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1 **Insights into C and H storage in the altered oceanic crust: results**
2 **from ODP/IODP Hole 1256D**

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33

34 **Abstract**

35

36 Carbon and hydrogen concentrations and isotopic compositions were measured in 19 samples
37 from altered oceanic crust cored in ODP/IODP Hole 1256D through lavas, dikes down to the
38 gabbroic rocks. Bulk water content varies from 0.32 to 2.14 wt% with δD values from -64 to -
39 25‰. All samples are enriched in water relative to fresh basalts. The δD values are interpreted
40 in terms of mixing between magmatic water and another source that can be either secondary
41 hydrous minerals and/or H contained in organic compounds such as hydrocarbons. Total CO_2 ,
42 extracted by step-heating technique, ranges between 564 and 2823 ppm with $\delta^{13}C$ values from
43 -14.9‰ to -26.6‰. As for water, these altered samples are enriched in carbon relative to fresh
44 basalts. The carbon isotope compositions are interpreted in terms of a mixing between two
45 components: (1) a carbonate with $\delta^{13}C = -4.5‰$ and (2) an organic compound with $\delta^{13}C = -$
46 26.6‰. A mixing model calculation indicates that, for most samples (17 of 19), more than
47 75% of the total C occurs as organic compounds while carbonates represent less than 25%.
48 This result is also supported by independent estimates of carbonate content from CO_2 yield
49 after H_3PO_4 attack. A comparison between the carbon concentration in our samples, seawater
50 DIC (Dissolved Inorganic Carbon) and DOC (Dissolved Organic Carbon), and hydrothermal
51 fluids suggests that CO_2 degassed from magmatic reservoirs is the main source of organic C
52 addition to the crust during the alteration process. A reduction step of dissolved CO_2 is thus
53 required, and can be either biologically mediated or not. Abiotic processes are necessary for
54 the deeper part of the crust (>1000 mbsf) because alteration temperatures are greater than any
55 hyperthermophilic living organism (i.e. $T > 110^\circ C$). Even if not required, we cannot rule out
56 the contribution of microbial activity in the low-temperature alteration zones. We propose a
57 two-step model for carbon cycling during crustal alteration: (1) when “fresh” oceanic crust
58 forms at or close to ridge axis, alteration starts with hot hydrothermal fluids enriched in
59 magmatic CO_2 , leading to the formation of organic compounds during Fischer-Tropsch-type
60 reactions; (2) when the crust moves away from the ridge axis, these interactions with hot
61 hydrothermal fluids decrease and are replaced by seawater interactions with carbonate
62 precipitation in fractures. Taking into account this organic carbon, we estimate C isotope
63 composition of mean altered oceanic crust at $\sim -4.7‰$, similar to the $\delta^{13}C$ of the C degassed
64 from the mantle at ridge axis, and discuss the global carbon budget. The total flux of C stored
65 in the altered oceanic crust, as carbonate and organic compound, is $2.9 \pm 0.4 \times 10^{12}$ molC/yr.

66

66

67 1. INTRODUCTION

68

69 Volatile elements such as C and H are studied in rocks since they control many
70 geological processes ranging from mantle melting to Earth's climate and origin of life. The
71 global geochemical cycles of volatile elements are dominated by exchanges between mantle
72 and exosphere (i.e. atmosphere, hydrosphere and crust) through volcanic and subduction
73 activities (e.g. Javoy, 1998). In detail, the generation, alteration and recycling of the oceanic
74 crust represent the main geodynamic vector of exchanges between mantle and surface
75 reservoirs. The alteration of oceanic crust on the seafloor, and its subsequent metamorphism
76 in subduction zones have a major impact on the chemical composition of the material
77 ultimately recycled to the deep mantle (e.g. Gregory and Taylor, 1981; Muehlenbachs, 1986;
78 Valley, 1986; Bebout, 1995; Shanks et al., 1995; Bach et al., 2003). Over the past decades,
79 stable isotopes systematic (C, H but also O, N and S) have been widely used to understand
80 physico-chemical processes associated with alteration of oceanic crust. Various questions
81 have been addressed such as volatile element speciation in altered rocks, chemical changes of
82 the rock and fluid during alteration, water-rock ratios, alteration temperature, or fluid source
83 and origin (e.g. Alt et al., 1986, 1996; Kawahata et al., 1987; Agrinier et al. 1995a, 1995b;
84 Charlou et al., 1996; Teagle et al., 1998; Bach et al., 2001; Busigny et al., 2005; Li et al.,
85 2007; Delacour et al., 2008).

86 Although it is largely accepted that volatile elements are incorporated into the oceanic
87 crust during alteration with seawater and/or hydrothermal fluids, the flux and speciation of
88 carbon involved in this transfer remains poorly known (e.g. Alt and Teagle, 1999; Staudigel,
89 2007; Delacour et al., 2008). Particularly, it is not known whether condensed carbon-rich
90 phases may form during seawater-crust interactions. The detailed study of altered rocks is a
91 key to better constrain the fate of C during alteration. Another interest for studying C
92 geochemical behavior and fluxes during alteration of oceanic crust is that CO₂-rich water
93 circulation into the crust may be considered as a natural analogue for CO₂ storage in basaltic
94 rocks. Indeed, fresh basalts forming the oceanic crust have low carbon concentration (given
95 an average value for glasses of 266 ppm CO₂; Matthey et al., 1984; Sakai et al., 1984; Pineau
96 and Javoy, 1994; Pineau et al., 2004; Aubaud et al., 2004), whereas seawater, responsible for
97 hydrothermal alteration of this crust, is relatively rich in CO₂ (2 mM in seawater; e.g. Bauer et
98 al., 1998). Water-rock interactions of such system are heavily explored from both experiments

99 and thermodynamic modelling, but studies on natural samples are still missing while they
100 could illustrate long-term reactions.

101 In the present contribution, we analyzed simultaneously concentration and isotopic
102 composition of C and H in altered basalts and gabbros cored in Ocean Drilling
103 Program/Integrated Ocean Drilling Program (ODP/IODP) Hole 1256D. Hole 1256D is quite
104 unique since it is the first drill hole to penetrate a continuous section into the deepest part of
105 the oceanic crust, i.e. the gabbroic section (Wilson et al., 2006). Accordingly, the present
106 study is the first to investigate chemical and isotopic variations of volatiles along a vertical
107 profile of in-situ oceanic crust from the lavas, through the sheeted dike complex, down to the
108 gabbros. The coupling approach between C and H isotopes is used to evaluate (i) qualitatively
109 their geochemical behavior during fluid-rock interactions and (ii) quantitatively constrain
110 their exchange fluxes between seawater and oceanic crust. It provides new insights into these
111 reactions as well as the nature of the carbon sources in bulk rocks from basaltic oceanic crust,
112 away from veins.

113

114 **2. GEOLOGICAL SETTING AND SAMPLING**

115

116 **2.1. Geological setting**

117

118 Ocean Drilling Program Hole 1256D (6°44.2'N, 91°56.1'W) is located on the eastern
119 flank of the East Pacific Rise (Figure 1). It lies on ~15 Ma oceanic lithosphere of the Cocos
120 plate under 3635 m of water in the Guatemala oceanic basin. ODP Hole 1256D has been
121 chosen in the hope to drill a complete section of oceanic crust because the crust at this site
122 was accreted at a superfast spreading rate (~200-220 mm/yr; Wilson, 1996) and the upper
123 gabbros were predicted to occur at relatively shallow depth (1100-1300 mbsf; Shipboard
124 Scientific Party, 2003). Hole 1256D was initiated in 2002 during Ocean Drilling Program Leg
125 206 (Shipboard Scientific Party, 2003). In 2005, Integrated Ocean Drilling Program
126 Expeditions 309 and 312 successfully deepened Hole 1256D, allowing for the first time to
127 reach gabbros along a continuous section of upper oceanic basement (Wilson et al., 2006).
128 ODP/IODP Hole 1256D reaches a depth of 1507.1 mbsf (meters below seafloor).

129

130 **2.2. Lithostratigraphy and alteration of Hole 1256D**

131

132 The lithostratigraphy and alteration of the crust drilled in Hole 1256D are detailed in
133 Teagle et al. (2006). They are summarized below. The lithostratigraphy of Hole 1256D shows
134 6 main units: (1) from 0 to 250 mbsf, a sediment blanket; (2) from 250 to 534 mbsf, a pile of
135 volcanics interpreted as being emplaced off-axis, composed of a ~100-m-thick sequence of
136 lava dominated by a single flow, up to 75 m thick (lava pond), overlying inflated lava flows
137 (Umino et al., 2000); (3) from 534 to 1004 mbsf, lavas that erupted at the ridge axis,
138 composed of sheet flows, massive flows and minor pillow lavas; (4) from 1004 to 1061 mbsf,
139 lithologic transition zone marked by subvertical intrusive contacts and mineralized breccias ;
140 (5) from 1061 to 1407 mbsf, relatively thin sheeted dike complex (some basalts have doleritic
141 textures, and many are cut by subvertical dikes with common strongly brecciated and
142 mineralized chilled margins); (6) from 1407 to 1507 mbsf, plutonic complex, composed of
143 two major bodies of gabbro, intrusive into dikes, with a 52-m-thick upper gabbro separated
144 from a 24-m thick lower gabbro by a 24-m screen of granoblastic dikes.

145 The main alteration features of the oceanic crust penetrated by Hole 1256D are
146 reported in Table 1 and can be summarized as follow. Similarly to other drill holes, the
147 volcanic section has been altered at low temperature (<150°C). Alteration by oxidizing
148 seawater is much less common than in Hole 504B (Alt, 1995, Alt et al., 2010) but similar to
149 other fast spreading crust (Alt and Teagle, 2003). The conditions were generally reducing (as
150 attested by smectite as the main secondary phase of the background alteration) except in
151 alteration halos adjacent to iron oxyhydroxides-bearing veins. There is a stepwise increase in
152 alteration grade downward from lavas into dikes, that are partially altered to chlorite and other
153 greenschist facies minerals at temperatures greater than ~250°C. Within the dikes the grade
154 and intensity of this hydrothermal alteration increase downward, with actinolite more
155 abundant than chlorite below 1300 mbsf and with hornblende present below 1350 mbsf,
156 indicating temperatures approaching ~400°C. The dikes have significantly lower porosity
157 (mostly 0.5–2%) than the volcanic section (2-10%). In the lower 60 m of the sheeted dikes
158 (1348 to 1407 mbsf), basalts are partially to completely recrystallized to distinctive
159 granoblastic textures resulting from contact metamorphism by underlying gabbroic intrusions
160 (Koepke et al., 2008; France et al., 2009). Both upper and lower gabbros are moderately to
161 highly altered by hydrothermal fluids to actinolitic hornblende, secondary plagioclase,
162 epidote, chlorite, prehnite, and laumontite. The intensity of hydrothermal alteration increases
163 with grain size and proximity to intrusive boundaries. Porosity increases stepwise downward
164 from lowermost dikes (0.1-0.3%) into the uppermost gabbro (1.0-2.2%), as the result of the

165 contact metamorphism of the granoblastic dikes and the strong hydrothermal alteration of the
166 uppermost gabbros. In the lower gabbros, porosity is then slightly lower (0.5-2%).

167

168 **2.3. Samples description**

169

170 In order to represent the various lithostratigraphic (lava, lava/dike transition, sheeted
171 dikes, gabbros) and alteration (low temperature, transition, hydrothermal alteration,
172 granoblastic) types, nineteen rock samples have been selected as regularly as possible
173 downhole (Table 1). We analyzed mostly background alteration samples, while veins and
174 alteration halos adjacent to veins were generally avoided. Only one carbonate-bearing vein
175 was analyzed in order to represent pure carbonate endmember (sample 149). In samples 16,
176 66 and 150, different parts were analyzed: one representing the background alteration
177 (samples 16b, 150b), the individual halo (66a) or background alteration associated with halo
178 (samples 16a, 66b, 150a).

179 Samples altered at low temperature (6, 16, 37, 52; Table 1) are composed mainly by
180 primary unaltered clinopyroxene and plagioclase. Secondary minerals occur in vesicles and
181 interstitial areas. Smectite is the dominant secondary mineral of the background rock, whereas
182 some amounts of Fe-oxyhydroxides and celadonite occur in an alteration halo (sample 16a)
183 adjacent to a Fe-oxyhydroxides + celadonite vein. Samples altered in conditions transitional
184 between low temperature and hydrothermal (66, 87, 102) present alteration features similar to
185 those described above, except the presence of minor amounts of hydroschorlomite in samples
186 66b and 102, and the presence of smectite/chlorite and vermiculite/chlorite mixtures instead
187 of smectite (Laverne et al. 2006). In samples affected by hydrothermal alteration (123 to 231)
188 primary phases are partly or completely replaced by greenschist facies minerals (Table 1).
189 Deeper samples (196, 207, 227) show the effects of both hydrothermal alteration and
190 granoblastic recrystallization. The latter is characterized by an assemblage of small rounded
191 crystals of plagioclase, clinopyroxene and orthopyroxene (Teagle et al., 2006; Koepke et al.,
192 2008). No carbonates were observed optically in the various studied samples, except in a vein
193 in sample 150 (but this vein was not analyzed, neither in 150a, nor in 150b) and in the vein of
194 sample 149. Chemical compositions of representative secondary minerals of samples
195 analyzed in this study are reported in Table 2.

196

197

198

199 3. ANALYTICAL METHOD

200

201 3.1. Step heating extraction

202

203 Step-heating experiments (Javoy and Pineau, 1991; Pineau and Javoy, 1994) have been
204 used for volatile extraction (CO₂ and H₂O) from silicate powders. Samples were crushed,
205 sieved to fraction <150 μm and homogenized. About 200 mg of powder were loaded in a
206 quartz tube and connected to a vacuum line. Step heating of the sample was obtained using a
207 vertical cylindrical furnace, with temperature stability of ±1-2°C. The main advantage of the
208 step heating technique is that it provides some means to differentiate various sources of
209 carbon, such as carbonate and reduced carbon phases that include non-carbonate carbon such
210 as graphite and various organic compounds *sensu stricto*. Hereafter we will use the term
211 “organic” for non-carbonate C. For every sample, the following procedure was used: after one
212 night degassing at room temperature, the samples were heated at 100°C during 1 hour to
213 remove surface contaminants (water and other adsorbed compounds). Then the volatiles were
214 extracted using 4 sequential steps: (1) heating at 250°C during 1 hour with 4 mbar partial
215 pressure of O₂ to oxidize some organic components, (2) then heating at 900°C during 1 hour
216 to extract CO₂ from carbonates. For this step, a little oxygen gas pressure (5×10⁻⁴ mbar) in the
217 line was provided to guarantee complete oxidation of CO also produced during
218 decarbonation. In our samples, which contain high water concentration, we noticed however
219 that organic compounds could also be extracted at this step because oxygen fugacity is raised.
220 (3) The samples were heated at 1170°C during 1 hour to ensure complete decarbonation (still
221 with 5×10⁻⁴ mbar of O₂) and (4) the oxygen pressure was then raised up to 4 mbar, while the
222 sample was maintained at 1170°C during 30 minutes, in order to oxidize all the reduced
223 carbon phases (e.g. graphite). For steps (2), (3) and (4), gases were extracted dynamically
224 using liquid nitrogen trap. After each step, gaseous CO₂ and H₂O were cryogenically
225 separated and collected. CO₂ was quantified by Baratron[®] or with a Toepler pressure gauge,
226 with a precision better than 5%. Mean blank values are 15, 33, 29 and 46 ppm CO₂ for the
227 250°C, 900°C, 1170°C without O₂ and 1170°C with O₂ steps, respectively.

228 Total accumulated water released during the four temperature steps, was converted to H₂
229 by reaction with hot uranium (800°C) and the H₂ yield was measured manometrically with a
230 Toepler pump. To report D/H ratios of water versus V-SMOW scale, the hot uranium has
231 been calibrated using a set of three waters calibrated versus SMOW and NBS30 biotite. For
232 sample 123, volatile extractions was performed twice in order to test reproducibility and

233 sample homogeneity (see Table 3). Blank measurements were carried out using the step
234 heating experimental protocol described above and corrections were made on all the data
235 reported in Table 3.

236

237 **3.2. H₃PO₄ acid attack**

238

239 In order to determine the carbonate content, approximately 200 mg of rock powder were
240 loaded in quartz tube and reacted under vacuum with 100% H₃PO₄ acid for 3 hours at 80°C to
241 extract CO₂ from carbonates (McCrea, 1950). CO₂ was then collected, purified to remove
242 trace of water and quantified by Baratron[®] pressure gauge, giving a precision better than 5%.
243 Blank measurements were carried out using the same experimental protocol and found to be
244 0.01 μmol CO₂ (i.e. about 3 ppm of CO₂ when compare to sample weight).

245

246 **3.3. Carbon and hydrogen isotope analyses**

247

248 The isotopic ratios have been measured on a Thermofisher Delta +XP and Mat 253.
249 They are reported in Table 3 using the conventional δ notation vs V-SMOW for hydrogen
250 isotopes and vs. PDB for carbon isotopes. For H₂, the H₃⁺ interference factor was estimated
251 before any hydrogen isotope measurements. The external repeatability of hydrogen isotopic
252 measurement is about ± 2 ‰ (2 σ). Repeated measurements of the international graphite
253 standard USGS24 gave $\delta^{13}\text{C}$ values of -15.96 ± 0.06 ‰ (2 σ ; n=10). This value is
254 indistinguishable from the recommended value (-15.99 ± 0.11 ‰ 2 σ ; Stichler, 1995). Thus,
255 the accuracy of the present procedure on $\delta^{13}\text{C}$ measurements is better than ± 0.1 ‰ (2 σ).

256

257

258 **4. RESULTS**

259

260 The amounts of water and carbon (as CO₂) extracted from the samples are listed in
261 Table 3, as well as the corresponding δD and $\delta^{13}\text{C}$. For carbon, the proportion extracted at
262 each of the four steps of the procedure is also displayed in Figure 2. Sample 123 was run
263 twice giving a good reproducibility for both carbon and water estimates via this step heating
264 methodology. In samples 16, 66 and 150, where three different alteration types were analyzed
265 (i.e. background alteration, individual halo and background alteration associated with halo),

266 no clear difference in terms of volatile concentrations or isotopic composition could be
267 evidenced. Sample 150, however, shows a significant enrichment in both water and CO₂
268 concentrations in the background alteration associated with halo (150a) relative to the
269 background alteration sample (150b).

270

271 **4.1 Carbon concentration and isotopic composition**

272

273 For the 250°C step, all the samples but two yield significant amount of CO₂ (i.e. 3 times
274 larger than the blank level); between 1 to 20 wt% of total CO₂ is recovered at this step. For
275 the 900°C step, all the samples yield significant amount of CO₂, which represents more than
276 60 % of total CO₂ (Figure 2). For the 1170°C step without O₂, a few samples yield significant
277 amount of CO₂, representing less than 20 % of total CO₂. At the 1170°C step with O₂, all the
278 samples yield CO₂ amount at the blank level, showing that essentially all the carbon of the
279 samples has been released by the 3 previous steps. Low temperature step (i.e. 250°C) may be
280 compromised by the addition of adsorbed atmospheric volatiles and/or organic contaminant
281 introduced after collection of the samples (Mattey et al., 1984; Sakai et al., 1984; Marty and
282 Zimmermann, 1999). However, the large variation in δ¹³C observed for this step may indicate
283 that this carbon is not derived from contamination (i.e. contamination may give similar δ¹³C
284 values for all samples). This point is still a matter of debate but has only a little consequence
285 in the case of Hole 1256D samples because the amount of CO₂ released at this step is always
286 less than 20 % of the total carbon of the sample. In the following discussion, the total carbon
287 concentration and isotopic composition will not include the 250°C step. Whether it is or not
288 included does not change significantly the value of the total amount of CO₂, nor its δ¹³C (see
289 Table 3).

290 Sample 149, which contains a vein of carbonate, yields a high amount of CO₂ (34254 ppm
291 CO₂) mainly released at the 900°C step. For all other samples, the total C content varies from
292 564 to 2823 ppm CO₂. The lowest C contents are observed for the deepest samples, where
293 alteration occurred at low water-rock ratios and higher temperatures (Figure 3 and Table 3).
294 The δ¹³C values show a large variation range between -26.6‰ to -10.9‰. The δ¹³C values are
295 slightly increasing with depth, with the most negative value closer to the surface (see Figure
296 3).

297 Six samples were reacted with H₃PO₄ (Table 4). In all samples except 149, carbonate
298 content was found to be very low (i.e. less than 200 ppm CO₂). This low amount of extracted

299 CO₂ limited our determination of C isotope composition to only one sample ($\delta^{13}\text{C} = -15.2\text{‰}$).
300 Sample 149, containing a carbonate vein, has a much higher carbon content and $\delta^{13}\text{C}$ value (-
301 4.5‰), similar to that of carbonate veins analyzed in shallow part of Hole 1256D (Coggon et
302 al., 2006). Generally carbonate content determined by acid attack is significantly smaller than
303 total carbon determined by the step-heating extraction, about 20 % or less, thus indicating that
304 non-carbonate carbon represents most of the carbon in these samples.

305

306 **4.2 Water concentration and hydrogen isotope composition**

307

308 The amount of water extracted from the samples also shows a large variation from 0.32
309 to 3 wt% (Table 3). The sheeted dike complex is significantly enriched in water (> 1.57 wt%)
310 relative to other parts of the section. The δD values range from -25.1 to -64.2 ‰, with a slight
311 increase with depth from the top of the volcanic section to the transition zone.

312

313 **5. DISCUSSION**

314

315 **5.1. Origin and speciation of carbon and hydrogen in the altered oceanic crust**

316

317 The origin and speciation of C and H in the oceanic crust are important questions
318 because it may help to (i) quantify exchange between seawater and oceanic lithosphere and
319 (ii) deduce the later fate of these elements in subduction environment. Carbon and hydrogen
320 in the altered oceanic crust may either be inherited from magmatic processes or be derived
321 from seawater-rock interaction.

322

323 *5.1.1. Carbon signature: a mixing between oxidized and reduced compounds*

324

325 Altered rocks from Hole 1256D have a bulk-rock carbon content from 564 to 2823
326 ppm CO₂ (average 1389 ppm CO₂) and $\delta^{13}\text{C}$ range from -10.9 to -26.6 ‰ with mean value of
327 $-22 \pm 2\text{‰}$ (1σ). In comparison, fresh basalt glasses from mid-ocean ridges have carbon
328 content from 44 to 613 ppm CO₂ (average 266 ppm CO₂; n=37) and $\delta^{13}\text{C}$ range from -12.2 to
329 -5.3 ‰, except two values at $\sim -24.5\text{‰}$ (Figure 4 and references therein). Accordingly, data
330 from Hole 1256D show an enrichment in C content with light isotopic signature relative to
331 fresh basalts. Contrasting with water-bearing phases that may be directly identified from

332 petrological observations on thin-section, the determination of carbon speciation is not
333 straightforward and mostly relies on C isotope analyses. In the oceanic crust, carbon can
334 occur in several phases either as oxidized or reduced compounds. Oxidized phases include
335 carbonates precipitating from dissolved inorganic carbon (DIC) in seawater (marine
336 carbonate); carbonates from microbially altered volcanic glasses (Furnes et al., 2001;
337 Banerjee et al., 2004) as well as CO₂ in vesicles and fluid inclusions (Pineau et al., 2004).
338 Reduced forms may include graphite, organic carbon (Tingle et al., 1991) and reduced carbon
339 gases such as methane trapped in bubbles and fluid inclusions (Charlou et al., 1996; Kelley
340 and Früh-Green, 2001). However in samples from Hole 1256D, fluid inclusions and bubbles
341 are rare, except for some quartz veins in the sheeted dikes and gabbros, and represent a
342 negligible amount of the total carbon at least in the analyzed samples. From an equilibrium
343 isotopic point of view, the reduced C phases (e.g. graphite, hydrocarbon) generally tend to be
344 depleted in the heavy isotope relative to the oxidized phases (carbonates and CO₂) (Bottinga,
345 1969; Des Marais et al., 1992). Oceanic crust carbonates occurring in veins usually have
346 carbon isotope composition between -3 and +3 ‰ (Coggon et al., 2006). Recently, however,
347 carbonates associated with microbially altered volcanic glasses have shown larger variations
348 with δ¹³C ranging from -16‰ up to +5‰ (Furnes et al., 2001). In contrast, reduced C phases
349 in oceanic rocks have lower δ¹³C around -25‰. For instance, Delacour et al. (2008) reported
350 δ¹³C values for total organic carbon (TOC) ranging from -28.9 to -21.5‰ in serpentinized
351 peridotites and gabbroic rocks from Lost City Hydrothermal System (Mid-Atlantic Ridge). In
352 these rocks, it was suggested that total carbon is a mixture of organic carbon and carbonates
353 of marine origin (Delacour et al., 2008). Likewise, the range of C isotope composition
354 observed in our samples (-14.9 to -26.6 ‰) can only be explained by the presence of reduced
355 C phase together with carbonate in relatively minor amounts. As the graphite stability field
356 (above 600°C; Libera and Gogotsi, 2001) was probably not reached, except for few samples
357 from the plutonic zone where hydrothermal metamorphism occurred at temperatures as high
358 as 900°-950°C (Koepke et al., 2008; Alt et al., 2010), it is not reasonable to invoke the
359 contribution of graphite in these samples. We derive consequently that most of carbon occurs
360 as “organic compounds” which have not necessarily a biogenic origin.

361 On the basis of the carbon isotope balance, an evaluation of the fraction of carbonate
362 (carb) and organic compound (OC) present in each sample can be calculated using:

363
$$\delta^{13}\text{C}_{\text{tot}} = n \delta^{13}\text{C}_{\text{OC}} + (1-n)\delta^{13}\text{C}_{\text{carb}} \quad (1)$$

364 where $\delta^{13}\text{C}_{\text{tot}}$ corresponds to the measured isotope composition of total carbon (as CO_2),
365 $\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{13}\text{C}_{\text{carb}}$ being the isotopic composition of organic compound and carbonate,
366 respectively; and n being the mole fraction of organic compound, i.e. $n = \text{C}_{\text{OC}}/\text{C}_{\text{tot}}$. In order to
367 estimate a value for n , and as $\delta^{13}\text{C}_{\text{tot}}$ is the only measured isotopic composition, we assigned
368 the most likely values to $\delta^{13}\text{C}_{\text{OC}}$ and $\delta^{13}\text{C}_{\text{carb}}$. For $\delta^{13}\text{C}_{\text{carb}}$ we considered two possible values:
369 (1) $\delta^{13}\text{C}_{\text{carb}} = -4.5\text{‰}$ which was measured using H_3PO_4 attack on a carbonate vein (sample
370 149) and (2) $\delta^{13}\text{C}_{\text{carb}} = 0.4\text{‰}$, the average value obtained by Coggon et al. (2006) on 37
371 carbonates veins from the same drilling hole. For $\delta^{13}\text{C}_{\text{OC}}$, we considered the lowest value
372 measured in the present sample set (-26.6‰). This value was also confirmed after analysis by
373 step heating on sample 123 which was previously cleaned with HCl to remove carbonates. In
374 this case, CO_2 obtained only comes from organic compounds: a $\delta^{13}\text{C}$ value of -25.7‰ was
375 measured. Table 5 gives the mol fraction " n " of organic compound (i.e. $\text{C}_{\text{OC}}/\text{C}_{\text{tot}}$) calculated
376 for the two different carbonate end-members and $\delta^{13}\text{C}_{\text{OC}}$ of -26.6‰ . The $\text{C}_{\text{OC}}/\text{C}_{\text{tot}}$ ratio varies
377 from 0.47 to 1 (Table 5). Among all samples, only two (150a and 220) have as much
378 carbonates as organic compounds ($\text{C}_{\text{OC}}/\text{C}_{\text{tot}} \approx 0.5$). All other samples ($n=16$) have $\text{C}_{\text{OC}}/\text{C}_{\text{tot}}$
379 between 0.74 and 1, indicating that more than 74% of the total C occur as organic
380 compounds. This result using the isotope balance approach is consistent with the comparison
381 between the CO_2 yield after H_3PO_4 attack (Table 4) and that of the total carbon (Table 3).

382 In a recent study of serpentized peridotites and gabbroic rocks from Mid-Atlantic
383 Ridge, Delacour et al. (2008) interpreted reduced carbon as organic compounds mainly from
384 marine biogenic origin. Gas chromatography allowed the authors to identify saturated
385 hydrocarbons, mostly as n -alkanes ranging from C_{15} to C_{30} . The nature and origin of an
386 organic carbon is still an open question for samples from Hole 1256D. Several hypotheses can
387 be considered: (1) direct incorporation of dissolved organic carbon (DOC) from seawater into
388 altered basalts, (2) biotic reduction of dissolved inorganic carbon (DIC) from seawater, (3)
389 abiotic reduction of DIC from seawater via Fischer-Tropsch reactions, or (4) incorporation
390 and reduction of magmatic carbon dissolved in hydrothermal fluid.

391 These different scenarios can be tested if we determine the total amount of fluid
392 interacting with our rock samples (i.e. water-rock ratio) and assuming that all DIC and/or
393 DOC of the fluid is incorporated into the rock. The lavas from volcanic section interacted with
394 seawater solutions so we assume seawater O, Sr and DIC compositions are representative of
395 the fluid endmember. Using traditional methods based on Sr and O isotopes (e.g. Taylor,
396 1978; McCulloch et al., 1981) and database available for Hole 1256D (Harris et al., 2008), we

397 estimated the seawater-rock ratio of our samples to be lower than 5 for all samples. A very
398 good agreement between independent O and Sr methods was observed for this calculation.
399 Deep seawater DIC and DOC concentrations are respectively ~2400 and 40 μM (Bauer et al.,
400 1998; Hansel and Carlson, 1998). Considering deep seawater infiltration through the oceanic
401 crust, with a seawater-rock ratio of 5 and a total precipitation/fixation of C from fluid to the
402 rock, the gain of C to the rock would be ~2.4 ppm from DOC and ~144 ppm from DIC.
403 Because altered basalts from the volcanic section in ODP Hole 1256D show an increase in C
404 concentration of the order of 1000 ppm, we conclude that C provided to the rock from the
405 fluid does not derive dominantly from seawater (either as DOC or DIC). Another source of
406 carbon is required. Residual magmatic carbon, occurring as reduced carbon, is not expected to
407 be a significant source of C since it represents a maximum of ~200 ppm CO_2 (e.g. Pineau et
408 al., 2004). The most likely source is magmatic C degassing and diffusing through the crust
409 mixed with or dissolved into hydrothermal fluid. This hypothesis is supported by East Pacific
410 Rise hydrothermal fluids whose dissolved CO_2 (DIC) concentration can be as high as 200,000
411 μM and $\delta^{13}\text{C}_{\text{DIC}}$ similar to that of fresh MORBs ($\delta^{13}\text{C}$ between -1.9 to -7.9‰) interpreted to
412 be of magmatic origin (Charlou et al., 1996; Proskurowski et al., 2008). Comparatively, CH_4
413 concentrations in EPR hydrothermal fluids are much lower than CO_2 and can be neglected
414 (Charlou et al., 1996; Proskurowski et al., 2008). In the deep part of the crust, rocks (i.e. dikes
415 and gabbros) interacted with hydrothermal fluids, which are highly reacted seawater
416 solutions. The rocks and vent fluids integrate the effects of fluid-rock interaction over a range
417 of conditions, but an endmember calculation can be made using the Sr and O isotope
418 composition of hydrothermal vent fluids. The ratio $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{18}\text{O}$ value of hydrothermal
419 fluids released at ridge axis from East Pacific Rise are on average ~0.7041 and +1‰, with
420 limited range of variation (Shanks et al., 1995; Ravizza et al., 2001). Using these parameters
421 and the data for Hole 1256D (Harris et al., 2008), fluid-rock ratios lower than 4 are obtained
422 from O isotopes, while those obtained from Sr isotopes are between 6 and 200. The apparent
423 discrepancy between calculations from O and Sr may result from the temperature effect on O
424 isotope fractionation since it is not taken into consideration in the models (McCulloch et al.,
425 1981). Fluid-rock ratios calculated from Sr isotopes are likely more reliable because Sr does
426 not depend on temperature. Assuming that all the CO_2 dissolved in hydrothermal fluid
427 (200,000 μM ; Charlou et al., 1996; Proskurowski et al., 2008) is transferred to the rock
428 during alteration, the C concentration of the rock is increased by ~48,000 ppm for a
429 hydrothermal fluid-rock ratio of 200. This C concentration is 30 times higher than the one
430 required to explain the enrichment observed in our dike and gabbro samples, thus showing

431 that only a limited part of the total C is transferred from the fluid to the rock. In addition, the
432 total transfer of carbon from the hydrothermal fluid to the rock would generate a C phase with
433 $\delta^{13}\text{C}$ between -1.9 and -7.9 ‰ which is not the case since the samples $\delta^{13}\text{C}$ are all below -17
434 ‰. This contrast shows that a C isotope fractionation occurred. The invoked C fractionation
435 must be in favor of an enrichment of ^{12}C in the organic carbon, which conforms to the
436 theoretical partition of C isotope among oxidized and reduced carbon phases. To conclude,
437 while $\delta^{13}\text{C}$ values measured in our samples suggest that C occurs mostly as organic
438 compounds, a comparison between the C concentrations in our samples, seawater DIC and
439 DOC, and hydrothermal fluids suggests that CO_2 degassed from magmatic reservoirs is likely
440 the main source of CO_2 addition during alteration process. A reduction step of dissolved CO_2
441 is thus required, and can be either biologically mediated or not as will be discussed in part 5.3.

442

443

444 *5.1.2. Hydrogen signature: from magmatic to secondary phases*

445

446 Like for carbon, hydrogen in altered oceanic crust can be either derived from
447 magmatic source or seawater. A compilation of bulk hydrogen analyzes in fresh degassed
448 MORB glasses and phenocrysts show water content from 0.12 to 0.52 wt% (average of $0.25 \pm$
449 0.09 wt%, 1σ ; $n = 47$) and δD values from -51 to -102 ‰ (average of -72.3 ± 9.9 ‰, 1σ ; $n =$
450 47) (Figure 5; Craig and Lupton, 1976; Kyser and O'Neil, 1984; Pineau et al., 2004). Altered
451 rocks from Hole 1256D have water content and δD values higher than the range defined by
452 fresh MORB, with some overlaps for few samples (see Figure 5). This confirms that alteration
453 of upper oceanic crust increases water content of the rocks as observed previously (e.g.
454 Kawahata et al., 1987; Agrinier et al., 1995a, 1995b; Alt, 2003). The high δD values relative
455 to fresh MORB are similar to those observed in other sites of the oceanic crust (Kawahata et
456 al., 1987; Agrinier et al., 1995a, 1995b; Javoy and Fouillac, 1979). However, it must be noted
457 that other studies found δD values in the upper oceanic crust (i.e. volcanic section) lower than
458 those of fresh MORB, with δD down to -170‰ (Hoernes and Friedrichsen, 1978;
459 Friedrichsen and Hoernes, 1979; Friedrichsen, 1985; Alt, 2003). The apparent discrepancy
460 between these data may arise either from (i) analytical problems (e.g. incomplete and
461 fractionated H isotope extraction) or (ii) heterogeneity of the upper oceanic crust because
462 different mineral phases can carry variable isotope signatures. This point will need to be
463 clarified in a near future by separating and analyzing individual mineral phases.

464 In the rocks of the present study, water is added either as OH or H₂O in secondary
 465 minerals such as smectite, celadonite and Fe-oxyhydroxides at low temperature of alteration
 466 (T < 150°C), and chlorite, amphibole, epidote, prehnite and zeolite under hydrothermal
 467 alteration (T > 250°C). Water can also occur in fluid inclusions trapped in newly formed
 468 minerals (Vanko, 1988). However, petrological observation of the samples analyzed in the
 469 present study indicates that fluid inclusions represent a negligible amount of the total water.
 470 We can thus consider that water in samples from Hole 1256D should represent a mixing
 471 between inherited/primary magmatic water and secondary H-bearing minerals. In a δD-H₂O
 472 diagram (Figure 5), samples from Hole 1256D plot along a curved trend typical of a mixing
 473 relationship between two end-members. The first end-member can be identified as fresh
 474 MORB and the second one shows a range of δD between -20 and -40‰, with water content
 475 up to ~10 wt%, which corresponds typically to hydrous minerals. Petrological study of the
 476 present samples set indicates that OH or H₂O-bearing secondary minerals are on a first order
 477 smectite in the upper part of the section, then chlorite, and amphibole ± chlorite in the deeper
 478 part. At the temperatures of alteration (Table 1), hydrogen isotope fractionation between a
 479 fluid and these secondary minerals is around -30 ± 10 ‰ (Graham et al., 1984, 1987; Hyeong
 480 and Capuano, 2004; Capuano, 1992; Chacko et al., 2001). Assuming that the fluid has
 481 seawater H isotope composition (i.e. δD = 0‰), the secondary minerals should be
 482 characterized by δD values around -30 ± 10 ‰, similar to the δD values of the end-member
 483 deduced from Figure 5. This observation supports the hypothesis that hydrogen content and
 484 isotopic composition correspond to a mixing between a magmatic component and secondary
 485 H-bearing minerals. However, in the present contribution, we analyzed hydrogen content and
 486 isotopic composition in bulk rock and this hydrogen may not be derived only from H-bearing
 487 minerals. For instance, if organic compounds such as hydrocarbon are present, H linked to C
 488 can be released during step heating and analyzed in the bulk sample gas as well. The potential
 489 proportion of H derived from organic compounds can be estimated from the amount of C
 490 calculated using the model described above (see equation 1). The predominant types of
 491 hydrocarbons forming through alteration of oceanic crust are alkanes (Kelley and Früh-Green,
 492 1999; Charlou et al., 1996, 2000; Delacour et al., 2008) and are defined by the general
 493 formula C_nH_{2n+2}. Since C/H molar ratio of alkanes varies in a well-defined range from 0.25
 494 for methane to ~0.5 for heaviest alkanes, the concentration of H (in mol/g) derived from
 495 organic compounds can be calculated as:

$$496 \quad H_{OC} = \frac{C_{OC}}{(C/H)_{alkane}} = \frac{n \times C_{tot}}{(C/H)_{alkane}} \quad (2)$$

497 where C_{OC} is the organic C content (in mol/g), $(C/H)_{alkane}$ is the C/H molar ratio of alkanes,
498 n is the molar fraction of organic C, and C_{tot} is the total C concentration measured in the
499 sample (in mol/g). The molar fraction of H present as hydrocarbon can then be calculated
500 from,

$$501 \quad X_{(H)OC} = \frac{H_{OC}}{H_{tot}} \quad (3)$$

502 where H_{tot} is the total H concentration measured in the sample by bulk extraction. From
503 equation (1), (2) and (3), we have estimated the maximum molar fraction of H possibly
504 present in organic compounds. The results are given in Table 5. Samples in the deeper part
505 (depth > 1000 mbsf) all have H_{OC}/H_{tot} lower than 10%, indicating a negligible amount of H
506 derived from organic compounds. In contrast, samples from the shallowest part (< 1000 mbsf)
507 have H_{OC}/H_{tot} ratios higher than 10%, with values up to 33% (sample 16b). This larger
508 proportion of hydrocarbon is also compatible with the observed variation in the $\delta^{13}C$ values,
509 being more negative in the shallower part of the sections. This significant proportion of H
510 from organic compounds may partly explain the negative δD values measured in samples
511 from the shallowest part because hydrocarbons formed during oceanic crust alteration have
512 very negative δD values (i.e. < -123‰; Welhan and Lupton, 1987). A plot of the measured
513 δD values versus calculated H_{OC}/H_{tot} ratio (not shown) displays a rough negative trend, which
514 is not statistically significant ($r^2 = 0.433$). This indicates that negative δD values observed in
515 samples from Hole 1256D cannot be explained only by the contribution of hydrocarbons but
516 also require the presence of inherited magmatic component. To summarize, H extracted from
517 the present sample set is interpreted as a mixing between (1) OH/H₂O bearing minerals
518 formed by interaction with seawater, (2) H derived from secondary hydrocarbons (such as
519 alkanes) and (3) a residual primary magmatic component.

520

521 **5.2. Physico-chemical conditions and spatial distribution of oceanic crust alteration at** 522 **Hole 1256D**

523

524 Carbon and hydrogen contents and isotopic composition can be useful to reconstruct
525 the physico-chemical conditions of oceanic crust alteration at Hole 1256D. The dominance of
526 an organic carbon component over carbonates in the host rocks suggests a reducing
527 environment where the system was mostly buffered by the rock but not by a fluid during
528 alteration. Low water-rock ratio of the volcanic zone (lava pond + inflated flows + sheet and

529 massive flows) is also supported by the low degree of alteration (typically ~10%; Teagle et
530 al., 2006; Alt et al., 2010), as reflected herein by petrology and low water content (only
531 slightly higher than fresh MORB). In contrast, the transition zone and the sheeted dike
532 complex (from 1030 to 1330 mbsf) show significant enrichment in water, indicating a higher
533 degree of alteration (~40%; Teagle et al., 2006; Alt et al., 2010). This spatial distribution of
534 alteration is in good agreement with results from other geochemical studies (e.g. Sr, O and U),
535 showing contrasting behavior between moderately altered volcanic zone and highly altered
536 sheeted dike complex (Harris et al., 2008; Flynn et al., 2008). From U isotopes, ^{234}U - ^{238}U
537 disequilibria were used to determine the timing and extent of off-axis alteration at Hole
538 1256D (Flynn et al., 2008). While the volcanic zone was in isotopic equilibrium and indicates
539 early alteration (i.e. close to the ridge axis), significant ^{234}U excess in the sheeted dike
540 complex suggests later alteration (< 1.25Myr; Flynn et al., 2008). The low degree of alteration
541 of the volcanic zone may be explained by early emplacement of a very massive lava flow,
542 called lava pond (see depth profile in Figure 3), covering all other inflated and sheet flows.
543 This may have set a sealing roof that would have considerably reduced the exchanges of
544 fluids between oceanic crust and seawater, at least for the immediately underlying lavas.
545 Moreover, fast spreading crust is smooth and rapidly buried, limiting oxidation by seawater
546 for the 800 m thick lava sequence (Alt and Teagle, 2003; Alt et al., 2010).

547 The physico-chemical conditions can also be discussed from the variability of $\delta^{13}\text{C}$
548 with depth (Figure 3). While mean $\delta^{13}\text{C}$ value increases with depth down to the bottom of the
549 volcanic section, the total C concentration does not show any specific trend and, on average,
550 is constant. These two features can be explained by changes in the proportion of carbonates
551 versus organic compounds, with an increase of carbonates associated to a decrease of organic
552 compounds. The variation of the $C_{\text{OC}}/C_{\text{carb}}$ ratio could result either from (1) a variation of the
553 oxygen fugacity ($f\text{O}_2$), with more reducing conditions on the surface (coupled to more organic
554 compounds) and more oxidizing conditions at depth coupled to carbonates precipitation; or
555 (2) a variation of temperature. The first hypothesis is unlikely since progressive water-rock
556 interaction with depth leads to more reducing fluids. Thus, we suggest that the variation of the
557 $C_{\text{OC}}/C_{\text{carb}}$ ratio is mostly controlled by temperature. The increase of temperature from lavas to
558 dikes is well established qualitatively from petrological observation (this study) and
559 quantitatively from O isotope measurements (Alt et al., 2008; Alt et al., 2010).

560

561 **5.3. Microbial or abiotic synthesis of organic compounds?**

562

563 An important question concerns the origin of the organic compounds detected in
564 samples from Hole 1256D, and particularly whether they are formed through microbial or
565 abiotic reactions. While this question may not be completely solved from the present data,
566 part of the answer can be brought by simple observations. In basement samples from Hole
567 1256D, the temperature of alteration from the top of the volcanic section to bottom gabbroic
568 rocks covers a wide range from ~50 to 950°C, respectively (Table 1; see also Alt et al., 2010).
569 Microbial activity is known to be limited to temperature lower than ~120°C, with the upper
570 temperature border of life organisms being represented by hyperthermophilic bacteria and
571 archaea (e.g. Stetter, 2006). In oceanic crust, bioalteration textures are abundant mostly in a
572 temperature range from 20°C to 80°C, and may occur up to ~110°C (Furnes and Staudigel,
573 1999). For samples from Hole 1256D, the temperatures of alteration (Table 1) reached more
574 than 110°C at depth greater than 1000 mbsf, indicating that microbial activity is not expected
575 to be sustained in deeper levels (i.e. Transition Zone, Sheeted Dike Complex and Gabbros).
576 The organic compounds identified in the deep zones are thus produced abiotically. In contrast,
577 for the low temperature (<110°C) zones of the section, we cannot preclude the formation of
578 these compounds through a biological process. Notably, the $\delta^{13}\text{C}$ value of the organic
579 endmember (~ -28‰) is compatible with typical C isotope fractionation of living organism.
580 For instance, hydrocarbons in petroleum typically have $\delta^{13}\text{C}$ ranging from -25‰ to -35‰
581 (e.g. Yeh and Epstein, 1981; see Galimov, 2006 and references therein).

582 Because the organic compound formation seems to be abiotic, at least in the deep
583 section of the oceanic crust, it is important to explore in detail this mechanism and test
584 whether this hypothesis is realistic. Since the evidence of large amounts of H_2 and CH_4 in
585 deep-sea hydrothermal fluids, the abiotic synthesis of organic compounds, such as light
586 hydrocarbons, has been widely studied over the last decades (e.g. Charlou et al., 1998; Kelley
587 and Früh-Green, 1999). The principle for such reactions is that hydrothermal alterations of
588 Fe-rich rocks produces large amounts of H_2 from coupling the oxidation of Fe (II) into Fe(III)
589 to the reduction of water into H_2 . Such reaction is efficient in the case of peridotite
590 serpentinization, where olivine reacts with water to form serpentine + brucite + magnetite.
591 This leads the iron to be oxidized and precipitate as magnetite; while in the meantime H_2 is
592 formed from reduction of water. Trying to quantify the H_2 production during these reactions,
593 which is controlled by the partitioning of iron and its oxidation state during the
594 serpentinization process, is still not an easy task. Recent detailed studies of altered peridotites
595 (Klein et al., 2009) as well as numerical models (McCollom and Bach, 2009) have shown for
596 example the importance of several parameters such as temperature, water-rock ratio, silica

597 activity in the fluid as well as rock composition. Moreover, magmatic events might also be
598 responsible for high H₂ production such as shown by Lilley et al. (2003) at vent of the fast
599 spreading EPR 9°N. We can conclude that in the most favorable cases, low oxygen fugacities
600 are generated in these systems, leading to the possible reduction of CO₂ (or DIC) via a series
601 of reactions leading to formic acid (HCOOH), CO, CH₄ and longer chain hydrocarbons. The
602 most widely invoked mechanism, even if it is not the unique one, to interpret this abiotic
603 synthesis of organic compounds is the Fischer-Tropsch-type (FTT) reaction which strictly
604 speaking concerns only the formation of organic compounds from a gaseous mixture of CO
605 and H₂. Hydrothermal alteration of more silica-rich basaltic rocks generally produces less H₂
606 since it produces minerals (like chlorite, amphibole) whose structures accept Fe(II) which is
607 then less easily oxidized to Fe(III). Even if serpentinites appear to be unique in their capacity
608 to generate high H₂ abundances, water-basalt interaction can produce moderately to strongly
609 reducing conditions with H₂ concentrations in the range 0.05-1.7 mmol/kg (measured in deep-
610 sea hydrothermal fluids that interacted with hot basalts; Von Damm, 1995) to be compared
611 with 12-16 mmol/kg in ultramafic rocks (e.g. Charlou et al., 2002). Whether such H₂
612 concentration is high enough to induce reduction of carbon from magmatic CO₂ and produce,
613 partly or completely, the organic compounds precipitated in our samples or not can be tested
614 via thermodynamic and isotope composition considerations.

615 Shock and Schulte (1998) studied thermodynamic equilibrium involved during organic
616 synthesis in deep-sea hydrothermal systems and showed that for temperatures below 400°C,
617 the reaction:



619 is displaced to the right side, suggesting that fluids equilibrated at low temperatures are CH₄-
620 rich. This reaction can be compared with calculated hydrogen fugacities set by the FMQ
621 (fayalite-magnetite-quartz) and PPM (pyrite-pyrrhotite-magnetite) buffer which are the two
622 main mineral buffers in seawater-basalt systems depending upon depth (Shock, 1990). From
623 this comparison, it appears that for pyrrhotite-pyrite-magnetite buffered systems, CO₂
624 reduction into CH₄ will be efficient at T <250-300°C. Even if methane is the most
625 thermodynamically favored stable organic compound at these conditions, kinetic barriers
626 existing at these temperature allow the metastable synthesis of others organic compounds.
627 This is coherent with the experimental work of Rushdi and Simoneit (2001) which shown that
628 the maximum lipid yield during an aqueous Fischer-Tropsch-type reactions was the 150-
629 250°C temperature window. This is in good agreement with the present observation that the
630 C_{OC}/C_{tot} ratio in Hole 1256D samples is larger in the upper part of the volcanic section and

631 decreases with depth as temperature increases. From these observations, the following
632 scenario can be proposed. Fluid-rock interaction during heating of seawater will increase H₂
633 concentrations. As fluids approach high-temperature reaction zone in the deeper part of the
634 crust, increased reaction rates may supply additional H₂ to the system from reaction with
635 basalts while injection of CO₂-dominated magmatic gases will provide additional carbon.
636 When these CO₂- and H₂-charged high temperature fluids cool down either by conduction
637 and/or mixing with seawater during ascent to the seafloor at the spreading axis, or close to the
638 spreading axis, it induces a large thermodynamic drive for the production of organic
639 compounds through equation 4. Even if abiotic synthesis is thermodynamically favored in
640 deep-sea hydrothermal systems, there are however large kinetic barriers for these reactions to
641 occur at temperatures below 350°C (McCollom and Seewald, 2007). Numerous experimental
642 works studied the FTS reactions (for comprehensive reviews of FTS research see Anderson,
643 1984; Dry, 1981) and in particular the most suitable catalysts to enhance the reaction (e.g.
644 magnetite, metal Fe, Fe-Ni alloys, chromite). If we consider the only experiments performed
645 in aqueous solution, which are the most appropriate for interpreting natural systems, the
646 presence of a vapor phase, existing when large amounts of H₂ and CO₂ are produced, as well
647 as chromite, could be the factor that allows FTT reactions to proceed rapidly and to enhance
648 the formation of complex hydrocarbons species (McCollom and Seewald, 2007, Foustoukos
649 and Seyfried, 2004). To conclude, all the experimental works indicate that FTT reactions can
650 proceed rapidly in hydrothermal environments.

651 Another argument that can be used to discuss the origin of the newly formed organic
652 compounds is its isotopic composition, mainly $\delta^{13}\text{C}$ since no measurements of δD were done
653 in any experimental work. In their study, McCollom and Seewald (2006) measured the
654 isotope composition of each carbon compound formed during reduction of formic acid in the
655 presence of Fe powder at 250°C and 325 bar. They showed that the synthesized hydrocarbons
656 were significantly depleted in ^{13}C relative to the dissolved CO₂, with a fractionation of ~ 36
657 ‰. The present data allow us to estimate the C isotope fractionation between oxidized
658 magmatic C and organic compounds formed in altered oceanic crust. Assuming that the
659 lowest $\delta^{13}\text{C}$ value measured in our samples represents the C isotope composition of organic
660 compounds (i.e. -26.6 ‰) and that magmatic C has a $\delta^{13}\text{C}$ value around -5‰, then the
661 calculated fractionation is ~21‰. Even if there might be kinetic effects that make this reaction
662 non-equilibrium, the present data are of similar direction (i.e. hydrocarbon depletion in ^{13}C)
663 and order of magnitude than the experimental value of ~ 36 ‰. We thus conclude that, taking

664 into account all these uncertainties, the $\delta^{13}\text{C}$ values measured in samples from Hole 1256D
665 are compatible with a production of organic compounds by FT synthesis. An abiotic process
666 is necessary for the deeper part of the crust but, even if not required, we cannot rule out the
667 contribution of microbial activity at low-temperature in the shallow alteration zones.

668

669 **5.4. Implication for the global C geodynamic cycle**

670

671 In good agreement with previous studies (Staudigel et al., 1989; Alt and Teagle,
672 1999), samples from Hole 1256D illustrate that background alteration of oceanic crust
673 induces a carbon-enrichment in the rocks. Alt and Teagle (1999) showed that, with aging,
674 oceanic crust is progressively enriched in carbonates by successive steps of seawater-crust
675 alteration. In the present paper, we studied a young section of oceanic crust (~15 Ma) that
676 experienced limited seawater-rock interaction. We show that carbon in Hole 1256D mainly
677 occurs as reduced species, i.e. organic compounds. The source of this C is likely magmatic
678 CO_2 (i) degassed from the mantle at or near ridge axis, (ii) subsequently mixed with
679 hydrothermal fluids and (iii) reduced through fluid-crust interaction (see discussion above in
680 part 5.1.1).

681 Integrating the present results with previous data, we can propose the following global
682 model for C cycling during oceanic crust alteration (Figure 6). First, when oceanic crust is
683 formed at ridge axis, it experiences interaction with hydrothermal fluids enriched in magmatic
684 CO_2 . These physico-chemical conditions promote the reduction of magmatic C to CH_4 and
685 other organic compounds during ascent and cooling of the fluid. While CH_4 is transferred to
686 seafloor vents by fluid flow, heavy insoluble organic compounds are trapped into the crust. It
687 is worth noting that the reduction of magmatic CO_2 into organic compounds is only partial
688 compared to the flux of degassed magmatic C since $\delta^{13}\text{C}_{\text{oc}}$ measured in our samples are ~ -25
689 ‰. In the case of total reduction, $\delta^{13}\text{C}_{\text{oc}}$ would have been similar to magmatic C (i.e. $\delta^{13}\text{C} \sim -$
690 5‰), which is not observed. This is also in good agreement with C isotope composition of
691 CO_2 in hydrothermal fluids released in seafloor vents, which show $\delta^{13}\text{C}$ values
692 undistinguishable from magmatic CO_2 (Charlou et al., 1996; Kelley and Früh-Green, 1999)..
693 In a second step of alteration, when the crust moves away from the ridge axis, the influence of
694 the hydrothermal convection of hot fluids enriched in magmatic CO_2 rapidly decreases and
695 becomes negligible. The C input into the crust is then mainly controlled by late carbonate
696 precipitation from seawater bicarbonates mostly in the volcanic section, which remains

697 sufficiently permeable to support ongoing convection even in old crust. In contrast, sheeted
698 dikes and gabbros are less permeable and not affected anymore by hydrothermal fluid
699 convection since they are far away from the heating source (i.e. magma chamber; e.g. Alt et
700 al., 1986, Alt et al., 1996). With aging, the volcanic section may experience successive
701 seawater infiltrations that enhance carbonate precipitation. In this model of alteration, C
702 contained as organic compounds would be mainly derived from outgassed mantle CO₂, while
703 C present as carbonates would be dominantly derived from seawater (Figure 6). If this model
704 is true, the amount of C as organic compounds added to a section of oceanic crust should not
705 evolve from few million years-old to hundred million years. We thus anticipate that if organic
706 carbon is measured in other drill-holes from the oceanic crust, a significant amount of organic
707 component will be revealed. This amount will probably be independent of the age of the crust
708 and may show values similar to those measured in Hole 1256D samples, i.e. at the level of
709 one thousand ppm CO₂ if no biotic organic C is added over this long period of time. This will
710 need to be confirmed in future studies on samples from other drill-holes such as DSDP/ODP
711 504B, ODP 896 or 801, in which the rocks are more heavily altered than in Hole 1256D.

712 On the basis of hundreds of bulk rock analyses combined with vein carbonate data, Alt
713 and Teagle (1999) estimated the flux of total C (including carbonate and organic carbon)
714 uptake during alteration of oceanic crust. While this value is quite robust considering the high
715 amount of data and the wide variety of sites taken into consideration, no distinction was made
716 between C components, particularly whether C occurs as carbonate or organic carbon. The
717 present study of Hole 1256D provide an opportunity to estimate the concentrations and
718 isotope composition of these C bearing phases. Using the global model for C cycling
719 presented above, we can assume that the flux of total C uptake determine by Alt and Teagle
720 (1999) is composed by carbonates and organic carbon. While carbonate content will depend
721 on the age of the crust, organic carbon will be produced and trapped mainly close to the ridge
722 axis if coming from magmatic CO₂. For biogenic organic carbon, there exist indirect
723 evidences from S isotopes (Rouxel et al., 2008; Alt et al., 2003, 2007) that support long
724 lasting microbial activity in oceanic crust. This microbial activity might contribute to add
725 organic carbon. At the present time, the production rate of such biogenic process is not
726 known. Thus on first order, Hole 1256D is considered as representative of the mean oceanic
727 crust for its organic carbon content. For each main lithological unit of the altered oceanic
728 crust, we have calculated a mean organic carbon content from the results obtained on our
729 samples (Table 6). The mean carbonate contents were then calculated as the difference
730 between total C content from previous estimate (Alt and Teagle, 1999) and organic C content

731 determined herein. Table 6 shows that in the upper part of the crust (volcanic section and
732 transition zone), C budget is dominated by the carbonate, while in the lower part (sheeted
733 dikes and gabbros) organic compounds are preponderant. This finding supports our model for
734 C cycling, where organic C is added close to the ridge while carbonate is mainly provided to
735 the upper crust by later alteration. For the bulk crust, the depth-weighted average C contents
736 for carbonates and organic compounds are 0.17 and 0.04 wt% CO₂ respectively, giving a total
737 carbon content at ~0.21 wt% CO₂ (Alt and Teagle, 1999). From these average concentrations
738 for carbonate and organic carbon, we can calculate δ¹³C value of the mean altered oceanic
739 crust assuming that (i) carbonate δ¹³C are ~0.4 ‰ (average value for carbonates occurring in
740 veins measured by Coggon et al., 2006), and (ii) organic carbon δ¹³C is -26.6 ‰ (the most
741 negative value measured in our samples from Hole 1256). This gives a mean altered oceanic
742 crust with δ¹³C = -4.7‰, similar to the δ¹³C of the carbon degassed from the mantle at mid-
743 ocean ridges (Mattey et al., 1984; Sakai et al., 1984; Pineau and Javoy, 1994; Pineau et al.,
744 2004; Aubaud et al., 2004). Considering a crustal production rate of 6.0±0.8 × 10¹⁶ g/year
745 (Mottl, 2003) and the average total C content of Alt and Teagle (1999), the total flux of C
746 stored in altered oceanic crust is 2.9±0.4 × 10¹² molC/yr; part of it being due to the alteration
747 process, while another part is the initial magmatic carbon. This flux can be compared with the
748 flux of C degassed from the mantle by mid-ocean ridge (MOR) systems. The flux of C
749 degassed from the mantle has been controversial for more than 20 years and various estimates
750 range over one order of magnitude from ~2 × 10¹² to 2 × 10¹³ molC/yr (e.g. Javoy et al., 1982,
751 1983; Des Marais, 1985; Javoy and Pineau, 1991; Marty and Tolstikhin, 1998; Cartigny et al.,
752 2001; Cartigny et al., 2008). Accordingly, the flux of C uptake in the altered oceanic crust is
753 either lower (≈ 0.15) or similar (≈ 1.5) to the flux degassed from the MOR. Another important
754 question is how this flux compares to the fluxes of C buried in subduction zone by
755 sedimentary material and C outgassed from subduction-related volcanism. The amount of C
756 in sedimentary material buried in subduction zones (~8.9 × 10¹¹ molC/yr; Plank and
757 Langmuir, 1998) is 3 times lower than the C flux transferred by subducting altered oceanic
758 crust (2.9±0.4 × 10¹² molC/yr; Alt and Teagle, 1999; this study). Thus, the altered oceanic
759 crust is the main carrier of C within the subducting slab. This illustrates again the importance
760 to determine precisely in future studies C concentration and isotopic composition of the bulk
761 altered oceanic crust. Including sediments and altered oceanic crust, the total flux of C buried
762 in the subducting oceanic lithosphere (~3.8 × 10¹² molC/yr) is more than twice higher than the
763 flux of C outgassed from volcanic arc in subduction zones (~1.6 × 10¹² molC/yr; Hilton et al.,

764 2002). This suggests that more than 50% of the C buried in subduction zones may be recycled
765 to the deep mantle and not transferred back to the surface via arc volcanism. This conclusion
766 is in good agreement with thermodynamic calculation on the stability of C-bearing phases in
767 various subducting lithologies, i.e. metasediments and metabasalts, showing that C is very
768 stable in the solid phases (i.e. carbonate and graphite) under pressure-temperature conditions
769 representative of subduction environments (e.g. Kerrick and Connolly, 2001a, 2001b). The
770 only way to induce decarbonation is by leaching of the rock through large flux of fluid
771 infiltration (Kerrick and Connolly, 2001a, 2001b). It can be noted that such a conclusion is
772 also supported from experiments under high-pressure (HP) to ultra-high pressure (UHP)
773 experiments (Poli et al., 2009). An important remaining question is whether part of the
774 subducting C is lost in early stages of subduction zone before reaching the depth locus of
775 island arc magmatism (i.e. 90-100 km). Studies of metamorphic rocks in paleo-subduction
776 zones show that volatile elements can be strongly affected by metamorphic devolatilization
777 when the rock experiences high-temperature metamorphism (e.g. Bebout, 1995). However,
778 the study of metamorphic suites subducted along “cool” geothermal gradient (8°C/km),
779 typical of present day peripacific subduction zone environment, show that volatile and fluid-
780 mobile elements can be preserved down to >90km depth (Busigny et al., 2003). Accordingly,
781 current subduction of altered oceanic crust may represent a way for natural transfer of huge C
782 amount from the surface to the deep mantle.

783

784

785 6. CONCLUSION

786

787 In the present contribution, C and H abundances as well as $\delta^{13}\text{C}$ and δD values are
788 reported for 19 samples of 15Ma oceanic crust cored at ODP/IODP Hole 1256D (Leg 206,
789 Expeditions 309 and 312). Hole 1256D is quite unique since it is the first hole drilled through
790 lavas, sheeted dike complex and gabbros, thus representing the most complete section of
791 oceanic crust ever sampled. While the present samples correspond to background alteration
792 (i.e. neither veins nor alteration halos adjacent to veins), significant enrichments of C and H
793 relative to fresh basalts are observed. Hydrogen isotopes are interpreted as a mixing between
794 primary magmatic hydrogen and a secondary source that can be secondary hydrous minerals
795 and/or hydrogen from organic molecules such as hydrocarbon. Carbon isotopes are
796 interpreted as a mixing between organic compounds with $\delta^{13}\text{C} \sim -27\%$, and carbonates with
797 $\delta^{13}\text{C} \sim 0\%$. The light C isotope signature of the present samples (average $\sim -22 \pm 2\%$, 1σ)

798 points to a dominant contribution of the organic compounds relative to carbonates. This
799 finding is also supported by independent measurement of carbonate abundances.
800 Considerations about C concentrations in various geological components (i.e. fresh and
801 altered rocks, DIC and DOC in seawater, hydrothermal fluids) drive us to the conclusion that
802 magmatic CO₂ added to hydrothermal fluids is the main source of C ultimately transferred to
803 the altered oceanic crust while seawater DIC and DOC represent only a minor source of C.
804 Since C in samples from Hole 1256D mainly occurs as reduced organic compounds, a CO₂
805 origin implies a reduction step during alteration that can be either biologically mediated or
806 not. If the making of this reduced organic compounds is restricted to the vicinity of the ridge
807 where magmatic CO₂-rich and low oxygen fugacity (H₂-rich) fluids are flushed through the
808 oceanic crust, it is likely that during the aging of the oceanic crust the dominance of reduced
809 organic compounds decrease to the profit of carbonates which gets progressively more
810 concentrated due to seawater inputs at the top of the oceanic crust (Staudigel et al., 1981; Alt
811 and Teagle 1999). Analysis of other young and older oceanic crust sections for both reduced
812 and carbonate carbon are needed to test this proposal.

813

814

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816

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1150
1151

1151 **FIGURE CAPTIONS**

1152

1153 Fig. 1. Bathymetric map showing the location of ODP/IODP Hole 1256D in the Cocos Plate
1154 (modified after Shipboard Scientific Party, 2003). Location of DSDP/ODP Hole 504B is
1155 reported for comparison.

1156

1157 Fig. 2. Spectrum of CO₂ released by step-heating experiments for samples analyzed in this
1158 study. The various colour bands represent different conditions of extraction (250°C with O₂
1159 pressure, 900°C without O₂, 1170°C without O₂ and 1170°C with O₂). It shows that, for all
1160 samples, most of the CO₂ is released in the step at 900°C without O₂ pressure.

1161

1162 Fig. 3. Depth profiles of water (a) and CO₂ (c) contents, and hydrogen (b) and carbon (d)
1163 isotope compositions in samples from Hole 1256D. Sample numbers reported in Fig. 3c are
1164 taken from Table 3, and correspond to the core-section in Tables 1 and 2.

1165

1166 Fig. 4. Carbon isotope composition vs CO₂ content in altered basalts from Hole 1256D. Fresh
1167 basalt glasses from Atlantic and Pacific mid oceanic ridges are represented for comparison
1168 (data from Matthey et al., 1984; Sakai et al., 1984; Pineau and Javoy, 1994; Pineau et al., 2004;
1169 Aubaud et al., 2004), as well as serpentinites from Lost City Hydrothermal System, MAR
1170 (Delacour et al., 2008).

1171

1172 Fig. 5. Hydrogen isotope composition vs H₂O content in altered basalts from Hole 1256D in
1173 comparison with fresh basalt glasses from Atlantic and Pacific mid oceanic ridges (data from
1174 Craig and Lupton, 1976; Kyser and O'Neil, 1984; Pineau et al., 2004), as well as altered
1175 oceanic rocks from Hess Deep, EPR (Agrinier et al., 1995b).

1176

1177 Fig. 6. Model of alteration based on C isotopic composition. A two-step model is proposed:
1178 (a) close to ridge axis where hot CO₂-rich hydrothermal fluids interact with rocks, promoting
1179 reducing conditions and CH₄ and other organic compounds production. This reaction is
1180 attested by the very negative δ¹³C values (~ -26‰) measured in our samples. (b) when crust
1181 moves away from ridge axis, the influence of these hot fluids becomes negligible. Carbon is
1182 incorporated into the crust only through seawater infiltration and carbonate precipitation,
1183 forming veins in the upper part of the volcanic section.

1184

1185

Table 1. Petrological, mineralogical and alteration features of samples from this study (ODP/IODP Hole 1256D).

Core-section, Interval (cm)	Depth (mbsf)	Spl #	Alteration zone	Rock type	Alteration Type	Estimated T (°C)	Secondary minerals (vol%)
6R-2, 75-78	296.65	6	bgr alt	LP	low-T	50-100	phyl (7)
16R-1, 37-42	369.27	16a	bgr alt + h	ILF	low-T	50-100	sm (3), cel (1), Fe-oxhydr (3)
16R-1, 37-42	369.27	16b	bgr alt	ILF	low-T	50-100	sm (7)
37R-2, 119-121	502.79	37	bgr alt	ILF	low-T	50-100	sm (5)
52R-2, 23-28	602.43	52	bgr alt	L	low-T	50-100	sm (3)
66R-1, 14-17	710.54	66a	h	L	tr	50-100	Fe-oxhydr (4)
66R-1, 14-17	710.54	66b	bgr alt + h	L	tr	50-100	sm (2), cel (3), hsch (<1)
87R-2, 75-79	832.85	87	bgr alt	L	tr	50-100	sm/chl (10), hsch (<1)
102R-2, 1-4	927.99	102	bgr alt	L	tr	50-100	sm./chl (7)
123R-1, 20-25	1032.30	123	bgr alt	LTZ	hydr	110-250	sm./chl (4)
138R-2, 38-43	1105.83	138	bgr alt	SD	hydr	250-380	chl (7), tit (<1)
149R-1, 73-76	1157.60	149	vein	SD	hydr	250-380	amph(18), ep (10), anh (9), chl(4) qtz(4), zeol(>1), tit(1), cc(3), pyr(1)
150R-1, 26-29	1160.56	150a	bgr alt + h	SD	hydr	250-380	amph(12), alb(6), chl(2), tit(1)
150R-1, 26-29	1160.56	150b	bgr alt	SD	hydr	250-380	amph(6), alb(4), chl(2), tit(<1)
170R-1, 69-73	1252.49	170	bgr alt	SD	hydr	250-400	amph(5), chl(6), tit(<1)
189R-1, 58-61	1334.48	189	bgr alt	SD	hydr	250-400	amph(45), chl(2)
196R-1, 27-30	1363.97	196	bgr alt	gSD	grbl	300-480	amph(30)
207R-1, 0-4	1390.70	207	bgr alt	gSD	grbl	300-480	amph(40)
214R-2, 37-42	1412.72	214	bgr alt	G	hydr	300-480	amph(20), alb(7), chl(1), ep(1), prh(1)
220R-1, 48-52	1435.48	220	bgr alt	G	hydr	300-480	amph(20)
227R-2, 21-23	1470.21	227	bgr alt	gSD	grbl	300-480	amph(20)
231R-3, 0-7	1490.56	231	bgr alt	G	hydr	300-480	amph(25), chl(1)

Column 2: mbsf: meters below seafloor. Column 3: sample number used in this study. Column 4: alteration zones are either background alteration (bgr alt), background alteration associated with halo (bgr alt+h), individual halo (h) or vein. Column 5: LP: lava pond; ILF: inflated lava flows, L: ridge-axis lavas; LTZ: lithostratigraphic transition zone; SD: sheeted dike; gSD: granoblastic sheeted dike; G: gabbro. Column 6: low-T: low temperature; tr: transitional between low T and hydrothermal alteration; hydr: hydrothermal; grbl: granoblastic. Column 7: temperatures estimated from oxygen isotope and fluid inclusion studies (Alt et al., 2010). Column 8: the values in brackets indicate the proportion of secondary minerals estimated from thin sections; phyl: phyllosilicate (see details in Alt and Laverne, 2006); sm: smectite; cel: celadonite; Fe-oxhydr: iron oxyhydroxide, hsch: hydroschorlomite (see details in Laverne et al., 2006); sm/chl: interlayered or mixed layered smectite/chlorite; chl: chlorite; amp: amphibole; ab: albite; ep: epidote; tit: titanite; prh: prehnite; anh: anhydrite; zeol: zeolite; qtz: quartz; pyr: pyrite; cc: calcite.

Table 2. Representative EMP chemical analyses of secondary minerals of samples from this study (ODP/IODP Hole 1256D). Complementary analyses from other samples (74R-2, 77R-1 and 89R-1) are also given.

Analysis run	B14	B14	B14	B7	B13	B9	B14	B14	B15	B15	B14	B14
Analysis #	85	32	67	46	115	331	41	126	16	19	26	30
Hole	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D
Core-section	6R-2	37R-2	52R-2	74R-2	77R-1	89R-1	102R-2	123R-1	138R-2	138R-2	150R-1	150R-1
Interval (cm)	75-78	119-121	23-28	81-85	103-106	16-22	1-4	20-25	38-43	38-43	26-29	26-29
Mineral type	sm	sm	sm	sm	cel	sm	sm	chl	prh	chl	cc	chl
Mineral color	gr bwr	or	or	or		or	p brw					
SiO ₂	33.18	47.63	47.00	40.00	48.42	41.88	46.14	31.00	41.20	28.33	0.00	29.00
TiO ₂	0.05	0.35	0.16	0.06	0.03	0.00	0.17	0.00	0.00	0.06	0.00	0.00
Al ₂ O ₃	10.43	3.42	7.67	8.78	6.35	8.01	5.57	13.58	22.64	15.53	0.00	17.92
CaO	1.08	1.70	2.49	4.69	0.77	2.66	2.68	0.66	22.10	0.84	59.11	0.22
Na ₂ O	0.31	0.36	0.13	0.20	0.20	0.06	0.14	0.03	0.01	0.06	0.03	0.03
K ₂ O	0.15	0.35	0.23	0.10	6.93	0.14	0.17	0.04	0.00	0.00	0.00	0.00
FeO	33.17	23.37	17.86	20.53	17.56	12.55	19.81	26.25	6.66	25.70	0.02	19.37
MgO	7.88	9.51	12.75	12.51	5.32	18.12	13.06	14.68	2.36	12.39	0.01	21.39
MnO	0.32	0.17	0.01	0.04	0.09	0.07	0.07	0.40	0.06	0.28	0.01	0.26
P ₂ O ₅	0.02	0.00	0.04	0.00	0.02	0.05	0.00	0.02	0.01	0.00	0.05	0.00
Cl	0.01	0.08	0.05	0.07	0.29	0.10	0.02	0.05	0.00	0.03	0.01	0.01
F	0.19	0.00	0.05	0.00	0.00	0.04	0.00	0.03	0.06	0.00	0.00	0.01
ZnO	na	na	na	na	na	na	na	0.03	0.06	0.00	na	na
Cr ₂ O ₃	0.03	0.00	0.00	0.04	0.11	0.00	0.01	na	na	na	0.00	0.03
ZrO ₂	na	na	na	0.02	0.01	0.00	na	na	na	na	na	na
PbO	na	na	na	0.11	na	na	na	na	na	na	na	na
Total	86.83	86.94	88.44	87.17	86.09	83.69	87.84	86.75	95.15	83.24	59.24	88.23

sm: smectite-rich phyllosilicate; cel: celadonite-rich phyllosilicate; prh: prehnite; chl: chlorite; cc: calcite; ep: epidote; ab: albite; amp: amphibole; tit: titanite; phyll: phyllosilicate; tlc: talc; gr: green; brw: brown; or: orange; p: pale; int; na: not analyzed.

Table 2. (Continued).

Analysis run	B14	B14	B14	B14	B14	B14	B14	P6	B14	B15	B15	B15
Analysis #	27	22	176	170	167	164	205	37	210	33	67	45
Hole	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D	1256D
Core-section	150R-1	150R-1	170R-1	170R-1	170R-1	170R-1	207R-1	220R-1	220R-1	227R-2	231R-3	231R-3
Interval (cm)	26-29	26-29	69-73	69-73	69-73	69-73	0-4	48-52	48-52	21-28	0-7	0-7
Mineral type	ep	ab	chl	amp	ab	tit	amp	amp	phyll	amp	amp	sm
Mineral color									dk gr		gr	dk brw
SiO ₂	37.68	66.57	29.39	48.23	66.05	29.88	52.10	52.90	44.88	53.90	50.36	38.31
TiO ₂	0.08	0.00	0.04	0.09	0.00	36.77	0.11	0.20	0.05	0.46	0.34	0.04
Al ₂ O ₃	24.89	20.58	17.10	6.25	21.80	1.71	2.21	2.80	0.02	2.16	5.52	9.75
CaO	23.37	1.18	0.29	2.50	2.46	29.30	12.53	9.16	0.51	11.82	11.06	2.04
Na ₂ O	0.02	10.78	0.00	0.65	10.01	0.02	0.27	0.69	0.02	0.55	0.87	0.07
K ₂ O	0.00	0.11	0.03	0.00	0.00	0.00	0.00	0.07	0.01	0.02	0.05	0.06
FeO	10.91	0.07	20.79	27.33	0.08	1.45	16.74	15.14	14.22	12.45	17.04	23.59
MgO	0.23	0.01	19.42	11.72	0.00	0.00	13.53	16.64	29.17	16.43	13.11	13.07
MnO	0.38	0.00	0.15	0.42	0.01	0.00	0.38	0.32	0.16	0.19	0.30	0.09
P ₂ O ₅	0.17	0.00	0.01	0.00	0.00	0.15	0.00	0.00	0.01	0.00	0.00	0.03
Cl	0.01	0.01	0.01	0.07	0.00	0.01	0.03	0.12	0.11	0.10	0.13	0.02
F	0.00	-0.09	0.06	0.00	0.00	0.42	0.10	0.00	0.00	0.00	0.04	0.10
ZnO	na	na	0.02	na	na	0.04	0.00	0.02	na	0.04	0.02	na
Cr ₂ O ₃	0.00	0.00	na	0.03	0.00	na	na	0.00	0.00	na	na	0.00
ZrO ₂	na	na	na	na	na	na	na	na	na	na	na	na
PbO	na	na	na	na	na	na	na	0.00	na	na	na	na
Total	97.74	99.33	87.20	97.28	100.42	99.76	98.01	98.05	89.15	98.10	98.85	87.19

Table 3. Abundance and isotope composition of hydrogen and carbon extracted during step-heating technique from samples of the Site 1256 (Leg 206, Expeditions 309, 312).

Spl #	H ₂ O (wt.%)	δD (‰)	CO ₂ (ppm)				δ ¹³ C (‰)		
			250°C with O ₂	900°C without O ₂	1170°C without O ₂	1170°C with O ₂	Total	250°C (900+1170)°C	
6	0.58	-64.2	95	1429	222	L.b.	1746	-20.9	-25.0
16a	0.61	-57.2	188	955	126	L.b.	1269	-26.5	-26.6
16b	0.66	-53.6	261	2511	89	L.b.	2823	n.a	-25.4
37	0.32	-56.3	96	471	102	L.b.	784	-22.7	-23.7
52	0.34	-63.7	142	918	46	L.b.	1126	-21.0	n.a
66a	0.65	-46.9	22	1376	186	39	1643	-21.3	-22.6
66b	0.51	-51.5	162	1652	80	L.b.	1895	-24.6	-21.3
87	0.83	-36.4	121	1272	97	L.b.	1594	-17.2	-21.7
102	0.43	-40.6	162	570	63	79	874	-22.7	-22.0
123	1.75	n.a	364	1456	193	L.b.	2409	n.a	n.a
123	1.83	-42.5	170	1751	403	11	2335	-26.4	-23.6
138	1.65	-28.9	101	1626	140	37	1839	-26.3	-19.9
149	3	-40.4	611	20230	10515	2898	34254	n.a	-10.9
150a	2.14	-25.5	149	2410	61	L.b.	2629	-25.4	-14.9
150b	1.75	-38.8	70	848	64	L.b.	973	-24.3	n.a
170	1.57	-25.1	87	1106	48	9	1209	-27.5	n.a
189	1.65	-30.5	59	502	100	L.b.	644	-28.4	-22.4
196	0.79	-41.7	57	489	43	2	564	n.a	-22.7
207	0.87	-43.1	111	974	90	L.b.	1158	n.a	-20.9
214	0.89	-55.0	57	593	62	L.b.	676	n.a	-22.1
220	0.91	-35.2	55	812	66	L.b.	945	-30.4	-17.3
227	0.7	-47.1	20	690	70	12	775	-28.1	-23.0
231	0.83	-40.0	20	524	93	L.b.	652	-25.4	-21.9
Blank*			15	33	29	46			

n.a =non analyzed

L.b.= Less than blank.

* Average blank was expressed in ppm for each step by dividing blank amount (in μmol) by average sample weight (~200 mg)

Table 4. CO₂ extracted from carbonates after H₃PO₄ attack at 80°C.

Spl #	CO ₂ (μmol)	Total CO ₂ (ppm)	δ ¹³ C (‰)
16a	0.97	38	n.d.
16a	1.32	58	n.d.
37	0.2	7	n.d.
66a	0.61	26	n.d.
123	0.74	106	-15.2
149	83.9	18312	-4.5
220	2.6	161	n.d.

Table 5. Results of the modeling for C and H speciation in rocks from Hole 1256D (see main text for details).

Spl #	Depth (mbsf)	C_{OC}/C_{tot} ⁽¹⁾ (molar ratio)	C_{OC}/C_{tot} ⁽²⁾ (molar ratio)	C_{OC} ⁽³⁾ ($\mu\text{mol/g}$)	$(H_{OC})_{max}$ ⁽⁴⁾ ($\mu\text{mol/g}$)	$(H_{OC})_{min}$ ⁽⁵⁾ ($\mu\text{mol/g}$)	H_{OC}/H_{tot} ⁽⁶⁾ (molar ratio)
6	296.65	0.93	0.94	37.4	149.6	74.8	0.23
16a	369.27	1.00	1.00	28.8	115.4	57.7	0.17
16b	369.27	0.95	0.96	61.4	245.4	122.7	0.33
37	502.79	0.87	0.89	15.9	63.8	31.9	0.18
66a	710.54	0.82	0.85	31.9	127.4	63.7	0.18
66b	710.54	0.76	0.81	34.7	138.9	69.4	0.25
87	832.85	0.78	0.82	29.7	118.8	59.4	0.13
102	927.99	0.79	0.83	16.5	66.2	33.1	0.14
123	1032.30	0.86	0.89	47.2	188.8	94.4	0.09
138	1105.83	0.70	0.75	31.5	126.0	63.0	0.07
150a	1160.56	0.47	0.57	33.8	135.4	67.7	0.06
189	1334.48	0.81	0.85	12.4	49.5	24.8	0.03
196	1363.97	0.82	0.86	11.0	43.9	21.9	0.05
207	1390.70	0.74	0.79	20.8	83.2	41.6	0.09
214	1412.72	0.80	0.84	12.8	51.4	25.7	0.05
220	1435.48	0.58	0.66	14.1	56.4	28.2	0.06
227	1470.21	0.84	0.87	15.3	61.3	30.7	0.08
231	1490.56	0.78	0.82	12.2	48.7	24.4	0.05

(1) Fraction of organic carbon calculated assuming C corresponds to a mixing between carbonates with $\delta^{13}\text{C}=-4.5\text{‰}$ and organic carbon with $\delta^{13}\text{C}=-26.6\text{‰}$.

(2) Fraction of organic carbon calculated assuming C corresponds to a mixing between carbonates with $\delta^{13}\text{C}=+0.4\text{‰}$ and organic carbon with $\delta^{13}\text{C}=-26.6\text{‰}$.

(3) Organic C content calculated from C_{org}/C_{tot} ⁽²⁾ and measured CO_2 concentration in bulk rock (given in Table 3).

(4) Maximum H content contained in organic compounds calculated for C/H molar ratio in alkane of 0.25.

(5) Minimum H content contained in organic compounds calculated for C/H molar ratio in alkane of 0.5.

(6) Maximum molar fraction of H present in organic compounds calculated from $(H_{org})_{max}$.

Table 6. Average C content in altered oceanic crust

Lithological unit	Thickness (km)	CO ₂ wt%		
		C _{tot} ^a	C _{org} ^b	C _{carb} ^c
Volcanic Section	0.6	2.00	0.12	1.87
Transition Zone	0.2	0.58	0.17	0.43
Sheeted Dikes	1.2	0.07	0.07	0
Gabbros	5	0.02	0.02	0
Mean crust	7	0.21	0.04	0.17

^a C_{tot}: total carbon, including carbonates and organic compounds - data from Alt and Teagle (1999)

^b C_{org}: organic compounds - determined from the average in Hole 1256 samples, except for the gabbros where values of 0.02 was assumed from Alt and Teagle data (1999). This assumption relies on the high number of analyses from Alt and Teagle and the fact that organic carbon content cannot be higher than total carbon content.

^c C_{carb}: calculated from the difference C_{tot} - C_{org}

FIGURE 1

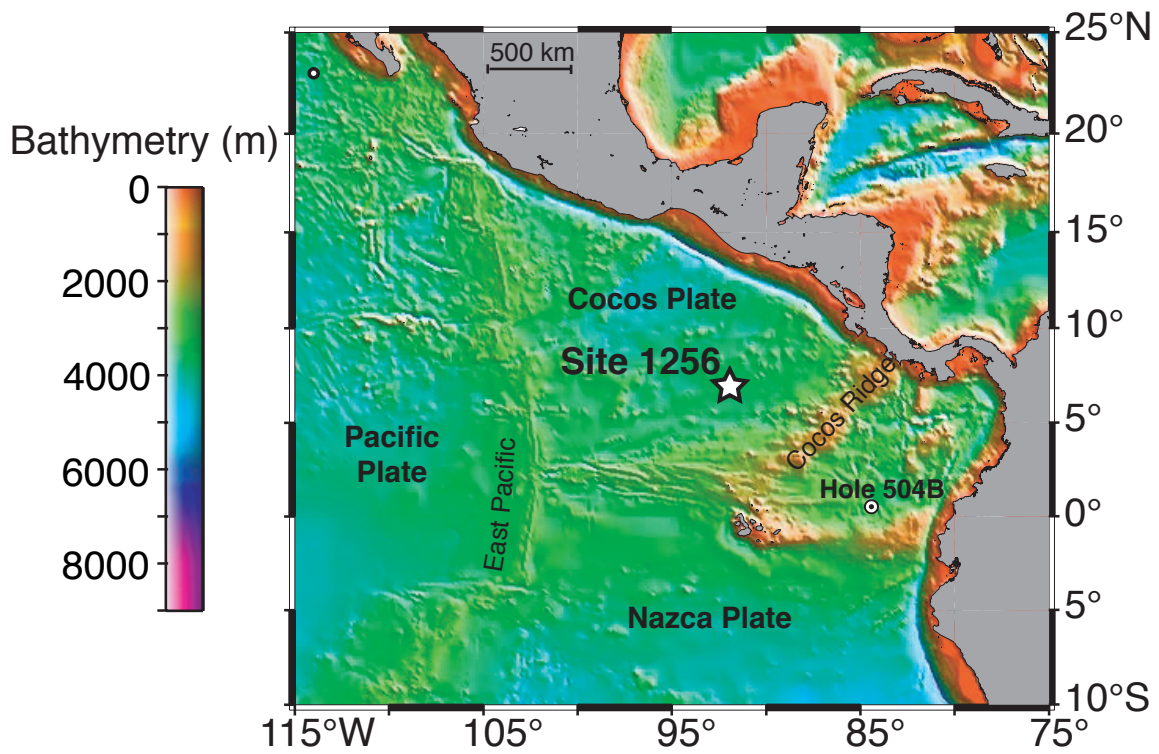


FIGURE 2

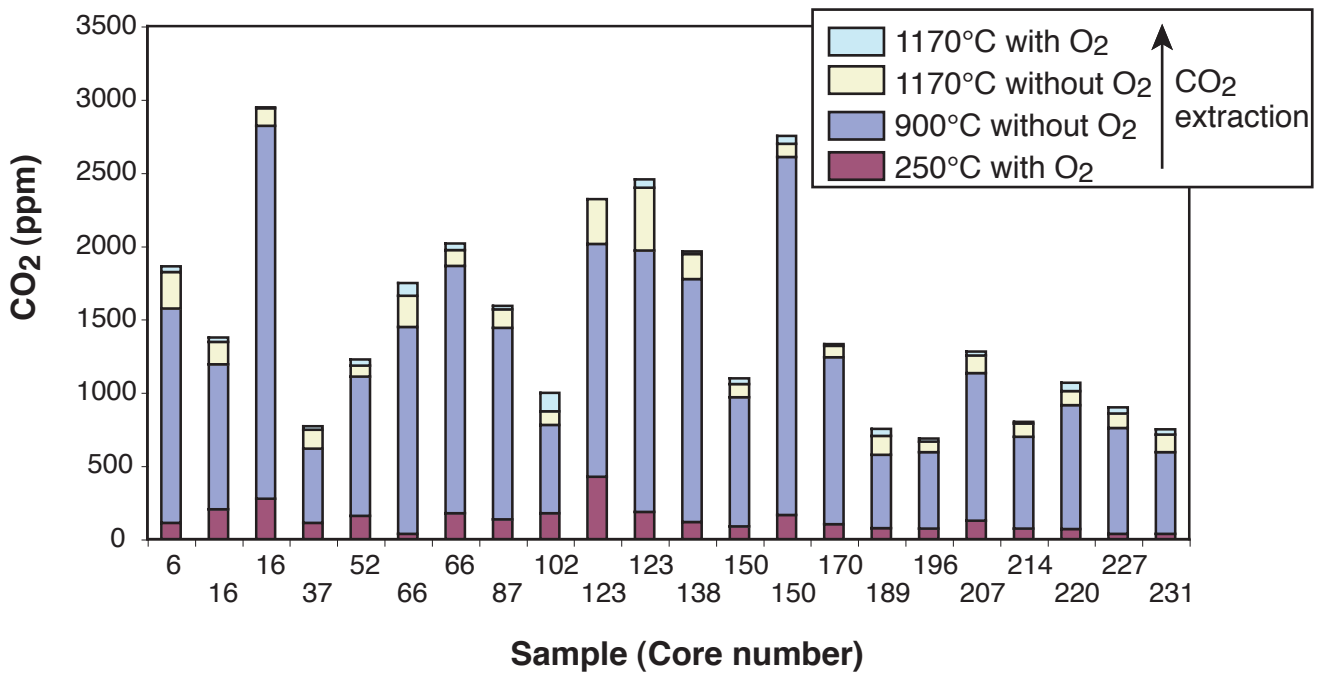


FIGURE 4

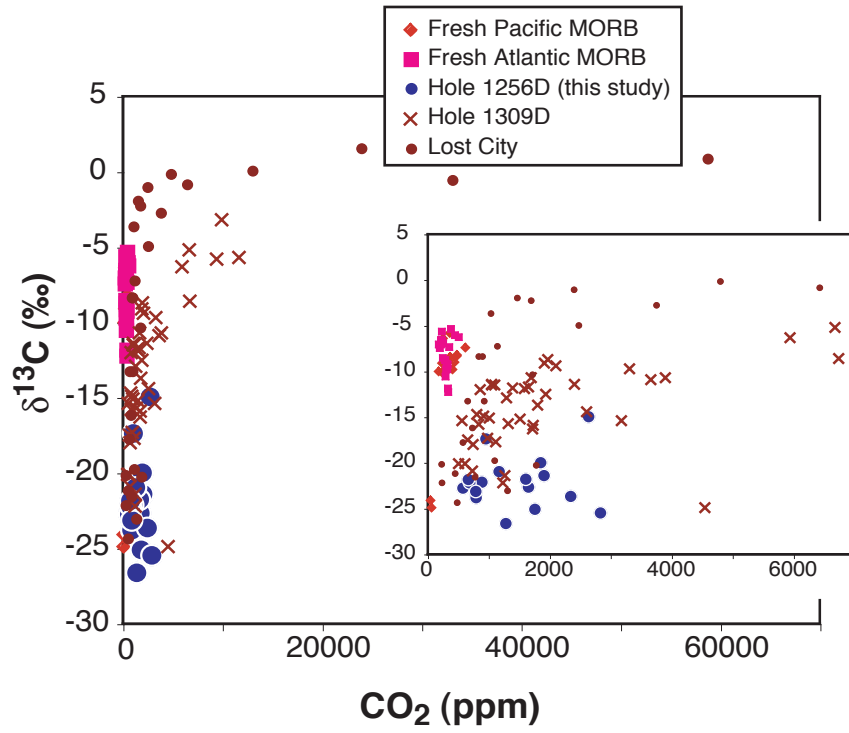


FIGURE 5

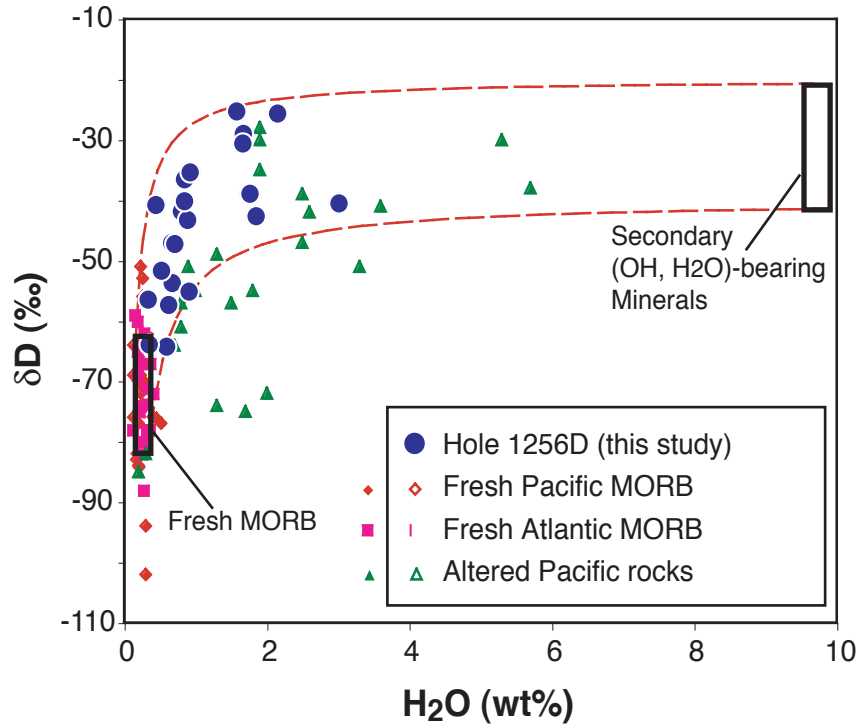


FIGURE 6

