sample}} (\text{‰}) =$
178 $[(^{15}\text{N}/^{14}\text{N})_{\text{sample}} / (^{15}\text{N}/^{14}\text{N})_{\text{standard}} - 1] \times 1000$, where the standard is atmospheric N₂. The quantity of N in
179 the analytical blank was low (0.65 ± 0.30 nmol) relative to samples (> 7 nmol), and its
180 isotopic composition averaged $-3.7 \pm 2.7 \text{‰}$ (2σ). The N concentrations and $\delta^{15}\text{N}$ values
181 reported here were corrected from the blank contribution. The precisions determined from
182 external reproducibility on internal and international standards were better than $\pm 8 \%$ and
183 $\pm 0.5 \text{‰}$ for nitrogen content and isotopic composition respectively.

184 For oxygen isotope analyses, 4 to 10 mg of bulk rock powders were loaded in Ni tubes under
185 vacuum and reacted overnight with bromine pentafluoride (BrF₅) at 550°C (Clayton and
186 Mayeda, 1963). The dioxygen produced from the reaction was separated and analyzed on a
187 Thermo-Finnigan™ Delta+XP mass spectrometer. During the course of the study, replicate
188 analyses of NBS-28 quartz standard gave a mean value of $9.45 \pm 0.1\text{‰}$ (1SD, n=17), in good
189 agreement with recommended value ($9.58 \pm 0.09\text{‰}$; Gonfiantini et al., 1995), thus providing
190 an estimation of the external precision and accuracy of the measurements.

191 Major element concentration of the 21 samples were measured in bulk rock using ICP-AES at
192 the Service d'Analyses des Roches et des Minéraux (SARM) of the Centre de Recherches
193 Pétrographiques et Géochimiques (CRPG) of Vandoeuvre, France. Analytical precision for all
194 elements can be found at <http://www.crpq.cnrs-nancy.fr/SARM>.

195 Whole rock K, Rb, Cs concentrations were analyzed in the Isotope Geochemistry
196 Laboratories of the National Oceanography Centre Southampton. Analyses were performed
197 on a VG Elemental Plasmaquad PQ2+ ICP-MS calibrated against international rock standard
198 reference materials and corrected for isobaric interferences and blanks. In run errors are
199 typically better than 3% RSD except for Cs where very low concentration samples may show
200 $\sim 10\%$ RSD. Samples with Rb concentrations < 0.05 ppm and Cs concentrations < 10 ppb are
201 approaching the detection limits of the techniques used with concentrations less than five
202 times blank levels.

203

204 **4. Results**

205

206 *4.1. Major and trace element concentrations*

207

208 Major and trace element concentrations of the samples from Hole 504B are given in Table 1.
209 They are similar to values reported by previous studies (*e.g.* Alt et al., 1996a; Bach et al.,
210 2003). SiO₂ and Al₂O₃ contents are very homogeneous within the section, with mean values of
211 49.1±0.7 and 15.1±0.8 wt% (1σ; n=21), respectively. Bulk Fe₂O₃ and MgO contents also show
212 a limited range, with values averaging 9.7±0.8 and 8.5±0.5 wt% (1σ; n=21), respectively. The
213 concentrations of CaO and Na₂O average 12.6±0.9 and 2.0±0.4 wt% respectively. Loss on
214 ignition (LOI) is more variable (0.6 to 3.2 wt%; avg. 1.5±0.7 wt%) and is not related to depth
215 in the crust. In contrast, the concentrations of K, Rb and Cs show a systematic decrease with
216 increasing depth in the crust (Table 1; Fig. 2).

217

218 *4.2. Nitrogen concentration and isotope composition*

219

220 Nitrogen content and isotope composition of the samples from Hole 504B are reported in
221 Table 2. Six of the 21 samples were duplicated by combustion at temperatures of 950 and
222 1050°C. The good reproducibility between duplicates confirms that N was completely
223 extracted by heating at temperature ≥ 950°C. Nitrogen content and δ¹⁵N value vary from 1.4 to
224 14.1 ppm and -0.9 to +7.3 ‰, respectively, a range similar to other altered oceanic basalts
225 (Busigny et al., 2005a; Li et al., 2007) and Mesozoic ophiolites (Bebout et al., 2018). Figure 2
226 illustrates downhole variations of bulk rock N contents and δ¹⁵N values in Hole 504B.
227 Nitrogen contents show a global decrease with increasing depth (Fig. 2d). The two deepest
228 samples have the lowest N-contents (~ 1.5 ppm) and are only slightly enriched compared to
229 the average of fresh degassed MORB (~1.1 ppm; Sakai et al., 1984; Exley et al., 1987; Marty
230 et al., 1995). Our N concentrations are higher than those obtained by Erzinger and Bach

231 (1996) on Hole 504B basalts (gray squares in Fig. 2d). The N concentrations of Hole 504B
232 basalts do not correlate with K_2O , Na_2O or $CaO+Na_2O$ concentrations, although N-rich
233 samples also have high K contents (Fig. 3). In contrast to N concentrations, the N isotopic
234 composition does not show a global trend with depth but some oscillation around a mean
235 value (Fig. 2e). The average N isotope composition calculated for the complete section is 3.0
236 ± 2.2 ‰ (1 SD), and overlaps modern oceanic sediments (most values from 4 to 6 ‰, but total
237 range from 2.5 to 16.6 ‰; *e.g.* Tesdal et al., 2013). The N isotope composition does not
238 correlate with N concentration (Fig. 4a).

239

240 *4.3. Oxygen isotope composition*

241

242 The oxygen isotope composition of altered basalts from Hole 504B varies over a large range,
243 with $\delta^{18}O$ values between 3.57 and 7.79‰ (average of 5.7 ± 1.1 ‰, 1σ ; $n=16$). The depth profile
244 displays a global decrease of $\delta^{18}O$ values with increasing depth, as already observed in
245 previous works (Barrett and Friedrichsen, 1982; Alt et al., 1986a, 1989, 1996; Kawahata et
246 al., 1987; Kusakabe et al., 1989; Mengel and Hoefs, 1990; Agrinier et al., 1995). A
247 comparison of previous and present data shows a good match of the $\delta^{18}O$ -depth trends (Fig.
248 2f). The upper volcanic zone is enriched in ^{18}O compared with typical mantle values and fresh
249 basaltic crust ($\delta^{18}O \sim 5.5$ ‰; *e.g.* Eiler et al., 2000) whereas the lower sheeted dike complex
250 exhibits low $\delta^{18}O$ values (Fig. 2f). We emphasize that there is a good positive correlation
251 between $\delta^{18}O$ values and N concentrations (Fig. 4b).

252

253 **5. Discussion**

254

255 *5.1. Ubiquitous N enrichment during alteration of oceanic basalts*

256

257 The present data can be used to re-assess the N geochemical behavior in altered basalts from
258 Hole 504B, and provide evidence for ubiquitous N enrichment during alteration of oceanic

259 crust. All N concentrations measured here are higher than those previously determined by
260 Erzinger and Bach (1996). Although analyses were not performed exactly on the same
261 samples, the trend of N content with depth allows a comparison between samples collected at
262 similar depths and indicates that N contents measured by Erzinger and Bach are lower by
263 more than one order of magnitude (Fig. 2d). This difference likely originates from an artifact
264 related to their analytical technique. Since the original publication of Erzinger and Bach
265 (1996), it has been demonstrated that the use of molybdenum crucible for heating the samples
266 leads to incomplete recovery of N. Indeed, laboratory experiments have shown that high
267 amounts of gaseous nitrogen (> 80%) are soluble in hot molybdenum (Yokochi and Marty,
268 2006) and molybdenum crucibles or wrapping foil should be avoided during the extraction
269 and quantification of N from rock samples. Instead the use of platinum is recommended for N
270 thermal extraction (Boyd and Pillinger, 1990; Yokochi and Marty, 2006). Moreover, the
271 incomplete recovery of N is associated with modification of the N isotope composition and
272 previous studies using molybdenum must be considered with caution. Numerous N data on
273 terrestrial and extraterrestrial samples should probably be re-evaluated, particularly for those
274 with N content at the ppm-level such as terrestrial basalts and peridotites (*e.g.* Mohapatra and
275 Murty, 2000; 2002) or meteorites (*e.g.* Murty and Marti, 1993; Mathew et al., 2000, 2005).

276
277 Nitrogen contents in altered basalts from Hole 504B vary from 1.4 to 14.1 ppm, and decrease
278 with increasing depth. The two deepest samples have N content (~1.4 ppm) similar to fresh
279 degassed MORB from other sites in the oceanic crust (~1.1 ppm; Sakai et al., 1984; Exley et
280 al., 1987; Marty et al., 1995). All other samples from Hole 504B have N content significantly
281 higher than fresh MORB, indicating that N was added to the ocean crust during hydrothermal
282 alteration. If the deepest samples are used as a reference of the background level of unaltered
283 N to evaluate the degree of enrichment during alteration, then N is enriched by at least one
284 order of magnitude. Therefore, the present data reconcile the apparent discrepancy among
285 former studies, with all data now indicating that N is incorporated into the rock, rather than
286 being leached, during interaction with external fluids (Hall, 1989; Busigny et al., 2005a; Li et
287 al., 2007; Bebout et al., 2018; this study; cf. Erzinger and Bach, 1996). All analyses of

288 oceanic basalts altered by seawater have concentrations in a limited range from 1.3 to 18.2
289 ppm (Busigny et al., 2005; Li et al., 2007; this study). These samples, including those from
290 the present study, represent typical background alteration but to date only two veins have been
291 analyzed (Busigny et al., 2005a). The two veins showed N content of several hundreds of ppm
292 (354 and 491 ppm), suggesting that a large portion of the N present in the altered upper crust
293 may be carried in secondary minerals (*e.g.* K-rich celadonite and Na-rich pyroxene; Busigny
294 et al., 2003) contained in veins. Further studies should therefore evaluate the vein contribution
295 to the total N amount of the crust.

296

297 *5.2. Factors controlling the N enrichment in altered oceanic basalts*

298

299 On the basis of N concentration and isotope composition, the sources of secondary N
300 enrichment can be attributed to deep seawater (*e.g.* NO_3^- or N_2 dissolved in seawater with $\delta^{15}\text{N}$
301 of +5‰ and 0‰ respectively), sediments intercalated in basalt layers ($\delta^{15}\text{N}$ ~4 to 8‰), and/or
302 mantle degassed N ($\delta^{15}\text{N}$ ~-5‰), reduced abiotically during hydrothermal alteration (Busigny
303 et al., 2005a; Li et al., 2007). The positive $\delta^{15}\text{N}$ values observed in Hole 504B samples (except
304 one sample at -0.9‰) supports that secondary N was derived from deep seawater or from NH_4^+
305 released by organic matter diagenesis in the overlying sediments.

306 To our knowledge, no N isotope data are available for the sediments cored in Hole 504B but a
307 previous study of ODP Legs 170 and 205 on the Costa Rica convergent margin reported $\delta^{15}\text{N}$
308 values between 2.4 to 8.5‰ (Li and Bebout, 2005), within the present range of variation.
309 Although the N speciation in altered basalts from Hole 504B is speculative, N is likely in the
310 form of NH_4^+ , which according to similarities in charge and ionic radius, substitutes for K^+ , Na
311 and/or Ca^{2+} (Honma and Itihara, 1981). Figure 3 shows that none of these element correlates
312 strictly with N in Hole 504B. However, the samples with high N concentrations also display
313 high K concentration (Figs. 2 and 3). Potassium is enriched in rocks from the uppermost 300
314 m of basement where the K-bearing mica celadonite and Mg-saponite are common alteration
315 phases (Alt et al., 1996a, 1996b; Bach et al., 2003). The concentrations of K are well

316 correlated with those of Rb and Cs (Fig. 2 a,b,c; Fig. 3b), reflecting as for NH_4^+ their
317 substitution with K in celadonite. The high N concentrations in K-rich samples are thus
318 compatible with N occurring as NH_4^+ in altered basalts. Although both K and N concentrations
319 decrease with depth in Hole 504B, the N content decrease is more continuous than for K, Rb
320 and Cs (Fig. 2). The same kinds of decoupled trends were observed for K and N along a depth
321 profile at Site 801 (Li et al., 2007). The decoupling between K and N concentrations indicates
322 that N enrichment in altered basalts is not only controlled by K concentration of the rocks but
323 requires one or several other parameters. For instance, N concentrations of altered basalts may
324 be influenced by local temperature and/or redox conditions, as suggested from highly
325 heterogeneous N contents and $\delta^{15}\text{N}$ values in several DSDP/ODP sites (Li et al., 2007). In the
326 upper part of the oceanic crust, the rocks are altered by interaction with seawater, and in some
327 cases chemically evolved, over a wide temperature range as the crust moves away from the
328 ridge. Thus the alteration process represents an aggregate record of fluid-rock interactions
329 over a temperature range (*e.g.* Alt et al., 1986a, 1996a). The correlation observed in Hole
330 504B basalts between $\delta^{18}\text{O}$ and N content ($r^2=0.73$; Fig. 4) suggests that N could be controlled
331 by local physico-chemical conditions. We explore below two possible scenarios for
332 explaining the depth-trend observed in N concentration (Fig. 2d). The first one is related to a
333 progressive evolution of the fluid composition with depth and the second is a temperature
334 control of the N speciation in the fluid.

335

336 *5.2.1. Evolution of the fluid composition with depth*

337

338 The decrease of N concentration with depth in samples from Hole 504B could reflect the
339 chemical evolution of the fluid due to fluid-rock exchanges that leads to the progressive
340 depletion of N. This could have resulted for instance from successive incorporation of N in
341 the rock, leaving the residual fluid depleted in nitrogen. In this case, one would also expect a
342 continuous evolution of the fluid $\delta^{15}\text{N}$, as observed in altered basalts from Leg 206 (Busigny et
343 al., 2005a). In contrast, the $\delta^{15}\text{N}$ values of altered basalts from Hole 504B do not display any

344 global trend with depth but instead oscillate around a mean value of $3.0 \pm 2.0\%$ (1SD; Fig.
345 2e). Moreover, a progressive evolution of a unique fluid with depth is not supported by
346 petrological observations documenting a complex multi-stage alteration history (*e.g.* Laverne
347 et al., 1995; Alt et al., 1986b, 1996a). Detailed petrographic description indicated that
348 alteration of the section penetrated by Hole 504B involves multiple phases of fluid-rock
349 reaction from the bare mid-ocean ridge crest to the thick sediment covered site today. At least
350 four stages of alteration occurred in the mineralized zone and the dike section, two stages in
351 the LPAZ, and three stages in the UPAZ. Therefore several fluids with different N isotope
352 compositions possibly interacted with the rocks, implying that N isotope signature recorded in
353 altered basalts integrated these various alteration stages. We conclude that a scenario
354 involving a chemical evolution of a single fluid with depth seems incompatible with
355 petrological and isotopic data on Hole 504B basalts, as well as with the knowledge on the
356 hydrology of the oceanic crust.

357

358 *5.2.2. A temperature control of the N speciation in the fluid*

359

360 The second scenario that we consider is a temperature control of the N speciation in
361 hydrothermal fluids. The evolution of oxygen isotope composition of oceanic basalts altered
362 by seawater has been studied for a long time and is well understood (*e.g.* Taylor, 1977;
363 Gregory and Taylor, 1981; Friedrichsen et al., 1985; Alt et al., 1986a; Kawahata et al., 1987;
364 Kusakabe et al., 1989; Agrinier et al., 1995; Gao et al., 2012). The $\delta^{18}\text{O}$ values of altered rocks
365 depend on a number of parameters such as (1) the temperature of alteration, (2) the isotopic
366 composition of the fluid interacting with the rock, (3) the water/rock ratio, (4) whether the
367 fluid-rock interaction happens in closed or open system and (5) the degree of isotopic
368 exchange between fluid and rock. In the case of Hole 504B, the water/rock (W/R) ratio of
369 altered basalts and dolerites (274 to 1350 mbsf) derived from O and Sr isotopes varies
370 between 1 and 5 (Friedrichsen et al., 1985; Kawahata et al., 1987). In contrast, dolerites from
371 the lower section of the sheeted dike complex, 1350 to 1991 mbsf, are characterized by lower
372 W/R ratios, mostly between 0.2 and 0.5 (Kusakabe et al., 1989; Agrinier et al., 1995). These

373 low W/R ratios are related to the lower permeability of the deeper rocks in the Sheeted Dike
 374 Complex (Alt et al., 1996a). Using the method developed by Taylor (1977), we have modeled
 375 the $\delta^{18}\text{O}$ of altered basalts for various W/R ratios and alteration temperatures (Fig. 5). We
 376 assumed that the initial isotopic compositions of the basalts and seawater were 5.5 and 0‰
 377 respectively, and that the water-rock interaction happened in a closed system. Overall, the
 378 strong decrease in O isotope composition with depth, from ^{18}O -enriched ($\sim 7.9\%$) to ^{18}O -
 379 depleted values ($\sim 3.5\%$), mainly reflects a temperature increase (Fig. 5). Together with the
 380 correlation between $\delta^{18}\text{O}$ value and N content, this suggests that the N geochemical behavior
 381 during alteration of basalts is controlled primarily by temperature variation. One possibility is
 382 that N speciation in the fluid, and thus availability for incorporation in secondary minerals, is
 383 controlled by temperature. It was shown that NH_4^+ can be stable in hydrothermal fluid at low
 384 temperature ($< 200^\circ\text{C}$) (Olofsson, 1975; Butterfield et al., 1997; Busigny et al., 2005a;
 385 Bourbonnais et al., 2012), thus suggesting that it represents a possible candidate explaining N
 386 enrichment in altered basalts. However, NH_4^+ in the fluid is in equilibrium with NH_3 and at
 387 high temperature ($> 200^\circ\text{C}$), NH_3 is efficiently transformed to N_2 and H_2 (Brown et al., 2018).
 388 We can thus hypothesize the following reaction chain, from left to right members, to illustrate
 389 the evolution of the hydrothermal fluid for increasing temperature:



391 Figure 6 reports the temperature dependence of the equilibrium constant for the
 392 transformation of NH_3 to N_2 and H_2 (Brown et al., 2018). It shows that NH_3 is stable ($K_p > 1$) at
 393 relatively low temperatures ($< 200^\circ\text{C}$) but becomes unstable ($K_p < 1$) at temperatures greater
 394 than 200°C . It is likely that NH_3 and NH_4^+ were both present in the low-T fluid and were thus
 395 partially enriched in the forming alteration phases, but then progressively disappeared with
 396 increasing temperature. A similar scenario has also been proposed from the study of
 397 hydrothermally altered gabbros from the French-Italian Alps (Busigny et al., 2018).

398

399

400 *5.3. Implication for the recycling of N in “warm” subduction zones*

401
402 The fate of N in subduction environments can be evaluated from the study of metamorphic
403 rocks in paleo-subduction zones (Bebout and Fogel, 1992; Mingram and Brauer, 2001;
404 Busigny et al., 2003; Halama et al., 2010, 2012; Bebout et al., 1997, 2013) but also from the
405 comparison of N fluxes input by subducting slabs with those output by volcanic arcs (*e.g.*
406 Fischer et al., 2002; Hilton et al., 2002; Zimmer et al., 2004; Mitchell et al., 2010; Li et al.,
407 2005, 2007). These approaches have led in the past to the conclusion that N can either be
408 efficiently lost (Bebout and Fogel, 1992) and quantitatively recycled to the surface *via* arc
409 volcanism (Fischer et al., 2002) or, on the contrary, largely transferred to the deep mantle
410 (Busigny et al., 2003; Li and Bebout, 2005; Li et al., 2007). These opposite conclusions can
411 be reconciled if the geothermal gradient of the subducting slab is taken into consideration
412 (Bebout et al., 1999; Busigny et al., 2003; Mitchel et al., 2010) because N as well as other
413 volatiles can be lost from the slab and migrate into the mantle wedge under high geothermal
414 gradients ($> 13^{\circ}\text{C}/\text{km}$), whereas N can be retained in the subducting slab under lower
415 geothermal gradients ($< 10^{\circ}\text{C}/\text{km}$). Moreover, it can be noted that Fischer et al. (2002) did
416 not consider reasonable estimates of the amount of N entering the subduction zone in
417 sediments but this has been re-estimated in later work (Li and Bebout, 2005). The studies of
418 subduction-zone metamorphic rocks have in general shown that, except in unusually warm
419 margins, the bulk of the initially subducted N bound into silicate minerals such as clays, then
420 micas, can be retained to depths approaching those beneath volcanic fronts (Busigny et al.,
421 2003; Bebout et al., 2013). However, there is no exposed metamorphic record of sediments or
422 altered oceanic crust that was present beneath an active arc. Thermal models indicate
423 significant heating of slabs over the 80-120 km depth range, due to exposure of the slabs and
424 sediments to the convecting part of the mantle wedge (*e.g.* Syracuse et al., 2010). A nitrogen
425 loss could therefore occur during this heating, eventually involving devolatilization and/or
426 partial melting. Mass balance approach based on the fluxes input and output in a specific
427 subduction zone can further help to characterize the N behavior in this type of environment.
428 The volcanic arc in Central America is a perfect site to build a global mass balance in a
429 “warm” subduction zone because N fluxes emitted by volcanoes (Fischer et al., 2002; Hilton

430 et al., 2002; Zimmer et al., 2004) and input by subducting sediments (Li and Bebout, 2005)
 431 have already been estimated in previous studies. The Central America margin is regarded as
 432 being non-accretionary, thus we do not need to consider accretion as a means of removing
 433 some of the sediment from the subducting section (see House et al., 2019, for a different
 434 situation in the Sunda margin). Some underplating of sediment could occur at greater depths
 435 but this effect cannot be estimated from the present knowledge. The data obtained here on
 436 Hole 504B provide the N concentration distribution within the upper crust, thus allowing us to
 437 include the upper mafic crust in the mass balance calculation of the Central America margin.
 438

439 In altered basalts from Hole 504B, N concentration shows an exponential decrease with depth
 440 (Fig. 7), which can be described by the following equation:

$$441 \quad N(z) = A \cdot e^{-Bz} \quad (\text{Eq. 2})$$

442 with $N(z)$ the N concentration, z the depth, and A and B two parameters determined by fitting
 443 the data in Figure 7. We can then calculate the flux of N input in Central American
 444 subduction zone by upper mafic crust as,

$$445 \quad \phi_N = \int_0^z N(z) \cdot \rho \cdot L \cdot r \cdot dz \quad (\text{Eq. 3})$$

446 where ρ is the density of upper oceanic crust, L is the length of the plate subducting in Central
 447 America, and r is the subduction rate. Combining equations 2 and 3 gives,

$$448 \quad \phi_N = (\rho \cdot L \cdot r) \int_0^z A \cdot e^{-Bz} dz \quad (\text{Eq. 4})$$

449 which can finally be solved and written as,

$$450 \quad \phi_N = (\rho \cdot L \cdot r) \cdot \left[\frac{A}{B} \times (1 - e^{-Bz}) \right] \quad (\text{Eq. 5})$$

451 In order to compare our results to previous studies (Fischer et al., 2002; Hilton et al., 2002;
 452 Zimmer et al., 2004; Li and Bebout, 2005), we adopted the average subducting rate (r) and
 453 trench length (L) used by Li and Bebout (2005) of 85 mm/yr and 1100 km, respectively. The
 454 density of the upper crust is on average 2900 kg/m³ (Carlson and Raskin, 1984). Considering a
 455 thickness of upper oceanic crust of 2 km, the flux of N transferred to the subduction is
 456 $\sim 2.9 \times 10^6$ g/yr. It should be noted here that this value represent a lower estimate since breccias,
 457 veins and alteration halos have not been included in our mass balance. Comparison of the N

458 input and output fluxes for the Central American subduction zone (Table 3) shows that altered
459 basalts from the upper crust represent more than 35% of the total flux of N released by arc
460 volcanoes in Central America (8.2×10^9 g/yr; Hilton et al., 2002). However, in comparison
461 with the sedimentary flux (1.3×10^{10} g/yr; Li and Bebout, 2005), the upper basaltic crust is a
462 minor reservoir (~20% of the total N input). Note, however, that there is presently no data for
463 the lower mafic and ultramafic crust subducting in Central America yet. Although mafic and
464 ultramafic rocks from intact crust formed at fast and intermediate spreading rates likely have
465 very low N concentrations (Yokochi et al., 2009; Halama et al., 2010, 2012) comparable to
466 the deeper rocks in Hole 504B, gabbroic rocks make up a significant volume of the ocean
467 crust (*e.g.* 4 km of gabbros in a typical crustal section). The total flux of N input by sediments
468 and upper oceanic crust in Central American trench amounts $\sim 16 \times 10^9$ g/yr although this is
469 likely to be significantly higher if phyllosilicate vein minerals and breccia cements are
470 accounted for. Our estimated flux is at least twice the flux of N degassed by arc volcanoes
471 (Hilton et al., 2002; Table 3). This suggests that in “warm” subduction zone like Central
472 America, up to 50% of the subducted N may be transferred to the deeper mantle. In
473 comparison, in “cold” subduction environments such as the Izu-Bonin-Mariana arc, 80 to
474 95% of the N input is preserved and likely buried in the deep mantle (Mitchell et al., 2010).

475

476 **6. Conclusion**

477

478 In the present contribution, we re-assessed the N concentration, and provide new data of N
479 isotope composition, of altered basaltic rocks from Hole 504B. The N of the upper crust is
480 clearly increased by seawater-rock interactions, a geochemical behavior similar to those
481 observed in other altered oceanic sections (Busigny et al., 2005a; Li et al., 2007). The
482 apparent contradiction with previous analyses by Erzinger and Bach (1996) likely derives
483 from their use of molybdenum crucible for heating the samples in vacuum line.

484 Whole rock basalt N concentrations decrease with depth, from ~ 15 ppm in the upper basalts
485 down to ~ 1 ppm in the deepest dolerites, the latter analyses being similar to fresh, unaltered
486 degassed oceanic crust (~ 1 ppm). In contrast, N isotope composition does not show specific

487 depth trend and displays a relatively large range around $+3.0 \pm 2.2\%$, similar to sedimentary
488 composition. The N concentration is well correlated with bulk-rock $\delta^{15}\text{O}$ values, which likely
489 indicates an evolution of N speciation in hydrothermal fluid with increasing temperature. If
490 the correlation between N content and $\delta^{15}\text{O}$ is verified in various DSDP/ODP sites, then $\delta^{15}\text{O}$
491 values could be used as a proxy to estimate the concentration of N content in the oceanic crust
492 in general.

493 Finally, mass balance calculation on subduction zones supports that the fate of N in subducted
494 slab is dependent on geothermal gradient of the subduction zone, as suggested by earlier
495 studies. In “cold” subduction like most modern environments, N is predominantly preserved
496 in the slab and does not return to the surface *via* arc volcanism. In contrast, in “warm”
497 subduction, N is strongly released but as much as 50% may still be preserved in the slab and
498 be transferred to the deep mantle. Once again, the temperature appears as the essential
499 parameter controlling the N behavior. These findings will need to be taken into consideration
500 in future modeling of the N geodynamic cycles for prediction of the atmosphere evolution and
501 reconstruction of the N distribution among Earth’s reservoirs.

502

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509

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705 **Figure caption**

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707 **Figure 1.** Map illustrating the location of DSDP/ODP Hole 504B, as well as other drill sites,
708 referred in the main text, near Central American convergent margin (modified from Busigny
709 et al., 2005).

710

711 **Figure 2.** Depth profiles of (A) potassium, (B) rubidium, (C) cesium and (D) nitrogen
712 concentrations (ppm), as well as (E) nitrogen (‰ vs Air) and (F) oxygen (‰ vs SMOW)
713 isotope compositions in altered basalts from Hole 504B (black circles). The main lithological
714 variations are reported on the left of the figure: volcanic zone (VZ), transition zone (TZ) and
715 sheeted Dike Complex (SDC). The main alteration zones are also reported on the left of the
716 figure: low-temperature oxidizing (LTO), low-temperature reducing (LTR), mineralized (M),
717 upper dikes (UD), lower dikes (LD). Horizontal dashed lines represent the depth range of the
718 five alteration zones as indicated on the right end side of the figure: Upper Pillow Alteration
719 Zone (UPAZ), Lower Pillow Alteration Zone (LPAZ), Mineralized Zone (MZ), Upper Dikes
720 (UD), Lower Dikes (LD). D: the gray squares represent the data reported by Erzinger and
721 Bach (1996) using Mo crucible for N extraction. The black vertical line represents N
722 concentration of the fresh (non-altered) mid ocean ridge basalts (MORB). E: the gray bar
723 represents the average $\delta^{15}\text{N}$ value of mantle nitrogen (-5‰; Cartigny and Marty, 2013). F: the
724 gray diamonds correspond to a compilation of data from the literature (Barrett and
725 Friedrichsen, 1982; Alt et al., 1986a, 1989, 1996; Kawahata et al., 1987; Kusakabe et al.,
726 1989; Mengel and Hoefs, 1990; Agrinier et al., 1995), and illustrates similar trend to the one
727 measured in our study (black circles). The gray bar represents the average $\delta^{18}\text{O}$ value of the
728 mantle (+5.5‰; Eiler et al., 2000).

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730 **Figure 3.** Relationships between N, K, Rb, Na_2O and $\text{CaO}+\text{Na}_2\text{O}$ concentrations in altered
731 basalts from Hole 504B.

732

733 **Figure 4.** Relations between N concentrations (ppm) and N (‰ vs Air) and O (‰ vs SMOW)
734 isotope compositions in altered basalts from Hole 504B.

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736 **Figure 5.** Calculated $\delta^{18}\text{O}$ values of altered basalts equilibrated with seawater at different
737 temperature (50 to 500°C) and water/rock ratios (W/R). The calculation assumes constant $\delta^{18}\text{O}$
738 value of seawater at ~0‰ and O isotope fractionation between water and rock defined as $\Delta_{\text{water-rock}} = 2.5(10^6)/T^2 - 3.70$ (e.g. Gregory and Taylor, 1981). The range of water/rock ratio reported
739 for Hole 504B in the literature is indicated by the light gray band (Friedrichsen et al., 1985;
740 Kawahata et al., 1987; Kusakabe et al., 1989; Agrinier et al., 1995).

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743 **Figure 6.** Equilibrium constant (K_p , expressed from gas pressure) as a function of temperature
744 for the reaction of ammonia formation from N_2 and H_2 (Brown et al., 2018). Ammonia is
745 favored at low temperature ($<200^\circ\text{C}$) whereas N_2 is more stable at temperatures $>200^\circ\text{C}$.

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747 **Figure 7.** Relation between N concentration (ppm) and depth in the oceanic crust (mbb: meter
748 below basement) for altered basalts from Hole 504B. The data are better fitted by an
749 exponential law ($R^2=0.82$) than a linear regression ($R^2=0.74$, not shown).

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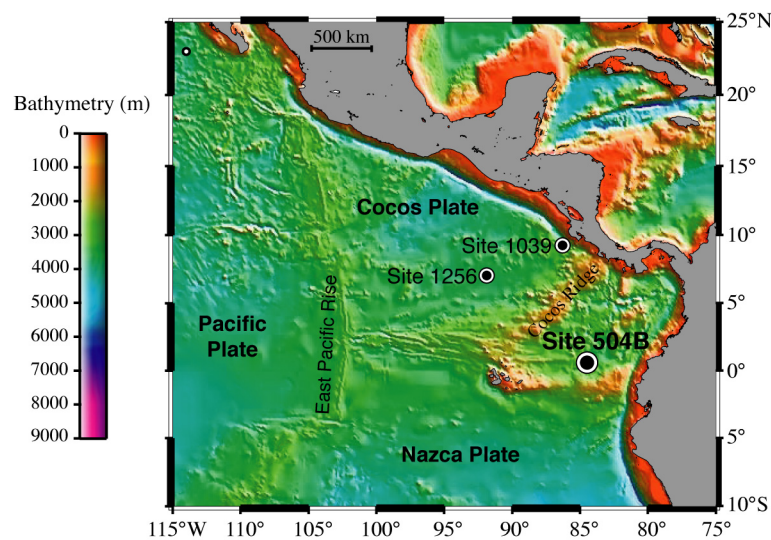


Figure 1

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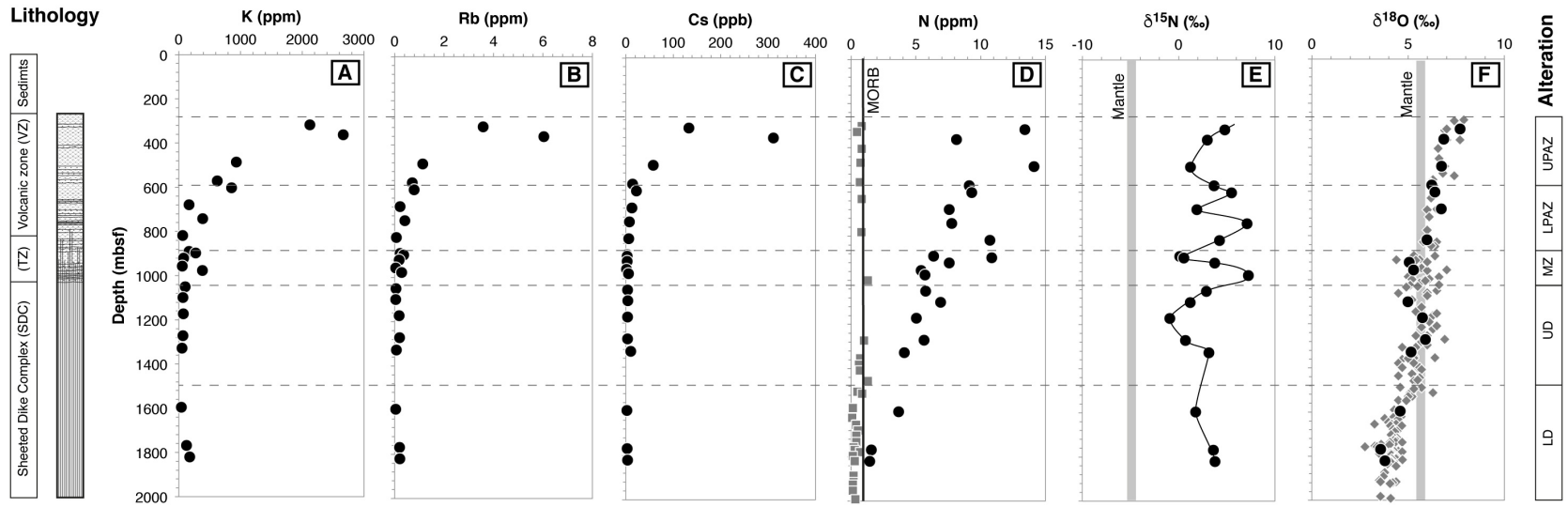


FIGURE 2

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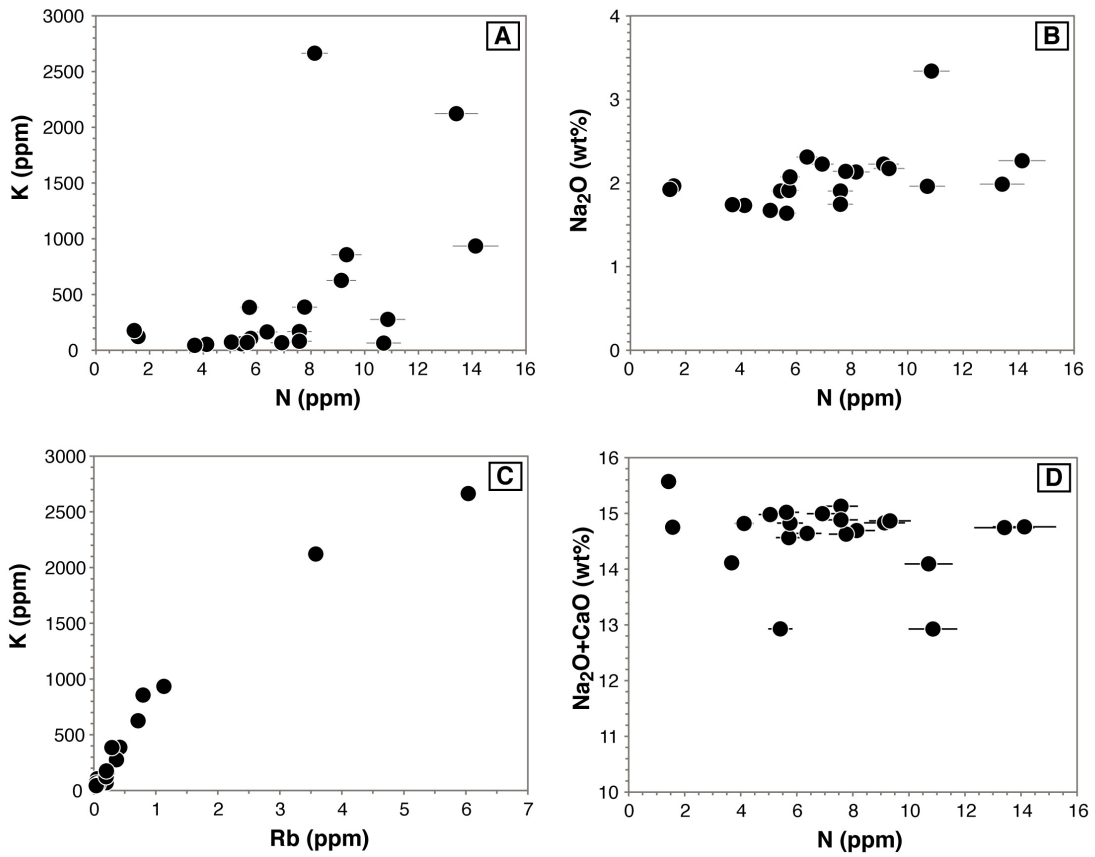


Figure 3

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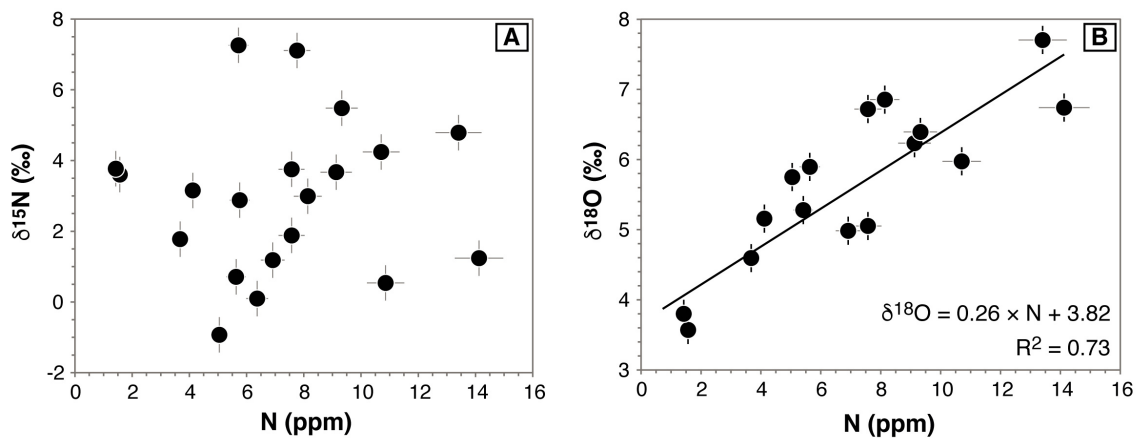


Figure 4

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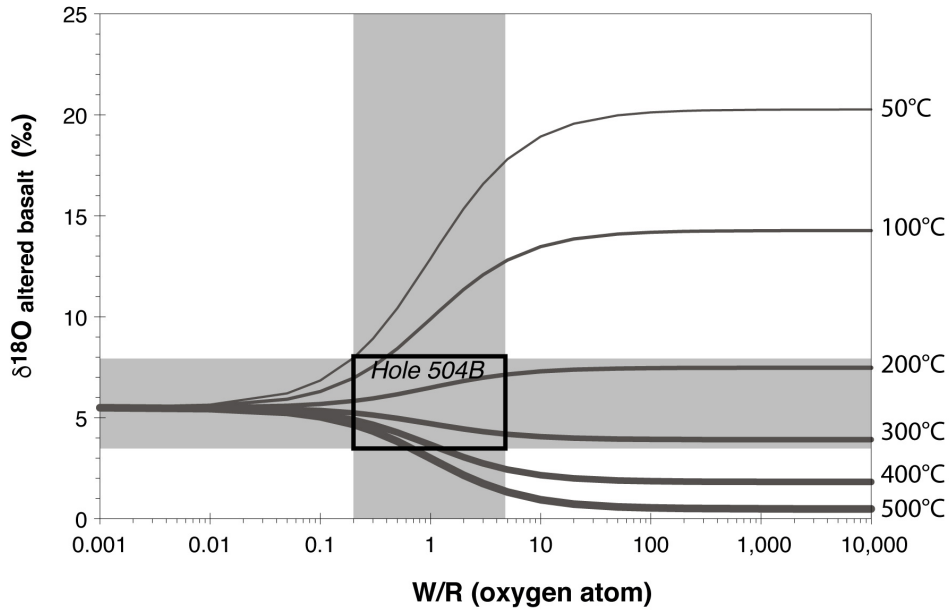


Figure 5

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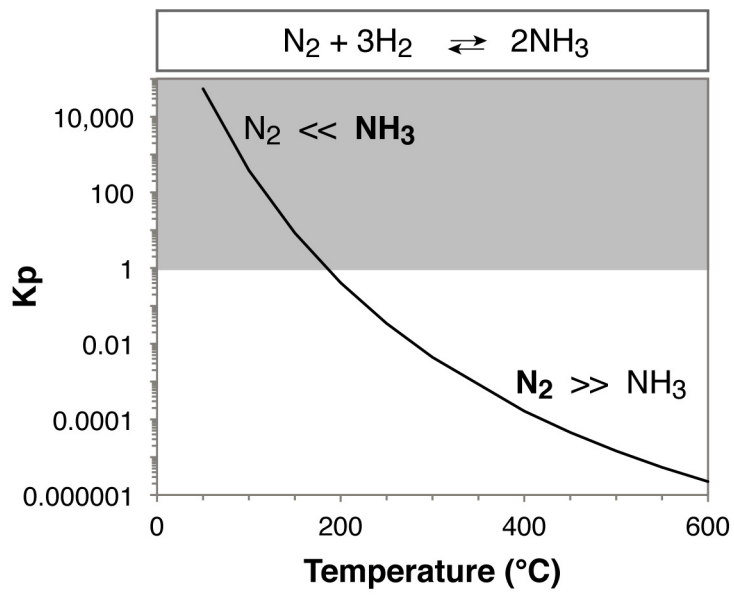


Figure 6

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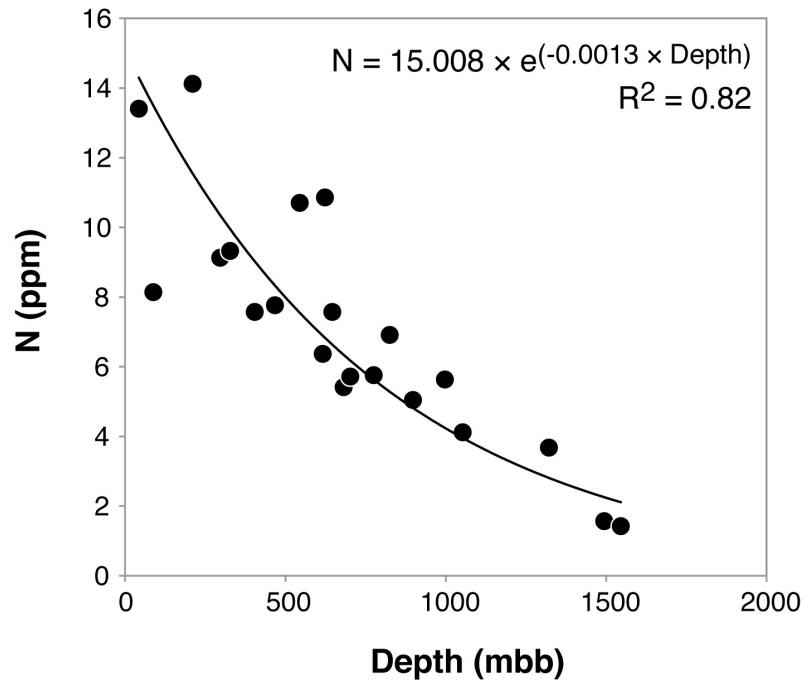


Figure 7

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Table 1

Depth, alteration zone, major and trace element concentrations and oxygen isotope composition (‰ vs SMOW) of altered basalts from Hole 504B.

| Core-section, Interval (cm) | Depth* (mbsf) | Alteration zone | SiO ₂ (wt%) | Al ₂ O ₃ (wt%) | FeO _T (wt%) | MnO (wt%) | MgO (wt%) | CaO (wt%) | Na ₂ O (wt%) | TiO ₂ (wt%) | P ₂ O ₅ (wt%) | LOI (wt%) | Total (wt%) | K (ppm) | Rb (ppb) | Cs (ppb) | δ ¹⁸ O (‰) |
|--------------------------------|------------------|--------------------|---------------------------|---|---------------------------|--------------|--------------|--------------|----------------------------|---------------------------|--|--------------|----------------|------------|-------------|-------------|--------------------------|
| 8-1, 69-72 | 317.2 | UPAZ | 48.50 | 15.71 | 10.03 | 0.16 | 7.72 | 12.76 | 1.99 | 0.86 | 0.09 | 0.65 | 98.63 | 2122.3 | 3578.3 | 132.7 | 7.70 |
| 13-1, 81-84 | 362.4 | UPAZ | 48.91 | 15.01 | 10.00 | 0.18 | 7.94 | 12.56 | 2.13 | 0.96 | 0.08 | 1.43 | 99.51 | 2664.2 | 6038.5 | 311.1 | 6.85 |
| 29-2, 16-19 | 485.2 | UPAZ | 49.03 | 14.71 | 9.51 | 0.17 | 8.41 | 12.49 | 2.27 | 1.00 | 0.08 | 1.57 | 99.32 | 934.5 | 1130.7 | 57.8 | 6.74 |
| 39-1, 62-66 | 571.2 | UPAZ | 49.64 | 15.91 | 9.25 | 0.18 | 7.98 | 12.60 | 2.23 | 0.93 | 0.09 | 1.41 | 100.21 | 626.1 | 713.3 | 14.1 | 6.23 |
| 43-1, 17-19 | 602.2 | LPAZ | 50.14 | 15.14 | 9.80 | 0.17 | 8.50 | 12.69 | 2.17 | 0.90 | 0.08 | 1.07 | 100.67 | 856.8 | 794.8 | 22.6 | 6.39 |
| 52-1, 38-40 | 678.9 | LPAZ | 48.79 | 16.51 | 8.77 | 0.15 | 7.92 | 13.22 | 1.91 | 0.82 | 0.07 | 1.36 | 99.51 | 167.7 | 223.8 | 13.2 | 6.72 |
| 60-1, 46-49 | 742 | LPAZ | 49.94 | 14.69 | 10.47 | 0.17 | 8.57 | 12.49 | 2.14 | 1.05 | 0.11 | 0.65 | 100.27 | 387.3 | 419.7 | 7.8 | n.a. |
| 69-1, 95-99 | 819 | LPAZ | 48.39 | 14.14 | 10.77 | 0.23 | 8.36 | 12.13 | 1.96 | 1.08 | 0.10 | 1.84 | 98.98 | 64.8 | 65.8 | 6.5 | 5.98 |
| 77-2, 71-73 | 890.8 | MZ | 49.40 | 14.45 | 10.85 | 0.20 | 8.38 | 12.33 | 2.31 | 1.04 | 0.10 | 1.17 | 100.22 | 164.1 | 218.5 | 3.1 | n.a. |
| 78-1, 6-11 | 897.6 | MZ | 49.59 | 14.88 | 10.25 | 0.17 | 8.19 | 9.59 | 3.34 | 0.95 | 0.09 | 3.22 | 100.27 | 276.7 | 365.5 | 2.9 | n.a. |
| 81-1, 128-132 | 920.8 | MZ | 48.88 | 14.98 | 9.73 | 0.23 | 8.53 | 13.14 | 1.75 | 0.88 | 0.09 | 1.42 | 99.62 | 80.6 | 183.4 | 3.1 | 5.05 |
| 85-1, 47-49 | 956 | MZ | 49.45 | 14.02 | 9.89 | 0.38 | 8.71 | 11.02 | 1.91 | 0.96 | 0.08 | 2.80 | 99.21 | 59.1 | 48.6 | 1.8 | 5.28 |
| 88-1, 12-16 | 976.7 | MZ | 47.48 | 15.20 | 9.48 | 0.23 | 8.72 | 12.65 | 1.91 | 0.99 | 0.12 | 3.03 | 99.82 | 384.8 | 291.3 | 5.4 | n.a. |
| 96-1, 125-127 | 1049.7 | MZ | 49.85 | 14.44 | 8.83 | 0.21 | 8.55 | 12.75 | 2.07 | 0.91 | 0.08 | 1.16 | 98.85 | 106.6 | 56.1 | 3.8 | n.a. |
| 101-1, 98-102 | 1099.5 | UD | 48.85 | 14.55 | 9.56 | 0.19 | 8.38 | 12.77 | 2.23 | 0.90 | 0.07 | 1.58 | 99.07 | 67.2 | 39.3 | 4.1 | 4.99 |
| 113-1, 122-126 | 1172.3 | UD | 49.80 | 15.15 | 10.09 | 0.17 | 8.96 | 13.31 | 1.67 | 0.84 | 0.08 | 0.70 | 100.76 | 72.6 | 184.3 | 3.4 | 5.75 |
| 129-2, 23-27 | 1271.8 | UD | 48.91 | 15.97 | 8.74 | 0.15 | 9.93 | 13.38 | 1.64 | 0.69 | 0.07 | 1.39 | 100.87 | 70.6 | 199.2 | 3.5 | 5.90 |
| 137-1, 31-34 | 1327.4 | UD | 48.44 | 15.87 | 8.96 | 0.15 | 8.98 | 13.09 | 1.73 | 0.79 | 0.07 | 1.16 | 99.23 | 53.5 | 69.7 | 10.3 | 5.16 |
| 176R-1, 85-89 | 1596.1 | LD | 49.42 | 14.30 | 10.82 | 0.17 | 7.95 | 12.37 | 1.74 | 0.97 | 0.08 | 0.86 | 98.69 | 44.1 | 37.7 | 2.2 | 4.60 |
| 207R-1, 0-4 | 1768.4 | LD | 49.79 | 14.28 | 10.71 | 0.19 | 8.32 | 12.79 | 1.97 | 1.00 | 0.09 | 0.58 | 99.70 | 122.9 | 200.3 | 3.2 | 3.57 |
| 214R-2, 29-32 | 1820.4 | LD | 48.55 | 16.97 | 7.88 | 0.12 | 9.07 | 13.65 | 1.92 | 0.69 | 0.06 | 1.53 | 100.42 | 176.6 | 204.1 | 3.6 | 3.80 |

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* mbsf: meters below seafloor; n.a.: not analyzed.

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Alteration zones: Upper Pillow Alteration Zone (UPAZ), Lower Pillow Alteration Zone (LPAZ), Mineralized Zone (MZ), Upper Dikes (UD), Lower Dikes (LD).

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Table 2
Nitrogen concentration and isotope composition of altered basalts from Hole 504B.

| Core-section, Interval (cm) | Piece # | Temp (°C) | N (ppm) | $\delta^{15}\text{N}$ (‰) |
|-----------------------------|---------|-----------|-------------|---------------------------|
| 8-1, 69-72 | 524 | 950 | 13.7 | 5.1 |
| 8-1, 69-72 | 524 | 1050 | 13.2 | 4.4 |
| | | | <i>13.4</i> | <i>4.8</i> |
| 13-1, 81-84 | 759 | 1050 | 8.1 | 3.0 |
| 29-2, 16-19 | 1581 | 1050 | 14.1 | 1.2 |
| 39-1, 62-66 | 463 | 950 | 9.1 | 3.7 |
| 43-1, 17-19 | | 950 | 9.2 | 5.1 |
| 43-1, 17-19 | | 1050 | 9.5 | 5.8 |
| | | | <i>9.3</i> | <i>5.5</i> |
| 60-1, 46-49 | 1260 | 950 | 7.8 | 7.1 |
| 69-1, 95-99 | 1547 | 1050 | 10.7 | 4.2 |
| 77-2, 71-73 | 6 | 950 | 6.2 | -0.1 |
| 77-2, 71-73 | 6 | 1050 | 6.5 | 0.3 |
| | | | <i>6.4</i> | <i>0.1</i> |
| 78-1, 6-11 | 2 | 950 | 10.9 | 0.5 |
| 81-1, 128-132 | 15 | 950 | 7.6 | 3.8 |
| 85-1, 47-49 | 6b | 1050 | 5.4 | n.a. |
| 88-1, 12-16 | 2A | 950 | 5.9 | 7.5 |
| 88-1, 12-16 | 2A | 1050 | 5.6 | 7.0 |
| | | | <i>5.7</i> | <i>7.3</i> |
| 96-1, 125-127 | 6b | 1050 | 5.8 | 2.9 |
| 101-1, 98-102 | 10a | 1050 | 6.9 | 1.2 |
| 113-1, 122-126 | 13 | 950 | 5.0 | -0.9 |
| 129-2, 23-27 | 1C | 950 | 5.6 | 0.7 |
| 137-1, 31-34 | 4 | 1050 | 4.1 | 3.2 |
| 176R-1, 85-89 | 16 | 1050 | 3.7 | 1.8 |
| 207R-1, 0-4 | | 950 | 1.5 | 3.8 |
| 207R-1, 0-4 | | 1050 | 1.6 | 3.4 |
| | | | <i>1.6</i> | <i>3.6</i> |
| 214R-2, 29-32 | 7 | 950 | 1.4 | 3.1 |
| 214R-2, 29-32 | 7 | 1050 | 1.4 | 4.5 |
| | | | <i>1.4</i> | <i>3.8</i> |

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Temp: temperature of N extraction from the sample during combustion in quartz sealed-tube.

Values in *italic*: mean values of replicate analyses; n.a.: not analyzed.

The precision on N content and $\delta^{15}\text{N}$ are better than 8% and 0.5‰, respectively.

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Table 3
Comparison of the nitrogen fluxes input in and output from Central American subduction zone.

| | | N flux, g/yr | Method used for estimating N flux | Reference |
|--------|----------------------------|-------------------|---|----------------------|
| Output | Volcanic arc | 8.2×10^6 | N ₂ degassed in Central American arc | Hilton et al., 2002 |
| | Volcanic arc | 3.6×10^6 | N ₂ degassed in Costa Rica only | Zimmer et al., 2004 |
| Input | Sediments | 6.4×10^6 | N concentration assumed for shales (100 ppm) and carbonates (0 ppm) | Fischer et al., 2002 |
| | Sediments | 1.3×10^6 | N concentration measured in sediments from ODP Site 1039 | Li and Bebout, 2005 |
| | Upper oceanic crust (2 km) | 2.9×10^6 | N concentration measured in altered basalts from DSDP/ODP Site 504B | This study |

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