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3 **Hf-Nd input flux in the Izu-Mariana subduction zone**  
4 **and recycling of subducted material in the mantle**

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22

## 22 **Abstract**

23 In subduction zones, two major mass fluxes compete: the input flux of altered oceanic  
24 crust and sediments subducted into the mantle and the output flux of magma that  
25 forms the volcanic arc. While the composition and the amount of material erupted  
26 along volcanic arcs are relatively well known, the chemical and isotopic composition  
27 of the subducted material (altered oceanic crust and sediments) is poorly constrained  
28 and is an important factor in the mass balance calculation. ODP Leg 185 in the  
29 Western Pacific used systematic sampling of the altered basaltic basement and  
30 sediment pile and the creation of composite mixtures to quantify the total chemical  
31 flux subducted at the Izu-Mariana margin. Here, we report Hf and Nd isotopic  
32 compositions of materials recovered from this Leg. The Hf and Nd isotopic  
33 compositions of altered basalts from Hole 801C are indistinguishable from those of  
34 recent unaltered Pacific MORB suggesting that hydrothermal alteration had no effect  
35 on either isotopic systems.

36 The complete Site 1149 sedimentary pile has a weighted average  $\epsilon_{Nd}$  of  $-5.9$  and  $\epsilon_{Hf}$   
37 of  $+4.4$ , values similar to those of Fe-Mn crusts and nodules. Therefore, the Hf and  
38 Nd isotopic compositions of the sediments collected at Site 1149 indicate minimal  
39 contributions from continental detrital material to the REE and HFSE. However, the  
40 Hf isotopic budget of the oldest sediments is more influenced by continental material  
41 than the younger sediments, despite the large distances to continental masses 130 Ma  
42 ago.

43 In the Izu subduction zone, we calculate a sedimentary input of less than about 2% in  
44 the volcanic lava source. In contrast, at least 85% of the sedimentary Nd and Hf are  
45 recycled into the mantle to affect its general composition. Assuming that sediments  
46 have been recycled in a similar manner into the mantle for millions of years, large  
47 chemical heterogeneities must be produced in the mantle. In addition, the depletion

48 of the mantle due to the extraction of continental crust must be partly counterbalanced  
49 by the injection of vast quantities of enriched sedimentary material.  
50

## 50 **Introduction**

51 Subduction zones are the principal sites for exchange between the mantle and surficial  
52 geochemical reservoirs: the crust, ocean and atmosphere. Magmas from subduction  
53 zones contribute to crustal growth and deliver volatile elements to the atmosphere. In  
54 return, the mantle is fertilized by subduction of altered oceanic crust and sediments  
55 containing elements derived from the continental crust and seawater (Armstrong,  
56 1968; Armstrong, 1991; VonHuene and Scholl, 1991; VonHuene and Scholl, 1993;  
57 Plank and Langmuir, 1998) .

58 Quantifying fluxes between material entering the subduction zone and volcanic  
59 outputs requires, on one hand, an accurate estimate of the chemical and isotopic  
60 composition of arc magmas and, on the other hand, a precise evaluation of the  
61 chemical and isotopic composition of subducted materials. Such evaluations have  
62 been made on a global scale by Plank and Langmuir (1998), who calculated average  
63 compositions for sediments subducted under various arcs as well as a global sediment  
64 composition called GLOSS. However, no complete section of basaltic crust and  
65 overlying sediments had ever been studied for its complete trace element and isotopic  
66 compositions. The primary scientific objective of ODP Leg 185, which was drilled in  
67 1999 in the western Pacific, outboard of the Izu-Bonin-Mariana arc, was to sample  
68 and characterize a complete section of altered basaltic crust and overlying  
69 sedimentary pile (Plank et al., 2000). Altered basaltic crust was drilled at Hole 801C,  
70 east of the Mariana arc, and the sedimentary pile and basaltic basement were sampled  
71 at Site 1149 in front of the Izu arc. As part of this joint international effort, we  
72 analyzed Nd and Hf isotopes of basaltic samples from Hole 801C and sediments  
73 collected at Site 1149 while other teams concentrated their efforts on the mobility of  
74 trace elements in the basaltic basement (Kelley et al., 2003; Reisberg et al., 2008), on  
75 the Sr, Nd, Pb isotopic systematics of both sediments and basalts (Hauff et al., 2003),

76 or on the trace element budget of the entire sedimentary pile (Plank et al., 2007).  
77 Comparing the Nd and Hf isotopic compositions of the old altered basaltic crust with  
78 those of fresh Pacific MORB should provide constraints on the behavior of rare earth  
79 elements (REE) and high field strength elements (HFSE) during alteration of oceanic  
80 crust. These data will also provide a composition for oceanic crust recycled into the  
81 mantle. In addition, Nd and Hf isotopic compositions measured on the Site 1149  
82 sediments provide constraints on the origin of REE and HFSE in sediments deposited  
83 in ocean basins, and can be used to evaluate the average composition of downgoing  
84 sedimentary material in intra-oceanic subduction zones. Our sediment results may  
85 also be compared to the pioneering Hf isotopic work on sediments from the western  
86 Pacific area of Woodhead (1989) and Pearce et al. (1999).

87 Our work constrains the composition of the subducted materials regionally, and can  
88 be used to understand the genesis of the Izu-Mariana arc lavas. Western Pacific arcs  
89 have been exceptionally well studied, particularly for Nd and Hf isotopes (White and  
90 Patchett, 1984; Woodhead, 1989; Elliott et al., 1997; Pearce et al., 1999; Woodhead et  
91 al., 2001; Tollstrup and Gill, 2005; Wade et al., 2005; Stern et al., 2006). In spite of  
92 this, there are no good estimates of the Nd-Hf input flux to these arc systems. More  
93 generally, such data on a complete section of subducted material provides an estimate  
94 of the flux of chemical elements recycled into the mantle and can help in  
95 understanding the long term evolution of the composition of the mantle as a result of  
96 the balance between melt extraction through volcanic activities, and recycling of  
97 basaltic crust and overlying sediments in subduction zones.

98

## 99 **Sample selection**

100 We focused our study on two different sets of samples: the first set is the suite of  
101 composite samples of basalts prepared by Kelley et al. (2003) to characterize the

102 basaltic crust entering the subduction zone and sampled at ODP Site 801C (see Figure  
103 1). This is the oldest crust formed at fast spreading rates, and so is the reference  
104 basement section for much of the subducting western Pacific oceanic crust (Ludden et  
105 al., 2006). The second set is a selection of sediment samples from ODP Site 1149  
106 which represent the sedimentary cover overlying the oceanic crust (Figure 1). This  
107 site reflects all the major types of pelagic sedimentation found in the western Pacific,  
108 including chert, clay, and carbonate lithologies (Plank et al., 2007). Samples were  
109 selected to cover the entire variability of the basaltic and sedimentary compositions  
110 along the cores and once weight averaged, they should represent the average  
111 composition of the old Pacific plate that enters subduction zones along a large sector  
112 of the western Pacific convergent margin.

113 • *The basaltic basement drilled at ODP Site 801C*

114 Hole 801C (18°38.5'N, 156°21.6'E) is located in the Pigafetta Basin (Figure 1), 950  
115 km east of the Mariana trench. This hole was first drilled in 1989 during ODP Leg  
116 129 (Lancelot et al., 1990). In 1999 during ODP Leg 185, the hole was deepened to  
117 collect a more complete section of the altered oceanic crust (Plank et al., 2000). A  
118 total thickness of 474 m was sampled and divided into eight major sequences based  
119 on petrological, mineralogical and geochemical characteristics. The uppermost  
120 sequence consists of alkalic basalts and dolerites (about 20m thick) while lower  
121 sequences are typical MORB with tholeiitic composition including massive flows or  
122 pillows associated with breccias, volcanoclastic material and silicic hydrothermal  
123 deposits (Plank et al., 2000; Barr et al., 2002; Fisk and Kelley, 2002). The upper  
124 alkalic basalts have an Ar-Ar age of 157 Ma and the underlying MORB have ages  
125 ranging from 162 to 171 Ma (Pringle, 1992; Koppers et al., 2003a). Most basaltic  
126 materials from hole 801C are altered by low temperature hydrothermal fluids and  
127 interaction with low-temperature seawater, and the material varies from highly altered

128 interpillow materials to better preserved massive flows. Some completely unaltered  
129 volcanic glasses also exist (Alt et al., 1992; Plank et al., 2000; Fisk and Kelley, 2002;  
130 Talbi and Honnorez, 2003).

131 A set of composite samples was prepared by mixing powders of the various  
132 lithologies (massive flows, pillows, breccias, volcanoclastic materials and  
133 hydrothermal deposits) according to their respective proportions in the hole. The  
134 procedure followed for sample preparation, as given by Kelley et al. (2003) led to the  
135 preparation of thirteen composites representing the flows and pillows units, the  
136 breccias and volcanoclastic sediments. A global composite representative of the entire  
137 basaltic column was also prepared. Major and trace element compositions of these  
138 composites were measured by Kelley et al. (2003), stable isotopes have been  
139 published by Alt (2003) and Re-Os results were reported by Reisberg et al. (2008).  
140 Our Hf and Nd isotopic compositions were obtained on the same composite samples.

141

142 • *The sedimentary pile drilled at ODP Site 1149*

143 The sedimentary cover subducted at the Mariana trench has been drilled and sampled  
144 during several DSDP and ODP campaigns (especially during the ODP Leg 129) and  
145 is one of the best studied sedimentary piles on a subducting oceanic plate (Plank and  
146 Langmuir, 1998). In contrast, the sedimentary pile subducted in the Izu-Bonin region,  
147 north of the Mariana arc, was largely unknown and was therefore drilled at Site 1149  
148 during ODP leg 185 (31°20.1'N, 143°21.8'E see Figure 1).

149 In the Izu-Bonin region the sediments covering the Pacific crust have a thickness of  
150 about 410 m and include several lithological units (figure 2):

151 -Unit I, at the top of the sediment pile, has a thickness of about 118 m. It  
152 consists of a mixture of clay minerals, siliceous planktonic microfossils (essentially

153 diatoms and radiolarians) and volcanic ash. Paleomagnetic data indicate an age from  
154 late Miocene (about 6.5 Ma) to late Pleistocene (younger than 0.2 Ma).

155 -Unit II (including subunits IIA and IIB) has a thickness of about 62 m, and  
156 consists almost exclusively of pelagic clays. However, in the upper part, defined as  
157 subunit IIA, some ash layers are present. The lowest part of unit II, called subunit IIB,  
158 is entirely composed of pelagic clays. The transition between subunit IIB and unit III  
159 is marked by the presence of zeolitic clays. The ages within unit II remain unknown  
160 by lack of paleomagnetic or biostratigraphic data but the unit reflects most of the age  
161 history of the site (from 6.6 Ma to 105 Ma (Plank et al., 2007)).

162 -Unit III mainly consists of biogenic siliceous deposits: radiolarian cherts and  
163 radiolarian porcelanite. Some claystones were also recovered, essentially in the  
164 uppermost and in the lowest part of the unit. The thickness of unit III is about 103 m  
165 and its deposition age ranges from 105 to 127 Ma (Plank et al., 2007).

166 -Unit IV has a thickness of 126 m and is characterized by a mixture of  
167 radiolarian cherts and porcelanite with calcareous sediments (marlstone and chalk).  
168 An isolated ash-rich level is also present at the top of the unit. Nannofossils preserved  
169 in marls and chinks indicate a late Valanginian (134 Ma) to late Hauterivian (127 Ma)  
170 age for this unit.

171 Discrete samples were selected along the entire Site 1149 sedimentary column from  
172 unit I to unit IV (Plank et al., 2000). Their major and trace element compositions were  
173 measured by Plank et al. (2007) and we report here Hf and Nd isotopic compositions  
174 on a selection of this sediment set. Eighteen samples from the various lithologies  
175 were selected in the different units to cover the entire compositional spectrum. This  
176 same subset of samples have been studied by several investigators, and so together,  
177 form a remarkably complete data set for elemental and isotopic compositions (Ludden



178 et al., 2006; Plank et al., 2007). The measured Hf and Nd isotopic variations should  
179 therefore be representative of the entire sedimentary pile.

180

## 181 **Analytical Procedure**

182 Hf and Nd chemical separation were performed in Grenoble and the isotopic  
183 compositions were measured using the VG Plasma 54 at ENS Lyon. Samples were  
184 dissolved in Savillex beakers but dissolution in Parr bombs were also performed on  
185 selected samples to check that complete dissolution of the sediments was achieved  
186 (see Table 2). The analytical procedure for Hf separation was based on the method  
187 published by Blichert-Toft et al. (1997) which proved to be highly efficient for most  
188 of the Site 801C composites and Site 1149 sediments, but this method failed for two  
189 particular sample groups (cherts and Ca-rich sediments) and had to be modified.  
190 Detailed suggestions relative to the isolation of Hf for these two groups of sediments  
191 are given in the appendix. Nd was isolated from the other REE using the classical  
192 Eichrom® HDEHP-coated teflon resin technique. Hf and Nd blanks were measured  
193 regularly by ICP-MS and were always lower than 80 pg for Hf and 235 pg for Nd;  
194 these values are negligible relative to the amounts of Hf and Nd present in the  
195 samples.

196 Accuracy of the isotopic measurements was monitored on the P54 at ENS Lyon using  
197 the JMC-475 Hf standard. The average measured  $^{176}\text{Hf}/^{177}\text{Hf}$  ratio was  $0.282163 \pm 11$   
198 ( $1\sigma$ , 32 runs). Two different standards were used during Nd analysis: an internal  
199 “home” Nd JMC standard which gave an average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  $0.512238 \pm 7$   
200 ( $1\sigma$ , 12 runs) and the Nd La Jolla standard which gave an average  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio of  
201  $0.511858 \pm 10$  ( $1\sigma$ , 8 runs). Several complete duplicate analyses were performed and  
202 results show that for both Nd and Hf isotopic ratios, the measurements reproduce  
203 within analytical errors ( $\leq 1\epsilon_{\text{Nd}}$  or  $\epsilon_{\text{Hf}}$ ) (see Tables 1 and 2).

204

## 205 **Results**

### 206 • *Site 801C basalt composites*

207 Hf and Nd isotopic compositions of Hole 801C composites are reported in Table 1  
208 together with calculated present-day and initial  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  values. The lithology of  
209 each composite is also indicated in the footnote. The measured and initial Hf and Nd  
210 isotopic compositions of Hole 801C samples are plotted in Figure 3 together with  
211 values for present-day mid-ocean ridge basalts (MORB) and oceanic island basalts  
212 (OIB). This figure shows that the MORB composites have Hf and Nd isotopes  
213 indistinguishable from those of present day Pacific MORB. The three alkali basalt  
214 composites have very different isotopic compositions and plot in the OIB field close  
215 to some of the Austral HIMU samples. When compared to the four samples from site  
216 801 (2 MORB and 2 OIB) analyzed by Pearce et al. (1999), a slight discrepancy is  
217 observed (see Figure 3): while the initial  $\epsilon_{\text{Hf}}$  are comparable, our analyses are  
218 systematically lower for Nd. The origin of the discrepancy is unclear because our Nd  
219 La Jolla measurements are similar to the value mentioned by Pearce et al. (1999).

220

### 221 • *Site 1149 sediments*

222 The measured Hf and Nd isotopic ratios for Site 1149 sediments are reported in Table  
223 2. Initial  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  values were also calculated using paleomagnetic and  
224 biostratigraphic ages (Bartolini, 2003) for samples from units I, III and IV. For units  
225 IIA and IIB, ages are unknown by lack of magnetostratigraphic or biostratigraphic  
226 record. However, the sedimentation rate was particularly slow during deposition of  
227 these units, at about 1 m/Ma if calculated over the entire time period and it does not  
228 seem to have varied through time. The initial Hf and Nd isotopic compositions of

229 samples from units IIA and IIB were therefore calculated using this sedimentation rate  
230 and the depth at which samples occur.

231 The initial  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  of all samples are plotted along the sedimentary column in  
232 Figure 4.  $\epsilon_{\text{Nd}(i)}$  values define a limited range between  $-8$  and  $-5$  with three exceptions,  
233 two samples from Unit I and one sample from Unit IV, which all have significantly  
234 more radiogenic Nd isotopic compositions ( $-3$  to  $-1.6$ ). Hauff et al. (2003) also  
235 reported Nd isotopic compositions obtained on samples from the same Leg and eight  
236 of our samples were also measured by them for Nd, Sr and Pb isotopes. Reported  
237 values are in excellent agreement and the difference between our values and those  
238 reported by Hauff et al. (2003) is always smaller than 50 ppm.

239 Hf isotopes do not define the same pattern as Nd isotopes: while sediments from the  
240 top of the column have positive  $\epsilon_{\text{Hf}(i)}$  values at about  $+6$ , samples from the bottom of  
241 the pile have negative  $\epsilon_{\text{Hf}(i)}$  values at about  $-5$ , and the change occurs gradually  
242 through time. Two samples from the bottom of the pile and one sample from the top  
243 of the pile do not follow the general trend and have significantly more positive  $\epsilon_{\text{Hf}(i)}$  at  
244  $+10.3$ ,  $+8$  and  $+12$  (see Table 2 and Figure 4). When plotted in a  $\epsilon_{\text{Hf}(i)}$  vs.  $\epsilon_{\text{Nd}(i)}$   
245 diagram (Figure 5), the Site 1149 sediments can be compared to the various types of  
246 oceanic sediments that have been published in the literature. This figure shows that  
247 almost all Site 1149 sediments plot in the Fe-Mn crusts and nodule field, above the  
248 “terrestrial array” defined by Vervoort et al. (1999). In addition, the progressive  
249 increase through time of  $\epsilon_{\text{Hf}(i)}$  at constant  $\epsilon_{\text{Nd}(i)}$  appears clearly: samples from unit IV  
250 are located next to the terrestrial array while samples from unit I have the most  
251 radiogenic Hf isotopes. Four exceptions exist, samples 7H4 and 10H3 from unit I and  
252 samples 16R1 and 29R1 from unit IV which have distinctively higher  $\epsilon_{\text{Hf}(i)}$  or  $\epsilon_{\text{Nd}(i)}$   
253 values and do not plot along the general sub-vertical trend (Figure 5).

254

## 255 Discussion

### 256 -A- COMPOSITION OF THE SUBDUCTED PILE

#### 257 • *The basalt composites*

258 In Site 801C, two volcanic sequences are distinguished, a thick pile of tholeiites  
259 overlain by a thin upper layer of more alkaline lavas. Composites of the tholeiitic  
260 rocks were prepared according to their depth along the drill core and according to the  
261 rock types (Kelley et al., 2003). Suffixes on the sample name in Table 1 indicate the  
262 depth range mixed in the composite while the type of material is indicated as being  
263 flows (FLO), volcanoclastics (VCL) or a mixture of the two (ALL). In addition, a  
264 composite representative of the entire tholeiitic section was prepared and called 801  
265 SUPER. All composites have near constant Hf and Nd isotopic compositions (see  
266 Figure 3) with  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  values similar to those of present-day Pacific MORB  
267 (Chauvel and Blichert-Toft, 2001), suggesting that the oceanic crust created about 167  
268 Ma ago (Pringle, 1992) originated from a mantle source equivalent to the present one.  
269 In addition, the similarity between this old Pacific oceanic crust and the basalts  
270 accreting today at the ridge suggests that alteration processes occurring after basalt  
271 formation at the ridge and during the 167 Ma of presence at the bottom of the Pacific  
272 ocean did not affect the Nd and Hf isotopes. In detail, small isotopic variations exist  
273 but no systematic trend can be found. In particular, no change occurs between  
274 composites from the upper, middle and lower part of the hole; in contrast, small but  
275 maybe systematic differences may exist between flow composites and volcanoclastic  
276 composites in terms of Hf isotopes alone with slightly more radiogenic values in the  
277 volcanoclastics than in the flows. However, the difference is so small that it might be  
278 an artifact due to the limited number of analyzed samples (see Table 1).

279 The top alkali basalt composites (TAB in Table 1) have  $\epsilon_{\text{Hf}(i)}$  and  $\epsilon_{\text{Nd}(i)}$  values lower  
280 than the tholeiitic composites and plot in the OIB field in Figure 3 close to data

281 reported for two Jurassic OIB samples drilled at Site 801 and analyzed by Pearce et al.  
282 (1999) and close to Rurutu and Raevavae, two islands in the Austral chain in  
283 Polynesia (Chauvel et al., 1992; Chauvel et al., 1997; Lassiter et al., 2004; Pfänder et  
284 al., 2007) confirming the OIB characteristics suggested by previous studies (Castillo  
285 et al., 1992; Floyd and Castillo, 1992; Hauff et al., 2003). In addition, the strong  
286 similarity between the Hf-Nd isotopic compositions of the alkali basalt composites  
287 and those of Rurutu and Raevavae supports Koppers et al. (2003b) reconstruction of  
288 the past history of the Austral HIMU hotspot in the Western Pacific.

289 The unmodified initial Hf and Nd isotopic compositions of Site 801C tholeiitic  
290 composites together with the preserved isotopes of the alkali composites demonstrate  
291 that, when considered on the bulk scale of the crust, the overall Hf and Nd isotopic  
292 budget of altered basalts remains unchanged during hydrothermal and low  
293 temperature alteration processes. This result extends to the Hf isotopic system the  
294 conclusions reached in previous studies by Staudigel et al. (1995) who demonstrated  
295 that provided samples are large enough to represent the whole rock (1-10 cm), Nd  
296 isotopes of ocean basalts were not modified by hydrothermal alteration.

297

298 • *The sedimentary column*

299 With the exception of four samples discussed later, the sediments sampled at Site  
300 1149 have initial Nd isotopic compositions that, irrespective of their lithology and  
301 age, remain remarkably constant during the entire sedimentation history ( $\epsilon_{Nd(i)}$  vary  
302 only between  $-6.6$  and  $-4$ , see Table 2 and Figure 4). In contrast, their initial  $\epsilon_{Hf}$   
303 values increase systematically through time: the oldest sediments from Unit IV have  
304 the lowest  $\epsilon_{Hf(i)}$  values at  $-5$  while the most recent sediments from Unit I have positive  
305  $\epsilon_{Hf(i)}$  values above  $+5$  (Figure 4). When combined in Figure 5, data points for the  
306 entire sediment pile fall in the field defined by the Fe-Mn crusts and nodules (Godfrey

307 et al., 1997; Albarède et al., 1998; David et al., 2001), and systematically above the  
308 terrestrial array of Vervoort et al. (1999). This suggests that during the 160 Ma of  
309 oceanic sedimentation, the Hf-Nd budget of the sediments was mainly dominated by  
310 sources with radiogenic Hf isotopes relative to their Nd isotopic compositions, as is  
311 the case with the Fe-Mn crusts and nodules, and was little influenced by direct detrital  
312 input from the continents. The reason why the older sediments register a more crustal  
313 signature than the younger sediments is unclear. Units III and IV are particularly poor  
314 in Hf and other trace elements due to the overwhelming presence of cherts and  
315 biogenic carbonates (Plank et al., 2007), while Units I and II contain a significant  
316 proportion of clays. The low  $\epsilon_{\text{Hf}}$  values of the older sediments are therefore not  
317 associated to a high proportion of silicates coming from a continental source. In  
318 addition, 130 Ma ago, the sediments were deposited far away from any continent, in  
319 the middle of the gigantic Pacific superocean (Bartolini and Larson, 2001).

320 There are four exceptions to this general trend: samples 29R1 and 16R1 from unit IV  
321 and samples 7H4 and 10H3 from unit I. Sample 29R1 is a calcareous marl located  
322 few centimeters above the basaltic basement. Plank et al. (2000; 2007) noticed that  
323 the lowermost sediments contain significant enrichments in metalliferous elements  
324 such as Mn and Fe and these sediments were interpreted as resulting from the  
325 presence of hydrothermal vents. While the Nd isotopic composition reported by  
326 Hauff et al. (2003) for sample 29R1 is similar to that of other samples, its Sr and Pb  
327 isotopic ratios are lower than in other samples. Our measured Hf isotopic composition  
328 for sample 29R1 is extremely radiogenic and approaches values obtained on the Site  
329 801 basaltic basement. We suggest therefore that the Hf isotopic value reported for  
330 this sample is strongly influenced by the underlying basaltic crust, most likely due to  
331 hydrothermal sedimentation.

332 Sample 16R1 from Unit IV and samples 7H4 and 10H3 from Unit I contain volcanic  
333 ashes in proportions varying between 10 and 15% (Plank et al., 2007), and their  
334 position in Figure 5 to the right of the trend defined by the other samples in the  
335 sedimentary pile can easily be explained by the contribution of volcanic products to  
336 the sediment composition. Plank et al. (2000) suggested that the volcanic ash present  
337 in samples 7H4 and 10H3 from Unit I could very well come from the Western Pacific  
338 volcanic arcs such as the Izu-Bonin-Marianne arc. This suggestion is entirely  
339 consistent with (a) the Hf and Nd isotopic compositions of the two samples from Unit  
340 I, which are displaced from the sediment pile field in Figure 5 towards more  
341 radiogenic isotopic compositions, and (b) the relationship between Sm/Nd and  $\epsilon_{Nd(t)}$   
342 values shown in Figure 6 where samples 7H4 and 10H3 fall in between the field  
343 defined by the other sediments and the field defined by the Izu-Mariana volcanics. For  
344 sample 16R1 from Unit IV, the origin of the volcanic material is more difficult to  
345 evaluate because at the time when the sediment was deposited on the ocean floor,  
346 about 125 Ma ago, it was located far from any known volcanic arc, volcanic island or  
347 continental arc (see Coffin et al. (2000) and Bartolini and Larson (2001) for  
348 paleogeographic reconstruction of the Pacific plate). However, its position in Figure  
349 6 together with the widespread recognition of OIB-type volcanic products in this part  
350 of the Pacific at that time (Staudigel et al., 1991; Castillo et al., 1992; Floyd et al.,  
351 1992; Lees et al., 1992; Koppers et al., 2003b) suggests that the volcanic ashes  
352 probably came from an ocean island located within a few hundreds of kilometers.

353 Our Hf and Nd isotopic measurements can be combined with trace element analyses  
354 published by Plank et al. (2007) to quantify the average composition of the entire  
355 sedimentary pile. Using an approach similar to that of Plank and Langmuir (1998) we  
356 use discrete measurements performed on carefully selected samples representative of  
357 each lithological unit to calculate the average composition of each lithology. A global

358 average of the entire sedimentary pile was then calculated using the composition of  
359 each unit composition and their relative proportion in the sediment column. Results  
360 are shown in Table 3 and presented in Figure 7. The sedimentary pile drilled at Site  
361 1149 was initially divided in five lithological units or subunits (see figure F17 in  
362 Plank et al. (2000)). However trace element analysis (Plank et al., 2007) and Hf and  
363 Nd isotopes indicate the presence of some distinctive layers within the original units:  
364 (a) The transition between subunit IIB and unit III consists of 10 meters of zeolitic  
365 clays highly enriched in REE compared to the rest of unit III and subunit IIB samples  
366 (Plank et al., 2007). We therefore treated this REE-rich layer individually when  
367 performing the average calculation.  
368 (b) Samples 16R1 93-98 and 29R1 28-35 from unit IV have radiogenic Hf isotopic  
369 compositions compared to the other unit IV sediments (Table 2) and were considered  
370 separately for the average calculation.  
371 The Site 1149 sedimentary column has an average  $\epsilon_{Nd}$  that is negative at -5.9, but its  
372  $\epsilon_{Hf}$  value is positive at about +4.4. In Figure 7, the combined values plot in the Fe-Mn  
373 crusts and nodules field significantly above the “terrestrial array” of Vervoort et al.  
374 (1999), suggesting that the REE and Hf budget for the entire history of sedimentation  
375 in the Pacific was dominated by mineral phases that registered a source with elevated  
376 Hf isotopes as is the case with the Fe-Mn crusts and nodules.  
377 Remarkably similar  $\epsilon_{Hf}$  and  $\epsilon_{Nd}$  values were obtained by White et al. (1986) and  
378 Woodhead (1989) who measured a composite sample from DSDP Site 452 located in  
379 front of the Mariana arc (see figures 1 & 7). It is also not very different from the  
380 estimated average Site 801 sediment value calculated by Wade et al. (2005). This  
381 suggests that the average isotopic compositions obtained in this study represent a  
382 common feature for the Western Pacific sedimentary cover. However, both at DSDP  
383 Site 452 in front of the Mariana arc and at ODP Site 1149 in front of the Izu arc, the



384 sedimentary columns do not include much volcanoclastic sediments (Hussong et al.,  
385 1982; Plank et al., 2000) whose presence would affect the average composition of the  
386 sediment cover. In other locations such as the West Pacific ODP sites 800, 801 and  
387 802 (see figure 1) thick volcanoclastic units are present (Lancelot et al., 1990; Lees et  
388 al., 1992) and there, the average Hf and Nd isotopic compositions would probably be  
389 different, with more radiogenic Nd and Hf isotopic values. The average Hf and Nd  
390 isotopic compositions of DSDP Site 452 and ODP Site 1149 should therefore be  
391 considered as representative of Pacific sedimentary columns dominated by pelagic  
392 sediments.

393

#### 394 **-B- RECYCLING OF THE SITE 1149 SEDIMENTS IN THE IZU-MARIANA ARC SYSTEM**

395

396 The trace element and isotopic characteristics of Izu arc lavas are reported a several  
397 papers (Notsu et al., 1983; Ikeda and Yuasa, 1989; Fryer et al., 1990; Hochstaedter et  
398 al., 1990a; Hochstaedter et al., 1990b; Tatsumi et al., 1992; Taylor and Nesbitt, 1998;  
399 Ishikawa and Tera, 1999; Hochstaedter et al., 2000; Hochstaedter et al., 2001;  
400 Schmidt, 2001; Straub and Layne, 2002; Straub, 2003; Straub et al., 2004) but the  
401 number of samples analyzed for Hf isotopes is quite limited. In terms of Hf and Nd  
402 isotopic compositions, Izu lavas, together with the Mariana arc lavas, are among the  
403 most radiogenic arc lavas studied up to now (White and Patchett, 1984; Woodhead,  
404 1989; Pearce et al., 1999; Woodhead et al., 2001; Tollstrup and Gill, 2005; Wade et  
405 al., 2005; Stern et al., 2006): their Hf and Nd isotopic characteristics are not very  
406 different from those of MORB (see Figure 8). Using our estimate of the average  
407 composition of the subducted sediments, we can evaluate the proportion of sediments  
408 involved in the genesis of the arc lavas. The composition of the mantle contaminated  
409 by the sediments is a matter of debate; it could either be Indian type MORB mantle as

410 suggested by Hickey-Vargas et al. (1998), Savov et al. (2006), Pearce et al. (1999)  
411 and by Woodhead et al. (2001), or Pacific type MORB mantle. Here we calculated  
412 mixing arrays using a Pacific mantle because this evaluation provides a higher  
413 proportion of sedimentary material due to the more radiogenic Nd isotopic  
414 composition of the Pacific mantle; it is therefore the maximum possible contribution  
415 from the sedimentary pile. In addition, some of the data used to suggest that the  
416 mantle wedge has “Indian” characteristics are ambiguous. The samples from the  
417 Philippine basement analyzed by Savov et al. (2006) and by Pearce et al. (1999) plot  
418 in between the Indian and the Pacific MORB fields in Nd-Hf isotopic space (see  
419 Figure 8). Moreover, the overlap between the Philippine plate and the Indian MORB  
420 as shown by Hickey-Vargas et al. (1998) and by Savov et al. (2006) is accentuated by  
421 using initial ratios of the 45 Ma volcanics vs. present-day isotopic ratios for MORB.  
422 The age correction has a significant impact on the  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios,  
423 but not on the  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  ratios. When the measured  
424 ratios are compared to the present-day MORB fields, data plot at an ambiguous  
425 intermediate position. Thus, while mantle of Indian affinity may have generated some  
426 Philippine basement, its distribution beneath the modern arcs is unknown, and given  
427 the subtle shifts in Nd and Hf that have been observed even in these “Indian”  
428 provinces, we chose the more extreme Pacific end-member to provide maximum  
429 sediment contributions.

430 Mixing arrays between the average subducted sediments and Pacific mantle are  
431 calculated using end-member compositions given in the caption of Figure 8 and  
432 shown in Figure 8. They fit well the data reported for both Izu and Mariana arc lavas  
433 and suggest that less than 2% of sediment mixed with depleted mantle can reproduce  
434 the island arc Hf-Nd isotopic array. This figure is very similar to the proportion of  
435 sediment suggested by Wade et al. (2005) for the Mariana arc and it is consistent with

436 estimates based on other trace elements or isotopic systems (i.e., (Tera et al., 1986;  
437 Ryan and Langmuir, 1988; Woodhead et al., 2001). If Indian type mantle were used  
438 instead of Pacific mantle composition, the proportion of sediment would be lower.  
439 The position of Site 1149 average sediment composition in the Hf-Nd isotopic space  
440 and the shape of the mixing array in Figure 8, also suggest that the displacement of  
441 the Izu-Bonin-Mariana arc lavas to the left of the 'MORB-OIB array' could be due to  
442 the composition of the subducted material and not necessarily due to changes of the  
443 Nd/Hf ratio during either dehydration or melting of the sediment component. This is  
444 consistent with the relationship between Hf isotopic compositions and the Hf/Hf\*  
445 ratios shown in Figure 9a. Wade et al. (2005) showed that by using their estimate of  
446 the sediment composition combined with the depleted mantle value recommended by  
447 Salters and Stracke (2004), mixing curves did not pass through the Mariana island arc  
448 data field (see figures 9a & b). They suggested that the Hf/Hf\* ratio of the depleted  
449 mantle might be too high, but also that the Nd/Hf ratio of the sediment involved in the  
450 source of the volcanic rocks had to be much higher than their sediment estimate (see  
451 Figure 9b and their figure 8). Using our estimate of the composition of the sediment  
452 pile, the discrepancy between mixing proportions given by the isotopic compositions  
453 (less than 2%, see Figure 8) and by the trace element ratios (less than 4%, see figures  
454 9a & b) is lower, but still exists. To have similar proportions of sediments in the two  
455 figures requires a mantle wedge with a slight Hf deficiency relative to its REE  
456 content. Most of the Izu-Mariana arc lava data points can be explained by mixing of  
457 depleted mantle and bulk sediment. Significant outliers are the Izu forearc lavas  
458 (Pearce et al., 1999) which have extremely high Hf/Hf\* and low Nd/Hf ratios and the  
459 Kasuga seamounts in the Mariana arc (Tollstrup and Gill, 2005) which have  
460 extremely low  $\epsilon_{\text{Hf}}$  and Hf/Hf\* values and high Nd/Hf ratios. These two datasets  
461 cannot be explained by any simple mixing relationship and require additional

462 processes to account for their arrays. Pearce et al. (1999) suggested that the elevated  
463 Hf/Hf\* values of the Izu protoarc lavas require a fractionation process that either  
464 added Hf or removed REE from the lavas while Tollstrup and Gill (2005) argued that  
465 residual rutile, zircon and monazite were necessary to explain the Kasuga seamount  
466 array.

467 Even if the site 1149 sediments have trace element contents and Nd-Hf isotopic  
468 compositions suggesting that simple bulk mixing between subducted sediments and  
469 mantle wedge could explain the Nd-Hf characteristics of the Izu-Mariana island arc  
470 lavas, things are more complex when other isotopic systems are considered. In  
471 particular, previous studies done by Elliot et al. (1997), Ishikawa and Tera (1999),  
472 Hochstaedter et al. (2001), Hauff et al. (2003) and by Straub et al. (2004) clearly  
473 demonstrated that some elements were transferred from the subducted material to the  
474 source of volcanics through fluid phases. Fractionation of trace elements like the  
475 REE and the HFSE by residual minerals during magma genesis is also required by  
476 the composition of both the Izu protoarc volcanics and the Kasuga seamounts in the  
477 Mariana arc (see figures 9a & b).

478 When site 1149 data are used as the sediment contaminant in the mantle wedge below  
479 the Izu arc, the modeling is quite satisfactory but the number of Nd-Hf isotopic  
480 analyses on the Izu volcanics is so low that the constraints are relatively weak. More  
481 analyses of the Izu volcanics would certainly help refine the general model. In the  
482 case of the Mariana arc, for which a significant number of Nd-Hf analyses has been  
483 published, the composition of the subducted sediment is poorly constrained: the  
484 estimate suggested by Wade et al. (2005) for Site 801 has an  $\epsilon_{\text{Hf}}$  and a Nd/Hf ratio  
485 that are too low to define a mixing array going through the arc data (see figures 8 and  
486 9). The Site 452 clay composite analyzed by Woodhead (1989) has  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  similar  
487 to the Site 1149 average values (Figure 8) but no trace element data have been

488 published. Finally, the Site 1149 sediments have trace element and isotopic  
489 compositions defining mixing arrays compatible with the Mariana arc data, but the  
490 drill site is not located in front of the Mariana arc, and contains different sedimentary  
491 units than found there (Plank et al., 2007). The main difference between the Site 1149  
492 and Site 801 sedimentary averages are the Cretaceous volcanoclastics that are a major  
493 part of the sedimentary input to the Marianas trench. These have isotopic  
494 compositions similar to OIB, and their inclusion in the Site 801 average is responsible  
495 for the lower  $\epsilon_{\text{Hf}}$  and Nd/Hf, and the misfits to the mixing lines. One possible solution  
496 to the mixing problem is that Nd and Hf are retained in the volcanoclastic unit, by the  
497 preferential stability of zircon and REE phases expected in these Zr- and REE-  
498 enriched materials (Klimm et al., 2008). Another possibility is simply that more data  
499 are necessary to establish whether a geographical variability exists. The average  
500 compositions of the subducted sediment pile in front of the Mariana arc and the Izu-  
501 Bonin arc could then be compared and a well constrained model could be developed.  
502 In 2003, Straub published an overview of the temporal changes in the chemical  
503 composition of the Izu Bonin–Mariana arc lavas (Straub, 2003). She demonstrated  
504 that over the past 50 Ma, the lava composition changed from boninitic to tholeiitic  
505 with an accompanying increase in  $\text{TiO}_2$  contents and  $\epsilon_{\text{Nd}}$  values. Because the Nd  
506 isotopic composition of the sedimentary pile is quite uniform at  $\epsilon_{\text{Nd}} \approx -6.5$  (see Table  
507 2 and Figure 4), secular changes in the sediment composition cannot explain the  
508 variation observed in the arc lavas. We suggest therefore that the increasingly  
509 depleted nature of the arc lavas might relate to a decreasing contribution of the  
510 sediment component through time.

511

512 **-C- RECYCLING OF SEDIMENTS IN ISLAND ARCS AND IN THE MANTLE**

513 • *Oceanic sediments and worldwide arc systems*

514 In more general terms, the Nd and Hf isotopic compositions of oceanic sediments can  
515 be compared to the arc lava isotopic array to evaluate their impact on the island arc  
516 compositions. In Figure 10, we show a compilation of available data published on  
517 island arcs. Not only do the data define an array that is significantly displaced to the  
518 left of the MORB-OIB array, but it also has a shallower slope:  $\epsilon_{\text{Hf}} = 1.23 \cdot \epsilon_{\text{Nd}} + 6.36$  vs.  
519  $\epsilon_{\text{Hf}} = 1.59 \cdot \epsilon_{\text{Nd}} + 1.28$ . While these values are slightly different from those published by  
520 Vervoort et al. (1999) mainly because of new data published within the last 10 years,  
521 they confirm the distinctive trend of arc volcanism relative to intra-plate volcanism. It  
522 can be argued, as is done by Pearce et al. (1999) and by Tollstrup (2005) that the  
523 slope of the “island arc array” results of a decoupling of Nd and Hf during  
524 dehydration and/or melting of the subducted slab with a sedimentary component  
525 characterized by elevated Nd/Hf ratios. However, we would like to suggest here that  
526 the “island arc array” could also be mainly controlled by the mixing of depleted  
527 mantle and subducted sediments. In Figure 10, we show mixing arrays between  
528 various sedimentary end-members and an average depleted mantle source.  
529 Contaminating the mantle wedge with the Leg 185 average sediment produces an  
530 array shown with a black striped line in Figure 10 that goes through the arc data with  
531 the highest  $\epsilon_{\text{Hf}}$  values but does not appear to be the best endmember to account for the  
532 composition of most island arcs even though it can explain some arcs data (e.g., Izu,  
533 Mariana and some of the Luzon arc data). Most arc lavas lie below this mixing line  
534 with the arcs located next to continents (the Lesser Antilles and the Aegean arc)  
535 defining the lower part of the arc array. We suggest therefore that depending on the  
536 nature of the subducted sediments (sands next to continental platforms, and clays,  
537 muds and Fe-Mn crusts further away from continental margins) a range of mixing  
538 lines can be calculated. In Figure 10, we show two end-member mixing lines

539 calculated using the Nd and Hf concentrations and Nd isotopic composition of  
540 GLOSS (Plank and Langmuir, 1998) for which no Hf isotopic composition is  
541 available. We therefore used a range of Hf isotopic compositions as shown by the  
542 vertical brown line in Figure 10. The mixing line between depleted mantle and the  
543 low  $\epsilon_{\text{Hf}}$  sand end-member reproduces well the Lesser Antilles and Aegean arcs  
544 compositions while mixtures of mantle wedge and high  $\epsilon_{\text{Hf}}$  sediments reproduce the  
545 compositions of arcs such as Luzon and Sunda. In most cases, the proportion of  
546 sediments involved in the source of arc volcanism is lower than 5% if straight bulk  
547 mixing between sediments and mantle is used. If the sediment component is extracted  
548 from the sedimentary material by either a fluid phase or a melt, the proportion of  
549 sediment will be lower. We realize that this mixing model is quite simplistic and that  
550 a better knowledge of the oceanic sediment compositions is really necessary. As  
551 mentioned by Plank and van Keken (2008), the diversity of  $\epsilon_{\text{Hf}}$ ,  $\epsilon_{\text{Nd}}$  and associated  
552 REE/HFSE ratios in oceanic sediments needs to be better documented to understand  
553 the way sediments are involved in the arc genesis.

554

555 • *Proportions of the incoming sediment flux injected back into the mantle*

556 Our average composition of the Site 1149 sedimentary pile can be used in conjunction  
557 with physical and chemical data to estimate the fraction of subducted sediments that is  
558 transferred directly into the arc system, and the fraction that is sent back into the  
559 convecting mantle.

560 The sediment input flux can be evaluated using the convergence rate of the Pacific  
561 plate, the thickness of the sediment pile, and its density, water content and average Nd  
562 and Hf concentrations. All these values, which are summarized in Table 4, allow  
563 estimates of the Nd input flux from the sediment at 857 kg/km of arc/yr and of the Hf  
564 input rate at 49 kg/km of arc/yr. The volcanic arc output flux can be evaluated using

565 the magmatic addition rates determined by Dimalanta et al. (2002) for the Izu-Bonin  
566 arc and the average Nd and Hf concentrations of arc lavas (White and Patchett, 1984;  
567 Pearce et al., 1999). Using the values listed in Table 4, we calculate a Nd output rate  
568 of about 1375 kg/km of arc/yr and a Hf output rate of about 312 kg/km of arc/yr. The  
569 Nd and Hf present in the arc lavas originate most probably from both the mantle  
570 wedge and the subducted material. Using the  $\epsilon_{Nd}$  values given in Table 4 for the  
571 average arc lavas, the mantle wedge and the subducted material, we can calculate that  
572 about  $10\% \pm 6\%$  of the Nd present in the arc lavas comes from the subducted  
573 sediment, i.e.,  $138 \pm 82$  kg/km of arc/yr. Subtracting this amount from the total  
574 amount of Nd present in the subducted sediment pile implies that about  $85\% \pm 9\%$  of  
575 the sedimentary Nd is sent back into the convecting mantle.

576 A similar calculation carried out for Hf does not provide well-constrained proportions  
577 because the  $\epsilon_{Hf}$  values of mantle wedge and arc lava are almost indistinguishable.  
578 However, using the Nd/Hf ratios of the three components, we can place limits to the  
579 proportion of Hf from the sediment pile that is transferred to the arc lavas and the  
580 amount that is recycled into the mantle. Assuming that the sedimentary material  
581 involved in the arc lava genesis has the same Nd/Hf ratio as the sediment itself, we  
582 evaluate the Hf flux from sediment to arc lava as 7.9 kg/km of arc/yr and calculate  
583 that  $85\% \pm 9\%$  of sedimentary Hf is recycled back into the mantle. It is very unlikely  
584 that the Nd/Hf of the material coming out of the subducted material is lower than that  
585 of the sediment because Nd is considered as more mobile in fluid phases than Hf  
586 (Kogiso et al., 1997; Johnson and Plank, 1999). Dehydration products are therefore  
587 likely to have a  $Nd/Hf \geq 17.5$  and transfer less than the 7.9 kg/km of arc/yr calculated  
588 above. This in turn suggests that a minimum of 85% of the sedimentary Hf is  
589 recycled back into the mantle.



590 In summary, the Nd and the Hf present in the sedimentary pile contribute to the arc  
591 lava composition but the vast majority ( $\geq 85\%$ ) is recycled into the mantle of the  
592 Earth to affect its general isotopic composition. Assuming that similar material has  
593 been recycled into the mantle over long periods of time during Earth history, its  
594 composition, which differs significantly from that of normal mantle, can create large  
595 chemical and isotopic heterogeneities. As already suggested by previous authors  
596 (Hofmann and White, 1982; Chauvel et al., 1992; Blichert-Toft and Albarède, 1999),  
597 such material could be present in the source of ocean island basalts. It could also be  
598 mixed into the normal depleted mantle and suppress the radiogenic growth of both Nd  
599 and Hf resulting from magmatic melt extraction of continental crust. Such modeling  
600 of the impact of recycled subducted oceanic basalt and sediments into the mantle over  
601 Earth history was performed recently by Chauvel et al. (2008) for the Nd and Hf  
602 isotopic systems and they showed that a combination of oceanic sediments and basalts  
603 could satisfactorily contribute to the mantle sources of both oceanic island basalts and  
604 mid-ocean ridge basalts and explain the “mantle array”.

## 605 **Conclusion**

606 Our Hf and Nd isotopic study of the Site 1149 sediments and the Hole 801C basaltic  
607 composites leads to the following main observations:

608 - The similarity between Hf and Nd isotopes measured on the Site 801C basalts and  
609 present-day Pacific MORB suggest that both isotopic systems are unaffected by  
610 hydrothermal processes and low temperature alteration for a period of more than 150  
611 Ma.

612 - The Hf and Nd isotopic compositions of Site 1149 sediments do not display a large  
613 range and the average composition of the entire sedimentary pile falls in the field of  
614 Fe-Mn crusts and nodules at  $\epsilon_{Nd} = -5.9$  and  $\epsilon_{Hf} = +4.4$ .

615 - The Hf and Nd isotopic composition of the Izu-Mariana arc lavas can be modeled by  
616 mixing a Pacific type mantle wedge and less than 2% sediments and the composition  
617 of most island arc lavas can be reproduced by mixing less than 5% oceanic sediments  
618 with an ordinary depleted mantle wedge.

619 - We evaluate that about 85% of the Nd present in the subducted sediments is  
620 recycled into the mantle. For Hf, the proportion is constrained to be similar (85%) or  
621 higher. Consequently, most of the Nd or Hf present in the oceanic sediments is  
622 recycled into the mantle to create chemical heterogeneities and affect its average  
623 composition.

624

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634

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926 **Figures captions**

927 **Figure 1** Map of the Western Pacific region with locations of ODP Sites 800, 801,  
928 802, 1149 and DSDP Site 452 (modified from Plank et al. (2000)).

929

930 **Figure 2** Lithostratigraphic column of Site 1149 with locations of samples analyzed  
931 for Hf and Nd isotopes. The transition between subunit IIB and unit III consists of  
932 zeolitic clays extremely enriched in REE relative to other Site 1149 sediments (Plank  
933 et al., 2007). They have been considered as a distinct unit in this study.

934

935 **Figure 3**  $\epsilon_{\text{Hf}}$  vs.  $\epsilon_{\text{Nd}}$  diagram showing the measured and initial isotopic compositions  
936 of the composite basalts from Hole 801C relative to measurements published by  
937 Pearce et al. (1999) and the fields of present-day MORB and OIB. For the MORB  
938 composites,  $\epsilon_{\text{Nd}}$  and  $\epsilon_{\text{Hf}}$ , and  $\epsilon_{\text{Nd}(i)}$  and  $\epsilon_{\text{Hf}(i)}$  are almost identical and are shown by only  
939 one symbol. In contrast, a difference of one to two  $\epsilon$  values is observed for the alkali  
940 basalts and the measured values are shown by the light color symbols while the initial  
941 values are shown by the orange dots. The HIMU islands in the Austral chain (Tubuai,  
942 Rurutu and Raevavae) are shown with darker symbols. The inset in the upper left  
943 corner presents the initial  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  with uncertainties of about  $\pm 0.65$  unit for the  
944  $\epsilon_{\text{Nd}(i)}$  values and about  $\pm 1$  unit for the  $\epsilon_{\text{Hf}(i)}$  values. MORB and OIB data are compiled  
945 from Georoc and PetDB databases (Georoc; PetDB) as well as unpublished data from  
946 C. Chauvel.

947

948 **Figure 4**  $\epsilon_{\text{Nd}(i)}$  and  $\epsilon_{\text{Hf}(i)}$  values of Site 1149 sediments plotted versus depth in the  
949 sedimentary pile.

950

951 **Figure 5**  $\epsilon_{\text{Hf}(i)}$  vs.  $\epsilon_{\text{Nd}(i)}$  diagram comparing the initial ratios calculated for Site 1149  
952 sediments with those of Fe-Mn crusts and nodules and other oceanic sediments.  
953 Samples 7H4 140-150, 10H3 140-150, 16R1 93-98 and 29R1 28-35, with distinct  
954 features are marked. The Nd isotopic composition of sample 29R1 is from Hauff et al.  
955 (2003). Fe-Mn crusts and nodules and other sediments data are from White et al.  
956 (1986), Ben Othman et al. (1989), McLennan et al. (1990), Godfrey et al. (1997),  
957 Albarède et al. (1998), Pearce et al. (1999), Vervoort et al. (1999) and David et al.  
958 (2001). “Terrestrial array” as defined by Vervoort et al. (1999) is also shown. MORB  
959 data sources as in Figure 3.

960

961 **Figure 6** Sm/Nd vs.  $\epsilon_{\text{Nd}(i)}$  diagram showing Site 1149 sediments together with the  
962 Pacific Seawater field, the Izu-Mariana arc lavas, the Site 800A alkali dolerites and  
963 OIB from Magellan seamounts. Trace element data of Site 1149 sediments are from  
964 Plank et al. (2007). The Pacific Seawater field has been drawn using data published  
965 by Piegras et al. (1988) and Shimizu et al. (1994). Izu-Mariana arc lavas are from  
966 White et al. (1984), Woodhead et al. (1989), Elliott et al. (1997), Pearce et al. (1999),  
967 Woodhead et al. (2001), Wade et al. (2005), Tollstrup and Gill (2005) and Stern et al.  
968 (2006). Four sediments analyzed by Pearce et al. (1999) are shown with small brown  
969 dots. Site 800A dolerites data are from Floyd et al. (1992) and Castillo et al. (1992).  
970 Magellan seamounts data are from Staudigel et al. (1991).

971

972 **Figure 7** Present-day  $\epsilon_{\text{Hf}}$  vs.  $\epsilon_{\text{Nd}}$  diagram of Site 1149 sediments together with Fe-Mn  
973 crusts and nodules and other oceanic sediments. Hf and Nd isotopes of a composite  
974 from DSDP Site 452 sedimentary pile are from Woodhead et al. (1989) while values  
975 for Site 801 are from Wade et al. (2005). Other data sources as in Figure 5. The  
976 positions of Site 1149 sediments in the figure differ slightly from their position in

977 Figure 5 because here we plot present-day measured ratios while initial ratios were  
978 reported in Figure 5.

979

980 **Figure 8**  $^{176}\text{Hf}/^{177}\text{Hf}$  vs.  $^{143}\text{Nd}/^{144}\text{Nd}$  for sediments, Izu-Bonin-Mariana arc lavas and  
981 Pacific and Indian MORB showing that less than 2% sediment combined with Pacific  
982 MORB mantle is enough to explain the composition of the arc lavas. The sediment  
983 composition of Site 1149 is given in Table 4 and the depleted mantle compositions  
984 are evaluated as follows: (a) Nd and Hf concentrations are from Salters and Stracke  
985 (2004); (b) three different isotopic compositions were selected: our estimated average  
986 composition for Pacific MORB:  $\epsilon_{\text{Nd}}=+9.7$  and  $\epsilon_{\text{Hf}}=+15$ , the sample with the most  
987 radiogenic Hf isotopes:  $\epsilon_{\text{Nd}}=+10.8$  and  $\epsilon_{\text{Hf}}=+20.1$ , and the sample with the least  
988 radiogenic Hf isotopes:  $\epsilon_{\text{Nd}}=+11.2$  and  $\epsilon_{\text{Hf}}=+12.1$ . Three mixing arrays are shown  
989 between sediment and the three depleted mantle sources. The mixing arrays were  
990 calculated assuming bulk mixtures of sediment and mantle. The sediment proportions  
991 are therefore maximum proportions because if the sediment component is extracted  
992 through either a melt or a fluid phase, the trace element concentrations of the  
993 contaminant should be higher than the starting sediment concentrations. The mixing  
994 array between Site 801 estimate (Wade et al., 2005) and average Pacific mantle  
995 shown with a dashed brown curve passes well below the arc lava fields. If an Indian-  
996 type mantle is used instead of a Pacific depleted mantle, the proportion of sediment  
997 required to explain the Izu-Mariana arc data is even lower, at less than 1%. Data  
998 sources as in figures 4, 5 and 6 plus sediment data from Vlastelic et al. (2005) and  
999 Philippine plate basement and volcanic clasts from Pearce et al. (1999) and Savov et  
1000 al. (2006).

1001

1002 **Figure 9** (a) Hf/Hf\* vs.  $\epsilon_{\text{Hf}}$  and (b) Nd/Hf vs.  $\epsilon_{\text{Hf}}$  showing mixing arrays between the  
1003 average Site 1149 sediment and the same three potential depleted mantle sources as in  
1004 Figure 8. With the exception of the Kasuga seamounts and the Izu protoarc volcanics,  
1005 most Izu and Mariana arc volcanics can be explained by less than 4% sediment in the  
1006 contaminated mantle source. Calculations were performed as in Figure 8 and the data  
1007 sources are as in figures 5,6,7 and 8. Hf/Hf\* measures the size of the primitive  
1008 mantle normalized Hf anomaly calculated using the following equation:  
1009  $\text{Hf}/\text{Hf}^* = \text{Hf}_N / ((\text{Nd}_N + \text{Sm}_N) / 2)$  and the normalizing values of Hofmann (1988) . As in  
1010 Figure 8, the mixing array between Site 801 estimate (Wade et al., 2005) and depleted  
1011 mantle does not intersect the island arc data field.

1012

1013 **Figure 10**  $\epsilon_{\text{Hf}}$  versus  $\epsilon_{\text{Nd}}$  diagram showing the relationship between island arc  
1014 volcanics and oceanic sediments. The island arc array is shown by an orange line  
1015 while the mantle array is shown by a grey line. Field for the three main types of  
1016 oceanic sediments are from Chauvel et al. (2008) and data on circum-Antarctic  
1017 sediments published by van de Flierdt et al. (2007) are also shown (light brown  
1018 diamonds) but could not be distributed among the fields due to the absence of  
1019 petrological description. Because no  $\epsilon_{\text{Hf}}$  value is available for GLOSS, its  
1020 composition is represented by a vertical brown bar at  $\epsilon_{\text{Nd}} = -8.9$ . Two typical mixing  
1021 arrays calculated using the GLOSS Nd and Hf concentrations and mantle values as  
1022 given in the caption of Figure 8 are shown as brown thin curves: one using an  
1023 elevated  $\epsilon_{\text{Hf}}$  value at about + 4 and one using a low  $\epsilon_{\text{Hf}}$  value at -13. A mixing curve  
1024 between Site 1149 and depleted mantle is also shown (black dashed curve). Data were  
1025 compiled using the Georoc database (Georoc, April 2008) for IAV and OIB and the  
1026 PetDB database (PetDB, April 2008) for MORB.

1027 **Table 1:** Hf and Nd isotopic compositions of Hole 801C Composites  
 1028

Composites <sup>a</sup>	Type	<sup>143</sup> Nd/ <sup>144</sup> Nd ± 2σ <sub>m</sub> <sup>b</sup>	ε <sub>Nd</sub> <sup>c</sup>	ε <sub>Nd(i)</sub> <sup>d</sup>	<sup>176</sup> Hf/ <sup>177</sup> Hf ± 2σ <sub>m</sub> <sup>b</sup>	ε <sub>Hf</sub> <sup>c</sup>	ε <sub>Hf(i)</sub> <sup>d</sup>
801-TAB-0-50	FLO	0.512845 ± 13	+4.0	+5.4	0.282979 ± 7	+7.3	+9.9
801-TAB-0-50	VCL	0.512848 ± 9	+4.1	+5.4	0.283019 ± 6	+8.7	+10.9
801-TAB-0-50	All	0.512896 ± 6	+5.0	+6.3	0.282973 ± 5	+7.1	+9.6
801-MORB-0-110	FLO	0.513154 ± 32	+10.1	+9.7	0.283206 ± 6	+15.3	+15.8
801-MORB-0-110	All	0.513081 ± 10	+8.6	+8.3	0.283201 ± 5	+15.2	+15.3
801-MORB-110-220	FLO	0.513128 ± 9	+9.6	+9.2	0.283171 ± 6	+14.1	+14.8
801-MORB-110-220	VCL	0.513080 ± 6	+8.6	+8.4	0.283219 ± 9	+15.8	+15.4
801-MORB-110-220	All	0.513103 ± 7	+9.1	+8.8	0.283194 ± 8	+14.9	+15.4
801-MORB-220-420	FLO	0.513154 ± 8	+10.1	+9.8	0.283172 ± 7	+14.1	+14.7
801-MORB-220-420	VCL	0.513157 ± 5	+10.1	+9.8	0.283201 ± 5	+15.2	+15.7
801-MORB-220-420	VCL <sup>e</sup>	0.513159 ± 4	+10.2	+9.9			
801-MORB-220-420	All	0.513132 ± 7	+9.6	+9.3	0.283161 ± 6	+13.8	+14.3
801	SUPER	0.513118 ± 6	+9.4	+9.1	0.283164 ± 7	+13.9	+14.3

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1030 Footnote:

1031 <sup>a</sup> TAB, top alkali basalts; MORB, mid-ocean ridge tholeiites; FLO, less altered flows and pillows; VCL, highly altered volcanoclastics; SUPER, all site  
 1032 801 tholeiite.

1033 <sup>b</sup> Normalized for mass fractionation to <sup>146</sup>Nd/<sup>144</sup>Nd=0.7219 and <sup>179</sup>Hf/<sup>177</sup>Hf=0.7325.

1034 <sup>c</sup> ε<sub>Hf</sub> and ε<sub>Nd</sub> have been calculated using <sup>176</sup>Hf/<sup>177</sup>Hf<sub>CHUR</sub>=0.282772 after Blichert-Toft and Albarède, 1997 and <sup>143</sup>Nd/<sup>144</sup>Nd<sub>CHUR</sub>=0.512638.

1035 <sup>d</sup> ε<sub>Hf(i)</sub> and ε<sub>Nd(i)</sub> have been calculated using the trace element data published by Kelley et al. (2003) and the following ages: alkali materials 157Ma  
 1036 and tholeiitic materials 167Ma (Pringle, 1992); <sup>176</sup>Lu/<sup>177</sup>Hf<sub>CHUR(0)}</sub>=0.0332 after Blichert-Toft and Albarède, 1997 and <sup>147</sup>Sm/<sup>144</sup>Nd<sub>CHUR(0)}</sub>=0.1967.

1037 <sup>e</sup> Complete duplicate analysis.

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**Table 2:** Hf and Nd isotopic compositions of Site 1149 sediments

Sample	Depth (mbsf) <sup>a</sup>	Unit	Dissolution	Protocol <sup>b</sup>	<sup>143</sup> Nd/ <sup>144</sup> Nd ± 2σ <sub>m</sub> <sup>c</sup>	ε <sub>Nd</sub> <sup>d</sup>	ε <sub>Nd(i)</sub> <sup>e</sup>	<sup>176</sup> Hf/ <sup>177</sup> Hf ± 2σ <sub>m</sub> <sup>c</sup>	ε <sub>Hf</sub> <sup>d</sup>	ε <sub>Hf(i)</sub> <sup>e</sup>
1149A 1H1 140-150	1.40	I		BT 97	0.512369 ± 10	-5.2	-5.2	0.282966 ± 8	+6.9	+6.9
1149A 1H1 140-150 <sup>f</sup>	1.40	I	in Parr Bomb	BT 97				0.282964 ± 5 <sup>g</sup>	+6.8	+6.8
1149A 4H2 140-150	26.10	I		BT 97	0.512307 ± 5	-6.5	-6.4	0.282939 ± 9	+5.9	+5.9
1149A 4H2 140-150 <sup>f</sup>	26.10	I		BT 97	0.512271 ± 6	-7.2	-7.2			
1149A 7H4 140-150	57.60	I		BT 97	0.512557 ± 6	-1.6	-1.6	0.283063 ± 8	+10.3	+10.3
1149A 10H3 140-150	84.60	I		BT 97	0.512483 ± 4	-3.0	-3.0	0.282973 ± 4 <sup>g</sup>	+7.1	+7.1
1149A 10H3 140-150 <sup>f</sup>	84.60	I		BT 97	0.512507 ± 5	-2.6	-2.5			
1149A 14H2 140-150	121.10	IIA		BT 97	0.512291 ± 11	-6.8	-6.6	0.282960 ± 6 <sup>g</sup>	+6.6	+6.7
1149A 18H3 140-150	160.40	IIB	in Parr Bomb	BT 97				0.282816 ± 8	+1.6	+1.6
1149A 18H3 140-150 <sup>f</sup>	160.40	IIB	in Parr Bomb	BT 97				0.282791 ± 4	+0.7	+0.7
1149A 20X1 140-150	171.20	IIB-III		BT 97	0.512342 ± 5	-5.8	-5.4	0.282936 ± 5 <sup>g</sup>	+5.8	+3.7
1149B 6R1 38-42	199.08	III	in Parr Bomb	Ca-Depl	0.512308 ± 6	-6.4	-5.8	0.282873 ± 8 <sup>g</sup>	+3.6	+2.2
1149B 12RCC 0-5	245.40	III	in Parr Bomb	Ca-Depl	0.512294 ± 5	-6.7	-5.8	0.282761 ± 3	-0.4	-1.4
1149B 16R1 93-98	283.23	IV		BT 97	0.512519 ± 6	-2.3	-1.1	0.282954 ± 6	+6.4	+8.0
1149B 17R1 14-17	292.14	IV		BT 97	0.512248 ± 12	-7.6	-6.3	0.282677 ± 4	-3.4	-2.7
1149B 17R1 14-17 <sup>f</sup>	292.14	IV		BT 97				0.282678 ± 3 <sup>g</sup>	-3.3	-2.7
1149B 18R1 41-43	302.01	IV		BT 97	0.512269 ± 5	-7.2	-5.9	0.282692 ± 5	-2.8	-3.1
1149B 20R1 25-35	321.15	IV		BT 97	0.512267 ± 7	-7.2	-5.8			
1149B 22R1 20-25	340.30	IV		BT 97	0.512240 ± 8	-7.8	-6.5	0.282671 ± 23	-3.6	-3.3
1149B 25R1 19-23	368.89	IV	in Parr Bomb	Ca-Rich				0.282715 ± 9 <sup>g</sup>	-2.0	-5.4
1149B 27R1 49-55	388.09	IV		Ca-Rich	0.512282 ± 12	-6.9	-5.5			
1149B 28R1 52-56	397.62	IV		BT 97	0.512353 ± 77	-5.6	-4.1			
1149B 28R2 48-66	398.90	IV		BT 97	0.512312 ± 24	-6.4	-4.9			
1149B 29R1 28-35	407.08	IV		BT 97				0.283244 ± 49	+16.7	+12.0

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Footnote:

|044 <sup>a</sup> mbsf, meters below surface seafloor.  
|045 <sup>b</sup> Protocol used for Hf separation: BT 97, original protocol of Blichert-Toft et al., 1997; Ca-Depl and Ca-Rich, protocols for Ca-depleted and Ca  
|046 enriched samples described in Fig. A in the appendix.  
|047 <sup>c</sup> Normalized for mass fractionation to  $^{146}\text{Nd}/^{144}\text{Nd}=0.7219$  and  $^{179}\text{Hf}/^{177}\text{Hf}=0.7325$ .  
|048 <sup>d</sup>  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  have been calculated using  $^{176}\text{Hf}/^{177}\text{Hf}_{\text{CHUR}}=0.282772$  after Blichert-Toft and Albarède, 1997 and  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}=0.512638$ .  
|049 <sup>e</sup>  $\epsilon_{\text{Nd}(i)}$  and  $\epsilon_{\text{Hf}(i)}$  have been calculated using the Sm/Nd and Lu/Hf ratios calculated from the trace element data published by Plank (2007) and for Unit I,  
|050 III and IV sediments paleomagnetic and biostratigraphic ages reported by Plank et al., 2000. Approximate ages of samples from unit II were  
|051 determined by linear extrapolation from ages of unit I and III samples using a constant sedimentation rate of 1 m/Ma,  $^{176}\text{Lu}/^{177}\text{Hf}_{\text{CHUR}(0)}=0.0332$  after  
|052 Blichert-Toft and Albarède, 1997 and  $^{147}\text{Sm}/^{144}\text{Nd}_{\text{CHUR}(0)}=0.1967$ . Assuming a 5% error on the measured parent/daughter ratios, the error propagation  
|053 on the calculated  $\epsilon_{(i)}$  due to the trace element ratio is always smaller than 0.1 epsilon unit.  
|054 <sup>f</sup> Complete duplicate analysis.  
|055 <sup>g</sup> Data published by Chauvel et al. (2008).  
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**Table 3:** Hf and Nd bulk isotopic compositions and trace element ratios for the Site 1149 sedimentary pile

Unit	Mass%	$^{143}\text{Nd}/^{144}\text{Nd}^{\text{a}}$	$\epsilon_{\text{Nd}}^{\text{b}}$	$^{176}\text{Hf}/^{177}\text{Hf}^{\text{a}}$	$\epsilon_{\text{Hf}}^{\text{b}}$	Nd (ppm) <sup>c</sup>	Sm (ppm) <sup>c</sup>	Lu (ppm) <sup>c</sup>	Hf (ppm) <sup>c</sup>	Sm/Nd	Nd/Hf	Lu/Hf
Site 1149	100	0.512336	-5.9	0.282897	+4.4	25.2	5.32	0.39	1.44	0.211	17.5	0.271
Unit I	30.2	0.512423	-4.2	0.282987	+7.6	21.5	4.72	0.414	2.62	0.220	8.2	0.158
Subunit IIA	6.5	0.512291	-6.8	0.282960	+6.6	26.5	5.90	0.521	3.05	0.223	8.7	0.171
Subunit IIB	4.3			0.282816	+1.6	59.4	13.3	0.994	4.14	0.224	14.3	0.240
Subunit IIB-III	2.2	0.512342	-5.8	0.282936	+5.8	193.5	44.0	3.19	4.47	0.227	43.3	0.714
Unit III	24.4	0.512296	-6.7	0.282779	+0.2	30.5	6.34	0.531	1.38	0.208	22.1	0.385
Sample 16R1 93-98	0.04	0.512519	-2.3	0.282954	+6.4	37.9	7.44	0.541	5.24	0.196	7.2	0.103
Unit IV	32.2	0.512277	-7.0	0.282680	-3.3	11.5	2.17	0.142	0.48	0.189	24.0	0.296
Sample 29R1 28-35	0.2			0.283244	+16.7	20.1	3.74	0.332	0.55	0.186	36.5	0.604

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Footnote:

<sup>a</sup>The isotopic composition of each unit has been calculated using the isotopic compositions and the Nd and Hf concentrations of discrete samples analyzed in each unit. The Nd and Hf isotopic compositions of the entire Site 1149 sedimentary pile have been calculated combining the isotopes, trace element compositions and mass % of each unit and the mixing equation of Langmuir et al. (1978). The trace element contents listed for the Site 1149 are from Plank et al. (2007).

<sup>b</sup> $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  have been calculated using  $^{176}\text{Hf}/^{177}\text{Hf}_{\text{CHUR}}=0.282772$  after Blichert-Toft and Albarède, 1997 and  $^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}=0.512638$ .

<sup>c</sup>Trace element data used for calculations. They differ slightly from values suggested by Plank et al. (2007) for individual units because we fell more comfortable calculating the average Nd and Hf isotopic compositions using samples that had been analyzed for isotopes instead of using the whole range of concentrations that vary quite widely in some of the units. The concentrations given on the first line for the entire Site 1149 are from Plank et al. (2007).



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**Table 4** Volcanic output and sediment input fluxes in the Izu subduction zone

	Output Flux	Sediment Flux	Mantle wedge
Volume ( $\times 10^{-6}$ km <sup>3</sup> /km/yr)	65.5 <sup>a</sup>	28.6 <sup>c</sup>	
Density (g/cm <sup>3</sup> )	2.8	1.74 <sup>d</sup>	
wt% water		31.6 <sup>d</sup>	
Total dry flux ( $\times 10^9$ kg/km/yr)	0.183	0.03399	
Average Nd conc. (ppm)	7.5 <sup>b</sup>	25.2 <sup>d</sup>	
$\epsilon_{Nd}$ value	+7 to +9 <sup>e</sup>	-5.9 <sup>e</sup>	+9.7 <sup>f</sup>
Nd flux (kg/km/yr)	1375	857	
Average Hf conc. (ppm)	1.7 <sup>b</sup>	1.44 <sup>d</sup>	
Hf flux (kg/km/yr)	312	49	
Nd/Hf	4.41	17.5	

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Footnote:

<sup>a</sup> Average value for Izu-Bonin of Dimalanta et al. (2002).

<sup>b</sup> Average values of data from White & Patchett (1984) and Pearce et al. (1999).

<sup>c</sup> Calculated with a subduction rate of 7 cm/yr and a sediment thickness of 410 m.

<sup>d</sup> Data from Plank et al. (2007).

<sup>e</sup> Range of values of data from White & Patchett (1984) and Pearce et al. (1999) for the arc lavas.

<sup>f</sup> Average value of Pacific MORB.

1086 **Appendix:**

1087 **Optimization of the chemical purification**

1088 The analytical procedure for Hf separation was based on the method published by  
1089 Blichert-Toft et al. (1997) which proved to be highly efficient for most of the Site  
1090 801C composites and Site 1149 sediments, but failed for two particular sample groups  
1091 and had to be modified: (1) The Hf isolation was unsuccessful for cherts and  
1092 porcelanites collected at Site 1149. For these samples, Hf was not efficiently  
1093 separated from heavy rare earth elements (HREE), and the Hf isotopic measurements  
1094 on the P54 were disturbed by isobaric interferences at mass 176 caused by Yb and Lu.  
1095 (2) The Hf chemical separation was poorly efficient for Ca-rich samples such as the  
1096 marl and chalk but also for two basalt composites containing calcareous interpillow  
1097 sediments. For these samples, the Hf recovery was extremely low and often  
1098 insufficient for a proper isotopic measurement on the P54.

1099 In the analytical procedure of Blichert-Toft et al. (1997) Hf is separated from the  
1100 HREE using a HF leaching technique after sample dissolution. The REE precipitate  
1101 into Ca-Mg fluoride salts while Hf remains in solution in the supernatant. For most  
1102 samples, this procedure allows an almost complete recovery of Hf in the supernatant  
1103 solution whereas virtually 100% of the REE are trapped into the Ca-Mg fluoride salts  
1104 (Blichert-Toft et al., 1997). However, Blichert-Toft (2001) has shown that this  
1105 procedure is inadequate to separate Hf from REE in Mg-rich samples (such as  
1106 komatiites or picrites) because during the fluoride precipitation stage, Hf is entrained  
1107 with the REE leading to low Hf recovery in the supernatant. Blichert-Toft (2001)  
1108 suggested that the presence of high concentrations of Hf in the fluorides salts was  
1109 probably due to high partition coefficients for Hf in Mg-rich fluorides.

1110 The low Hf recovery we experienced for Ca-rich samples suggests that a similar Hf  
1111 precipitation occurs during HF leaching of Ca-rich materials. On the other hand, the  
1112 very low Mg and Ca contents of cherts and porcelanites (CaO and MgO usually lower  
1113 than 1%) could explain why HREE did not quantitatively precipitate into the fluoride  
1114 salts during the HF leaching procedure. To confirm this interpretation, we performed  
1115 experiments on the partitioning of Zr, Hf and REE during HF leaching and fluoride  
1116 precipitation in Ca-rich and Ca-depleted samples. Three test samples were selected on  
1117 the basis of their major elements (Table A): one basalt from the Sunda arc moderately  
1118 enriched in CaO (CaO = 8.38%), one limestone from southeast France rich in CaO  
1119 (CaO = 50.61%) and one andesite from the Sunda arc with a particularly low CaO  
1120 (CaO = 0.7%). All three samples have low MgO (3.8%, 0.6% and 5.24% respectively)  
1121 precluding potential trapping of HFSE in Mg-rich fluorides.

1122 Powders of the three samples were dissolved in savillex beakers with an HF:HNO<sub>3</sub>  
1123 mixture (≈ 6:1) at about 140°C for 48h and residues were leached 3 times with  
1124 concentrated HF as recommended by Blichert-Toft et al. (1997). HF supernatant  
1125 solutions and Ca-Mg fluoride salts were prepared for ICP-MS analysis with the  
1126 exception of the fluorides formed by the Ca-rich sample because this residue resisted  
1127 acid digestion and could not be put into solution. Percentages of REE, Zr and Hf  
1128 recovered in each fraction are given in Table A and plotted in figures A 1&2. For the  
1129 basalt moderately enriched in Ca, the measured REE, Hf and Zr partitioning between  
1130 Ca-Mg fluoride salts and HF supernatant are similar to the results of Blichert-Toft et  
1131 al. (1997). More than 97% of Zr and Hf are in the HF supernatant (figure A.1) while  
1132 over 95% of the REE are in the fluoride precipitate. Among the REE, Ce is an  
1133 exception with only 71% in the salt, probably because of the presence of both Ce<sup>3+</sup>  
1134 and Ce<sup>4+</sup>. As mentioned above, the fluoride salts of the Ca-rich sample could not be  
1135 analyzed but nevertheless only 2.2% of Zr and 0.9% of Hf were recovered in the HF

1136 supernatant solution (Table A). This result demonstrates that during HF leaching of  
1137 Ca-rich material, Zr and Hf are partitioned into the fluoride residue instead of staying  
1138 in solution in HF. This suggests that Zr and Hf have significantly higher partition  
1139 coefficients for Ca-rich fluorides than for Ca-poor fluorides. In contrast to the other  
1140 two samples, the Ca-depleted andesite shows distinctive features (see Figure A.2): Zr  
1141 and Hf are almost exclusively present in the HF supernatant (more than 99% of Zr  
1142 and Hf) but the REE are also present in the leachate and show a progressive  
1143 fractionation with the LREE mainly concentrated in the fluoride salt (over 80%) and  
1144 the HREE distributed equally between the residue and the leachate (59% of Yb in the  
1145 supernatant). Such distribution suggests a progressive decrease of the partition  
1146 coefficient from LREE to HREE in the Ca-depleted fluoride salts and an inefficient  
1147 separation of the REE from the HFSE using the HF leaching technique in such  
1148 samples.

1149 Our experiments demonstrate therefore that the Ca content plays a fundamental role  
1150 on the distribution of HFSE and REE between fluoride salts and supernatant solution  
1151 during HF leaching. For moderately Ca-rich matrices, HFSE are preferentially  
1152 concentrated in the leachate while REE precipitate in the fluorides; for Ca-rich  
1153 samples, HFSE and REE precipitate together in the fluoride residue; and finally for  
1154 Ca-depleted samples, HFSE remain in the leachate while REE are evenly distributed  
1155 between fluoride salts and HF supernatant solution. Despite providing excellent  
1156 results for most rocks, the HF leaching procedure of Blichert-Toft et al. (1997) proves  
1157 not to be efficient to separate Hf from REE in Ca-rich and Ca-poor samples and the  
1158 original protocol of Blichert-Toft et al.(1997) has to be modified for this type of rock  
1159 samples.

1160 For Ca-rich samples, the HF leaching and fluoride precipitation step should be  
1161 replaced by a cation-exchange column separation as published by Patchett (1980) and

1162 modified by Revillon et al. (Revillon, 2000). However this modified protocol  
1163 succeeds only if Ca-rich fluorides salts do not precipitate during dissolution of the  
1164 sample. These fluorides, very resistant to acid dissolution, are likely to contain large  
1165 amounts of Hf leading to low Hf recovery. We suggest therefore that dissolution of  
1166 Ca-rich samples should be achieved either using the procedure recommended by  
1167 Bizimis et al. (2003) or using concentrated HF associated to large amounts of HClO<sub>4</sub>  
1168 or using lithium metaborate fusion as described in Lefèvre and Pin (2001). For Ca-  
1169 depleted samples, the modified procedure consists simply in a column separation  
1170 using cation-exchange resin instead of Hf leaching. In this case, REE are recovered  
1171 from the cation-exchange column. In all cases, Nd is further isolated from the other  
1172 REE using Eichrom® HDEHP-coated teflon resin.

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1176 **Appendix Figure A** REE, Zr and Hf distributions between supernatant and fluoride  
1177 salts after HF leaching of (1) a sample moderately enriched in Ca and (2) a Ca-  
1178 depleted sample.

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|180 **Appendix Table A:** Trace element distributions after HF leaching of Ca-moderately enriched, Ca-highly enriched and Ca-depleted samples.

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Sample	80J102 <sup>a</sup>	287C <sup>b</sup>	PC6B <sup>a</sup>
Rock Type	Basalt	Limestone	Andesite
Location	Sunda arc	SE France	Sunda arc
CaO%	8.38	50.61	0.70
MgO%	3.80	0.60	5.24

Element <sup>c</sup>	Fluoride (%)	Supernatant (%)	Supernatant (%)	Fluoride (%)	Supernatant (%)
La	93.4	6.6	0	89.5	10.5
Ce	71.5	28.5	0	6.2	93.8
Pr	95.8	4.2	0	86.5	13.5
Nd	96.2	3.8	0	84.7	15.3
Sm	96.8	3.2	0	74.7	25.3
Zr	3.7	96.3	0.2	0.6	99.4
Hf	3.6	96.4	0	1.0	99.0
Eu	95.8	4.2	0.1	68.2	31.8
Gd	94.9	5.1	0	61.9	38.1
Tb	96.9	3.1	0	55.2	44.8
Dy	97.1	2.9	0	50.5	49.5
Ho	97.1	2.9	0	47.0	53.0
Er	97.1	2.9	0	43.7	56.3
Yb	96.3	3.7	0	40.9	59.1
Lu	96.4	3.6	0.6	39.4	60.6

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|183 Footnote:

|184 <sup>a</sup>CaO and MgO compositions after Polvé and Maury, Unpublished data.

|185 <sup>b</sup>CaO and MgO compositions after Nicod and Chauvel, Unpublished data.

|186 <sup>c</sup>Determined by ICP-MS (VG Plasma Quad, University of Grenoble). Analytical precision is  $\pm 5\%$ .

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Figure A

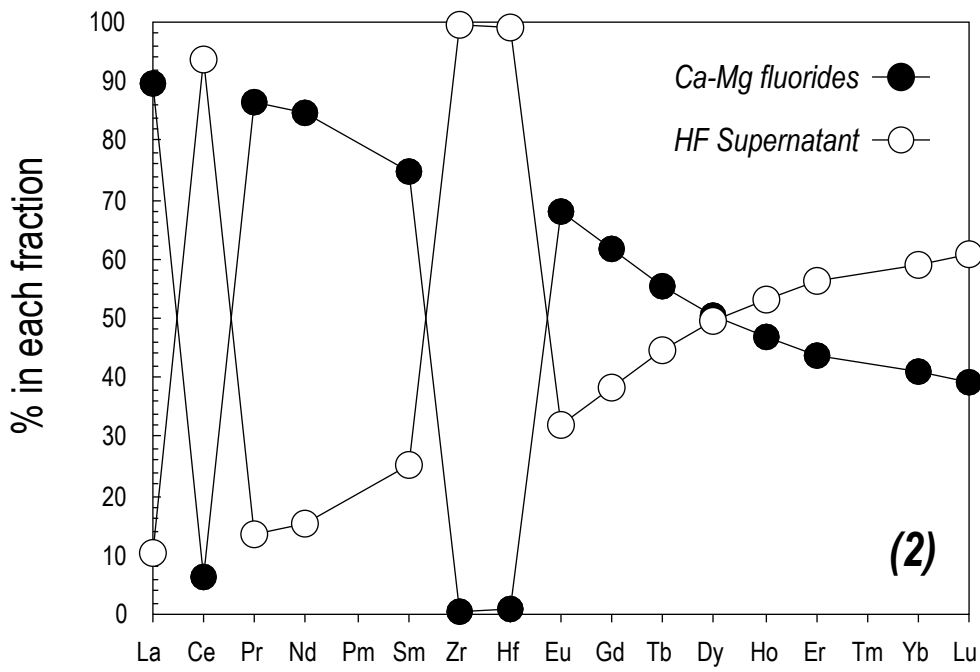
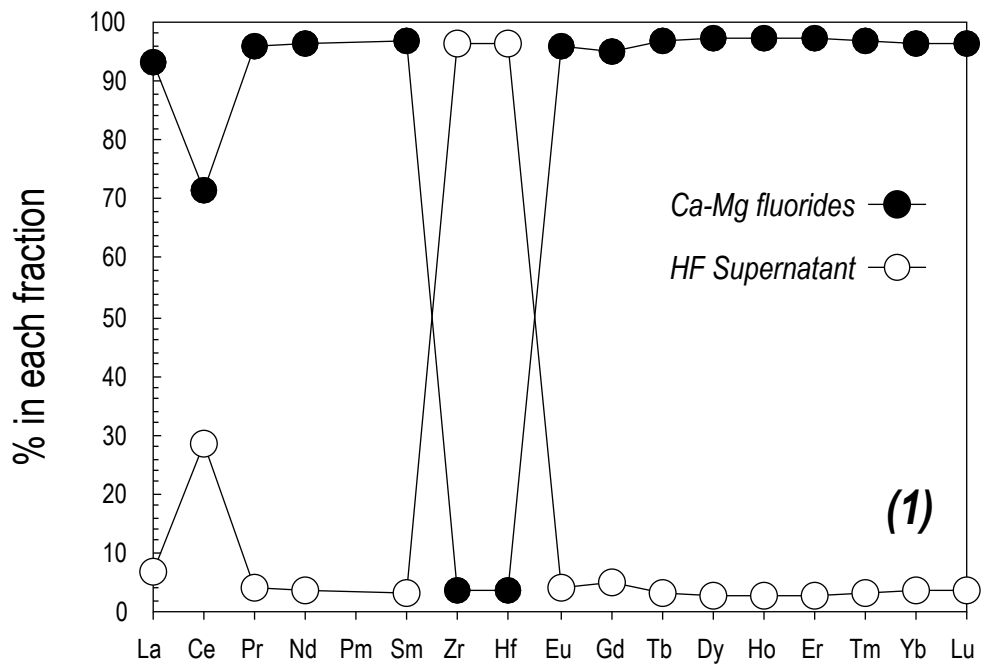


Figure 1

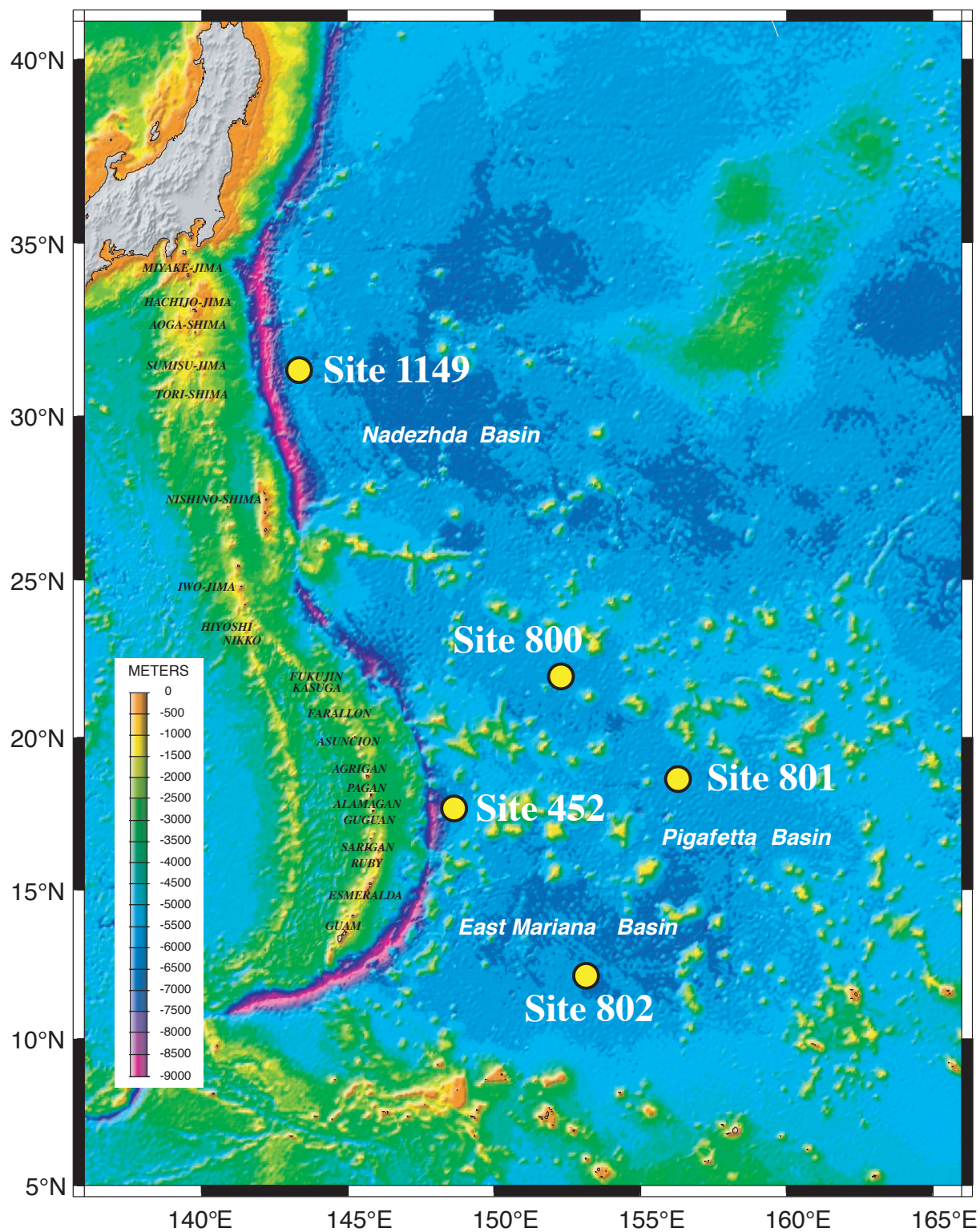
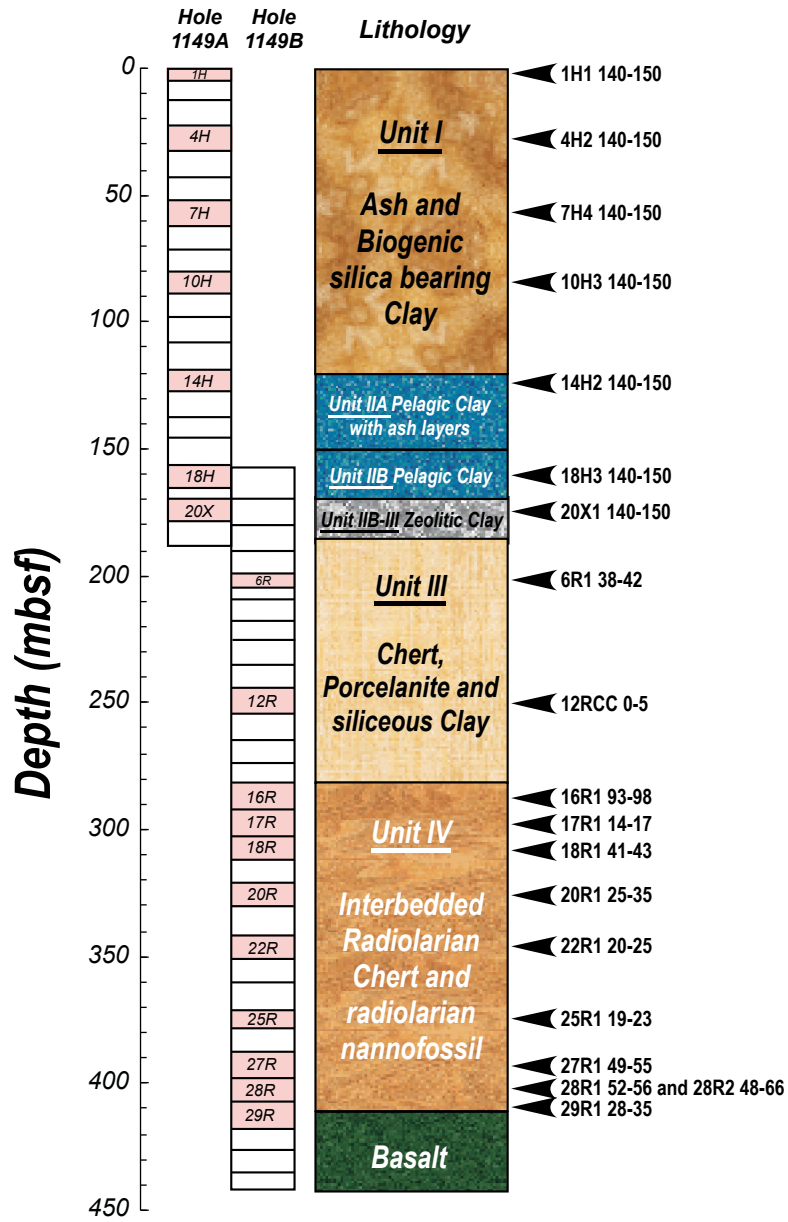




Figure 2



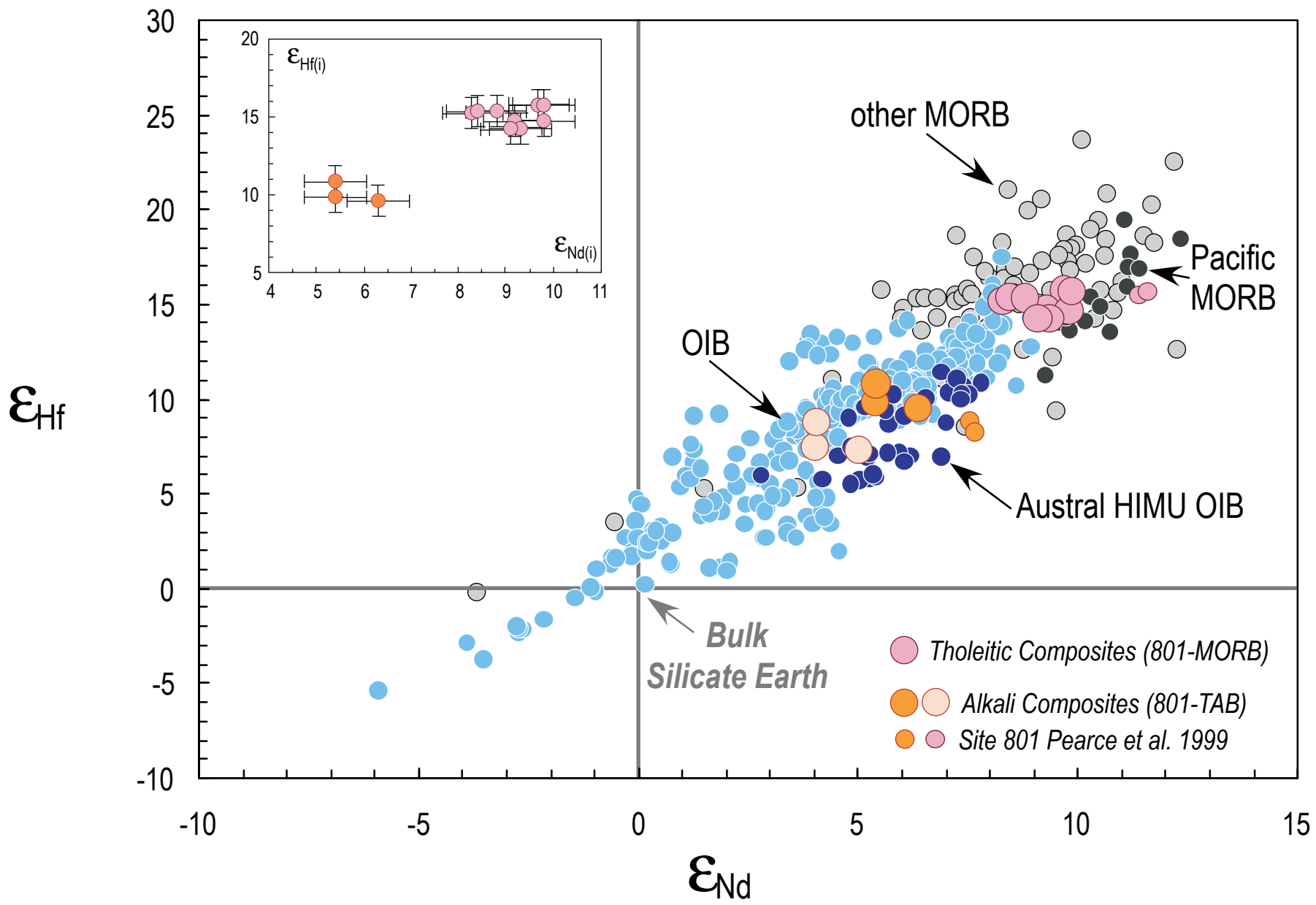


Figure 3

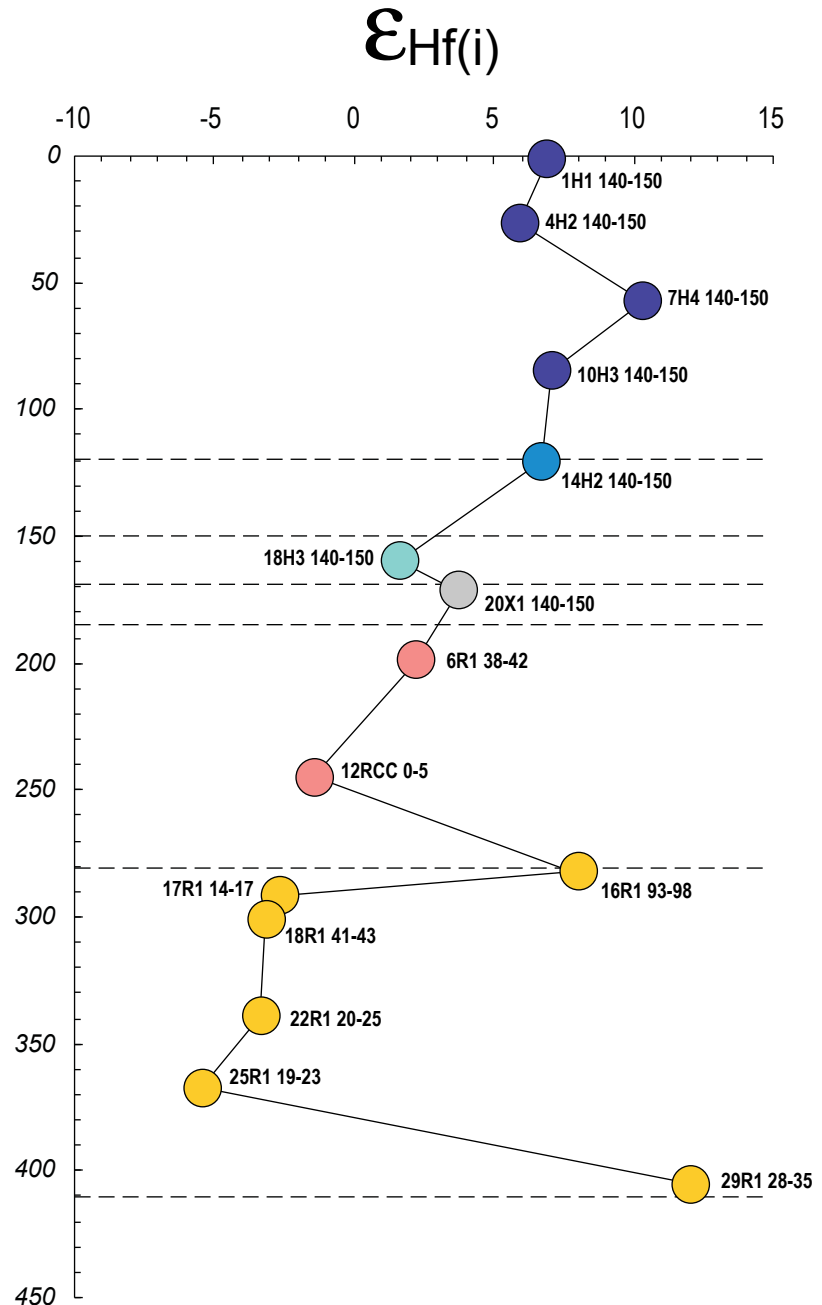
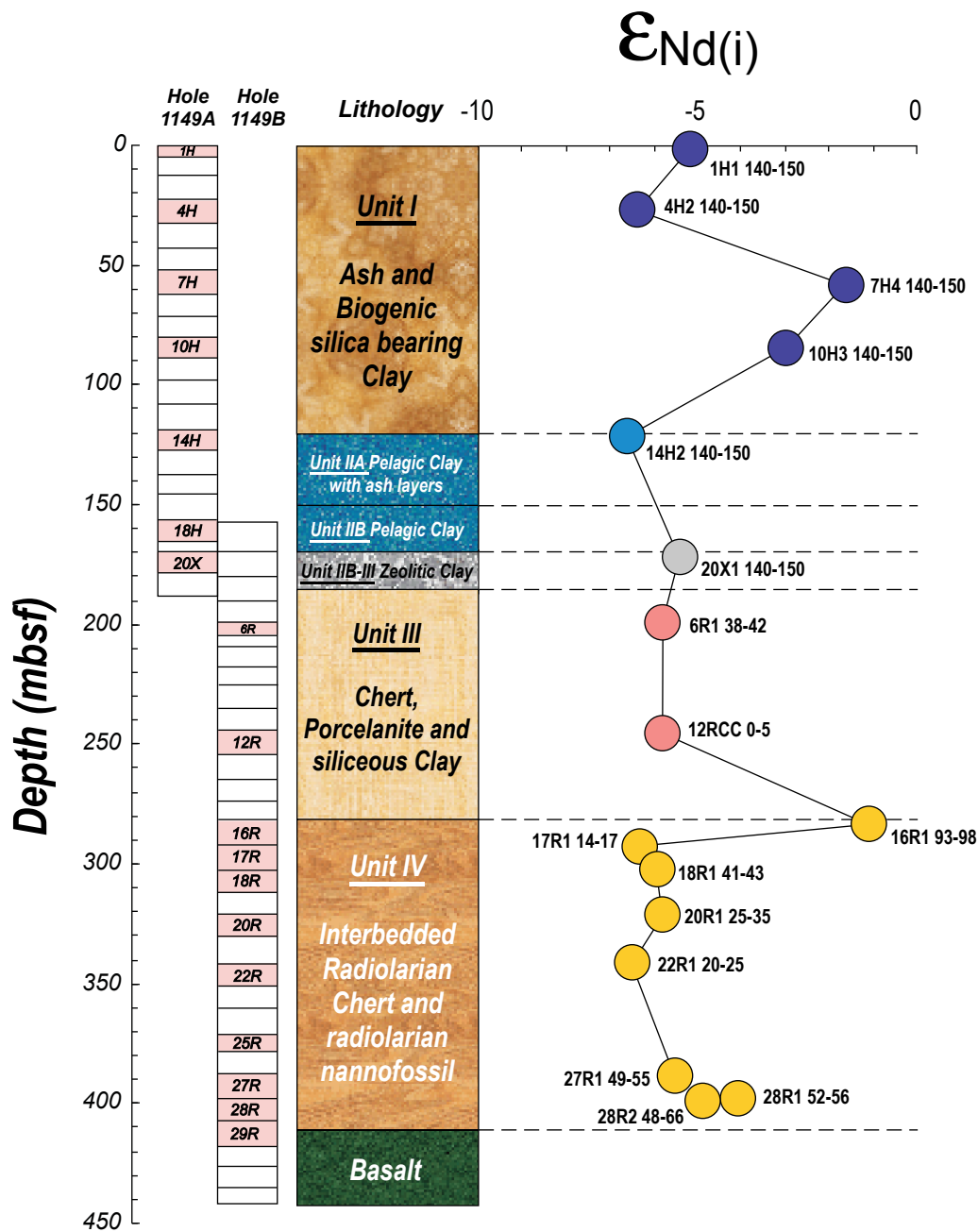


Figure 4

Figure 5

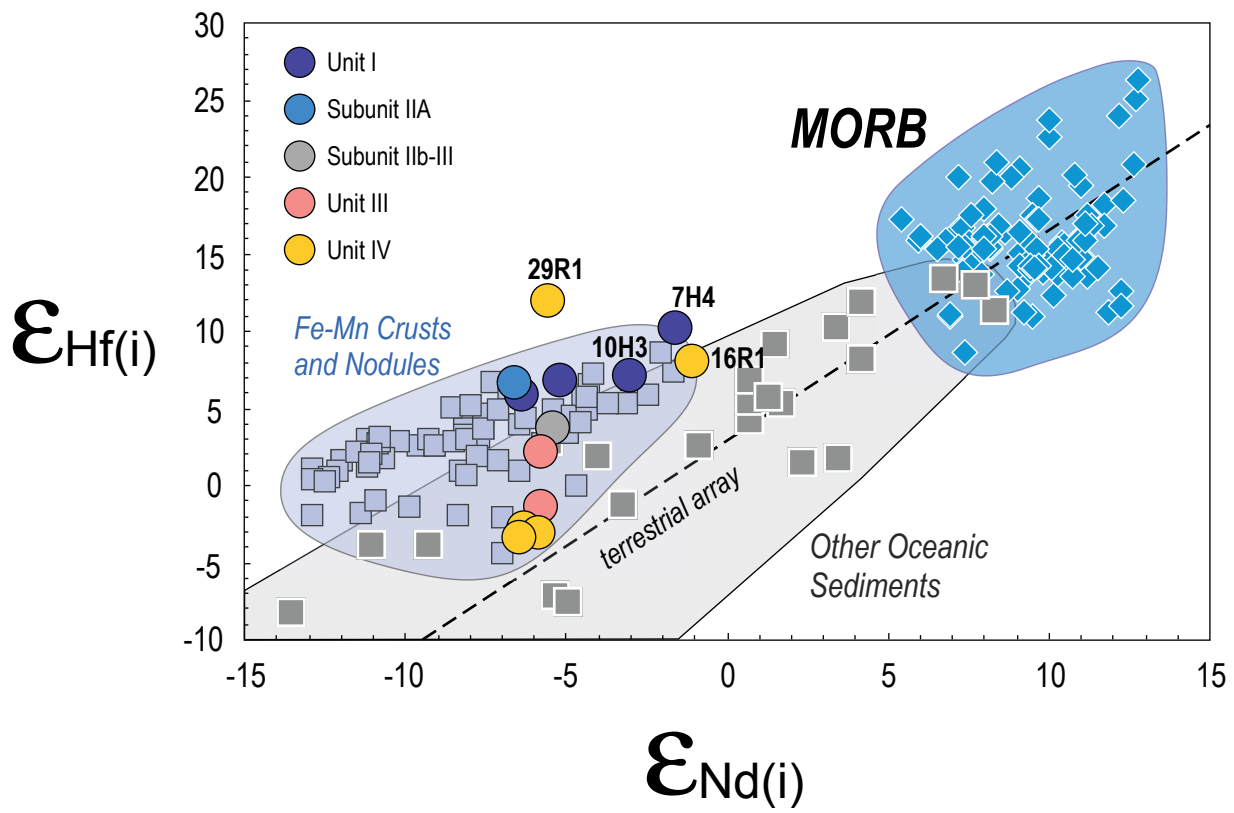


Figure 6

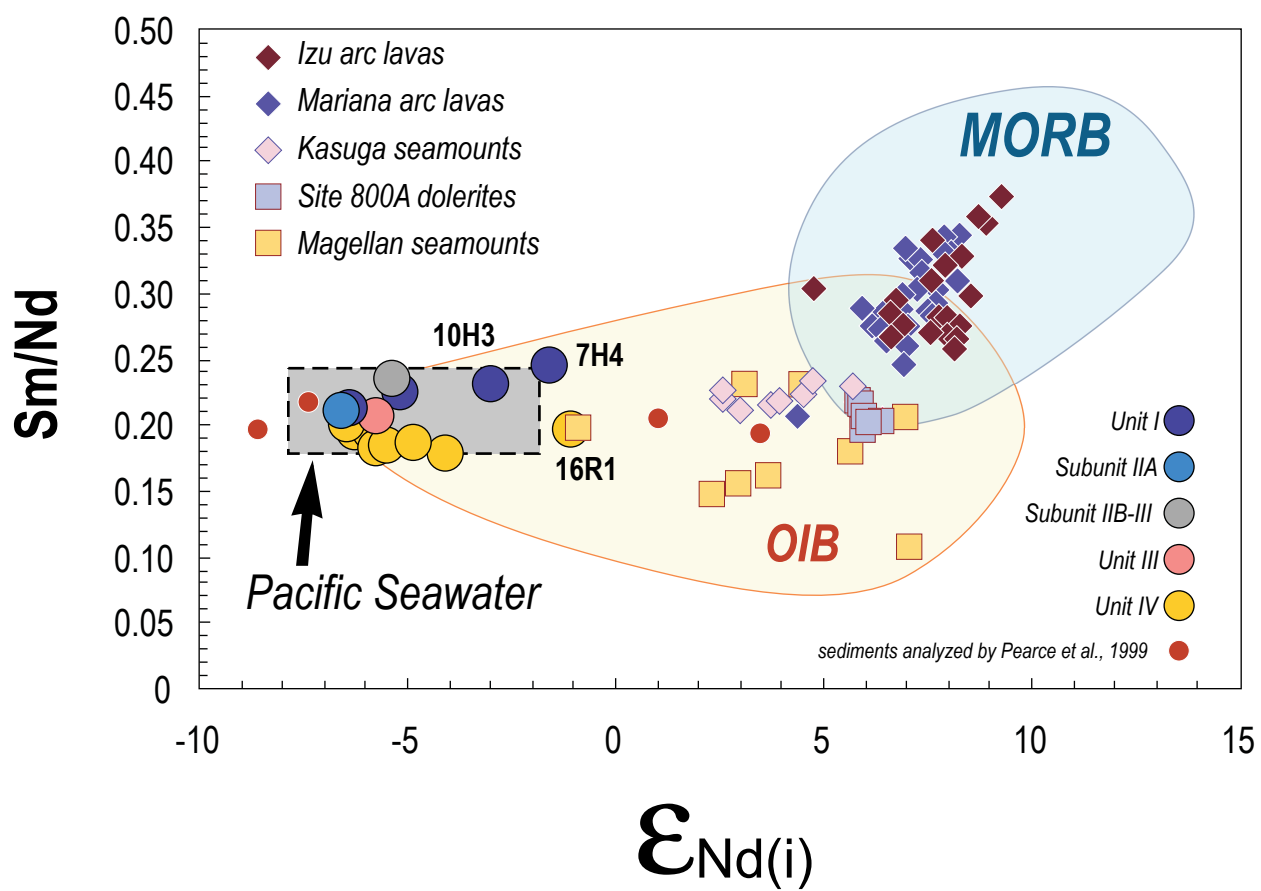
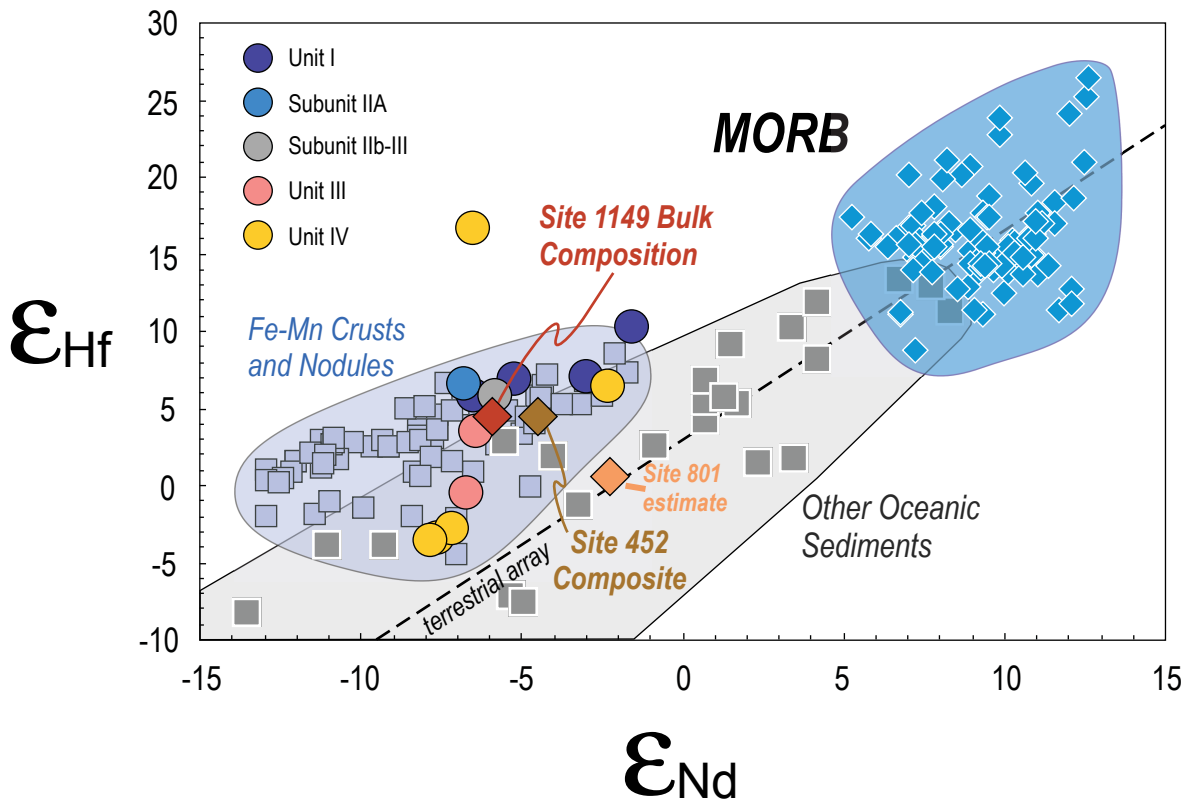


Figure 7



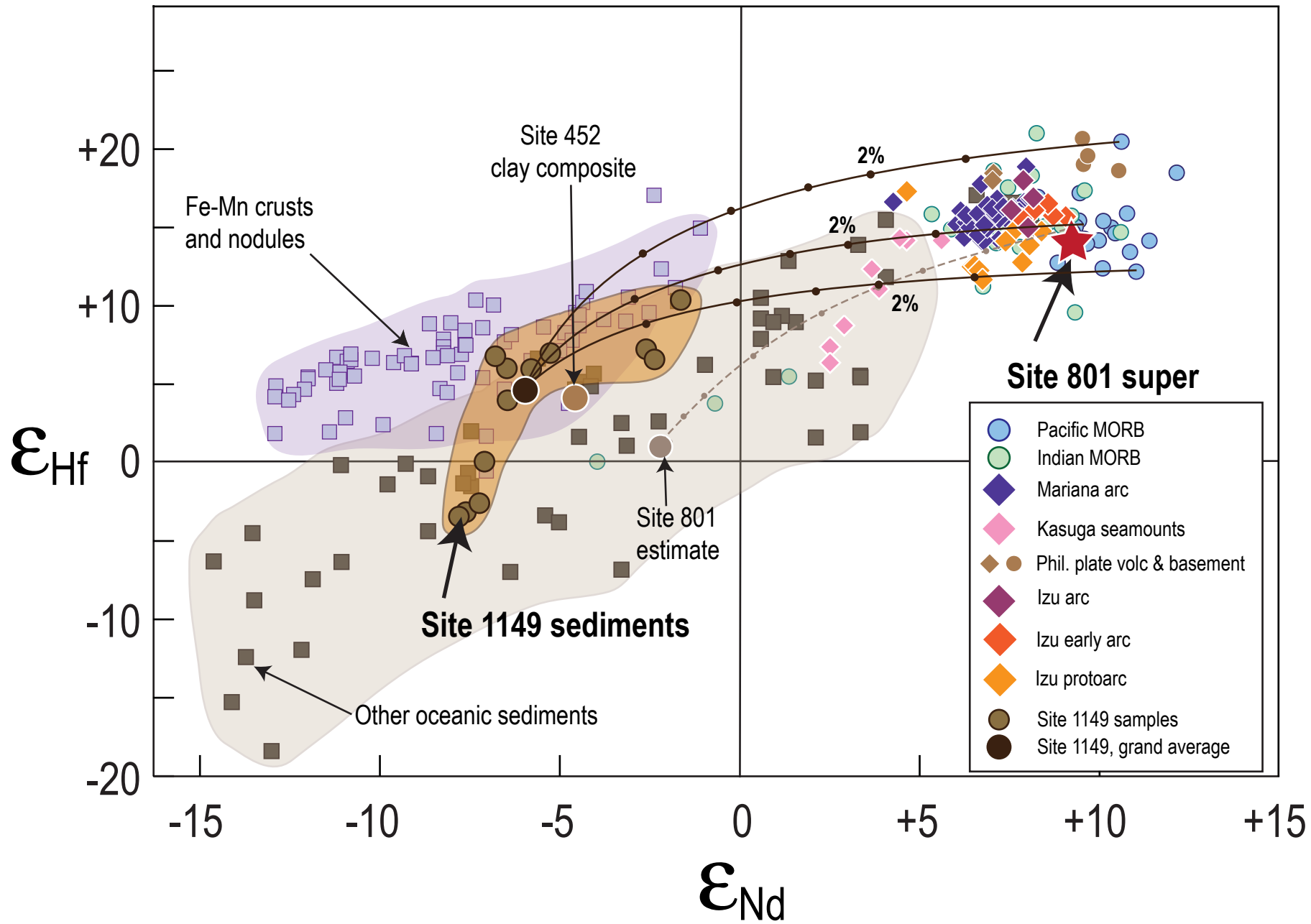
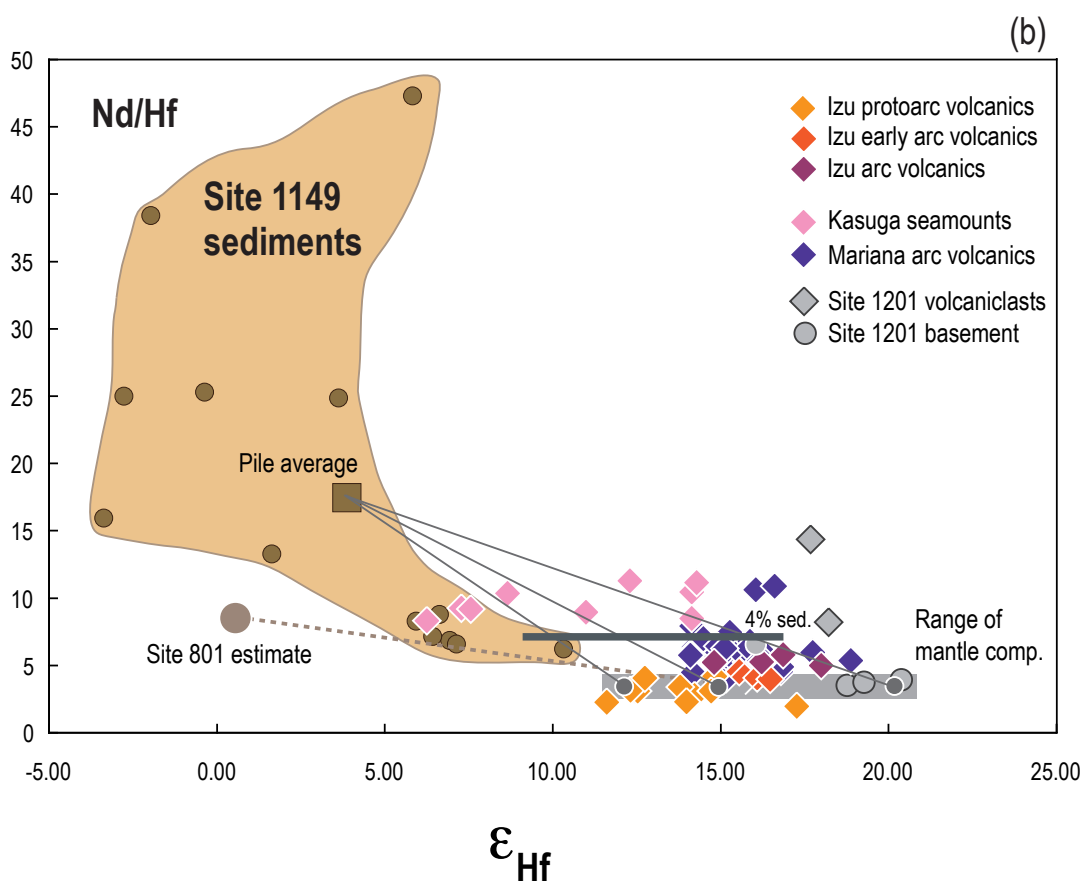
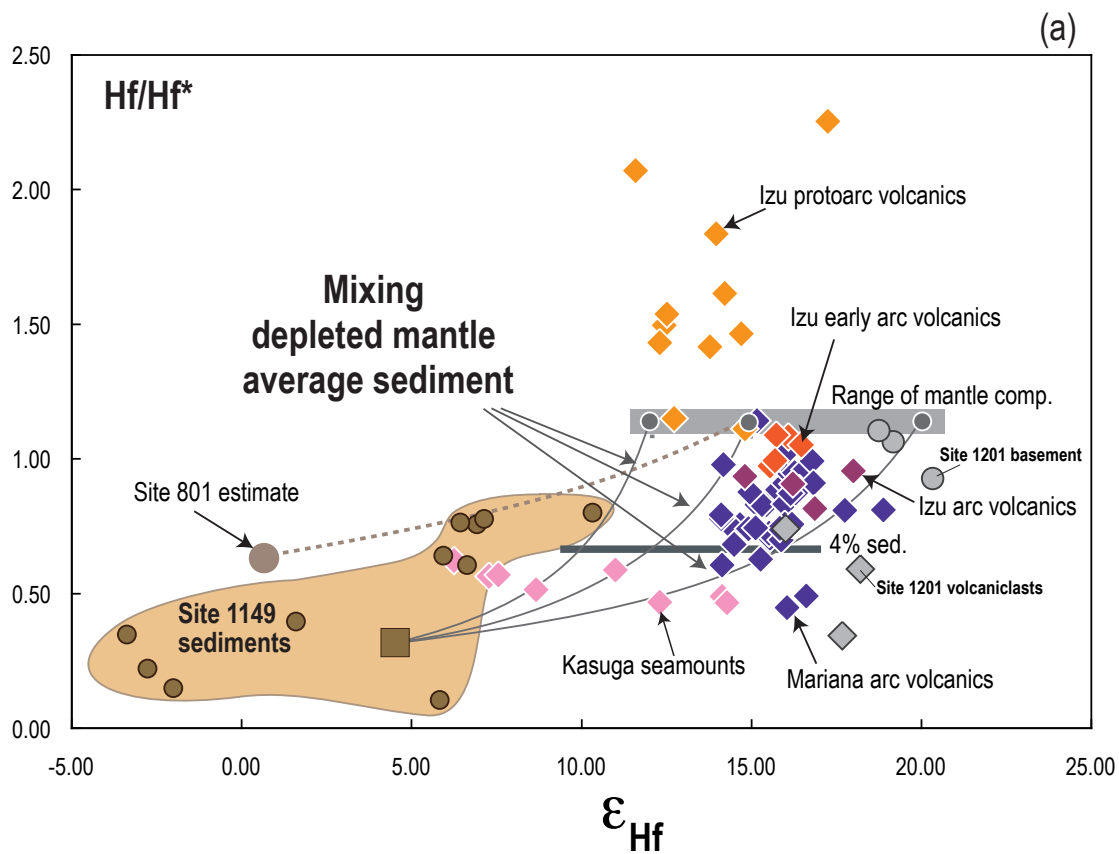


Figure 8

Figure 9





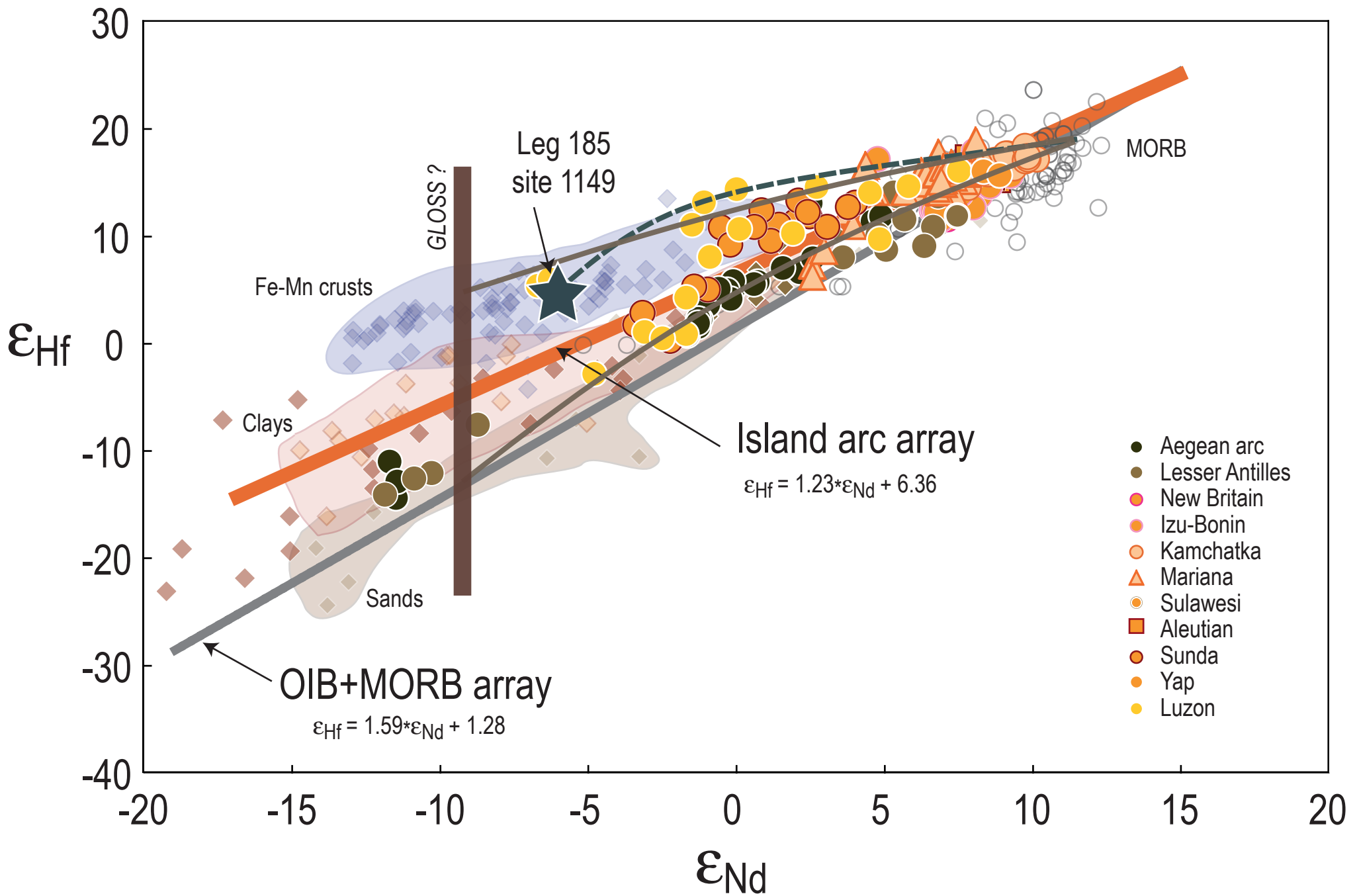


Figure 10