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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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29  
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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  $3.0 \pm 2.2$  ‰ (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  $\text{NH}_3/\text{NH}_4$  at low temperature (<200°C)  
53 but is transformed to  $\text{N}_2$ , associated with  $\text{H}_2$ , 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, CO<sub>2</sub> and H<sub>2</sub>O, 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  $300^{\circ}\text{C}$  under vacuum during one night and then  
167 saturated with  $\text{O}_2$  pressure generated with CuO heated to  $900^{\circ}\text{C}$ . These steps allow removing  
168 any organic contamination and/or atmospheric  $\text{N}_2$  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  $1050^{\circ}\text{C}$  during 6 h (Busigny et al., 2005b). A comparison of the combustion at  $950$  and  
171  $1050^{\circ}\text{C}$  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  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) using Cu, CuO and CaO  
174 (Kendall and Grim, 1990). It was then quantified as dinitrogen  $\text{N}_2$  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 N<sub>2</sub>. Nitrogen  
177 isotopic composition was expressed in the usual  $\delta$  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 N<sub>2</sub>. The quantity of N in  
179 the analytical blank was low ( $0.65 \pm 0.30$  nmol) relative to samples ( $> 7$  nmol), and its  
180 isotopic composition averaged  $-3.7 \pm 2.7 \text{‰}$  ( $2\sigma$ ). 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 (BrF<sub>5</sub>) 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.cprg.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). SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> 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 Fe<sub>2</sub>O<sub>3</sub> 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 Na<sub>2</sub>O 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 δ<sup>15</sup>N 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 δ<sup>15</sup>N 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  $\pm 2.2$  ‰ (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  $5.7 \pm 1.1$ ‰,  $1\sigma$ ;  $n=16$ ). 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.*  $\text{NO}_3^-$  or  $\text{N}_2$  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  $\text{NH}_4^+$   
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  $\text{NH}_4^+$ , which according to similarities in charge and ionic radius, substitutes for  $\text{K}^+$ , Na  
311 and/or  $\text{Ca}^{2+}$  (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  $\text{NH}_4^+$  their  
317 substitution with K in celadonite. The high N concentrations in K-rich samples are thus  
318 compatible with N occurring as  $\text{NH}_4^+$  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  $^{18}\text{O}$ -enriched ( $\sim 7.9\%$ ) to  $^{18}\text{O}$ -  
 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  $\text{NH}_4^+$  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,  $\text{NH}_4^+$  in the fluid is in equilibrium with  $\text{NH}_3$  and at  
 387 high temperature ( $> 200^\circ\text{C}$ ),  $\text{NH}_3$  is efficiently transformed to  $\text{N}_2$  and  $\text{H}_2$  (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  $\text{NH}_3$  to  $\text{N}_2$  and  $\text{H}_2$  (Brown et al., 2018). It shows that  $\text{NH}_3$  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  $200^\circ\text{C}$ . It is likely that  $\text{NH}_3$  and  $\text{NH}_4^+$  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  $\rho$  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/m<sup>3</sup> (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 ( $8.2 \times 10^9$  g/yr; Hilton et al., 2002). However, in comparison  
461 with the sedimentary flux ( $1.3 \times 10^{10}$  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  $\sim 15$  ppm in the upper basalts  
485 down to  $\sim 1$  ppm in the deepest dolerites, the latter analyses being similar to fresh, unaltered  
486 degassed oceanic crust ( $\sim 1$  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).

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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).

729

730 **Figure 3.** Relationships between N, K, Rb,  $\text{Na}_2\text{O}$  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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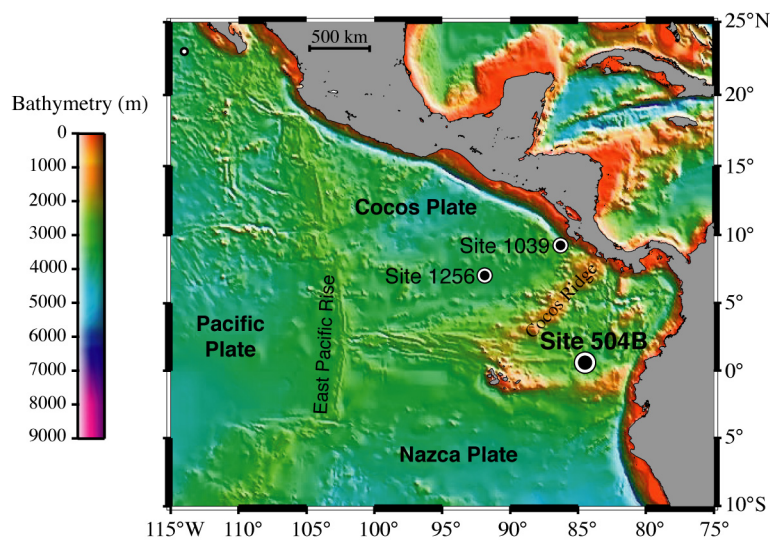


Figure 1

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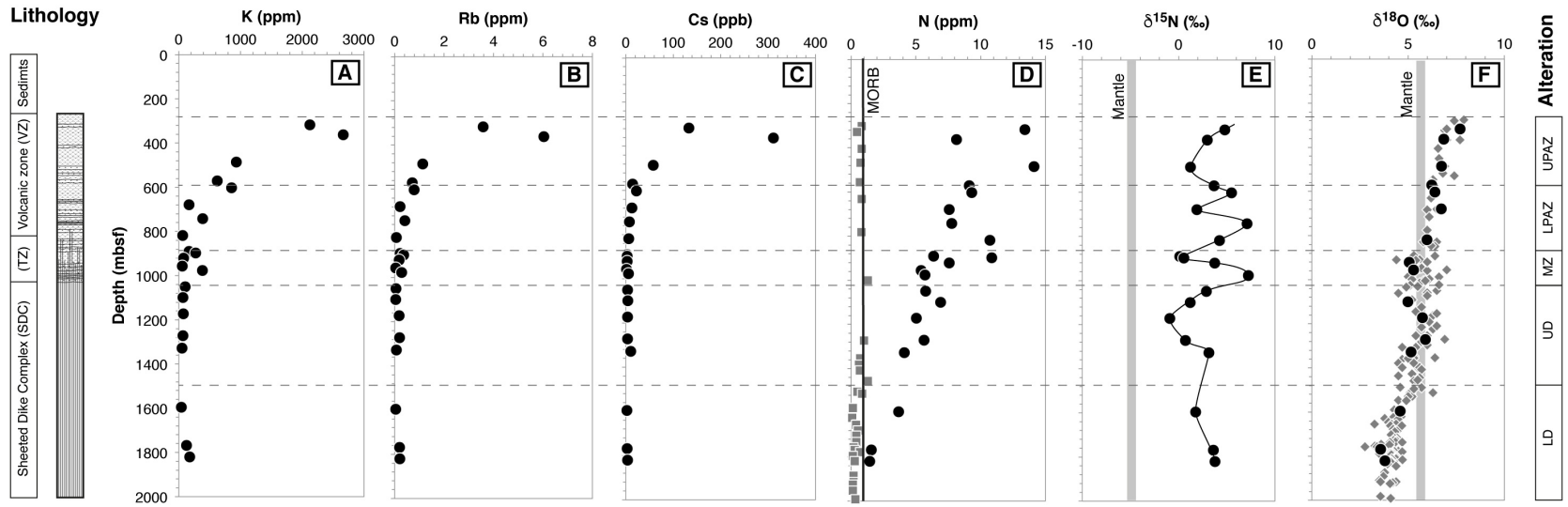


FIGURE 2

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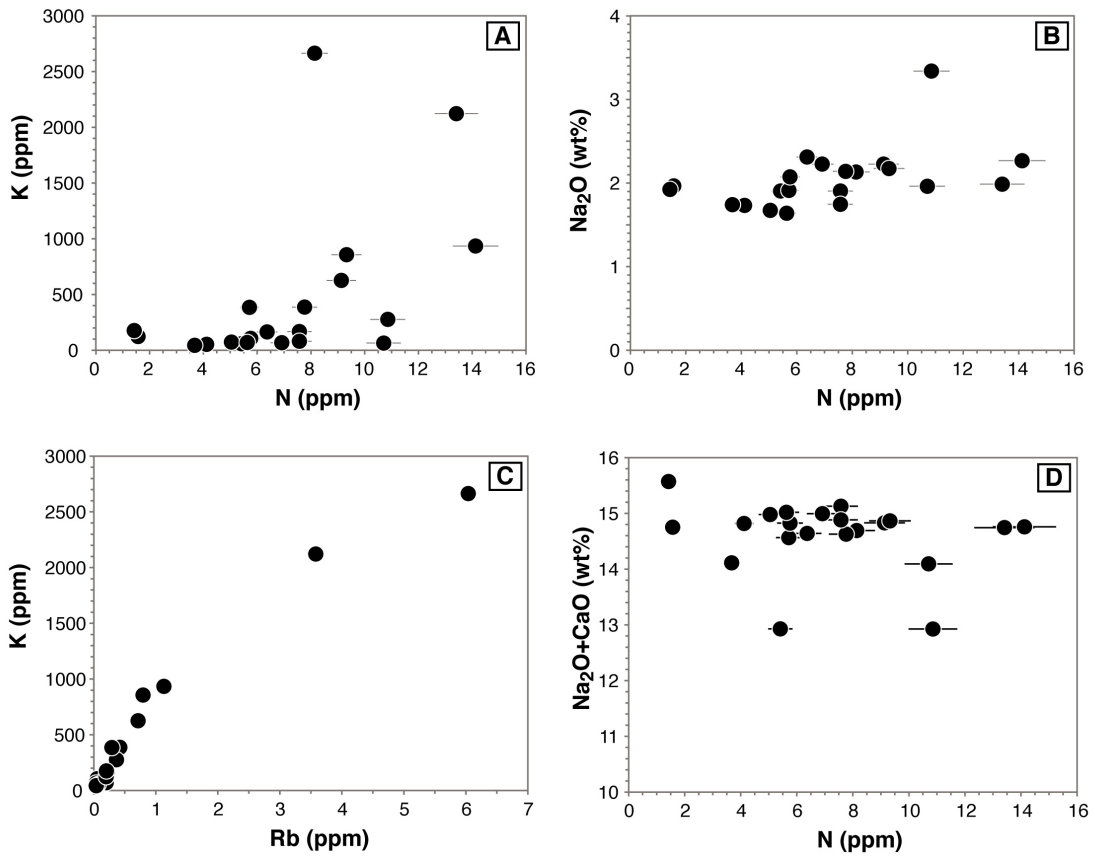


Figure 3

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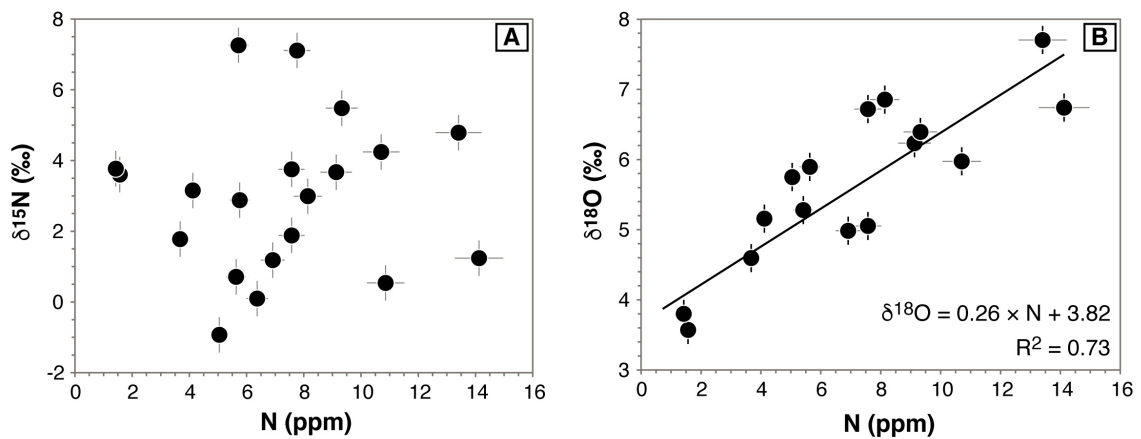


Figure 4

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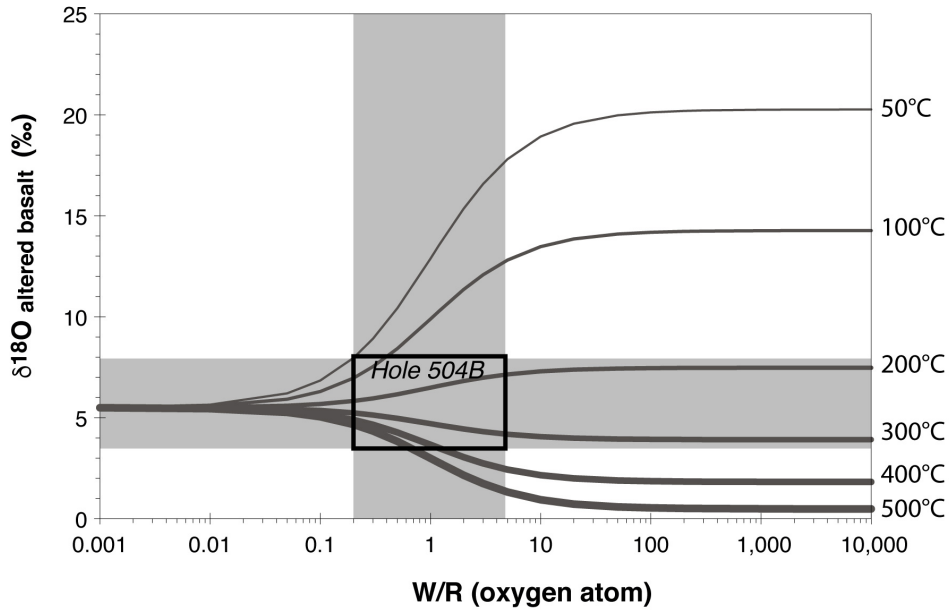


Figure 5

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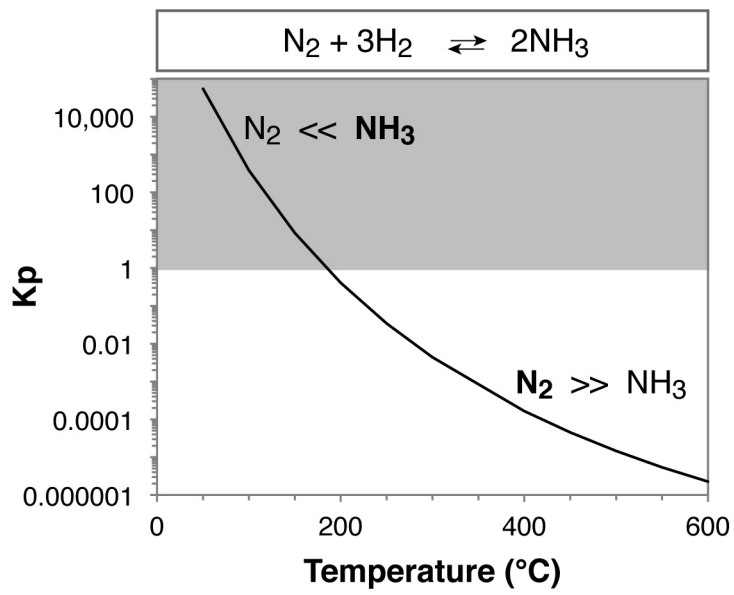
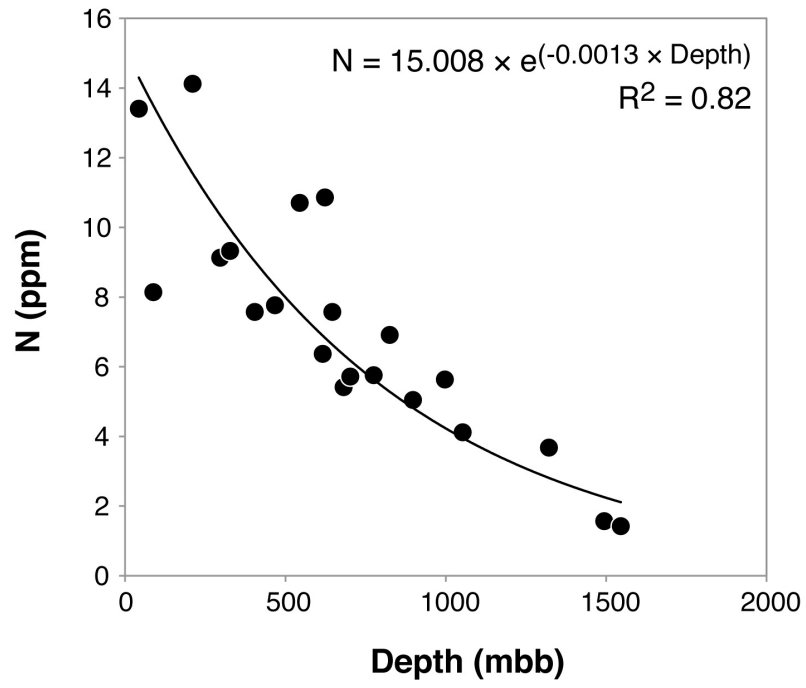


Figure 6

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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 <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na <sub>2</sub> O (wt%)	TiO <sub>2</sub> (wt%)	P <sub>2</sub> O <sub>5</sub> (wt%)	LOI (wt%)	Total (wt%)	K (ppm)	Rb (ppb)	Cs (ppb)	δ <sup>18</sup> 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	$8.2 \times 10^6$	N <sub>2</sub> degassed in Central American arc	Hilton et al., 2002
	Volcanic arc	$3.6 \times 10^6$	N <sub>2</sub> degassed in Costa Rica only	Zimmer et al., 2004
Input	Sediments	$6.4 \times 10^6$	N concentration assumed for shales (100 ppm) and carbonates (0 ppm)	Fischer et al., 2002
	Sediments	$1.3 \times 10^6$	N concentration measured in sediments from ODP Site 1039	Li and Bebout, 2005
	Upper oceanic crust (2 km)	$2.9 \times 10^6$	N concentration measured in altered basalts from DSDP/ODP Site 504B	This study

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