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The hydrogen isotopic composition and water content of southern Pacific MORB: A reassessment of the D/H ratio of the depleted mantle reservoir

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Abstract:

In this paper, we re-investigate the isotopic composition of hydrogen in MORB and the possible effects of contamination on δD and water content. A suite of 40 N-MORB from the Pacific–Antarctic ridge, far from any hotspot, was analyzed for chlorine content by electron microprobe and for water content and δD with silica tubes. Cl concentrations (from 29 to 2400 ppm) indicate widespread contamination, more intense with faster spreading rates, while water contents (from 840 to 7800 ppm) are mainly controlled by igneous processes. δD values range from -76 to -48‰ , with an average value of -61‰ . The lack of correlation between Cl content and either H_2O/Ce or δD indicate that contamination has a negligible effect on δD for our samples, which is therefore characteristic of the mantle below the Pacific–Antarctic ridge. We suggest that the 20‰ lower δD value reported for the North Pacific and North Atlantic is highly unlikely from geodynamical arguments. We propose that the convecting mantle is characterized by a δD of $-60 \pm 5\text{‰}$, as supported by the most recent data from North Atlantic N-MORB.

Highlights

► A suite of 40 MORB was analyzed for δD , water and Cl content. ► Degassing and contamination have negligible effect on D/H. ► Average δD is $\sim -60\text{‰}$, 15‰ higher than earlier studies. ► High regional D are unlikely, analytical artifacts may be responsible. ► We propose an updated value for mantle D/H.

Keywords: hydrogen isotopes ; mantle geochemistry ; mantle water

1. Introduction

Based on the pioneer work of Kyser and O’Neil (1984), the isotopic composition of hydrogen in the convective mantle is commonly assumed to be characterized by a δD of $-80 \pm 10\%$ (compared to SMOW). The D/H variations were attributed to secondary processes, especially contamination by seawater and seawater-derived fluids, both with higher δD than the mantle. Hence, in any given area, the value most likely to characterize mantle hydrogen would be the lowest observed, typically -80% . Several studies (Poreda et al., 1986; Kingsley et al., 2002; Pineau et al., 2004) have however since shown co variations between δD -values (ranging from -80 to -40%) and tracers of mantle source heterogeneities (either ratios of rare-earth elements or Pb isotopes), demonstrating that source heterogeneity rather than contamination is the main factor controlling the variations of δD and H_2O in MORB, OIB and seamount chain basalts. This is also consistent with studies of water to light rare earth element ratios of similar incompatibilities (Michael, 1995; Kent et al., 1999b; Danyushevsky et al., 2000; Le Roux et al., 2006), which showed that MORB H_2O/Ce (or $/La$) are regionally homogeneous and characteristic of the local MORB mantle source. How δD -values may vary remain however typically unaddressed (except for Kingsley et al. (2002)). Moreover, a recent study has shown that extracting water by induction heating of basaltic glasses in a Pt-crucible (which was the preferred method in the 80’s, Kyser and O’Neil (1984)) can lower the measured δD by more than 10% (Clog et al., 2012). It further illustrates the need to re-evaluate the hydrogen isotopic composition of the mantle and its variability.

In the present study we reinvestigate the current consensus that the δD -

26 value of the MORB mantle is equal to -80% and propose that a value of
27 $\approx -60\%$ is more appropriate.

28 **2. Samples locality background and analytical techniques**

29 The Pacific-Antarctic ridge is ideal to re-investigate the D/H isotope com-
30 position of the depleted upper mantle. Two large supersegments (from 65
31 to 56°S and from 52 to 41°S , sampled respectively by the French missions
32 PACANTARCTIC 1 (1996) and 2 (2005)) present MORB compositions char-
33 acterizing a rather homogeneous mantle devoid of hotspot influence (see
34 Vlastélic et al. (2000) for the southern one ; Moreira et al. (2008) and Hamelin
35 et al. (2010) for the northern one). They are separated by a region with sev-
36 eral fracture zones which record interactions with the Louisville hotspot, as
37 illustrated by the greater variability of MORB compositions in radiogenic
38 isotope ratios (Castillo et al., 1998; Géli et al., 1998; Vlastélic et al., 1998).
39 Spectral analysis of the variations in isotopic compositions of Pb, Sr and Nd
40 along the Pacific-Antarctic and East-Pacific ridges showed that the compo-
41 sition of MORB from those supersegments reflects subtle variations within
42 the range of N-MORB compositions, consistent with a gradual greater con-
43 tribution of the HIMU component northwards (Hamelin et al., 2011).

44 Except for helium analyses (Moreira et al., 2008; Hamelin et al., 2011),
45 which show homogeneous isotopic composition typical of the depleted man-
46 tle ($R/R_a = 7.29 \pm 0.19$), there has been no study of volatile elements in this
47 region. Moreira et al. (2008) also noted limited variations and in particu-
48 lar that the northern supersegment is the most homogeneous ridge portion
49 studied with respect to He isotopic compositions.

50 The variations in structure and spreading rate in this area are also of
51 importance. The spreading rate increases northwards, from 54 mm/yr at
52 70°S to 111 mm/yr at 40°S (DeMets et al., 1990) and is associated with a
53 change in the structure of the ridge in the southern supersegment, from a cen-
54 tral valley typical of slow-spreading ridges to a central dome typical of faster
55 ridges. As noted by Vlastélic et al. (2000), the morphology appears to be pri-
56 marily controlled by the spreading rate, rather than by the potential mantle
57 temperature. On the whole northern supersegment, the structure is typical
58 of a fast-spreading ridge (Klingelhoefer et al., 2006; Hamelin et al., 2010).
59 Faster ridges have typically more important and widespread hydrothermal
60 circulation, leading to a more pronounced chlorine contamination (Michael
61 and Cornell, 1998; Bonifacie et al., 2008). Therefore, for water studies, the
62 structure of the ridge could also be of importance, particularly in assessing
63 the effect of contamination of seawater derived-fluids on δD -values.

64 *2.1. Sample suite*

65 All samples in this study are glassy rims of pillow lavas dredged at the
66 axis of the ridge, at depths between 1500 and 2800 meters below sea level,
67 except PAC1CV07 which was dredged on an off-axis seamount (figure 1).

68 Forty basalts were analyzed for water and chlorine contents, and for δD .
69 All the samples are N-MORB ($La/Sm_N < 1$, where $_N$ marks normalization
70 to the primitive mantle, McDonough and Sun (1995)), with a slightly higher
71 alkali content for samples collected near the Menard Transform Fault Frac-
72 ture (samples PAC2 DR7 and PAC2 DR20) due to greater extents of crystal
73 fractionation. Most samples were previously analyzed for their compositions
74 in major ($n = 37$), trace ($n = 35$) and radiogenic (Sr, Nd, Pb) elements iso-

75 topic compositions ($n = 37$) and some ($n = 16$) for helium concentrations and
76 isotopic compositions (tables 1 and 2, Vlastélic et al. (1999, 2000); Moreira
77 et al. (2008); Hamelin et al. (2010, 2011)). We report new cerium data mea-
78 sured by NAA (Neutron Activation Analysis) for the samples of the southern
79 supersegment, with the same technique as used for La and Sm by (Vlastélic
80 et al., 2000). Tables 3 and 4 report the δD , H_2O , Cl and Ce concentrations,
81 along with geographic coordinates and depth of collection.

82 *2.2. Water content and δD measurements*

83 The technique used in this study has been described in Clog et al. (2012)
84 and is summarized here. It is based on the original method described by
85 Vennemann and O’Neil (1993). Glass samples were crushed to shards of
86 100 to 250 μm , washed in distilled water, ultrasonically cleaned and dried.
87 Most of the plagioclase, olivine and altered grains were discarded using a
88 Frantz magnetic sorting apparatus. Remaining minerals and altered chips
89 were removed by careful handpicking under a binocular, to select only fresh
90 glass shards.

91 The mass of sample typically used was 350 mg for each analysis. The sam-
92 ple was introduced into a pre-cleaned sealed quartz tube (2 hours at 1150°C)
93 connected to a vacuum line and heated to 250°C for half an hour to eliminate
94 any adsorbed water. Then the samples were heated to 950°C for 45 minutes
95 under a pressure of 400 Pa of pure O_2 obtained by thermal decomposition of
96 CuO . The released CO_2 and H_2O (and other condensable gases such as SO_2)
97 are held in a cold trap at -196°C (liquid nitrogen) and separated by setting
98 the temperature at -140°C to keep only H_2O , while incondensable gases and
99 CO_2 are pumped out of the line. Water is then reduced on hot uranium fur-

100 nace held at 800°C to obtain H₂ (Bigeleisen et al., 1952). The amount of gas
101 is measured by manometry and it is then concentrated into a sampling tube
102 with a Toepler pump. The gas is analyzed with a dual-inlet mass spectrom-
103 eter (Delta Plus XP). The typical reproducibility on the measurements was
104 $\pm 5\%$ for water content and $\pm 3\%$ for δD (both 2σ , as established from the 10
105 analysis of the PAC2DR20-1-1 sample). Procedural blanks amount to ≈ 0.4
106 μmol . Re-heating a sample that had previously been heated to 900°C for half
107 an hour produced amounts of water equal to the value of our experimental
108 blanks, demonstrating that we reached quantitative water recovery.

109 The uranium furnace was calibrated with three standard waters : ROSS
110 ($\delta D = -114.9\%$), EPB-5 ($\delta D = -44.4\%$) and ORSMOW ($\delta D = +2.4\%$). These
111 in-house standards were obtained from the LSCE (Laboratoire des Sciences
112 du Climat et l'Environnement, Saclay, France) where they are regularly cali-
113 brated against IAEA standards (VSLAP, $\delta D = -428\%$ and VSMOW, $\delta D = 0\%$).
114 During the course of this study, we checked the accuracy of our analytical
115 protocol by regularly measuring the δD -value of the standard NBS-30. We
116 obtain an average value of $-63.4 \pm 2\%$ (2σ , $n=6$), in agreement, within ana-
117 lytical uncertainties, with the recommended value of $-65.7 \pm 0.6\%$ (2σ).

118 All samples were at least duplicated, reported values representing their
119 averages, and all were within $\pm 3\%$.

120 *2.3. Chlorine content measurements*

121 Fresh glass shards were mounted in epoxy and polished for analysis.
122 Chlorine concentrations were determined using electron microprobe with a
123 CAMECA SX50 at the CAMPARIS analytical facility in Paris, France, using
124 well-established techniques (e.g. Jambon et al., 1995). Analyses were made

125 using a 20 μm diameter, 500 nA electron beam intensity, at 30 kV accelera-
126 tion voltage and with a counting time of 60 s for chlorine and for backgrounds.
127 All four spectrometers were used simultaneously. Calibration was determined
128 using a scapolite standard (Cl content 4.04 wt%). Ten points were measured
129 for each sample along a transect, avoiding visible cracks or imperfection in the
130 polished surface. The detection limit is 13 ppm, as determined on an olivine
131 standard and the reproducibility in chlorine concentration range from 5 to
132 10 ppm (1σ).

133 **3. Results**

134 *3.1. Water concentrations*

135 Water concentrations range from 840 to 7800 ppm ($n = 40$), which is
136 within the typical range for MORB (2300_{-1600}^{+3500} ppm, PetDB database (Lehn-
137 ert et al., 2000) and Kyser and O’Neil (1984); Poreda et al. (1986); Jambon
138 and Zimmermann (1990); Pineau and Javoy (1994); Michael (1995); Dixon
139 et al. (2002); Pineau et al. (2004); Le Roux et al. (2006)). High water samples
140 are rare, with only four having more than 4000 ppm H_2O (tables 3 and 4,
141 figure 2b). $\text{H}_2\text{O}/\text{Ce}$ ratios range from 112 to 254 (figure 3a, 186 ± 30 on the
142 southern supersegment and 173 ± 15 on the northern supersegment), within
143 the range observed in MORB (from 100 to 350, Michael (1995)). The typical
144 range for Pacific MORB is 180 ± 30 (Michael, 1995; Le Roux et al., 2006),
145 and only samples south of 63°S present $\text{H}_2\text{O}/\text{Ce}$ ratios outside this range.
146 No systematic variation of water content or $\text{H}_2\text{O}/\text{Ce}$ with latitude was found
147 (figure 2).

148 *3.2. Hydrogen isotopic compositions*

149 δD range from -76 to -48‰ (tables 3 and 4, figure 2a), within the range of
150 previously studied MORB (from -92 to -44‰ (Kyser and O’Neil, 1984; Poreda
151 et al., 1986; Chaussidon et al., 1991; Pineau and Javoy, 1994; Kingsley et al.,
152 2002; Pineau et al., 2004; Hauri et al., 2006b; Cartigny et al., 2008)). The
153 δD values show no significant correlation to either water contents or water
154 to cerium ratios. It is however worth noting that more than >90% of the
155 N-MORB from the North Pacific and Atlantic previously published have δD
156 between -85 and -65 ‰ (Kyser and O’Neil, 1984; Pineau et al., 2004; Hauri
157 et al., 2006b; Cartigny et al., 2008). The values measured here are thus
158 more comparable to previously analyzed E-MORB from other oceanic basins
159 (Poreda et al., 1986; Kingsley et al., 2002), though N-MORB from the East
160 Pacific Rise near 22°N and the west rift of the Easter microplate have δD
161 close to -65‰ (Kingsley et al., 2002). There is also no correlation with Sr,
162 Nd, Hf Pb or He isotope data on these samples (figure 3b) or with the
163 La/Sm ratio.

164 *3.3. Chlorine concentrations*

165 Cl concentrations vary from 23 to 2000 ppm (figure 3c), within the MORB
166 range (from 10 (below the detection level) to more than 4000 ppm (Jambon
167 et al., 1995; Michael and Cornell, 1998; Soule et al., 2006), 90% of measured
168 MORB falling below 800 ppm (PetDB database)). On average, samples
169 from the northern supersegment, where the spreading rate is higher, have
170 higher Cl/K than samples from the southern supersegment (modes $0.32^{+0.58}_{-0.21}$
171 vs $0.16^{+0.22}_{-0.09}$, figure 3d). Potassium and chlorine having similar bulk partition

172 coefficient during partial melting and crystal fractionation (Michael and Cor-
173 nell, 1998), the variations are thus too large to depend only upon variations
174 in igneous processes, but reflect contamination or assimilation, as discussed
175 in the next section.

176 4. Discussion

177 4.1. Degassing

178 Contrary to CO₂ which can degas at high pressure, water is much more
179 soluble in silicate melts and typically remains under-saturated in typical
180 MORB settings (e.g., Dixon and Stolper, 1995; Jendrzejewski et al., 1996).
181 Kyser and O'Neil (1984) suggested that loss of hydrogen could occur either
182 as degassing of H₂ or CH₄. Subsequent studies have actually shown that
183 MORB are more oxydized than was originally thought (Bézos and Humler,
184 2005; Kelley and Cottrell, 2009), and therefore, H₂/CH₄ degassing is not sig-
185 nificant. Furthermore all samples present very low vesicularity (<1%), are
186 under-saturated with respect to water (figure 4), and can be calculated to be
187 in equilibrium with a gas phase containing less than 5% of water for all but
188 4 of the samples. The sample PAC1DR10-1 is in equilibrium with a vapor
189 phase containing more than 20% of water, and is thus the most likely to
190 have experienced some degassing. However, its δD is indistinguishable from
191 the δD of the sample PAC1DR10-2 which comes from the same dredge and
192 argues against any significant degassing-induced change in δD values. The
193 homogeneity of the H₂O/Ce ratios observed along the supersegments is also
194 a compelling argument against degassing. Degassing of water thus appears
195 negligible for all of our samples.

196 *4.2. Effects of contamination on volatile contents*

197 It should be first noted that previous studies established that variations
198 in major and trace elements in this sample suite are mostly due to crystal
199 fractionation (Vlastélic et al., 2000; Hamelin et al., 2010). This is also illus-
200 trated by the evolution of La and Ce content with MgO wt% (figure 5a and
201 b). In this section we investigate to what extent are non-igneous processes
202 responsible for variations in water and chlorine content.

203 Ratios of Cl and H₂O to elements of similar incompatibilities (typically
204 K, La or Ce) can be used to quantify the degree of interaction with brines or
205 hydrated rocks during ascent (e.g., Michael, 1995; Michael and Cornell, 1998).
206 This is because contamination of lavas by seawater-derived fluids results in
207 an increase in chlorine content, while water content appears comparatively
208 less (or not) affected (Michael and Cornell, 1998; Kent et al., 1999a,b; Dixon
209 and Clague, 2001; Soule et al., 2006).

210 Constraining the interaction with brines or hydrated rock on the basis of
211 the δD alone is difficult, as the isotopic composition of the brines deep in the
212 crust is unconstrained, while hydrated rocks can have δD similar to those
213 measured in our samples (e.g., Agrinier et al., 1995). It is worth noting that
214 experiments led to the suggestion that high-Cl brines should be depleted in D,
215 with $\Delta D_{vapor-brine}$ fractionation between 2 and 8‰ according to Berndt et al.
216 (1996), but the same study also highlighted the difficulty in trying to relate
217 the measured fractionation and the δD of outwards fluxes at hydrothermal
218 vents due to uncertainties in mixing processes, temperature of the reaction,
219 closed versus open system consideration and concurrent processes of inter-
220 action with the crustal rocks. In summary, from available studies, the D/H

221 ratio of brines is still difficult to anticipate. Yet, it should also be noted that
222 contamination by either brines or hydrothermally altered rocks cannot buffer
223 the δD of our samples as they are all under-saturated with respect to water.

224 In the following discussion, we therefore focus on the the H_2O/Ce and
225 Cl/K ratios.

226 *4.2.1. H_2O/Ce ratios*

227 Water content increases smoothly with decreasing MgO wt% (figure 5c),
228 suggesting that water content is primarily controlled by igneous processes
229 rather than contamination. We also observed that the H_2O/Ce ratios are
230 rather homogeneous on our sample suite. The average H_2O/Ce ratio is
231 $\approx 185 \pm 30$ on the southern supersegment and $\approx 175 \pm 15$ on the northern one,
232 which is, within this small range, the opposite of what would be expected
233 from the relationship between ridge structure and degree of assimilation
234 (Michael and Cornell, 1998). All this evidence argues against substantial
235 hydrogen contamination by either seawater-derived fluids or hydrated rocks
236 during ascent (see also figure 6).

237 *4.2.2. Cl/K ratios*

238 Contrary to water, the chlorine content variations cannot be explained
239 solely by crystal fractionation (figure 5d). We observe that the majority of
240 samples have incurred a greater extent of crystal fractionation ($MgO < 7.5$
241 wt.%) have Cl content much higher than the crystal fractionation trend,
242 which contrasts with samples where $MgO > 8.0$ wt.%. Cl/K ratios are also
243 higher in the northern supersegment (modes $0.32^{+0.58}_{-0.21}$ in the northern su-
244 persegment and $0.16^{+0.22}_{-0.09}$ in the southern supersegment, figure 3d), which

245 points to more intense contamination with an increasing spreading rate, as
246 has been proposed by Michael and Cornell (1998) and Bonifacie et al. (2008).
247 It should be noted that this difference is however mostly driven by a couple
248 of extremely Cl-enriched samples (PAC2 DR34-1 and PAC2 DR28-2).

249 A recent study (Kendrick et al., 2012), based on a global compilation
250 of Cl and K concentrations, has proposed that the average Cl/K of uncon-
251 taminated MORB is close to 0.08. When comparing to modes of 0.16 and
252 0.32 on respectively the southern and northern supersegments, this would
253 indicate that our samples are extensively contaminated with respect to Cl.
254 Conversely, the lowest Cl/K measured on our samples are, for both segments,
255 ≈ 0.03 , illustrating the non-uniformity of the contamination. This would im-
256 ply, for chlorine budget, that the details of the ascent and eruption scenarii
257 are at least of equal importance to the spreading rate. Lowest Cl/K were ob-
258 served in both cases where the magmatic activity is less vigorous : a near-axis
259 seamount in the south and a sample from the S2 segment, whose structure is
260 described as poorly defined (Hamelin et al., 2010) due to interaction with the
261 Menard Fracture Zone in the north. Assuming that the smallest Cl/K mea-
262 sured correspond to uncontaminated samples, we conclude that more than
263 80% of Cl comes from contamination in our sample suites (versus more than
264 50% of Cl from contamination if we use the average value of Kendrick et al.
265 (2012)).

266 The contrast between the behavior of water and chlorine suggests that
267 contamination in our sample suite is not due to assimilation of hydrated
268 wall-rock or contribution from seawater or diluted brines, but due to either
269 very concentrated brines or pure halite left in the crust by hydrothermal

270 circulation (figure 6). It should also be noted that samples with low Cl
271 content (<100 ppm, 12 samples) or low Cl/K (<1.6 , 12 samples) present a
272 range of δD from -76 to -51% , and an average δD of -63% . Those values are
273 close to those observed for the complete sample suite (δD from -75 to -48%
274 and $\bar{\delta D} \approx -61\%$). This is consistent with a very minor effect of contamination
275 on the D/H ratio of our samples.

276 *4.3. Incompatibility of water relative to La and Ce*

277 Although it is well described that the bulk partition coefficient of wa-
278 ter during mantle partial melting is close to Ce and La (Michael, 1995), the
279 rare-earth element whose behavior is closest to water actually depends on the
280 degree of enrichment of the source in incompatible elements (Danyushevsky
281 et al., 2000). In the extreme case of Macquarie Island, where the primitive,
282 weakly fractionated basalts have $(La/Sm)_N > 2$, it was recently proposed that
283 Pr was the element whose behavior was the most similar to water (Kamenet-
284 sky and Eggins, 2012), emphasizing the need to carefully choose the element
285 for normalization.

286 For our sample suite, the incompatibility of water is more closer to that of
287 Ce rather than of La, as illustrated on figure 7. The regression line defined by
288 our samples in $H_2O/Ce-Ce$ space is actually flatter (slope of -0.6 ± 0.7 , origin
289 190 ± 12) than the one in $H_2O/La-La$ space (slope -13 ± 9 , origin 624 ± 54).
290 This justifies the normalization to Ce rather than La chosen in the previous
291 section as well as in the rest of this article.

292 Considering the range of $(La/Sm)_N$ observed here (between 0.45 and
293 0.95), our results contrasts with those of Danyushevsky et al. (2000) which
294 suggested that La should be more appropriate. It should be noted that there

295 is no requirement for disagreement. Partition coefficient for individual min-
296 erals (olivine, garnet, pyroxene) are not similar between water and La/Ce
297 (Aubaud et al., 2004; Hauri et al., 2006a; Kohn, 2006; Grant et al., 2007).
298 Therefore source mineralogy affect the bulk partition coefficient for H₂O, La
299 or Ce, and as a matter of consequence, the preference for Ce over La in this
300 sample suite.

301 *4.4. Crystal fractionation and partial melting effects*

302 In the southernmost area, the H₂O/Ce ratio is more variable (standard
303 deviation of 50 south of the Saint-Exupery fracture zone versus standard de-
304 viation of 15 for the rest of the sample set, see also figure 3). This could mean
305 that the source region is heterogeneous at the scale of sampling (≈ 100 km be-
306 tween two samples). We also observe that the average MgO% is higher (≈ 8.1
307 versus ≈ 6.9). This is indicative of more primitive melts, and an alternative
308 model to heterogeneities in the source is that we observe un-mixed melting
309 products of an heterogeneous source, as proposed by Langmuir and Bender
310 (1984), and that northwards, those melts are pooled in magma chambers
311 where they differentiate before eruption.

312 We calculated the water content of the source by correcting to 8% of MgO
313 (Weaver and Langmuir, 1990; Kelley et al., 2006) and using a simple batch
314 melting model, assuming a constant Na content of the source. The results are
315 illustrated in figure 8, whose caption contains the details of the calculation.

316 For most ($>80\%$) of the samples, the calculated water content is in the
317 range 150-250 ppm. The obvious limitations of this method are the assumed
318 homogeneity of Na content and the variations of solidus temperature with
319 water content. A posteriori, the influence of the latter is negligible consid-

320 ering the limited range of calculated $\text{H}_2\text{O}_{\text{source}}$. The variations observed in
321 water content are thus consistent with a source containing 200 ± 50 ppm of
322 water with an extent of melting between 8 and 10%, followed by various
323 extents of crystal fractionation.

324 Despite the relative homogeneity of our sample suite, we discuss in the
325 next section the consequence of melting a heterogeneous mantle source in
326 terms of δD -variability.

327 *4.5. Hydrogen heterogeneities in the source*

328 As water behaves as a very incompatible element during igneous pro-
329 cesses ($D_{\text{peridotite-melt}} \approx 0.012$ Aubaud et al., 2004; Kohn, 2006; Grant et al.,
330 2007), hydrogen isotopes are not significantly fractionated during melting at
331 ridges (where the extent of melting is typically higher than 5%, Asimow and
332 Langmuir (2003)) and crystal fractionation, even though the isotopic frac-
333 tionation factor of H between liquid and silicate minerals is higher than 10‰
334 at magmatic temperatures (Dobson et al., 1989; Bell and Ihinger, 2000). Our
335 data shows that the mantle is not perfectly homogeneous for water concen-
336 trations and δD , but north of the Saint-Exupery fracture zone, we mainly
337 observe homogeneous compositions, suggesting that the characteristic size
338 of the heterogeneities is close to the characteristic mixing length along the
339 ridge.

340 As illustrated by the $(\text{La}/\text{Sm})_{\text{N}}$ ratio, our samples fall within the field
341 of N-MORB. The gradual increase of $^{206}\text{Pb}/^{204}\text{Pb}$ ratio northwards illus-
342 trates the slightly higher amount of HIMU-type component in the source
343 (Hamelin et al., 2010). Despite the two samples with the lowest $^{206}\text{Pb}/^{204}\text{Pb}$
344 (PAC1CV04 and PAC1DR12-1) also display low δD , there is no correlation

345 between δD and $(La/Sm)_N$ or $^{206}Pb/^{204}Pb$ (figure 9), so no enriched source
346 with high $(La/Sm)_N$, δD and H_2O content can be inferred, in contrast with
347 observations near Iceland (Poreda et al., 1986) or along the Salas y Gomez
348 seamount chain (Kingsley et al., 2002). This suggests that the heterogene-
349 ity in water contents and δD relates to a distinct process, and the lack of
350 relationship with Pb-isotopes (seen as a tracer for a HIMU-type component)
351 precludes the use of the δD variability to constrain the D/H ratio of the
352 HIMU component.

353 The only apparent relationship is a negative correlation between δD and
354 TiO_2/H_2O -ratios (figure 9), driven by two samples from the area south of
355 the Saint Exupery fracture zone (PAC1CV04 and PAC1CV07). These two
356 samples have the lowest H_2O/Ce of the sample suite (134 and 112), the
357 lowest calculated H_2O_{source} and low δD (-76.6 and -69.6‰). Interestingly,
358 their H_2O/TiO_2 and K_2O/TiO_2 are comparable to samples from the Siqueiros
359 fracture zone (Saal et al., 2002, among others). These last two characteristics
360 have been interpreted as resulting from a prior melting event of the source
361 (Perfit et al., 1996; Danyushevsky et al., 2000; Cartigny et al., 2008), and
362 their δD would suggest that the hydrogen left in the residue after partial
363 melting is depleted in D. However, the apparent correlation is not significant
364 if those two samples are not taken into account, as might be expected if the
365 high TiO_2/H_2O ratios reflect a specific process.

366 Despite having little evidence for significant variability in major and trace
367 elements, we investigate the possibility that the ranges in water content and
368 δD observed reflect a heterogeneous source, containing two distinct compo-
369 nents. Without making any a priori hypothesis on the characteristic size

370 or shape of the heterogeneities, we expect that for higher spreading rates,
371 the more abundant production of basaltic liquids and the existence of more
372 permanent magma chambers will lead to more homogeneous lavas erupted
373 on the sea floor. If different water contents are assumed, the most water-rich
374 component would be more fusible, and for low amounts of melting a second
375 episode of melting would be necessary to express the characteristic water
376 content and δD of the more refractory component. Samples PAC1CV04,
377 CV06 and CV07 present low δD and low calculated water in the source, so
378 this explanation looks promising, but we would expect samples with melting
379 rate scaling to water content of the source. Yet the calculated melting rates
380 range for a homogeneous mantle (with respect to major elements) is limited,
381 only from 8 to 11% (figure 8), and previous studies do not suggest a major
382 element concentration contrast in the southernmost section of the sampling
383 area.

384 The size of possible heterogeneities is limited by the diffusion rate of
385 hydrogen in the conditions of the upper mantle. For the fast axis of olivines
386 at mantle temperatures, it is of the order of $10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$ (Hercule and Ingrin,
387 1999; Ingrin, 2006). For residence times of 10^8 years, heterogeneities must be
388 larger than 5 km, three orders of magnitude greater than the heterogeneities
389 limit for trace elements (about 2 m, Allègre and Turcotte (1986)). This 5
390 km figure is smaller than the scale of sampling, although fracture zones can
391 also play the role of barriers between different mantle domains.

392 So far, the lack of relationship between $\text{H}_2\text{O}/\text{Ce}$, δD and Pb isotopes sug-
393 gest that for this sample suite, the variability observed cannot be accounted
394 for by the presence of an uniquely defined component richer in water and/or

395 D and with a distinct $^{206}\text{Pb}/^{204}\text{Pb}$.

396 *4.6. A reference zone for the study of the N-MORB source*

397 Previous studies on the δD -values of N-MORB have mainly focused on
398 samples from the north Atlantic and Pacific oceans (Kyser and O’Neil, 1984;
399 Poreda et al., 1986; Pineau and Javoy, 1994; Pineau et al., 2004; Hauri et al.,
400 2006b; Cartigny et al., 2008). These studies concluded that the uncontam-
401 inated N-MORB source had a δD of $-80\pm 10\text{‰}$ (even if the average value
402 measured in those studies is closer to -70‰). Most of those studies also used
403 an extraction technique (induction-heating in Pt crucibles) which can cause
404 biases of more than 10‰ (Clog et al., 2012). The recent study of (Binde-
405 man et al., 2012), which does not use crucibles however, found the δD of
406 Macquarie Island basalts to be close to $-75\pm 5\text{‰}$. Although falling within
407 the canonical mantle range, it must be noted that those samples are very
408 enriched compared to N-MORB ($\text{La}/\text{Sm}_\text{N} > 1.3$ for the most depleted one)
409 and are therefore not representative of the depleted mantle.

410 N-MORB from the North Atlantic measured with the same protocol as
411 in this study (Clog et al., 2012) have δD of $\approx -60\text{‰}$ and do not outline the
412 existence of a distinct δD between the Pacific-Antarctic and the North Pa-
413 cific or Atlantic mantles. Nonetheless, the dataset is still restricted and we
414 are going to evaluate whether this part of the upper depleted mantle can
415 plausibly have a distinct δD .

416 *4.6.1. Geodynamic model*

417 There are two ways to consider mantle water degassing flux at ridges.
418 The first is that we observe degassing of some primordial water from the

419 upper mantle (as for Craig and Lupton (1976)). In this case the apparent
420 contrast with the North Atlantic and North Pacific could be inherited from
421 the processes of crust extraction. This proposition is however unlikely. First,
422 the South Pacific, the North Atlantic and the North Pacific mantle domains
423 have very similar e.g. Sr-isotopes compositions, suggesting an overall similar
424 history and homogeneity resulting from mantle convection (van Keken et al.,
425 2002; Hamelin et al., 2011, among others). Second, water is recycled in the
426 mantle at subduction zones, which is likely to erase any primitive signature.
427 This is illustrated by the high H₂O/Ce ratios in the North Atlantic due to
428 recent rapid subduction (Michael, 1995) or by the distribution of δ D observed
429 in the Manus basin glasses (Shaw et al., 2012). It is thus unlikely that the
430 southern Pacific mantle present a strong, inherited, δ D contrast compared to
431 the rest of the upper mantle.

432 The alternative, generally accepted model considers the hydrogen cycle as
433 in equilibrium chemically and isotopically (steady state), with water recycled
434 to the convecting mantle at subduction zones (Ito et al., 1983; Bebout, 1995;
435 Williams and Hemley, 2001; Dixon et al., 2002). This is supported by the
436 stable continental freeboard in the last half-billion years and analysis of old
437 hydrated rocks (Galer, 1991; Lécuyer et al., 1998). Recent estimates range
438 from 0.2 to 2 ocean masses contained in the mantle, (between 0.3 et 2.8
439 10^{24} g Bolfan-Casanova et al., 2000; Bolfan-Casanova, 2005; Javoy, 2005;
440 Keppler, 2006; Hirschmann, 2006), with half in the transition zone and very
441 little in the lower mantle (less than 5% of the total water, although this
442 number depends on the oxygen fugacity of the lower mantle). The large
443 range in mantle water budget reflects that several hypotheses are considered.

444 With the current ridge and hotspot water output (10^{14} g/an), the residence
445 time is thus between 3 and 28 Gyr, but fluxes were probably greater during
446 the Hadean and Archean and the equilibrium may have been reached early
447 in Earth history. In this model, changing the composition of the upper
448 mantle is possible by changing how recycling occurs, i.e., how much water is
449 devolatilized, which P-T path the subducting slab follows, or depending on
450 the thickness and extent of serpentinization, for the mantle domains of the
451 South Pacific and North Atlantic.

452 It should be noted that we have few direct constraints on the inward flux
453 of water in the mantle, and especially on its isotopic composition. The sub-
454 ducting slab must lose more than 80% of its water (Nadeau et al., 1993;
455 Chaussidon and Jambon, 1994; Dixon et al., 2002) to the arc system, and
456 for the Pacific ocean, flux towards the mantle wedges is not relevant as the
457 subduction zones are directed outwards. The water content of the hydrated
458 oceanic crust is between 0.5 and 5% with a δD between -30 and -50‰ (Kawa-
459 hata et al., 1987; Kusakabe et al., 1989; Agrinier et al., 1995; Shilobreeva
460 et al., 2011), but the sampling is very sparse, especially with respect to
461 depth, and the hydration of the lower oceanic lithosphere is hard to con-
462 strain (Rüpke et al., 2004). To reach isotopic equilibrium of the water cycle,
463 the final average δD of slabs after dehydration should be equal to the average
464 δD of the ridges flux (e.g. -60‰ as measured in this study), but studies have
465 given possible ranges from -30 to -200‰ for effectively recycled hydrogen
466 (Kingsley et al., 2002; Shaw et al., 2008, 2012).

467 *4.6.2. Changing the δD of the slab*

468 The first obvious answer to obtain a higher δD is to increase the δD of
469 the recycled crust before dehydration, either with a different δD of the ocean
470 or by changing the average temperature of alteration. Both are extremely
471 unlikely for the following reasons.

472 The first is at odds with results on Phanerozoic and Proterozoic ophiolites
473 suggesting little variability of oceans δD values (Lécuyer et al., 1998). It
474 would also require, for a difference between the north and south Pacific to
475 be apparent today, that the recycling timescale differs markedly between the
476 different mantle domains.

477 The second would require a hydrothermal alteration temperature several
478 hundreds of degrees higher (Suzuoki and Epstein, 1976) than the one which
479 produces the altered crust studied by Kawahata et al. (1987); Kusakabe et al.
480 (1989); Agrinier et al. (1995). There is at present no compelling argument
481 suggesting that oceanic basalts could have been altered at such higher tem-
482 peratures. Moreover, given that present hydration of the ocean crust depends
483 upon spreading rate, it is worth noting that there is again no evidence for sig-
484 nificant change in spreading rate at least since 180 Ma (Cogné and Humler,
485 2004).

486 *4.6.3. Subduction processes*

487 The H_2O/Ce ratios on the two supersegments studied here (186 ± 30 and
488 173 ± 15) are similar to those measured in the rest of the Pacific ridges sys-
489 tem (between 150 and 220, Michael (1995); Le Roux et al. (2006)). A smaller
490 extent of dehydration during subduction is therefore not a possible explana-
491 tion for the apparent North Pacific/South Pacific δD contrast. Nevertheless,

492 the exact P-T path followed by the slab depends on the dipping angle of
493 the subduction zone (Hager and O'connell, 1978; Cahill and Isacks, 1992).
494 This could be critical for the final δD of the slab, as destabilisation of the
495 water-bearing minerals will occur at different pressures and temperatures
496 (Schmidt and Poli, 1998; Kawamoto, 2006; Smyth, 2006). Water solubility
497 in nominally anhydrous minerals depends on the pressure, so even for the
498 same amount of dehydration (Kohlstedt et al., 1996; Mierdel et al., 2007),
499 the final δD could differ. Indeed, even at 900°C, fractionation of hydrogen
500 isotopes between minerals is significant (up to 10‰ : Suzuoki and Epstein,
501 1976; Graham et al., 1984; Dobson et al., 1989; Vennemann and O'Neil, 1996).
502 This type of scenario would also create differences for other fluid-mobile ele-
503 ments like Li and B, and could explain the small differences between the two
504 supersegments ($\overline{\delta D} \approx -63\text{‰}$ in the south and $\overline{\delta D} \approx -58\text{‰}$ in the north).

505 Yet this scenario can hardly lead to the 20‰ contrast between our results
506 and those of Kyser and O'Neil (1984). If we model the slab dehydration as
507 an open-system loss of water, the average fractionation of water would need
508 to differ by 10‰. Experiments on fractionation factors between water and
509 hydrated minerals indicate that it corresponds to a $\approx 150^\circ\text{C}$ change in the
510 range 500-900°C (Suzuoki and Epstein, 1976). This explanation is therefore
511 not satisfactory with the current view of P-T paths and and dehydration of
512 recycled ocean crust.

513 *4.6.4. Revising the δD of the upper depleted mantle*

514 We have shown that previous measurements could suffer from an experi-
515 mental bias (Clog et al., 2012), and have not been able to find a satisfactory
516 scenario explaining why the south Pacific would be enriched in D compared

517 to previous data and other locations while being otherwise a perfect exam-
518 ple of the upper depleted mantle, unaffected by mantle plumes. Our view
519 is therefore that slight variations in δD (and H_2O/Ce) can be produced by
520 dehydration and recycling of water, but that the large contrast with previous
521 data reflects analytical artifacts.

522 This sample suite presents many advantages to characterize the isotopic
523 composition of the depleted mantle. Previous researchers have shown that
524 the source composition is typical of the depleted mantle with limited and
525 gradual variations in compositions in the area. Most of the variations are due
526 to igneous processes, and the variation in spreading rate and ridge structure
527 strengthen the conclusion that contamination is not a major obstacle to the
528 determination of hydrogen isotopic composition of the source of N-MORB.
529 Finally, the high number of samples (40 in this area compared to less than
530 70 N-MORB measured in a variety of locations in the literature, Craig and
531 Lupton (1976); Satake and Matsuda (1979); Kyser and O'Neil (1984); Poreda
532 et al. (1986); Chaussidon et al. (1991); Pineau and Javoy (1994); Kingsley
533 et al. (2002); Pineau et al. (2004); Cartigny et al. (2008)) limits the possibility
534 of sample bias when calculating averages.

535 On the basis of this study, we propose that the average δD of the up-
536 per depleted mantle is rather $-60 \pm 5\%$. Although the same average value
537 and a similar range were observed on 8 N-MORB from the Middle Atlantic
538 Ridge (Clog et al., 2012), further studies on other ridges are necessary to
539 confirm this figure. Variations observed in isotopic composition and water
540 content shows that the upper mantle is not homogeneous, but present both
541 small scales heterogeneities which are averaged by melts pooling when the

542 spreading rate is higher than 7 cm/year, and zonations at a larger scale lead-
543 ing to different average values on the northern and southern supersegments,
544 illustrating the distribution of heterogeneities in the convecting mantle.

545 **5. Conclusions**

546 Despite widespread Cl contamination, assimilation of seawater-derived
547 fluids or interaction with hydrated rocks did not significantly affect concen-
548 trations or isotopic compositions of hydrogen for our suite of samples. An
549 increase in Cl contamination with spreading rate was observed. All samples
550 are N-MORB with no evidence of influence from hotspots. Samples were
551 undersaturated with respect to H₂O, and variations in concentrations of wa-
552 ter are mainly due to igneous processes. The water content in the source
553 ranges from 150 to 250 ppm. The average δD are -63 and -58‰ and the
554 water to cerium ratios of 186 ± 30 and 173 ± 15 for the southern and northern
555 supersegments respectively. This apparent enrichment compared to previous
556 studies ($\delta D \approx -70\%$) is not due to difference during the recycling of water. It
557 is rather explained by a combination of a potential experimental bias and
558 different interpretation on the influence of contamination. The δD of the up-
559 per depleted mantle is close to $-60\pm 5\%$, with variations in δD and H₂O/Ce
560 at different length scales resulting from recycling and ridge processes.

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866 **6. TABLES**

Table 1: Previous data for the southern supersegment : major elements (Vlastélic et al., 2000) and segment number.

	SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Total	Segment
PAC1 CV1	49.78	15.70	9.79	0.18	8.45	11.71	2.49	0.04	1.10	99.24	1
PAC1 CV2	50.78	14.37	10.49	0.19	7.74	11.25	2.55	0.06	1.67	99.10	1
PAC1 CV3	50.70	15.53	8.60	0.16	8.57	11.91	2.53	0.08	1.20	99.28	1
PAC1 CV4	50.30	15.46	8.55	0.16	8.78	12.32	2.46	0.04	1.05	99.12	1
PAC1 CV6	50.44	15.37	9.31	0.17	8.51	12.01	2.50	0.04	1.23	99.58	1
PAC1 CV7	51.06	14.50	9.80	0.19	7.88	12.03	2.71	0.04	1.31	99.52	1
PAC1 DR3	51.18	14.51	9.88	0.18	7.30	11.21	3.00	0.15	1.59	99.00	2
PAC1 DR4	49.13	15.71	10.08	0.18	7.25	11.83	2.87	0.12	1.35	98.52	3
PAC1 DR5-1	51.00	15.45	8.42	0.15	8.33	12.01	2.82	0.09	1.19	99.46	4
PAC1 DR6	50.99	13.99	11.20	0.20	6.93	10.58	2.86	0.12	2.02	98.89	4
PAC1 DR7-1	50.75	14.43	10.70	0.22	6.83	10.58	3.03	0.19	1.94	98.67	4
PAC1 DR7-2	50.83	14.43	10.52	0.18	7.35	11.29	2.91	0.12	1.69	99.32	4
PAC1 DR9	50.75	13.42	12.15	0.22	6.36	10.44	3.09	0.12	2.20	98.75	5
PAC1 DR10-1	53.79	14.10	10.77	0.21	4.83	8.59	3.43	0.48	1.73	97.93	5
PAC1 DR10-2	51.46	14.10	10.87	0.20	6.22	10.36	3.37	0.25	1.75	98.58	5
PAC1 DR11-1	50.21	14.32	9.25	0.17	7.33	11.34	2.70	0.06	1.31	96.69	6
PAC1 DR12-1	50.94	15.62	8.49	0.15	8.85	12.31	2.32	0.03	1.03	99.74	6
PAC1 DR13-1	50.37	14.60	10.89	0.18	7.38	10.76	2.82	0.09	1.64	98.73	6
PAC1 DR13-2	50.50	14.52	11.01	0.19	7.42	10.73	2.85	0.09	1.65	98.96	6

Table 2: Previous data for the northern supersegment : major elements (Hamelin et al., 2010) and segment names.

	SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	Total	Segment
PAC2 DR 1-1	50.20	14.60	10.75	0.18	7.30	11.90	2.82	0.20	1.58	99.53	S1
PAC2 DR3-1											S1
PAC2 DR4-2	50.40	14.28	11.70	0.20	7.08	11.20	2.83	0.12	1.79	99.60	S1
PAC2 DR5-2	49.90	13.65	13.45	0.22	6.52	10.40	2.74	0.18	2.13	99.19	S2
PAC2 DR6-6	51.30	12.56	15.70	0.26	4.34	8.66	3.46	0.31	2.88	99.47	S2
PAC2 DR7-2											S3
PAC2 DR8-1	49.40	14.40	12.65	0.20	7.05	11.70	2.87	0.20	1.66	100.13	S3
PAC2 DR20-1	51.15	13.90	14.20	0.24	4.60	9.35	3.34	0.25	2.40	99.43	N1
PAC2 DR21-2	50.30	13.88	12.50	0.21	6.73	11.10	2.79	0.15	2.00	99.66	N1
PAC2 DR22-1	49.90	14.60	11.70	0.20	7.25	11.60	2.78	0.17	1.87	100.07	N1
PAC2 DR28-2	49.70	15.00	11.15	0.19	7.85	12.10	2.52	0.08	1.39	99.98	N3
PAC2 DR29-1	49.90	13.37	13.80	0.23	6.16	10.75	2.83	0.19	2.31	99.54	N3
PAC2 DR30-1	50.00	14.05	12.45	0.21	7.00	11.70	2.64	0.17	1.94	100.16	N3
PAC2 DR31-3	49.85	14.70	11.70	0.19	7.55	11.45	2.56	0.10	1.74	99.83	N3
PAC2 DR32-1	50.50	14.00	12.60	0.21	6.80	11.10	2.84	0.16	2.02	100.23	N4
PAC2 DR33-1	50.20	13.90	12.80	0.21	6.63	10.95	2.84	0.15	2.10	99.78	N4
PAC2 DR34-1	50.00	15.10	10.44	0.18	8.00	12.08	2.60	0.06	1.30	99.76	N4
PAC2 DR35-1a	49.50	13.15	15.05	0.23	5.65	9.93	3.05	0.17	2.93	99.66	N5
PAC2 DR36-1	49.60	14.25	12.50	0.20	7.07	11.30	2.80	0.15	2.09	99.96	N5
PAC2 DR37-2											N5
PAC2 DR38-1	49.10	15.7	10.80	0.18	8.35	11.70	2.67	0.09	1.42	99.72	N6

Table 3: Data table for the southern supersegment : K_2O , La and Sm content from Vlastélic et al. (2000); H_2O , Cl, Ce and δD from this study.

	Long. (°W)	Lat. (°S)	Depth (m)	H_2O (ppm)	δD (‰)	Cl (ppm)	Ce (ppm)	H_2O/Ce	$(La/Sm)_N$	Cl/K
PAC1 CV1	173.75	-65.10	2863	1192	-63.2	56	5.6	213	0.49	0.169
PAC1 CV2	172.43	-64.83	2936	2070	-60.5	61	10.5	197	0.47	0.122
PAC1 CV3	171.88	-64.53	2576	2217	-54.5	55	8.7	255	0.64	0.083
PAC1 CV4	169.40	-64.40	2340	844	-76.6	52	6.3	134	0.49	0.157
PAC1 CV6	166.06	-63.45	2755	1030	-65.7	53	5.2	198	0.44	0.160
PAC1 CV7	165.96	-63.54	1603	1182	-69.5	218	10.5	113	0.85	0.656
PAC1 DR3	156.08	-62.32	2219	2672	-66.4	175	14.8	181	0.84	0.140
PAC1 DR4	153.04	-62.41	1587	2151	-66.5	29	10.7	201	0.65	0.029
PAC1 DR5-1	154.54	-62	2344	1585	-61.3	43	10.2	155	0.77	0.058
PAC1 DR6	153.21	-60.94	2527	2705	-71.7	39	14.6	185	0.61	0.039
PAC1 DR7-1	152.08	-60	2362	3112	-60.8	533	17.9	174	0.76	0.338
PAC1 DR7-2	152.08	-60	2362	2437	-66.0	206	13.1	186	0.63	0.207
PAC1 DR9	149.14	-58.85	2484	2956	-65.2	380	15.9	186	0.56	0.381
PAC1 DR10-1	148.50	-57.89	2319	7808	-58.1	2395	39.6	197	0.94	0.601
PAC1 DR10-2	148.50	-57.89	2319	3835	-57.7	1008	23.1	166	0.80	0.485
PAC1 DR11-1	146.80	-57.63	2500	1889	-48.7	162	9.6	197	0.56	0.325
PAC1 DR12-1	146.29	-57.18	2539	1175	-69.0	48	6.0	196	0.45	0.193
PAC1 DR13-1	145.74	-56.57	2674	2112	-56.1	76	11.7	181	0.54	0.102
PAC1 DR13-2	145.74	-56.57	2674	2345	-65.4	66	11.1	211	0.61	0.088

Table 4: Data table for the northern supersegment. K_2O , La, Sm and Ce from Hamelin et al. (2010); H_2O , Cl and δD from this study.

	Long. (°W)	Lat. (°S)	Depth (m)	H_2O (ppm)	δD (‰)	Cl (ppm)	Ce (ppm)	H_2O/Ce	$(La/Sm)_N$	Cl/K
PAC2 DR 1-1	118.4	-52.52	2323	2397	-60.1	256	14.4	166.47	0.78556	0.154
PAC2 DR3-1	118.0	-51.79	2396	2783	-59.8	309	13.6	205.21		
PAC2 DR4-2	117.8	-51.42	2409	2310	-64.8	257	12.8	180.67	0.60379	0.258
PAC2 DR5-2g	117.4	-50.98	2784	3296	-60.9	309	17.6	186.92	0.81617	0.207
PAC2 DR6-6	117.2	-50.70	2610	6546	-51.2	78	39.0	168.01	0.86064	0.030
PAC2 DR7-2g	117.1	-50.24	2229	2764	-58.4	479				
PAC2 DR8-1	117.0	-49.99	2220	3012	-51.8	271	15.8	190.61	0.90177	0.163
PAC2 DR20-1	113.8	-49.73	2440	4797	-55.2	1631	34.2	140.34	0.80392	0.786
PAC2 DR21-2	113.6	-49.26	2338	2384	-56.2	308	14.0	170.82	0.65922	0.247
PAC2 DR22-1	113.4	-48.73	2413	2646	-56.6	348	14.6	180.83	0.60670	0.246
PAC2 DR28-2	113.3	-47.51	2488	1656	-56.2	1397	8.6	191.77	0.57468	2.103
PAC2 DR29-1	113.1	-47.01	2407	2933	-68.2	439	17.1	171.94	0.68383	0.278
PAC2 DR30-1	112.9	-46.40	2345	2446	-60.1	385	14.9	164.14	0.66544	0.273
PAC2 DR31-3	112.7	-45.85	2414	1983	-65.5	530	12.7	156.74	0.61245	0.672
PAC2 DR32-1	112.4	-45.39	2384	2695	-61.0	356	16.2	166.78	0.69091	0.268
PAC2 DR33-1	112.3	-44.87	2374	2657	-56.8	294	16.2	164.05	0.70567	0.236
PAC2 DR34-1	112.0	-44.24	2467	1276	-61.4	1516	8.1	158.20	0.46939	3.042
PAC2 DR35-1a	111.8	-43.59	2463	4808	-51.7	259	24.9	192.85		0.183
PAC2 DR36-1	111.6	-42.95	2503	2804	-55.6	548	16.2	173.59	0.64663	0.440
PAC2 DR37-2	111.3	-42.27	2474	2462	-58.2	439	15.1	163.35		
PAC2 DR38-1	113.3	-41.8	2524	1751	-57.8	151	10.2	172.343		0.214

867 **7. FIGURES CAPTIONS**

868 Figure 1. Map of the sampling area, illustrating the position of the sam-
869 ples with respect to the local geographical and geological features. The
870 symbols representing the samples will remain the same in the whole arti-
871 cle. The figure was created with the GeoMapApp application and the depths
872 databases included therein.

873 Figure 2. δD (in ‰, top panel) and water content (in ppm, bottom panel)
874 along the sampling area. Error bars are smaller than the symbols for water
875 content.

876 Figure 3. From top to bottom : H_2O/Ce , $^{206}Pb/^{204}Pb$, Cl content and
877 Cl/K along the sampling area. Except south of Saint-Exupery fracture zone,
878 all H_2O/Ce ratio are in the range of North Pacific basalts.

879 Figure 4. Water content as a function of eruption pressure and curves
880 illustrating the composition of the vapor in equilibrium with the magma for
881 a given water content and pressure. This figure illustrate that all but sample
882 PAC1DR10-1 were not significantly affected by degassing.

883 Figure 5. Incompatible species content as a function of MgO wt%. From
884 top to bottom, Ce, La, H_2O and Cl. Continuous lines are best linear fits,
885 while dotted lines illustrate the differentiation trend predicted for a perfectly
886 incompatible species. Note that we observe over-enrichment for H_2O , La
887 and Ce, as commonly observed in numerous sample suites (e.g. Sours-Page
888 et al., 1999). However the over-enrichment happens for both H_2O and Ce,
889 as illustrated here and by the constant H_2O/Ce ratios, and is thus not due
890 to an increase in assimilation with increasing differentiation.

891 Figure 6. Cl/ H_2O versus Ce/ H_2O and curves resulting from the addition

892 of seawater, brines with various concentrations or a serpentine with 10 wt.%
893 H₂O, 1000 ppm Cl and 10 ppm Ce to a typical MORB composition (2000
894 ppm H₂O, H₂O/Ce = 200, 1000 ppm K, K/Cl = 12.5 (Kendrick et al., 2012)).
895 The figure illustrate that the observed variations are not compatible with the
896 addition of diluted brines, seawater or hydrated mafic rock. Shaded outlines
897 illustrate the dispersion of the data in the southern (continuous outline) and
898 the northern (dotted outline) supersegments.

899 Figure 7. Sodium content as a function of water content, both corrected to
900 8 wt.% MgO. Continuous lines represent constant water content in the source,
901 and dotted lines correspond to constant melting rate. Both where calculated
902 using a simple batch melting model with 0.29 wt.% of Na in the source (Klein
903 and Langmuir, 1987; Kelley et al., 2006). We assumed incompatibilities of
904 0.012 for water (Aubaud et al., 2004; Kohn, 2006; Grant et al., 2007) and
905 0.02 for sodium (Kelley et al., 2006).

906 Figure 8. Ratios of water to Ce (top) and La (bottom) as function of Ce
907 and La contents respectively. Straight lines are best linear fits and dotted
908 lines represent the 95% confidence envelope.

909 Figure 9. From top to bottom, δD as a function of La/Sm_N, ²⁰⁶Pb/²⁰⁴Pb
910 and TiO₂/H₂O. There are no correlation in the top two panels, while the
911 negative correlation in the bottom panel is controlled by the two samples
912 PAC1CV04 and PAC1CV07 (which may reflect source re-melting, see text).

913 8. FIGURES

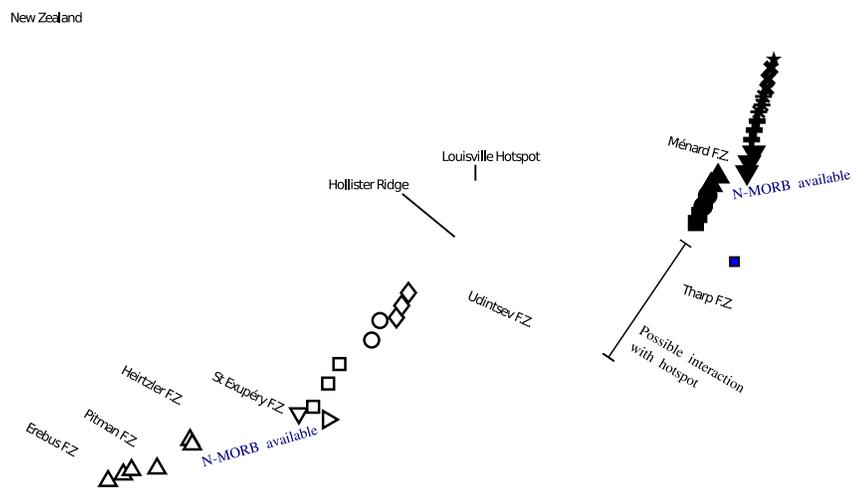


Figure 1:

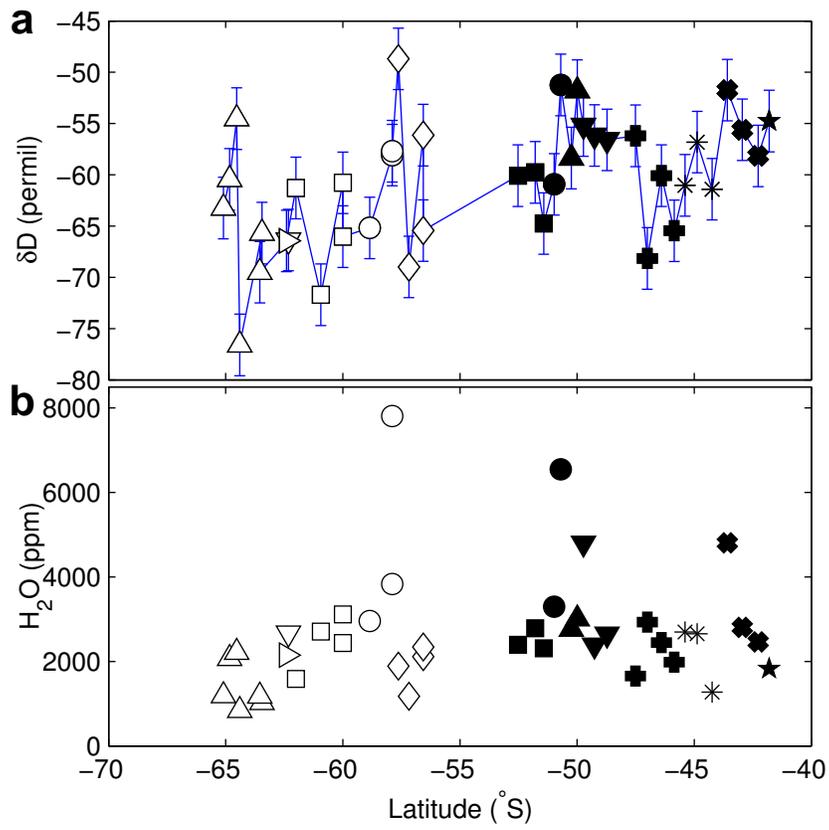


Figure 2:

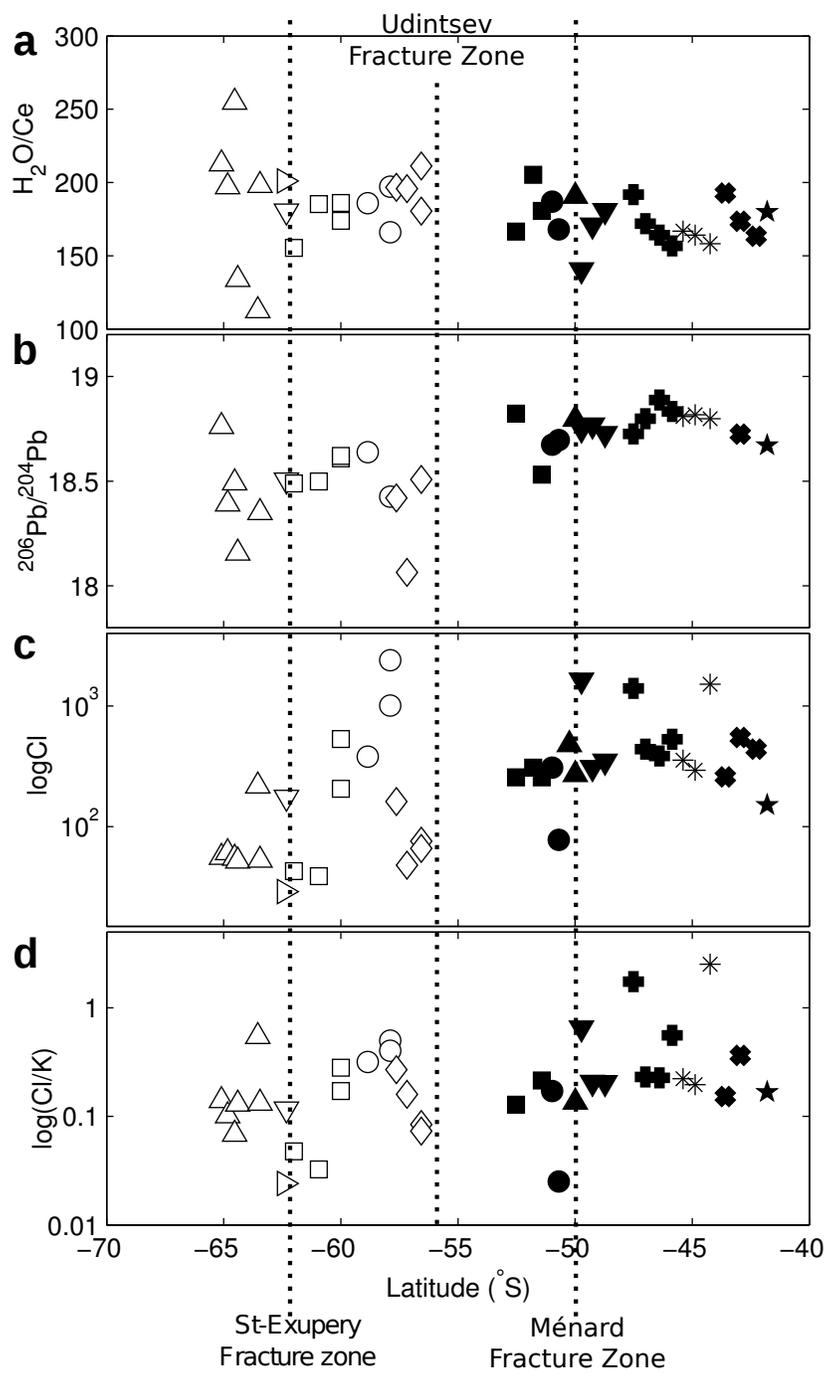


Figure 3:

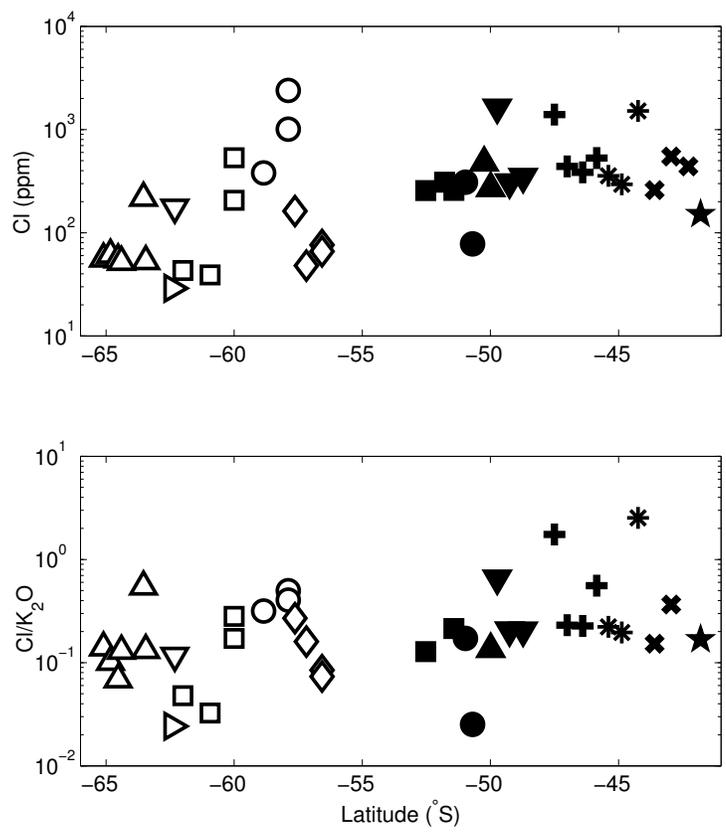


Figure 4:

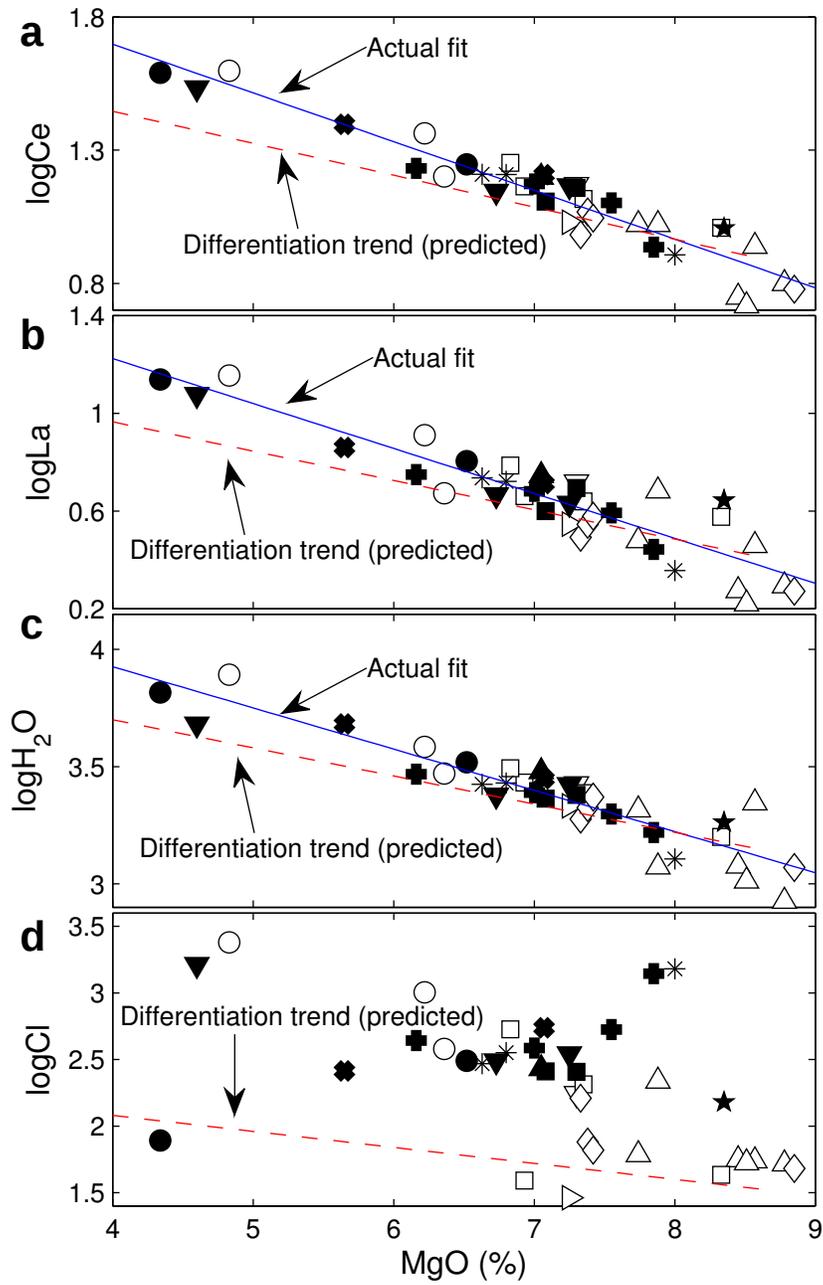


Figure 5:

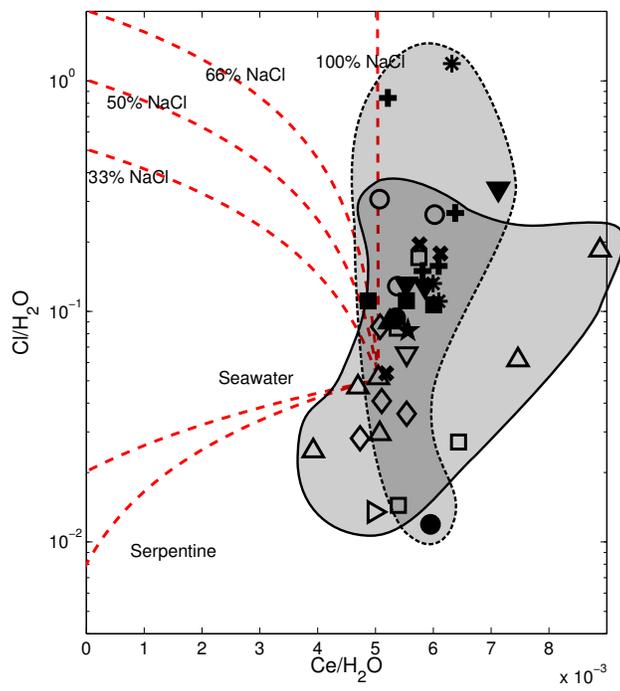


Figure 6:

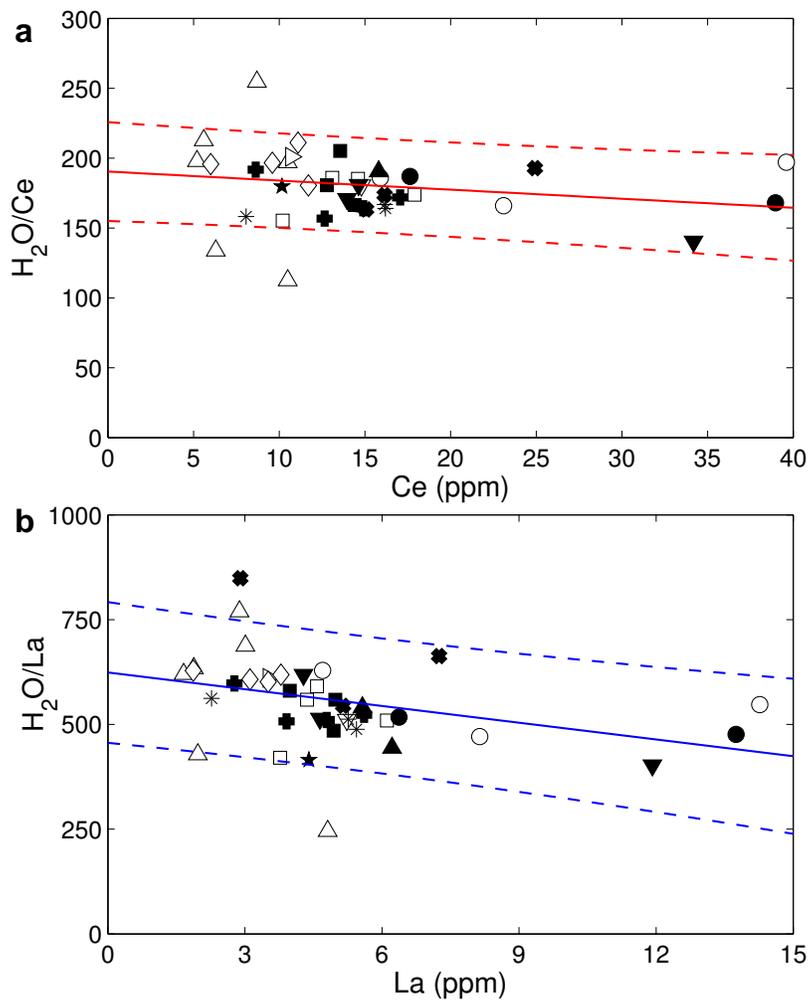


Figure 7:

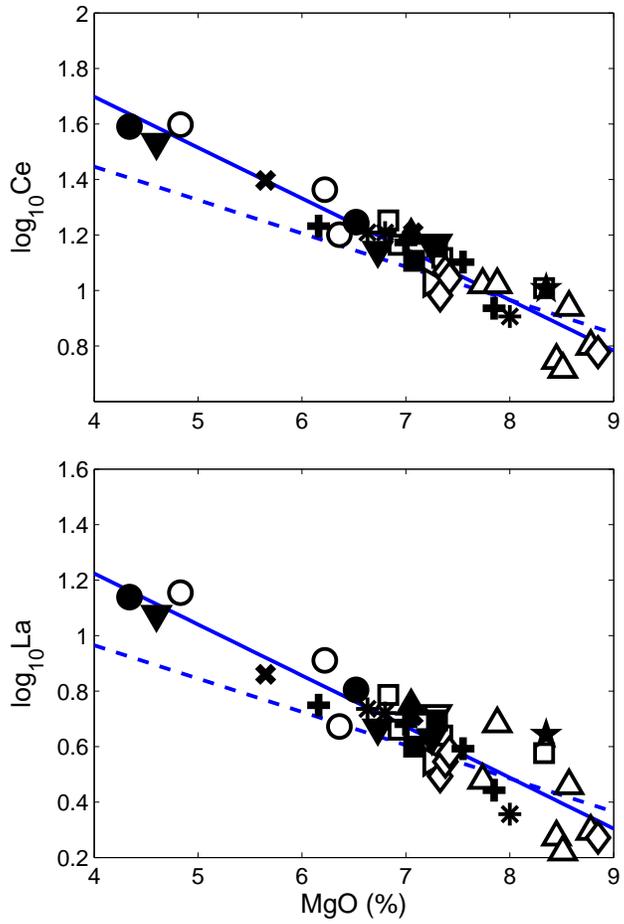


Figure 8:

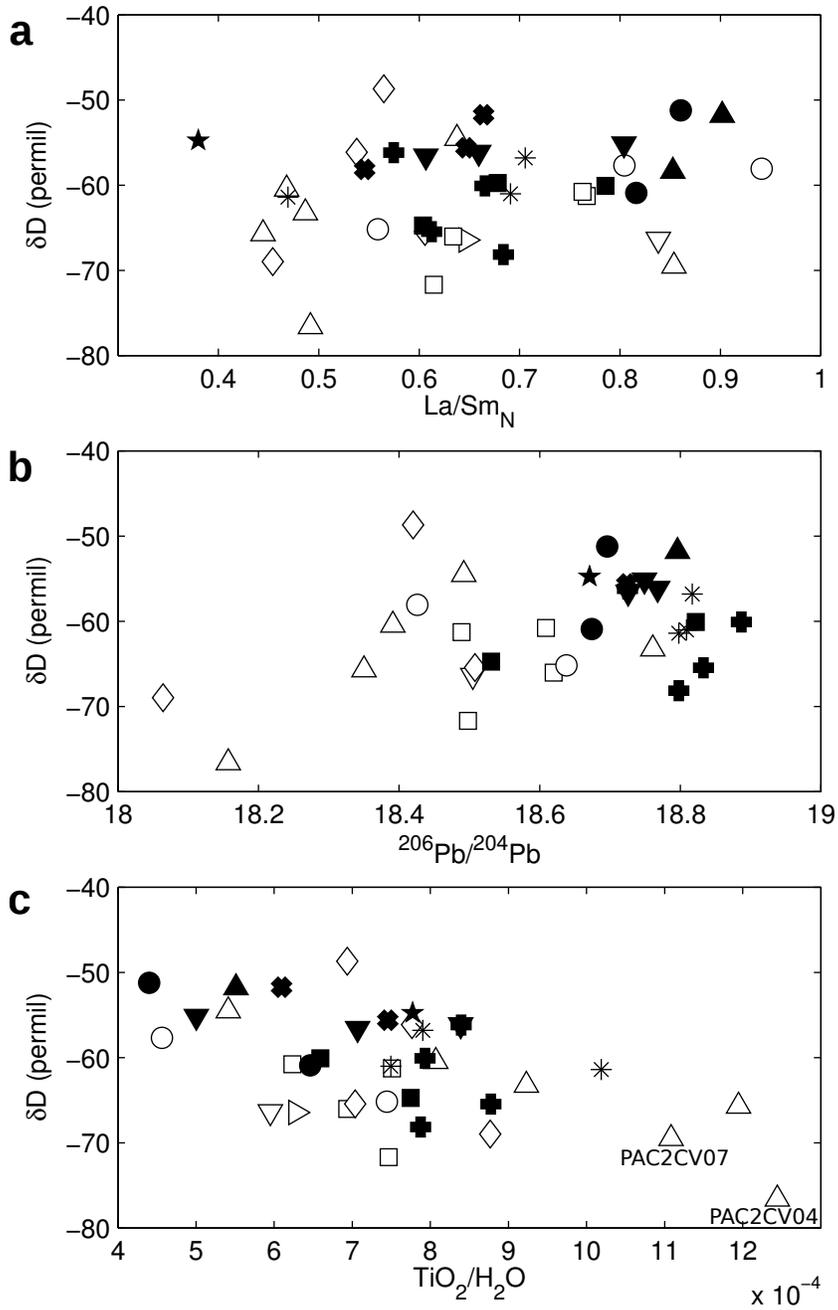


Figure 9: