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# Multi-isotopic composition ( $\delta^7\text{Li}$ - $\delta^{11}\text{B}$ - $\delta\text{D}$ - $\delta^{18}\text{O}$ ) of rainwaters in France: origin and spatio-temporal characterization

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## Abstract

Lithium (Li) and boron (B) concentrations and isotope measurements for 45 monthly rainwater samples collected over a 1-year period from four different sites in France, from coastal and inland locations (Brest, Dax, Orléans and Clermont-Ferrand) are reported. This is the first study of Li and B isotope ratios in rainwater samples collected over a long time period at a national scale. The range of Li and B isotopic variations in these rainwaters are measured to enable the determination of the origin of these elements in rainwaters and the characterization of both the seasonal and spatio-temporal effects for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  signatures in rainwaters. Lithium and boron concentrations are low in rainwater samples, ranging from 0.004 to 0.292  $\mu\text{mol/L}$  and from 0.029 to 6.184  $\mu\text{mol/L}$ , respectively.  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values in rainwaters also show a great range of variation between +3.2 and +95.6‰ and between -3.3 and +40.6‰ over a period of one year, respectively, for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$ , clearly different from the signature of seawater. Seasonal effects (i.e. rainfall amount and month) is not the main factor controlling element concentrations and isotopic variations.  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values in rainwaters are clearly different from one site to another, indicating the variable contribution of sea salts in the rainwater depending on the sampling site (coastal vs. inland: also called the distance-from-the-coast-effect). This is well illustrated when wind direction data (origin of air masses) is included. We found that seawater is not the main supplier of dissolved atmospheric lithium and boron, and non-sea-salt sources (i.e. crustal, anthropogenic, biogenic) should also be taken into account when Li and B isotopes are considered in hydrogeochemistry as an input to surface waters and groundwater bodies as a recharge. The isotopic variations of the water molecule, vector of the dissolved B and Li, are also investigated and reported as a contour map for  $\delta^{18}\text{O}$  values based on compiled data including more than 400  $\delta^{18}\text{O}$  values from throughout France. This  $\delta^{18}\text{O}$  map could be used as a reference for future studies dealing with  $\delta^{18}\text{O}$  recharge signature in relation the characterization of surface waters and/or groundwater bodies.

**Keywords:** lithium isotopes, boron isotopes, hydrogen isotopes, oxygen isotopes, rainwaters, France

*8 365 words (without references and captions)*

## 40 1. INTRODUCTION

41  
42 Atmospheric aerosols including sea salts, crustal dusts, biogenic materials and  
43 anthropogenic emissions are the main sources of chemical elements in rainwaters (Junge  
44 1963). The determination of the chemical composition of rainwater provides an  
45 understanding of the source types that contribute to rainwater chemistry and enhances our  
46 understanding of the dispersion of elements, whether pollutants or not, and their potential  
47 impact on hydrosystems through precipitation and wet deposition processes (Berner and  
48 Berner 1987).

49 The aim of this study is to present the results of the first study of both Li and B isotope ratios  
50 in rainwater samples collected over a long time period (i.e. monthly rainfall events over one  
51 year, Négrel et al. 2007) at a national scale. In addition, the stable isotopes of the water  
52 molecule ( $\delta D$  and  $\delta^{18}O$ ) are also reported here for the same locations (Brest, Dax and  
53 Orléans) so that we can discuss the Li and B isotope data in the same context and to provide  
54 a framework for the main processes affecting the isotope signatures of the rainwater. Since  
55 rainwater is the main input in hydrogeological systems, monitoring the H-O-Li-B isotopic  
56 compositions of rainwater at the national scale should enable us to compile a reference  
57 system of meteoric isotopic signatures for all of France, as an addition to the Sr isotopes  
58 data previously reported by Négrel et al. (2007).

59 The recent development of new isotopic techniques (e.g. lithium and boron:  $\delta^7Li$ ,  $\delta^{11}B$ ) to  
60 investigate aquifer systems has highlighted the gap in knowledge of the atmospheric inputs  
61 that are the major contributor to groundwater recharge (Widory et al. 2005, Millot et al. 2007).  
62 In this context, a knowledge of the spatial and temporal variability of the isotopic  
63 compositions of rainwater appears to be essential for hydrogeological investigations and also  
64 for sustainable water management.

65 This paper presents, firstly, the hydrogen and oxygen isotope data from the French Isotopic  
66 Data Base (BDISO, 2007), in the form of a contour map linked to data from neighboring  
67 countries and, secondly, boron and lithium isotopic data on selected samples from this  
68 French monitoring network, part of the international database of the Global Network of  
69 Isotopes in Precipitation (GNIP, 2007) managed by the International Agency of the Atomic  
70 Energy (IAEA).

71 The characterization of  $\delta^7Li$  and  $\delta^{11}B$  signatures in rainwaters is of major importance if we  
72 wish to increase our knowledge of the external cycles of these elements and, more  
73 specifically in the field of hydrogeochemistry, characterize the Li and B isotope signatures of  
74 the rainwater input to surface waters and/or groundwater bodies as a recharge.

75 To date, one measurement of  $\delta^7Li$  (+14.3‰  $\pm$  0.7) has been reported in the literature for a  
76 rainwater event collected in Hawaii (Pistiner and Henderson 2003) and another (+33.3‰),

77 slightly higher than the seawater signature, for a snow sample collected in Iceland (Pogge  
78 von Strandmann et al. 2006).

79 On the other hand,  $\delta^{11}\text{B}$  signatures of rainwaters are more circumscribed (Miyata et al. 2000,  
80 Chetelat et al. 2005, Rose-Koga et al. 2006, Chetelat et al. 2009). Indeed, previous work on  
81 the characterization of  $\delta^{11}\text{B}$  signatures in rainwaters have shown that seawater may be a  
82 major supplier of atmospheric boron, and that boron isotopic fractionation during evaporation  
83 from seawater and removal from the atmosphere may account for the large variations of  $\delta^{11}\text{B}$   
84 signatures observed in the atmosphere and in rainwater (Miyata et al. 2000). In addition, it  
85 has been also shown that boron isotopes in rainwater are potentially good tracers of biomass  
86 burning (Chetelat et al. 2005) and anthropogenic contamination of the atmosphere in a  
87 polluted environment (Chetelat et al. 2009).

88 The present study aims, therefore, at investigating Li and B isotope signatures in the rainfall  
89 input, which should be identified in either surface water or groundwater since the sources of  
90 Li and B both are atmospheric, the dissolution of Li- and B-bearing minerals, biogenic and/or  
91 anthropogenic. This study also aims to more accurately define the input of Li and B to either  
92 surface water or groundwater and place constraints on the  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values, which  
93 should be corrected for atmospheric input, in order to characterize the anthropogenic  
94 signature and/or the signature derived from water-rock interactions.

95

96

## 2. RAINWATER SAMPLES

97

### 2.1. Sampling sites

98

100 Monthly rain water samples were collected at five different locations throughout France  
101 (Brest, Dax, Orléans, Thonon and Avignon, Fig. 1). They constitute the French monitoring  
102 network, which is part of the IAEA/IOW Global Network for Isotopes in Précipitation (GNIP  
103 2007) for isotopes of the water molecule. The long-term monthly monitoring consists in  
104 sampling rainwater in Avignon (from May-97 to Dec-02, n=60), Brest (from Apr-96 to May-03,  
105 n=83), Dax (from Oct-97 to Apr-04, n=74), Orléans (from Mar-96 to May-04, n=96) and  
106 Thonon (from Mar-95 to Dec-02, n=89).

107 Three of these sampling sites were monitored between 2003 and 2004 for B and Li isotopes.  
108 One, Brest, is located in the northwest of France (N 48.24, W 04.31), less than 5 km from the  
109 Atlantic Ocean. Another, Dax, is located in the southwest of France (N 43.44, W 01.03), 30  
110 km from the Atlantic Ocean. The third, Orléans (N 47.54, E 01.52), is located 400 km from  
111 the Atlantic Ocean. A fourth B and Li isotope sampling site is located near Clermont-Ferrand  
112 (N 45.46, E 03.04), in the Massif Central, 200 km upstream from Orléans. Rainwater

113 samples were monitored here between 1994 and 1995. The Mediterranean Sea is 300 km to  
114 the south and the Atlantic Ocean is 380 km to the west.

115

## 116 **2.2. Sampling technique**

117

118 A direct polycarbonate funnel (Négrel et al. 1997), 12 cm in diameter and with an area of ~  
119 110 cm<sup>2</sup>, was used to collect the rainfall samples in Brest, Dax and Orléans. This apparatus  
120 enables precipitation measurement by direct reading, without the need for preliminary  
121 transfer into a measurement test tube. The rainwater was stored in a polypropylene jerrycan  
122 to avoid any evaporation or modification of the sample. The accumulation of daily samples  
123 enabled a monthly sample of rain to be obtained.

124 An automatic precipitation sampler was also designed for collecting rainwater samples at the  
125 site near Clermont-Ferrand (Négrel and Roy 1998). The basic requirements for our collector  
126 were automatic detection and collection of rainfall, elimination of dry fallout, collection of  
127 frozen precipitation and prevention of sample contamination. A removable PVC lid covers the  
128 funnel when no rain is falling. The cover opens to expose the funnel when electrical contact  
129 is made in the rain detector. A polypropylene funnel (45 cm in diameter) was used to collect  
130 the rainfall.

131 After monthly sample collection, 100 mL were used for  $\delta D$  and  $\delta^{18}O$  determination. The rest  
132 of the rainwater samples were filtered through pre-cleaned 0.45  $\mu m$  acetate filters using a  
133 pre-cleaned Nalgene filter apparatus and the filtrate was separated into two aliquots. From  
134 this: (i) 100 and 1000 mL were acidified with double-distilled nitric acid (pH = 2) and stored in  
135 pre-cleaned polyethylene bottles for major-cation analysis and lithium isotope ratio and  
136 elemental Li and B determinations, and (ii) 500 mL were stored unacidified in polyethylene  
137 bottles for anion analysis and B isotope ratio measurements.

138

139

## 139 **3. ANALYTICAL METHODS**

140

### 141 **3.1. Chemical parameters and stable isotopes of the water molecule**

142

143 The rainwater samples were chemically analysed by atomic absorption spectrometry (Ca,  
144 Na, K, and Mg concentrations, accuracy 5%), ion chromatography (Cl, SO<sub>4</sub> and NO<sub>3</sub>  
145 concentrations, accuracy 5%) and inductively coupled plasma mass spectrometry (Li and B  
146 concentrations, accuracy 5%). Accuracy and precision for major and trace elements was  
147 verified by repeated measurements of standard materials during the course of this study:  
148 namely Ion96-3 and LGC6020 for cations and anions and pure Li and B standard solutions  
149 (Merck) for Li and B determinations.

150 Oxygen and deuterium measurements were performed by various French laboratories using  
151 a standardised method. At BRGM's laboratory, a Finnigan MAT 252 mass spectrometer was  
152 used with a precision of 0.1‰ for  $\delta^{18}\text{O}$  and 0.8‰ for  $\delta\text{D}$  (vs. SMOW). Isotopic compositions  
153 are reported in the usual  $\delta$ -scale (in ‰) according to  $\delta_{\text{sample}} (\text{‰}) = \{(R_{\text{sample}}/R_{\text{standard}}) - 1\} \times 10^3$ ,  
154 where R is either the  $^2\text{H}/^1\text{H}$  or the  $^{18}\text{O}/^{16}\text{O}$  atomic ratio.

155 In the present work, it was challenging to measure Li and B isotope compositions in  
156 rainwater samples due to their low content (a few  $\mu\text{mol/L}$ ). We, therefore, developed new  
157 sensitive techniques (Millot et al. 2004a, 2004b, Guerrot et al. 2010) in order to be able to  
158 accurately and precisely determine  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  for rainwater samples.

159

### 160 **3.2. Lithium isotopes**

161

162 Lithium isotopic compositions were measured using a Neptune Multi Collector ICP-MS  
163 (Thermo Fischer Scientific).  $^7\text{Li}/^6\text{Li}$  ratios were normalized to the L-SVEC standard solution  
164 (NIST SRM 8545, Flesch et al. 1973) following the standard-sample bracketing method (see  
165 Millot et al. 2004a for more details). The analytical protocol involves the acquisition of 15  
166 ratios with 16 s integration time per ratio, and yields in-run precision better than 0.2‰ ( $2\sigma_m$ , 2  
167 x Standard Error). Blank values are low, (i.e. 0.2‰), and 5 minutes wash time is enough to  
168 reach a stable background value.

169 The samples must be prepared beforehand with chemical separation/purification by ion  
170 chromatography in order to produce a pure mono-elemental solution. Chemical separation of  
171 Li from the matrix was done prior to the mass analysis, following a procedure modified from  
172 the technique of James and Palmer (2000), using a cationic resin (a single column filled with  
173 3 mL of BioRad AG<sup>®</sup> 50W-X12 resin, 200-400 mesh) and HCl acid media (0.2N) for 30 ng of  
174 Li. Blanks for the total chemical extraction were less than 30 pg of Li, which is negligible  
175 since it represents a  $10^{-3}$  blank/sample ratio.

176 Successful quantitative measurement of Li isotopic compositions requires 100% Li recovery  
177 during laboratory processing. Therefore, frequent column calibration was done and repeated  
178 analyses of L-SVEC standard processed through columns shows 100% Li recovery and no  
179 induced isotope fractionation due to the purification process.

180 Accuracy and reproducibility of the entire method (purification procedure + mass analysis)  
181 were tested by repeated measurements of a seawater sample (IRMM BCR-403) after  
182 separation of Li from the matrix, for which we obtained a mean value of  $\delta^7\text{Li} = +30.9\text{‰} \pm 0.4$   
183 ( $2\sigma$ , 2 x Standard Deviation,  $n = 12$ ) over the period of the duration of the analyses. This  
184 mean value is in good agreement with our long-term measurement ( $\delta^7\text{Li} = +31.0\text{‰} \pm 0.5$ ,  $2\sigma$ ,  
185  $n = 30$ , Millot et al. 2004a) and with other values reported in the literature (see, for example,

186 Tomascak 2004 for a compilation). Consequently, based on long term measurements of the  
187 seawater standard, we estimate the external reproducibility of our method to be around  $\pm$   
188 0.5‰ ( $2\sigma$ ).

189 In addition, reproducibility of the method was also tested by repeated measurements of a  
190 rainwater standard solution (TMRAIN-95, Environment Canada, National Water Research  
191 Institute) after separation/purification by ion chromatography, for which we obtained a mean  
192 value of  $\delta^7\text{Li} = +445.9\text{‰} \pm 0.6$  ( $2\sigma$ ,  $n = 10$ ) over the period of the duration of the analyses.  
193 This mean value could not, however, be compared either to literature data or to certified  
194 values because this reference material is not certified for Li isotopes (only for Li  
195 concentration). In spite of this, it is of interest to note that this rainwater standard solution is  
196 significantly enriched in heavy lithium ( $^7\text{Li}$ ). This is, however, not surprising because this  
197 reference material is a synthetic rainwater solution (namely: *TMRAIN-95: a simulated rain*  
198 *sample for trace elements*). Consequently, it is likely that lithium in this standard solution  
199 could come from an  $^7\text{Li}$ -rich reagent, as was pointed out by Qi et al. 1997, who showed that  
200  $\delta^7\text{Li}$  values in laboratory reagents could range between -11 and +3013‰. Indeed, it is well  
201 known that lithium can be isotopically fractionated due to the removal of  $^6\text{Li}$  for use in  
202 hydrogen bombs. The remaining lithium is therefore substantially enriched in  $^7\text{Li}$  and some of  
203 this lithium has found its way into laboratory reagents and into the environment (Coplen et al.  
204 2002). In addition, we also measured an ICP  $^7\text{Li}$ -rich standard solution (Spex) that has a  
205 mean value of  $\delta^7\text{Li} = +241.4\text{‰} \pm 0.5$  ( $2\sigma$ ,  $n = 38$ , Millot et al. 2004b), which confirms the  
206 results found by Qi et al. 1997.

207 Finally, concerning the lithium concentration of this rainwater standard solution (TMRAIN-95),  
208 we obtained a good agreement between the values measured by ICP-MS in our laboratory  
209 ( $0.059 \mu\text{mol/L} \pm 0.003$ ,  $2\sigma$   $n = 10$ ) and the certified value ( $0.056 \mu\text{mol/L} \pm 0.011$ ).

210

### 211 **3.3. Boron isotopes**

212

213 Boron isotope composition were determined following a newly-developed methodology for  
214 precise and accurate measurement using a Neptune double-focusing multi-collector sector  
215 ICP-MS (Guerrot et al. 2010).

216 To avoid any drift of the mass bias induced by the sample matrix, chemical purification of 100  
217 ng B was done before the mass analysis, following a procedure described in Guerrot et al.  
218 (2010), using the specific boron resin IRA743 and 0.42N  $\text{HNO}_3$  acid media with a final boron  
219 concentration of 50 ng/mL.  $^{11}\text{B}/^{10}\text{B}$  ratios were normalized, following the standard-sample  
220 bracketing method, to the NIST SRM-951 standard solution (Catanzaro et al. 1970) run  
221 through chemistry (Guerrot et al. 2010). Analytical uncertainty for each individual

222 determination was better than 0.1‰ at  $2\sigma_m$  ( $n = 20$ ). Accuracy and reproducibility of the  
223 whole process were determined by repeated measurements of a seawater solution (IAEA-  
224 B1) with a mean value of  $\delta^{11}\text{B} = +39.36\text{‰} \pm 0.43$  ( $2\sigma$ ,  $n = 20$ ). This mean value is in good  
225 agreement with our measurements using the positive-TIMS- $\text{Cs}_2\text{BO}_2$  technique ( $\delta^{11}\text{B} =$   
226  $+39.24\text{‰} \pm 0.36$  ( $2\sigma$ ,  $n = 19$ ), as well as with the data compilation obtained for an  
227 intercomparison exercise (Gonfiantini et al. 2003) and with the worldwide accepted value for  
228 seawater.

229 Consequently, based on long term measurements of seawater standards, we estimate the  
230 external reproducibility of our method around  $\pm 0.5\text{‰}$  ( $2\sigma$ ).

231

232

## 4. RESULTS AND COMMENTS

233

### 4.1. Stable isotopes of the water molecule: $\delta\text{D}$ and $\delta^{18}\text{O}$

234

235  
236 The main processes controlling the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  isotopic signatures in precipitations were  
237 summarized by Rozanski et al. (1993): i.e. the rainfall amount, continental and altitude  
238 effects and the origins of air masses. The morphology of France is complex with the Massif  
239 Central in the centre, the Alps to the East and the Pyrénées to the South, together with the  
240 influences of both the Atlantic Ocean and the Mediterranean Sea, which have very different  
241 characteristics, as evidenced by Celle-Jeanton et al. (2001) and Ladouche et al. (2009). It is,  
242 therefore, of primary importance to constrain the signature of the atmospheric signal in  
243 different geographical and geomorphological contexts by means of a rainfall-monitoring  
244 network.

245 The five monitoring stations (Brest, Dax, Orléans, Thonon and Avignon) were selected in  
246 order to have a good distribution over the national territory (Fig. 1). This enables, firstly, to  
247 follow the evolution of the isotopic signal over a West-East transect from Brest to Thonon via  
248 Orléans, and, secondly, to observe the influence of Mediterranean versus Atlantic air  
249 masses.

250 The equation of the Global Meteoric Water Line (GMWL) is  $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$  (Craig 1961).  
251 The arithmetic (unweighted) means of isotopic ratios in precipitation from nearly 410 stations  
252 are described by the following equation:  $\delta\text{D} = 8.07 (\pm 0.02) \times \delta^{18}\text{O} + 9.9 (\pm 0.1)$ ,  $R^2 = 0.98$ .  
253 Long-term means weighted by the amount of precipitation were calculated only for the year  
254 for which more than 70% of the rainfall was analysed and at least one year of observation  
255 was available (Gourcy et al. 2005). The correlation between the weighted means is:  $\delta\text{D}_{\text{weighted}}$   
256  $= 8.14 (\pm 0.02) \times \delta^{18}\text{O} + 10.9 (\pm 0.2)$ ,  $R^2 = 0.98$ . When all the available data from the 5  
257 French monitoring stations are plotted in a  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  diagram (Fig. 2a), the following



258 equation can be calculated:  $\delta D = 7.727 (\pm 0.066) \times \delta^{18}O + 7.033 (\pm 0.451)$ ,  $R^2 = 0.97$ ,  $n =$   
259 411. When only annual weighted mean values are used for each monitoring station (Fig. 2b),  
260 the equation becomes:  $\delta D = 8.347 (\pm 0.153) \times \delta^{18}O + 11.662 (\pm 1.048)$ ,  $R^2 = 0.99$ ,  $n = 31$ .

261 These global results are close to the Global Meteoric Water Line despite the variability that  
262 can be found at each French station.

263 The weighted mean for each station integrates all the available data over the monitoring  
264 period. The Avignon weighted mean for the period 1997-2002,  $\delta^{18}O = -5.81\text{‰}$ , is similar to  
265 the one calculated during the 1997-1998 period, i.e.  $\delta^{18}O = -6.1\text{‰}$  (Celle et al. 2000). These  
266 weighted means are reported in figure 3f, in which all points plot very close to the GMWL,  
267 and highlight the continental effect (also called the distance-from-the-coast-effect) with  
268 progressive depletion in heavy isotopes from Brest (Atlantic coast) to Thonon via Orléans  
269 (Fig. 1). It is worth noting that the best fit regression lines of the annual weighted means of  
270 these three stations described a quasi-straight line very close to the GMWL (Fig. 2b),  
271 suggesting a genetic link of rainfall for the three stations.

272 In greater detail, the continental effect can be assessed between Brest and Thonon samples  
273 (355 km apart) after removing the altitude effect for the Thonon station (at an altitude of 385  
274 m). Blavoux (1978) calculated an altitudinal gradient of  $-0.3\text{‰}/100$  m in this region (Chablais,  
275 pre-Alpes), leading to a continental effect of  $-3.2\text{‰} \delta^{18}O/1000$  km in an eastward direction  
276 from the French Atlantic Coast. This value is in good agreement with the assessment of  
277 Lécalle (1985) over the French territory. The continental effect varies considerably from place  
278 to place and from season to season (Ladouche et al. 2009), even over a low-relief profile. It  
279 is also strongly correlated with the temperature gradient and depends on both the  
280 topography and the climate regime.

281 Average annual  $\delta^{18}O$  values vary from year to year (Fig. 2b). For the 5 French monitoring  
282 stations, the  $\delta^{18}O$  values vary between 1 and 2‰ over the monitoring period, as was  
283 observed in Wallingford, UK (Darling and Talbot 2003). This is typical of temperate climates  
284 where a large part of the spread is caused by variations in the average annual temperature  
285 (Gat et al. 2001). These variations from year to year show why it is difficult to assess the real  
286 signature of precipitation in a given place without long-term monitoring. This should be kept  
287 in mind when drawing a contour map of  $\delta^{18}O$  for a vast territory for which only a few long-  
288 term monitoring data are available.

## 289 **4.2. Lithium and boron concentrations in rainwaters**

291  
292 Major elements (cations and anions) and lithium and boron concentrations in rainwater  
293 samples collected in Brest, Dax, Orléans and Clermont-Ferrand are given in table 1. When  
294 Cl concentrations are plotted as a function of Na concentrations (Fig. 4, Négrel et al. 2007),

295 we observe a good correlation for the rainwater samples. The regression line between these  
296 two major elements is also shown in figure 4. A 95% confidence level is assigned to the data  
297 that falls between the two lines. The seawater dilution line is also shown in figure 4. Cl  
298 concentrations show a very strong correlation with Na concentrations ( $R^2 = 0.99$ ). All the  
299 samples lie near the seawater dilution line, indicating that both the Na and Cl in these  
300 samples come from sea salt. The Brest and the Dax rainwater samples have the highest Na  
301 and Cl concentrations, whereas those collected near Clermont-Ferrand have the lowest  
302 concentrations in both Na and Cl.

303 Lithium and boron concentrations in rainwater samples range from 0.004 to 0.292  $\mu\text{mol/L}$   
304 and from 0.029 to 6.184  $\mu\text{mol/L}$ , respectively. This range of variation for Li concentrations is  
305 significantly lower than the only other value reported for rainwater (i.e. Li = 0.520  $\mu\text{mol/L}$ , in  
306 Hawaii, Pistiner and Henderson 2003). On the other hand, boron concentrations reported in  
307 here are in agreement with literature data, with values sometimes higher in the present case  
308 (Chetelat et al. 2005, Rose-Koga et al. 2006, Chetelat et al. 2009).

309 Li concentrations are more homogeneous than boron concentrations from one sampling site  
310 to another. The mean lithium concentration values for the various sites are quite similar  
311 (0.058, 0.066, 0.053 and 0.057  $\mu\text{mol/L}$  for rainwaters collected at Brest, Dax, Orléans and  
312 near Clermont-Ferrand, respectively), whereas they are more heterogeneous for boron (i.e.  
313 0.66, 0.90, 1.51 and 0.20  $\mu\text{mol/L}$  for rainwaters collected at Brest, Dax, Orléans and near  
314 Clermont-Ferrand, respectively).

315 The overall range of variation for Li and B concentrations can be seen in figure 5a and 5b,  
316 where lithium and boron concentrations are plotted as a function of the Na concentrations as  
317 seasalt tracer (Négrel and Roy, 1998). Again, we see that these rainwater samples are rather  
318 homogenous for lithium concentrations (with the exception of 2 Li-rich samples). Moreover, it  
319 appears that rainwaters are slightly enriched in Li and B compared to Na derived from  
320 seawater. No correlation could be found, however, between Li and B concentrations in  
321 rainwater samples (Fig. 5c).

322

### 323 **4.3. Lithium and boron isotopes**

324

325 Lithium and boron isotope compositions are reported in table 1 and figure 6. The most  
326 striking outcome of this study is that there is a very large range of variation (between +3.2  
327 and +95.6‰) for  $\delta^7\text{Li}$  in rainwaters. Mean  $\delta^7\text{Li}$  values are +22.5, +22.8, +16.1 and +26.2‰ for  
328 samples collected in Brest, Dax, Orléans and near Clermont-Ferrand, respectively. This  
329 range of variation is consistent with the only other value reported for rainwater ( $\delta^7\text{Li} =$

330 +14.3‰, in Hawaii, Pistiner and Henderson, 2003). Furthermore,  $\delta^7\text{Li}$  values in rainwaters  
331 are significantly different from the  $\delta^7\text{Li}$  signature of seawater (+31‰, Millot et al. 2004a).

332  $\delta^{11}\text{B}$  in rainwaters also shows a very wide range of variation, between -3.3 and +40.6‰. The  
333 mean  $\delta^{11}\text{B}$  values are +37.4, +11.4, +8.4 and +23.2‰ for rainwaters collected in Brest, Dax,  
334 Orléans and near Clermont-Ferrand, respectively. This is in agreement with literature data  
335 (Chetelat et al. 2005, Rose-Koga et al. 2006, Chetelat et al. 2009) and is significantly  
336 different from the  $\delta^{11}\text{B}$  signature of seawater (+39.5‰, see data compilation reported by  
337 Aggarwal et al. 2004), except for Brest.

338 In figures 7a and 7b,  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values are plotted as a function of Li and B  
339 concentrations, respectively. No general correlation is observed between  $\delta^7\text{Li}$  and Li  
340 concentrations (Fig. 7a). Indeed, the range of  $\delta^7\text{Li}$  variation is covered at both low and high Li  
341 concentrations (with the exception of the three  $^7\text{Li}$ -rich samples from Clermont-Ferrand). On  
342 the other hand, there seems to be an inverse correlation between  $\delta^{11}\text{B}$  and B concentrations  
343 (Fig. 7b). Initially high  $\delta^{11}\text{B}$  values (close to seawater signature, i.e. corresponding to  
344 rainwater samples from Brest, which is near the ocean) tend to decrease down to nearly -3‰  
345 as B concentrations increase. This also means that high B concentrations in rainwaters are  
346 associated with low  $\delta^{11}\text{B}$  values, especially for Orléans rainwater samples.

347 The overall range of variation for both  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values is very great (over 90‰ and 40‰,  
348 respectively, for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$ , Fig. 6), and these isotopic signatures for rainwater samples  
349 are significantly different from the isotopic signature of seawater (+31.0 and +39.5‰,  
350 respectively, for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values). Seawater might, therefore, be a major source of  
351 dissolved atmospheric lithium and boron (especially for rainwater collected near the ocean),  
352 but other sources must also be considered.

353

354

## 5. DISCUSSION

355

### 356 5.1. Contour map of the stable isotopic signature of oxygen ( $\delta^{18}\text{O}$ )

357

358 The world map developed by the IAEA from GNIP data (GNIP 2007) is one of the few  
359 contour maps of the stable atmospheric signal that exist today. In France, a  $\delta^{18}\text{O}$  contour  
360 map was drawn by Lécolle (1985), based on the oxygen isotopic composition of the  
361 carbonate shell of landsnails, which have been shown to be directly linked to the annual  
362 mean  $\delta^{18}\text{O}$  of rainwater. A second map, based on a few rainwater and groundwater  
363 measurements, was drawn by Razafindrakoto (1988).

364 In the present work, the stations in Brest, Dax, Orléans, Avignon and Thonon (Fig. 1) were  
365 monitored monthly for the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  atmospheric signal. Rain samples from the BDISO  
366 databank are from studies dedicated to the knowledge and functioning of specific aquifers,  
367 often represent only a few months of monitoring, and are not for the same time periods. From  
368 all the available data, we selected data points with the following criteria: (1) there must be at  
369 least one year of monitoring; (2) isotopic data should be associated with the rainfall amount  
370 (if rainfall values are unavailable, data are weighted by those from the nearest meteorological  
371 station at the same altitude); (3) when two points are close, only the longest and more recent  
372 monitoring campaign is selected, as well as the lowest altitude point to minimize the altitude  
373 effect when drawing the map. Rain data from 44 points were selected (Fig. 8). Some regions  
374 are poorly documented and additional data were selected. In the Southwest of France, lakes  
375 considered to be natural rain gages under well-defined conditions (lakes in pristine  
376 environments located in the upper parts of drainage basins to limit runoff, Petelet-Giraud et  
377 al. 2005) are used after data has been corrected for evaporation. Data from 13 lakes were  
378 used. In other regions, recent groundwater (i.e. Tritium values  $>0$  and  $^{14}\text{C}$  Activity close to  
379 100%) was used as a reference material as it has been shown to be often reasonably  
380 representative of long-term rainfall (Darling et al. 2003). Data for 12 groundwater bodies  
381 were used. No data are available for the Rhône River Valley. We, therefore, used a signature  
382 calculated from that of a landsnail shell from the Northern part of the valley (Lécolle 1985).  
383 To better determine the isotopic signature at the French border, we used data from the  
384 literature or long-term rain monitoring data in the GNIP database for neighbouring countries  
385 (GNIP 2007, Plata-Bedmar 1994, Longinelli and Selmo 2003, Longinelli et al. 2006, Darling  
386 and Talbot 2003, Darling et al. 2003, Schurch et al. 2003).

387 The contour map of  $\delta^{18}\text{O}$  values was drawn manually for the following reasons: (1) to take  
388 into account the altitude from the topographic digital terrain model (DTM) for a better  
389 interpolation, reflecting the altitude affect and (2) to give a greater weight to the most  
390 representative samples (length of the monitoring campaign, altitude, etc.) when large isotopic  
391 variations were observed at small scale. Our attempts to automatically generate the map with  
392 dedicated software with kriging methods were rather inconclusive mainly because, as the  
393 data including the altitude effect, it was impossible to take into account the DTM in the  
394 interpolation without a risk of taking the altitude effect into account twice.

395 The resulting map of the meteoric  $\delta^{18}\text{O}$  signal (Fig. 8) clearly shows the main effects that  
396 could affect the isotopic signature of rainwater. The continental and altitude effects are  
397 clearly visible. It is also in good agreement with the map drawn by Lécolle (1985), with a high  
398 degree of precision, especially in the North. The new contour map still remains quite  
399 schematic because of the limited number of available data points and the complexity of the  
400 French topography. This is especially true in mountainous regions, where the density of data

401 is too low and the relief too uneven for us to draw reliable lines.  $\delta^{18}\text{O}$  iso-value lines are,  
402 therefore, represented by dotted lines in the Pyrénées and the Alps.

403 The map also shows that the signature along the Atlantic coast is relatively homogeneous  
404 with a  $\delta^{18}\text{O}$  value of around  $-5\text{‰}$ , despite the difference in latitude and the known climatic  
405 differences. The same phenomenon is observed on the Mediterranean coast of Italy  
406 (Longinelli and Selmo 2003) and can be at least partially related to the contribution of  
407 seawater vapor to the coastal precipitation, with values characteristic of a first condensate of  
408 vapor (Gat et al. 2001). While the isotopic signal on the Mediterranean coast is not  
409 significantly different from that on the Atlantic coast, the Mediterranean signature is more  
410 rapidly depleted in heavy isotopes as we move inland from the coast. This could be due to  
411 the presence of mountains close to the coast, which generate rainfall. Rainwater in and  
412 around Paris is less depleted in heavy isotopes than available data indicates for the  
413 surrounding area. This might be explained by a slightly higher temperature induced by the  
414 high population density and intensive industrial activity. Such a phenomenon has been  
415 described in Rome (Italy) (Longinelli and Selmo 2003). The Northern coast presents a  $\delta^{18}\text{O}$   
416 signal, depleted in heavy isotopes compared to the Atlantic coast ( $-6.5\text{‰}$  vs.  $-5.3\text{‰}$  in Brest  
417 and  $-5.6\text{‰}$  in Dax), which suggests that clouds that produce rainfall are already depleted in  
418 heavy isotopes. This phenomenon has been observed over the British Isles. The  $\delta^{18}\text{O}$   
419 contour lines are parallel on each side of the Chanel.

420 This map is the first one drawn at the national scale based on most of the isotopic data  
421 available in France, and which takes into account data for neighbouring countries in order to  
422 better constrain the contour lines along the borders. It is, therefore, a unique tool for  
423 assessing the stable isotopic signature of aquifer recharge for oxygen isotopes.  
424 Nevertheless, it is worth noting that the rainwater data used often integrate only one year of  
425 rainfall and we have shown that the mean annual weighted  $\delta^{18}\text{O}$  values vary from 1 to  $2\text{‰}$   
426 due to variations in the average annual temperature typical of temperate climates. This map  
427 can, therefore, be a valuable addition to local rain monitoring when a specific aquifer is being  
428 studied.

429 In this paper, we report only the  $\delta^{18}\text{O}$  signature for France. However,  $\delta\text{D}$  can be determined  
430 using the global correlation between  $\delta\text{D}$  and  $\delta^{18}\text{O}$  (the Global Meteoric Water Line) since all  
431 the data considered plot, for the most part, along this line.

432

## 433 **5.2. Lithium and boron isotopes variations**

434

### 435 *5.2.1. Seasonal and spatio-temporal variations*

436

437 Monitoring rainwater samples over a period of one year at different locations allows us to  
438 study seasonal effects on the range of variation for both Li and B isotopes. We have plotted  
439 Li and B isotopes as a function of the rainfall amount (mm) (Figs. 9a and b) and the month  
440 (Figs. 9c and d). The rainfall amount seems to have no effect on  $\delta^7\text{Li}$  variations (Fig. 9a). The  
441 total range of variation for  $\delta^7\text{Li}$  values seems to be independent of the rainfall amount, and  
442 this is especially true for Orléans, Brest and Dax. On the other hand, for Brest and Dax  
443 samples (sampling points on or near the coast), the rainfall amount does seem to control  
444  $\delta^{11}\text{B}$  variations to some extent (Fig. 9b). When the rainfall amount increases, the  $\delta^{11}\text{B}$  values  
445 increase for the Brest samples but decrease for the Dax samples. It is very likely that when  
446 the rainfall amount is great, there is a large contribution of sea salts derived from seawater.  
447 This is especially true for the Brest rainwater samples (sampling point less than 5 km from  
448 the Atlantic Ocean). However, the trend observed for  $\delta^{11}\text{B}$  the rainwater samples from Dax  
449 (30 km inland) is more complex. We know that, in this area, rainfall comes not only from the  
450 Atlantic Ocean to the West, but also from the Pyrénées Mountains to the South. Therefore,  
451 we can assume that for the Dax rainwater samples: (i) during the summer and winter (low  
452 rainfall amount),  $\delta^{11}\text{B}$  is controlled mainly by the sea salt contribution coming from the  
453 Atlantic Ocean, whereas (ii) during spring and autumn when rainfall is heavier,  $\delta^{11}\text{B}$  might  
454 also be controlled by rain coming from the mountains that has been in contact with local dust  
455 (i.e. silicate, carbonate and/or evaporite particulates from the Pyrénées), lowering  $\delta^{11}\text{B}$   
456 values. In addition, like Négrel et al. (2007) have observed for Sr isotopes at the same  
457 sampling site, biogenic sources might also contribute to the  $\delta^{11}\text{B}$  signature of the Dax  
458 samples, also lowering the  $\delta^{11}\text{B}$  values. Indeed, Dax is located in a huge maritime pine forest  
459 (*Pinus pinaster*) that covers 860,000 hectares, the trees growing in sand containing chlorite,  
460 micas, feldspars and quartz (Righi and De Connick 1977).

461 Rainwater samples from inland sampling points (Orléans and Clermont-Ferrand) do not show  
462 any correlation of  $\delta^{11}\text{B}$  values with the rainfall amount (Fig. 9b). Likewise, the month does not  
463 appear to have any effect on  $\delta^7\text{Li}$  values (Fig. 9c). However,  $^7\text{Li}$ -rich values for Clermont-  
464 Ferrand rainwater are observed during the winter and spring seasons (December, February  
465 and April).

466 There appears to be no correlation between  $\delta^{11}\text{B}$  values and the month (Fig. 9d). The range  
467 of variation for  $\delta^{11}\text{B}$  is controlled, first of all, by the location (inland vs. coastal) of the  
468 sampling point.

469

470 *5.2.2. Wind direction and air mass origin*

471

472 The origin of the air masses for the French rainwater under consideration was studied using  
473 the French Meteorological Institute database ([www.meteofrance.com](http://www.meteofrance.com)). Daily maximum wind  
474 direction (0 to 360°) and rainfall (mm) were considered. Average monthly wind direction data  
475 are given in table 1 for each sampling point. These average values were calculated by  
476 weighting daily maximum wind directions by the corresponding rainfall amount and only rainy  
477 days were considered.

478 The effect of wind direction, and thus the origin of the air masses, at each sampling site was  
479 investigated by identifying correlations between wind direction and Li-B concentrations and  
480 their isotopes.

481

#### 482 *5.2.2.1. Lithium*

483

484 Li concentrations and  $\delta^7\text{Li}$  values were plotted as a function of the wind direction (Fig. 10).  
485 The wind direction does not control Li content in Brest and Clermont-Ferrand rainwater  
486 samples (Figs. 10b and 10h). For Dax and Orléans sampling sites, however, there is a  
487 correlation between Li concentration and wind direction (Figs. 10d and 10f). The lithium  
488 concentration is controlled by the origin of the air masses for these rainwater samples, with  
489 higher Li concentrations in rainwater coming from the ocean (wind direction around 270°, i.e.  
490 W). Concerning  $\delta^7\text{Li}$  values, no effect is observed, here again, for Brest rainwaters (Fig. 10a),  
491 which means that most of rainwater at this site is homogeneous for both Li and its isotopes,  
492 even though the wind direction can range significantly (from 50 to 240°, i.e., NE to WSW).  
493 For Dax and Orléans samples, opposite phenomena are observed concerning Li isotopes.  
494 When the air masses have a Western origin (oceanic input),  $\delta^7\text{Li}$  values tend to increase  
495 slightly for Dax rainwaters but decrease slightly for Orléans rainwaters (Figs. 10c and 10e).  
496 The most striking observation concerns Clermont-Ferrand rainwaters, for which  $\delta^7\text{Li}$  values  
497 display two interesting trends as a function of the wind direction (Fig. 10g). In winter and  
498 spring samples, there is a positive correlation between  $\delta^7\text{Li}$  and wind direction. However,  
499 autumn and summer samples show no change in the  $\delta^7\text{Li}$  signature when the wind direction  
500 is between 120 and 300°. This means that the  $^7\text{Li}$ -rich rainwaters are characterized by air  
501 masses coming from SSW of the sampling site during the winter and spring.

502

#### 503 *5.2.2.2. Boron*

504

505 B concentrations and  $\delta^{11}\text{B}$  values were plotted as a function of the wind direction (Fig. 11). B  
506 concentrations in Brest and Clermont-Ferrand rainwaters are not controlled primarily by the  
507 wind direction (Figs. 11b and 11h, respectively). However, for Dax and Orléans rainwaters, B

508 concentrations increase when the wind comes from West of the sampling site (marine origin,  
509 Figs. 11d and 11f). There is no evidence that  $\delta^{11}\text{B}$  values in Brest and Clermont-Ferrand  
510 rainwaters are controlled by the wind direction (Figs. 11a and 11g), whereas  $\delta^{11}\text{B}$  values in  
511 Dax rainwaters increase when the wind direction ranges from  $210^\circ$  (SW) to  $270^\circ$  (W) (Fig.  
512 11c), in agreement with our conclusions in section 5.2.1. concerning the two major origins of  
513 boron at this site (sea salt from the Atlantic Ocean (W) and rainfall from the Pyrénées (SW)  
514 having lower  $\delta^{11}\text{B}$  values).  $\delta^{11}\text{B}$  values in rainwater in Orléans decrease slightly when the  
515 wind direction ranges from  $180^\circ$  (S) to  $270^\circ$  (W) (Fig. 11e).

516 The origin of the air masses is, therefore, an important factor that can control the dissolved  
517 concentration of Li and B for the Dax and Orléans sampling sites, but seems to have no  
518 effect on Clermont-Ferrand and Brest rainwaters. This is probably due to the homogeneity of  
519 the rainfall for the Brest sampling site. On the other hand, for Dax, rainwater could have two  
520 main origins – the SSW (with lower  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values) or the W (with higher  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$   
521 values), which reflects the contribution of marine sea salts. For Clermont-Ferrand, the wind  
522 direction has no significant effect on either Li or B concentrations, whereas we have seen  
523 that the  $^7\text{Li}$ -rich rainwaters are characterized by air masses coming from the SSW of the  
524 sampling site during the winter and spring.

525 The spatial range of variation for Li and B isotopes could then be studied because we  
526 monitored rainwater samples at different locations in France (coastal and inland). The  
527 rainwaters sampled at Brest, near the sea, have both  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values close to the  
528 seawater signature (Figs. 6 and 12), whereas those sampled at Dax, Orléans and Clermont-  
529 Ferrand have a very broad range of variation for both  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values – from crustal  
530 values (i.e. from -2 to +2‰ and from -5 to +10‰, respectively, for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$ , Teng et al.  
531 2004, Tomascak 2004, Barth 1993, Barth 2000 and Millot et al. 2007) up to the  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$   
532 signatures of seawater (+31.0 and +39.5‰, respectively, for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$ ). However, higher  
533  $\delta^7\text{Li}$  values are measured in some rainwater samples collected near Clermont-Ferrand. We,  
534 therefore, discuss below the origins of lithium and boron in rainwaters, and the associated  
535 isotope signatures, that might explain the observed range of variation for both Li and B  
536 isotope systematics.

537

### 538 **5.3. Origin of lithium and boron in rainwaters**

539

540 Seawater (by contributing sea salts) might be one of the major suppliers of atmospheric  
541 lithium and boron, but other sources must also to be taken into account. We, therefore,  
542 determined the contribution of sea salts to lithium and boron in rainwater samples.



543 Na concentrations in rainwater samples can be used to estimate the sea salt contribution of  
544 other ions because Na is the best tracer of sea salt input in rainwater (Keene et al. 1986,  
545 Négrel and Roy 1998, Basak and Alagha 2004, Rastogi and Sarin 2005). Distinguishing  
546 between the sea salt (ss) and non-sea salt (nss) component contributions in rainwater (rw) is  
547 essential if we wish to characterize the chemistry of precipitation (Négrel and Roy 1998,  
548 Schmitt and Stille 2005, Al-Khashman 2005, Rastogi and Sarin 2005, Négrel et al. 2007).  
549 To calculate the contribution of Li and B (X in equation 1) in the sea salt component (ss) with  
550 seawater (sw) characteristics, the following equation is used:

551

$$X_{ss} = Na_{rw} \times \left( \frac{X}{Na} \right)_{sw} \quad (1)$$

552

553

554 Na is used as a marine tracer in rainwater (see Négrel and Roy 1998 and references  
555 therein). The contribution of the non-sea salt component (nss) is the difference between the  
556 total composition of rainwater (rw) and the sea salt (ss) contribution:

557

$$X_{nss} = X_{rw} - X_{ss} \quad (2)$$

558

559 This equation enables us to determine the contribution of sea salts for lithium and boron  
560 concentrations in rainwaters (Fig. 13). Results show that the contribution of sea salt for boron  
561 concentrations in rainwaters is greater than for lithium concentrations. Indeed, considering  
562 average values for the 4 different sampling sites, we see that the marine contribution (sea  
563 salt) to B in rainwaters is twice that to Li (22.3% and 12.0%, respectively, Fig. 13). The  
564 distance-from-the-coast-effect (inland vs. coastal location) is the key parameter controlling  
565 the marine contribution for both Li and B to rainwater concentrations. Samples collected  
566 inland (Orléans and Clermont-Ferrand) show the lowest sea salt contributions. Rainwaters  
567 from Dax have intermediate values (Fig. 13), whereas rainwaters collected at Brest have the  
568 highest contributions of marine sea salt to Li and B concentrations (25% and 49.8% on  
569 average, respectively, for Li and B).

570 Although these results are not surprising, they show that although seawater does, indeed,  
571 supply dissolved atmospheric lithium and boron, non sea salt sources represent the major  
572 source of Li and B in rainwaters.

573 This could be of importance in hydrogeochemical studies of surface water and groundwater  
574 bodies because rainwater is an input for the former and a recharge for the latter. The non  
575 sea salt signature for Li and B isotopes should, therefore, be taken into consideration for  
576 future studies in the investigation of their isotope systematics in water.

577

#### 578 **5.4. Lithium isotopes in rainwaters**

579  
580 The fact that most of dissolved Li in rainwaters does not have a marine origin is in agreement  
581 with the range observed in  $\delta^7\text{Li}$  in our samples (+3.2 and +95.6‰) compared to the marine  
582 signature of Li isotopes ( $\sim +31\text{‰}$ ).

583  $\delta^7\text{Li}$  values in rainwater samples were plotted as a function of Li derived from sea salt (Fig.  
584 14a) in an attempt to identify the different sources contributing to the rainwaters Li isotopes  
585 signature. For rainwater sampled at a coastal location (Brest), the marine contribution is  
586 relatively great (9 to 45%), but another source or other sources is/are needed in order to  
587 explain the range of variation in these  $\delta^7\text{Li}$  values (+15.1 to +28.6‰). The same is observed  
588 for rainwaters collected at Dax and Orléans, but at these locations the non sea salt  
589 contribution should be even greater since these sites are located inland (especially Orléans)  
590 and show lower marine contributions. The dissolution of either Li-bearing minerals or  
591 anthropogenic inputs might explain lower  $\delta^7\text{Li}$  values compared to the seawater signature ( $\sim$   
592 +31‰).

593 Continental rocks have  $\delta^7\text{Li}$  values ranging from -4 to +8‰ (Teng et al. 2004 and references  
594 therein) and might contribute to rainwater signatures by interaction in the atmosphere  
595 between continental particles and water molecules. In addition, most carbonates analysed to  
596 date show  $\delta^7\text{Li}$  values between +6 and >25‰ (e.g. Hoefs and Sywall 1997, Hall et al. 2005,  
597 Hathorne and James 2006, Vigier et al. 2007) and could also be cited there. It is, however,  
598 more likely that multiple sources exist for the crustal component at the scale of France.

599 The three rainwater samples from Clermont-Ferrand having a  $^7\text{Li}$ -rich signature ( $\delta^7\text{Li}$  values  
600 of +63.8, +77.6 and +95.6‰) are, however, notable because they have significantly heavier  
601 Li isotopic compositions than seawater. Négrel and Roy (1998) and Roy and Négrel (2001)  
602 have shown that rainwater in this area is likely to record an anthropogenic input due to  
603 agricultural activities (e.g. fertilizers application). These high  $\delta^7\text{Li}$  values might, therefore, be  
604 explained by the contribution of a local input derived from fertilizers and/or soil amendments  
605 used by farmers in this area. This is also in good agreement with recent results of Négrel et  
606 al. (2009) concerning the Li isotopic characterization of a peat bog located near our sampling  
607 site. In this study, the  $^7\text{Li}$ -rich contribution to surface waters is explained by the dissolution of  
608 fertilizers and soil amendments having  $\delta^7\text{Li}$  values higher than +215‰ (Négrel et al. 2009).  
609 This heavy lithium component is attributed to synthetic Li added into fertilizers and soil  
610 amendments, derived from a  $^7\text{Li}$ -rich reagent, as was reported by Qi et al. (1997). In addition,  
611 we have seen (section 5.2.2) that these  $^7\text{Li}$ -rich rainwaters are characterized by air masses  
612 coming from the SSW of the sampling site during the winter and spring, which is when soils  
613 are fertilized and amended.

614 When Li isotopes are plotted as a function of the Na/Li molar ratio (Fig. 15), we observe that  
615 samples from Clermont-Ferrand seem to indicate a mixing of a crustal component (granite  
616 and/or carbonate) and an anthropogenic component ( $^7\text{Li}$ -rich end-member), whereas  
617 samples from Brest, Dax and Orléans seem to indicate a mixing of a crustal component  
618 (complex due to the relative contribution of different particles derived from carbonate or  
619 granite) and a marine end-member.

620

## 621 **5.5. Boron isotopes in rainwaters**

622

623 As stated above, most of the dissolved B in rainwater is not of marine origin (for rainwater  
624 samples collected at inland locations in Orléans and Clermont-Ferrand, in particular). This is  
625 in agreement with the range observed in  $\delta^{11}\text{B}$  values in our samples (-3.3 and +40.6‰)  
626 compared to the marine signature of B isotopes (+39.5‰, Aggarwal et al. 2004 and data  
627 therein).

628  $\delta^{11}\text{B}$  values in rainwater samples have been plotted as a function of B derived from sea salt  
629 (Fig. 14b). Seawater seems, nevertheless, to be a major supplier of rainwater boron in Brest,  
630 near the ocean. However, the rainwater sample collected at Brest in August 2003 is notable  
631 (the lowest  $\delta^{11}\text{B}$  value: +27.5‰). It was collected at a time when France and Western Europe  
632 were having an exceptionally severe heat wave with record temperatures and little rainfall  
633 (Luterbacher et al. 2004, Chase et al. 2006), and it is very likely that this sample is not  
634 representative.

635 Concerning the Dax, Orléans and Clermont-Ferrand rainwater samples, another source or  
636 other sources is/are needed in order to explain the range of variation in  $\delta^{11}\text{B}$  values. As for  
637 lithium, the dissolution of either B-bearing minerals or anthropogenic inputs might explain  
638  $\delta^{11}\text{B}$  values lower than the seawater signature (+39.5‰). A crustal component probably  
639 contributes to rainwater signatures by the interaction in the atmosphere of continental  
640 particles and water molecules. B isotopic compositions for the main crustal lithologies have  
641 been well identified, with  $\delta^{11}\text{B}$  values ranging from -5 to +10‰, from +15 to +30‰ and from 0  
642 to +35‰, for granite and gneiss, marine evaporite and carbonate, respectively (Barth 1993,  
643 2000). This crustal component is expected to contribute to the B isotopic rainwater signature,  
644 although the crustal component is probably made up of a combination of several sources  
645 (different particles coming from different lithologies).

646 Plotting B isotopic compositions as a function of  $\text{NO}_3/\text{B}$  molar ratios ( $\text{NO}_3$  being a good tracer  
647 of fertilizer) provides additional and important information (Fig. 16). Samples from Dax, for  
648 which we have already suggested a possible biogenic input, are in agreement with field data  
649 reported by Chetelat et al. (2005) for the biomass-derived end-member (this is also true for

650 most samples from Orléans, located near a large forested area, “La Sologne”, an area  
651 covering 500,000 ha). In addition, the B values in rainwaters from this study are little affected  
652 by anthropogenic emissions compared to those of rainwater sampled in Paris that have an  
653 urban aerosol component (Chetelat et al. 2009). Most rainwater samples from Clermont-  
654 Ferrand (for which we have cited a possible fertilizer input based on Li isotope data) also  
655 reveal a mixing trend toward a fertilizer end-member (Fig. 16) based on B isotopes tracing.

656

657

## 6. CONCLUSIONS

658

659 This work has made it possible to better characterize Li, B, H and O isotopes in rainwaters.

660 The main results of this study are:

661 • Li and B concentrations and  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  signatures in rainwater samples collected over  
662 one year in four stations (Brest, Dax, Orléans and Clermont-Ferrand) varied greatly over the  
663 sampling period.

664 • Lithium and boron concentrations are low and comprised between 0.004 and 0.292  $\mu\text{mol/L}$   
665 and 0.029 and 6.184  $\mu\text{mol/L}$ , respectively.

666 •  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  values in rainwaters also vary greatly between +3.2 and +95.6‰ and -3.3 and  
667 +40.6‰ over a period of one year, respectively.

668 • The seasonal effect (i.e. the month or rainfall amount) is not the main controlling factor for  
669 these isotopic variations. However, the continental effect (distance from the coast) is a key  
670 parameter, determining the origin of both lithium and boron derived from marine sea salts. In  
671 addition, the origin of air masses (wind direction) is also a key parameter that controls the  
672 contribution of sea salts derived from the Ocean.

673 • The most striking outcome of this study is that most lithium and boron in rainwaters does  
674 not have a marine origin. Seawater is not the major supplier of atmospheric lithium and boron  
675 and a non-sea-salt source, such as a crustal component and/or an anthropogenic  
676 contribution, should also be taken into account when Li and B isotopes are studied in  
677 hydrogeochemistry as an input to surface waters and a recharge to groundwater bodies. This  
678 may be important in the understanding of dissolved Li and B distributions in ground- and  
679 formation waters, and should be taken into account in future studies.

680 • A contour map of France for  $\delta^{18}\text{O}$  was drawn after compiling data that included more than  
681 400 values from all of France. This map could be used as a reference for future studies  
682 concerning the recharge  $\delta^{18}\text{O}$  signature in surface water and groundwater body  
683 characterization. It represents a unique tool for assessing the stable isotopic signature of the  
684 recharge of aquifers for oxygen isotopes.

685

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687

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691 University of Avignon, Centre de Recherches Géodynamiques (Thonon-les-Bains), CEA  
692 (Saclay) and BRGM in Orléans. BDISO aims at gathering isotopic data (mainly  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ,  $^3\text{H}$ ,  
693  $^{14}\text{C}$ ,  $\delta^{13}\text{C}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{11}\text{B}$  and  $\delta^{15}\text{N}$ ) on French groundwater, surface water and rainwater. We  
694 thank J. Garnier for compiling most of the  $\delta^{18}\text{O}$  and  $\delta\text{D}$  data and drawing the first version of  
695 the  $\delta^{18}\text{O}$  contour map presented here. We thank Météo France (Direction de la Production)  
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- 863

864 **Table caption**

865

866 **Table 1**

867 Major cations and anions (Na, K, Mg, Ca, Cl, SO<sub>4</sub>, NO<sub>3</sub>, μmol/L), Li and B concentrations  
868 (μmol/L) and Li and B isotope compositions of rainwaters by location and sampling date.  
869 Rainfall amount (mm) and wind direction are also reported in this table. The prevailing wind  
870 direction data (in °) at each sample location were obtained from the Météo France database.  
871 Data reported for monthly average values in this table are weighted by the rainfall amount  
872 and only days with precipitation are considered.

873

874

875 **Figure captions**

876

877 **Figure 1**

878 Map of the rainwater sampling sites for lithium and boron isotopes (Brest, Dax, Orléans and  
879 Clermont-Ferrand). Graphs show the monthly mean rainfall amount (mm) at each site  
880 (modified from Négrel et al. 2007). Long-term monitoring stations for hydrogen and oxygen  
881 isotopes of the water molecule, at Thonon and Avignon, are also shown on this map.

882

883 **Figure 2**

884 2a:  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  for all the monthly samples from the 5 long-term monitoring stations (Orléans,  
885 Brest, Dax, Thonon and Avignon. 2b: Annual weighted means of the same 5 stations. The  
886 Global Meteoric Water Line is also drawn (GMWL,  $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$ ).

887

888 **Figure 3**

889 3a to 3e:  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  for the monthly samples for each station. 3f: Mean weighted values for  
890 the period considered at each station. Blue diamonds correspond to individual data, red stars  
891 are the weight mean values and the grey dashed line is the Global Meteoric Water Line  
892 (GMWL) is  $\delta\text{D} = 8 \times \delta^{18}\text{O} + 10$ .

893

894 **Figure 4**

895 Cl concentrations in rainwaters ( $\mu\text{mol/L}$ ) plotted as a function of the Na concentrations in  
896 rainwaters ( $\mu\text{mol/L}$ ). The seawater dilution line and the linear relationship between Cl and Na  
897 are represented. A 95% confidence level is assigned to the data that falls between the two  
898 lines (modified from Négrel et al. 2007).

899

900 **Figure 5**

901 5a and 5b: Lithium and boron concentrations in rainwaters ( $\mu\text{mol/L}$ ) vs. sodium  
902 concentrations in rainwaters ( $\mu\text{mol/L}$ ). 5c: Lithium concentrations in rainwaters ( $\mu\text{mol/L}$ )  
903 plotted as a function of boron concentrations in rainwaters ( $\mu\text{mol/L}$ ).

904

905 **Figure 6**

906 Histograms for  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  (‰) values in rainwater samples.

907

908 **Figure 7**

909 7a and 7b:  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  (‰) values plotted as a function of lithium and boron concentrations,  
910 respectively, in rainwaters ( $\mu\text{mol/L}$ ).

911

912 **Figure 8**

913 Isovalue contour lines of the mean annual oxygen isotopic composition ( $\delta^{18}\text{O}$ ) of rainwater in  
914 France. This map is based on rainwater, groundwater, lake (corrected for evaporation) and  
915 landsnail shell data. Contour lines from Spain (Plata-Bedmar 1994), Italy (Longinelli and  
916 Selmo 2003, Longinelli et al. 2006) and United Kingdom (Darling and Talbot 2003, Darling et  
917 al. 2003), together with Swiss data (Schurch et al. 2003) where also used to constrain lines  
918 at the French borders. The location of rainwater sampling stations for  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  is also  
919 shown on this map (blue: short-term monitoring; red: long-term monitoring).

920

921 **Figure 9**

922 9a and 9b:  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$  (‰) values plotted as a function of rainfall amount (mm); 9c and 9d:  
923 and sampling month.

924

925 **Figure 10**

926  $\delta^7\text{Li}$  (‰) values and Li concentrations ( $\mu\text{mol/L}$ ) plotted as a function of wind direction for each  
927 sampling site. Bold lines represent parameter trends as a function of wind direction.

928

929 **Figure 11**

930  $\delta^{11}\text{B}$  (‰) values and B concentrations ( $\mu\text{mol/L}$ ) plotted as a function of wind direction for  
931 each sampling site. Bold lines represent parameter trends as a function of wind direction.

932

933 **Figure 12**

934  $\delta^7\text{Li}$  (‰) plotted as a function of  $\delta^{11}\text{B}$  (‰) in rainwater samples.

935

936 **Figure 13**

937 Histograms for Li and B contribution of marine sea salts (%) in rainwater samples.

938

939 **Figure 14**

940 14a and 14b: Li and B isotopic compositions plotted as a function of Li and B contribution of  
941 marine sea salts in rainwater samples, respectively.

942

943 **Figure 15**

944  $\delta^7\text{Li}$  (‰) plotted as a function of the Na/Li molar ratio.

945

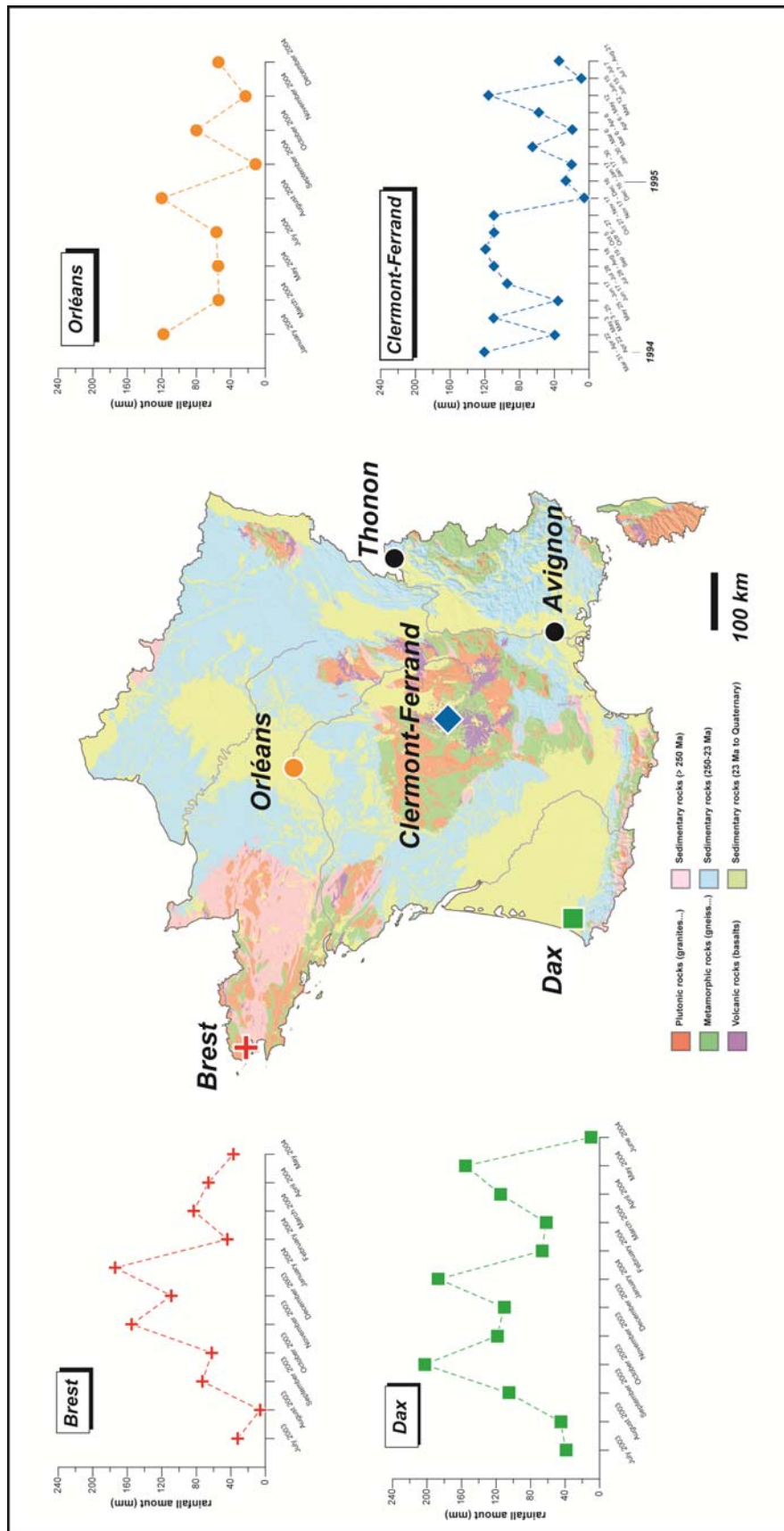
946 **Figure 16**

947  $\delta^{11}\text{B}$  (‰) plotted as a function of  $\text{NO}_3/\text{B}$  molar ratios. The anthropogenic end-member (urban  
948 aerosols) is from Chetelat et al. (2009), the biomass-derived end-member is from Chetelat et  
949 al. (2005) and the fertilizer end-member is from Widory (pers. comm.).  
950

**Table 1**

Location / Sampling date	Reference	Rainfall amount mm	Main Wind direction °	Na μmol/L	K μmol/L	Mg μmol/L	Ca μmol/L	Cl μmol/L	SO <sub>4</sub> μmol/L	NO <sub>3</sub> μmol/L	Li μmol/L	B μmol/L	δ <sup>13</sup> C ‰	δ <sup>15</sup> N ‰
<b>BREST</b>														
July 2003	03-E-524	32	223	117.5	5.8	16.1	8.5	117.7	21.3	36.7	0.051	0.398	23.4	35.1
August 2003	03-E-525	6	105	235.0	31.9	62.8	65.8	228.6	113.9	172.0	0.142	3.793	19.3	27.5
September 2003	03-E-526	73	176	74.3	2.8	10.9	7.9	75.2	22.3	68.9	0.051	0.262	15.1	38.1
October 2003	03-E-527	62	193	208.3	5.6	23.8	11.4	218.9	32.2	58.9	0.052	0.329	22.2	39.6
November 2003	03-E-528	155	129	142.6	10.2	17.2	6.0	150.1	23.2	10.2	0.053	0.207	17.7	40.3
December 2003	03-E-529	109	174	292.7	7.6	33.1	6.2	322.3	31.3	32.1	0.060	0.298	27.2	40.6
January 2004	04-E-52	174	232	231.7	5.1	25.7	7.0	243.1	25.5	6.8	0.050	0.214	28.6	40.1
February 2004	04-E-53	44	57	393.8	10.3	47.8	15.9	450.1	46.0	36.0	0.059	0.355	26.3	37.8
March 2004	04-E-54	83	209	346.2	11.0	40.6	12.6	390.4	42.3	47.0	0.042	0.449	25.8	39.5
April 2004	04-E-55	66	150	227.7	4.8	27.6	10.2	236.3	39.3	57.8	0.033	0.357	22.7	37.5
May 2004	04-E-56	37	234	323.9	10.7	39.5	12.6	366.2	42.1	80.3	0.045	0.599	19.4	35.2
<b>DAX</b>														
July 2003	03-E-164	39	256	204.3	63.6	24.4	55.2	156.6	43.9	-	0.069	1.013	34.1	15.9
August 2003	03-E-165	45.4	248	89.5	9.2	14.9	33.8	50.7	40.8	49.7	0.078	1.167	21.5	7.9
September 2003	03-E-166	105.4	225	196.1	14.3	18.0	23.2	176.3	32.5	2.6	0.067	0.717	21.1	12.9
October 2003	03-E-147	203.1	207	273.6	50.2	26.9	57.8	272.3	33.8	110.6	0.077	1.174	25.2	8.3
November 2003	03-E-148	118.7	238	155.7	15.9	15.2	25.7	136.6	24.8	-	0.062	0.830	19.8	2.0
December 2003	03-E-149	110.7	230	194.2	11.5	16.9	44.6	167.0	30.6	2.9	0.058	0.595	21.0	11.8
January 2004	03-E-150	187.3	242	176.4	9.3	16.9	20.8	164.8	25.9	-	0.047	0.997	23.0	7.1
February 2004	03-E-151	66.8	212	203.9	51.0	29.6	49.2	198.3	44.9	28.7	0.058	0.369	23.5	19.8
March 2004	03-E-152	62.1	210	137.4	41.9	27.1	64.5	135.5	36.9	3.5	0.055	0.662	17.2	9.4
April 2004	03-E-153	115.1	255	255.2	53.8	33.7	65.0	247.3	18.3	3.0	0.068	1.099	18.9	7.9
May 2004	03-E-154	155.1	243	160.1	10.9	19.8	31.4	163.7	23.5	-	0.050	0.898	22.8	7.8
June 2004	03-E-155	10.2	268	108.3	26.8	22.8	114.4	113.5	42.0	-	0.079	1.340	25.3	26.5
<b>ORLEANS</b>														
January 2004	04-E-46	118	221	38.7	6.9	5.8	8.9	32.7	8.4	-	0.041	0.029	13.0	29.8
March 2004	04-E-48	54	231	61.4	11.3	10.8	21.4	49.6	22.6	39.4	0.055	0.408	14.2	13.1
May 2004	04-E-50	55	243	52.4	17.0	8.2	12.7	39.4	14.1	9.5	0.046	0.818	19.2	6.0
July 2004	04-E-295	57	220	53.4	13.5	12.0	23.3	30.4	21.0	-	0.068	1.987	11.2	-0.3
August 2004	04-E-296	120	267	34.5	6.6	11.6	21.0	16.6	14.0	-	0.057	2.430	9.2	-2.4
September 2004	04-E-297	11.5	234	96.9	19.4	22.8	39.4	98.3	27.9	-	0.081	6.184	19.4	-3.3
October 2004	04-E-298	80	175	59.0	14.4	8.9	12.9	41.7	16.5	12.9	0.038	1.246	14.3	0.0
November 2004	04-E-299	23	219	92.3	60.5	13.3	17.8	66.8	39.5	59.0	0.052	0.281	22.9	22.7
December 2004	04-E-300	54	201	51.0	17.8	6.3	9.4	50.1	13.0	19.8	0.036	0.217	21.9	9.8
<b>CLERMONT-FERRAND</b>														
March 31 - April 22 1994	PSM1	120	288	39.1	4.1	4.4	12.3	39.4	51.0	74.6	0.049	0.312	77.6	11.9
April 22 - May 3 1994	PSM2	40	173	6.1	4.1	2.1	10.5	7.0	23.4	16.7	0.041	0.156	6.7	22.9
May 3 - 25 1994	PSM3	110	239	3.9	2.6	1.7	8.0	7.0	16.1	34.1	0.004	0.116	8.7	28.7
May 25 - June 17 1994	PSM4	37	256	9.1	7.2	0.2	14.8	16.9	19.8	-	0.075	0.191	4.9	25.0
June 17 - July 28 1994	PSM5	95	256	20.0	23.8	4.3	79.0	31.0	47.9	42.9	-	-	-	-
July 28 - August 18 1994	PSM6	110	243	4.8	3.3	0.9	16.0	16.9	33.3	30.2	0.033	0.248	6.7	32.8
September 19 - October 5 1994	PSM7	120	294	4.3	2.3	1.9	16.8	7.9	7.1	12.7	0.027	0.106	9.0	32.0
October 5 - 27 1994	PSM8	110	152	8.7	2.6	0.8	15.0	10.1	7.3	-	0.027	0.050	14.7	19.5
October 27 - November 17 1994	PSM9	110	172	0.4	13.6	6.3	1.0	13.5	4.2	-	-	-	-	-
November 17 - December 16 1994	PSM10	5	246	6.5	3.8	6.3	9.5	13.0	36.6	53.8	-	-	-	-
December 16 1994 - January 17 1995	PSM11	28	197	32.2	1.8	8.3	12.0	44.2	21.6	38.7	0.044	0.172	63.8	27.2
January 17 - 30 1995	PSM12	20	195	8.7	3.1	5.8	3.3	14.1	6.1	-	0.041	0.104	33.2	25.4
January 30 - March 6 1995	PSM13	65	214	43.0	2.3	4.0	5.8	21.7	13.2	19.0	0.292	0.520	95.6	4.8
March 6 - April 6 1995	PSM14	20	258	23.0	5.1	3.2	12.3	25.4	14.2	17.5	-	-	-	-
April 6 - May 12 1995	PSM15	58	302	8.3	4.1	2.3	11.0	11.8	39.4	47.0	0.022	0.160	3.2	19.8
May 12 - June 15 1995	PSM16	115	229	8.7	4.9	2.6	18.0	-	-	-	0.044	0.226	7.8	25.2
June 15 - July 7 1995	PSM17	10	124	4.8	9.0	-	12.0	37.5	13.9	69.2	0.037	0.239	8.3	26.8

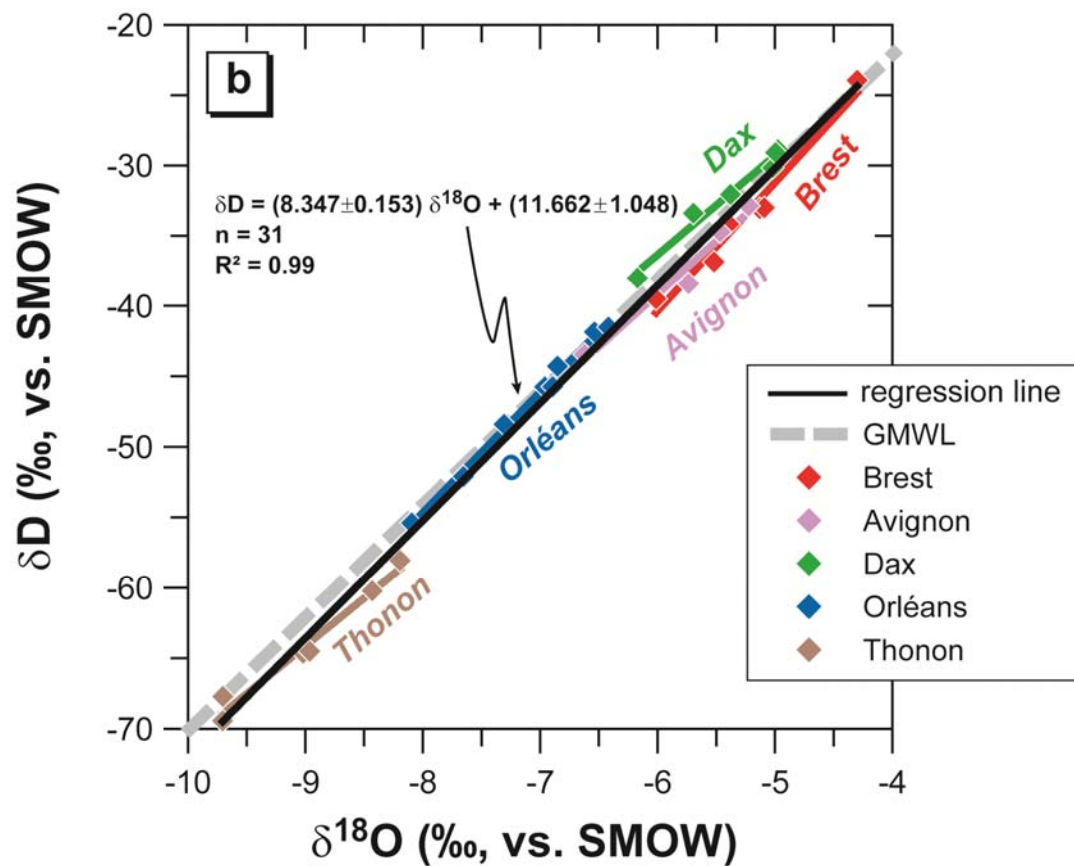
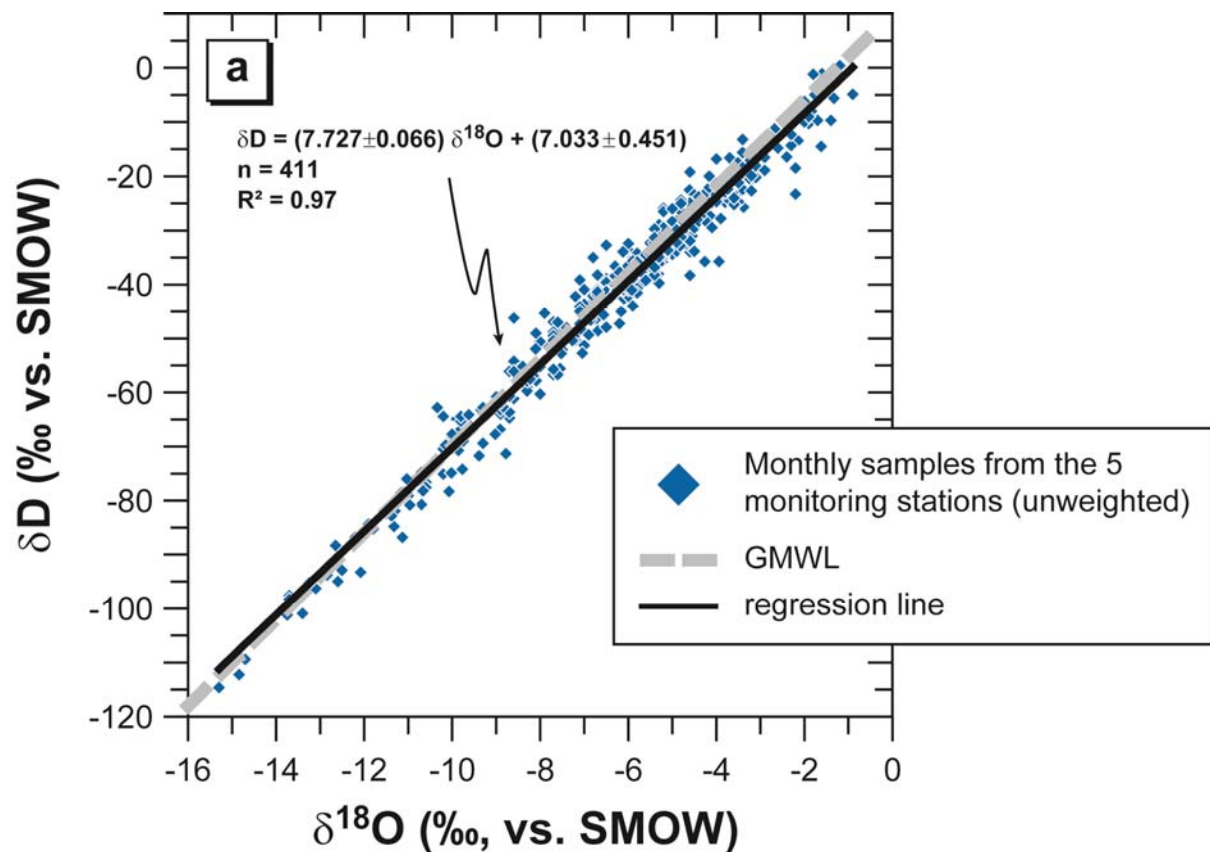
Figure 1





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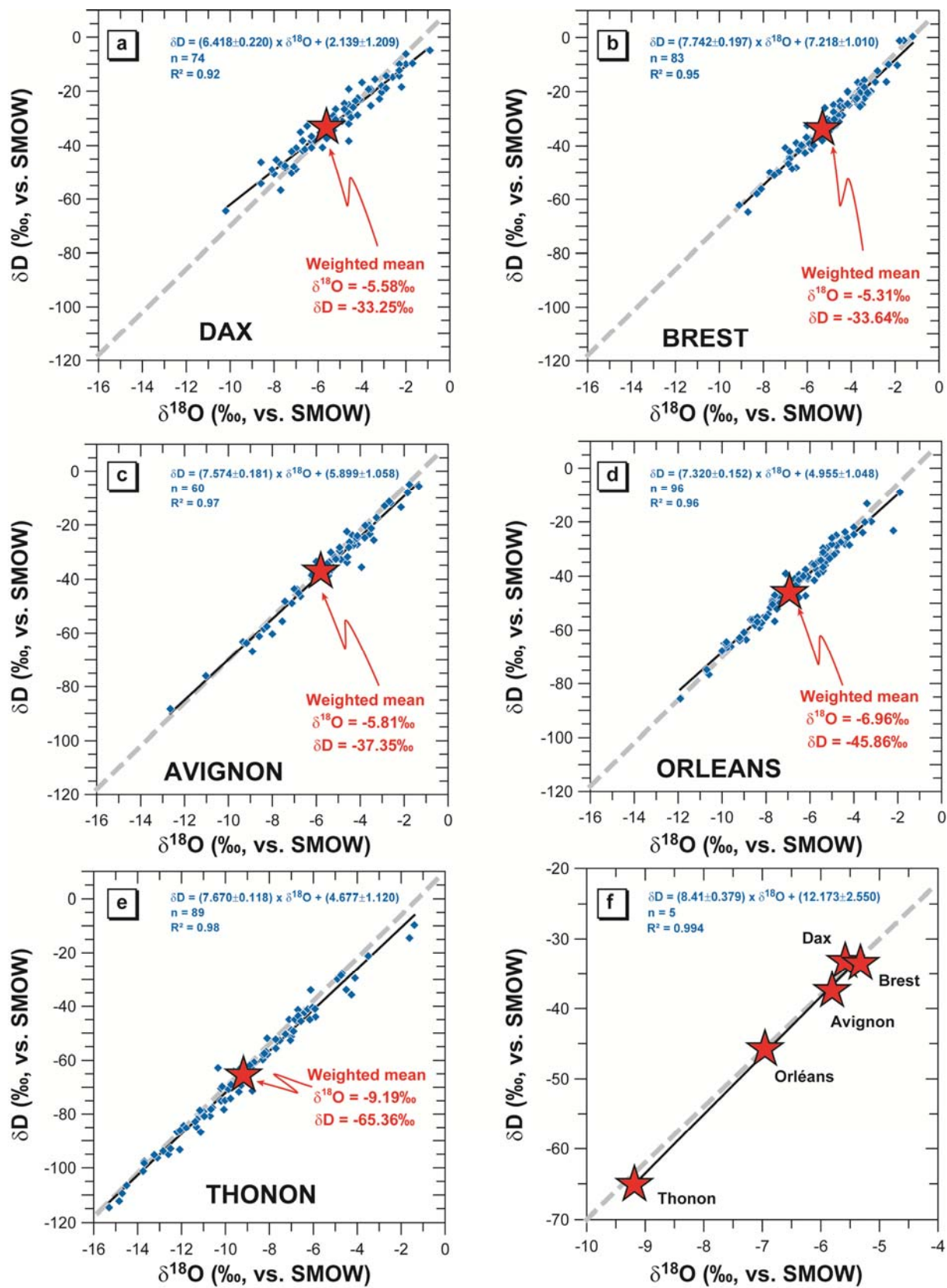
Figure 2



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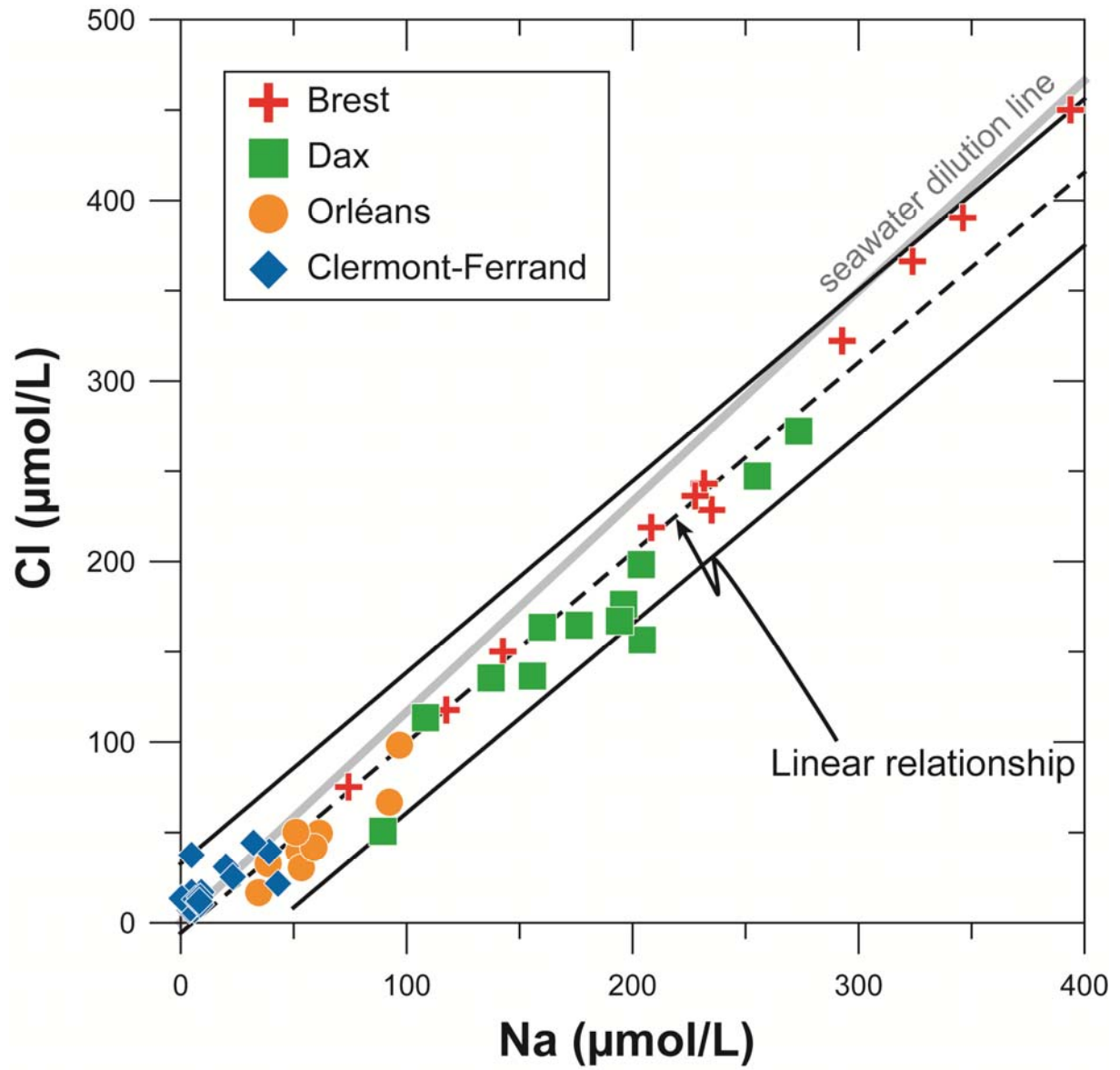
**Figure 3**



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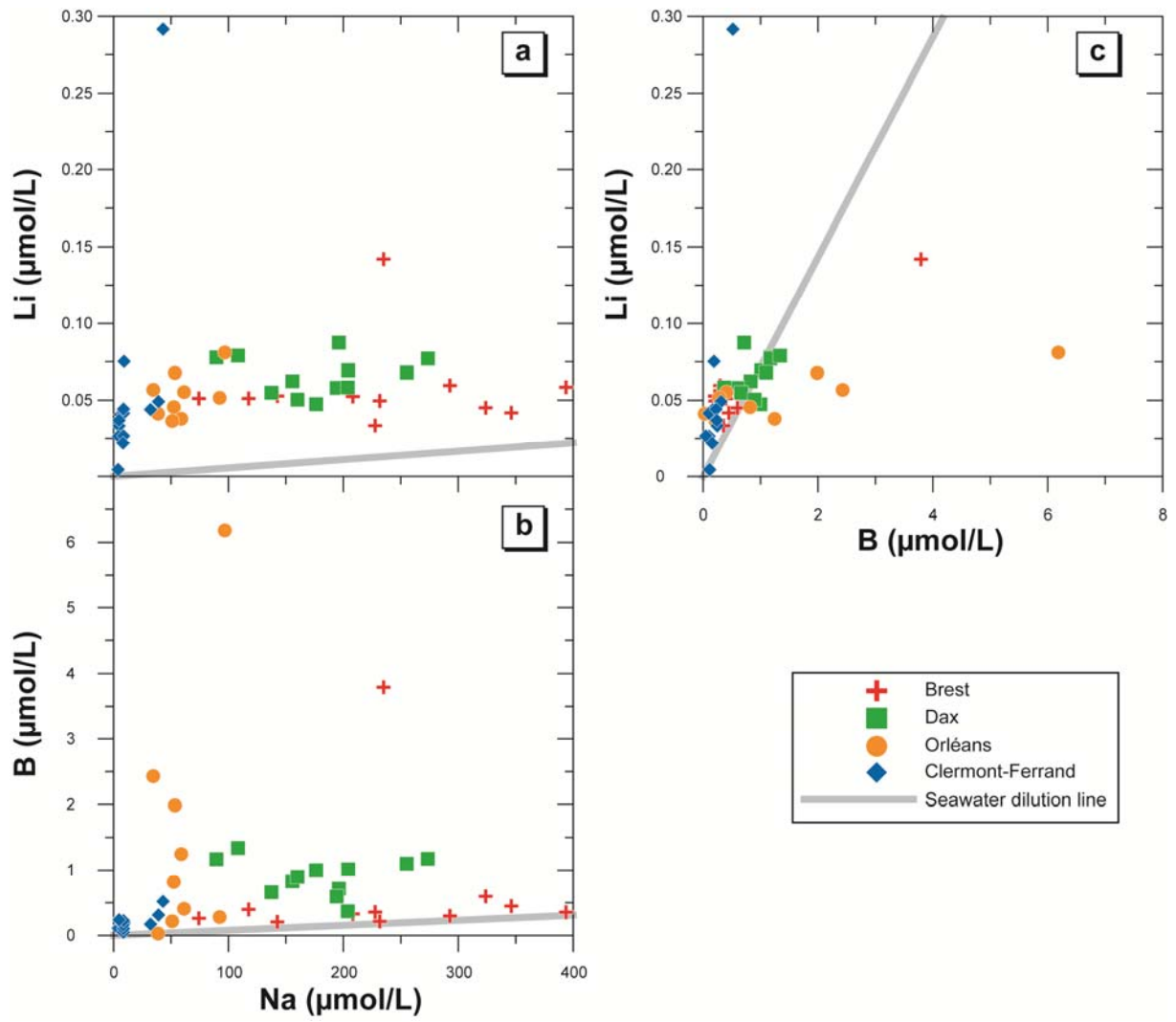
Figure 4



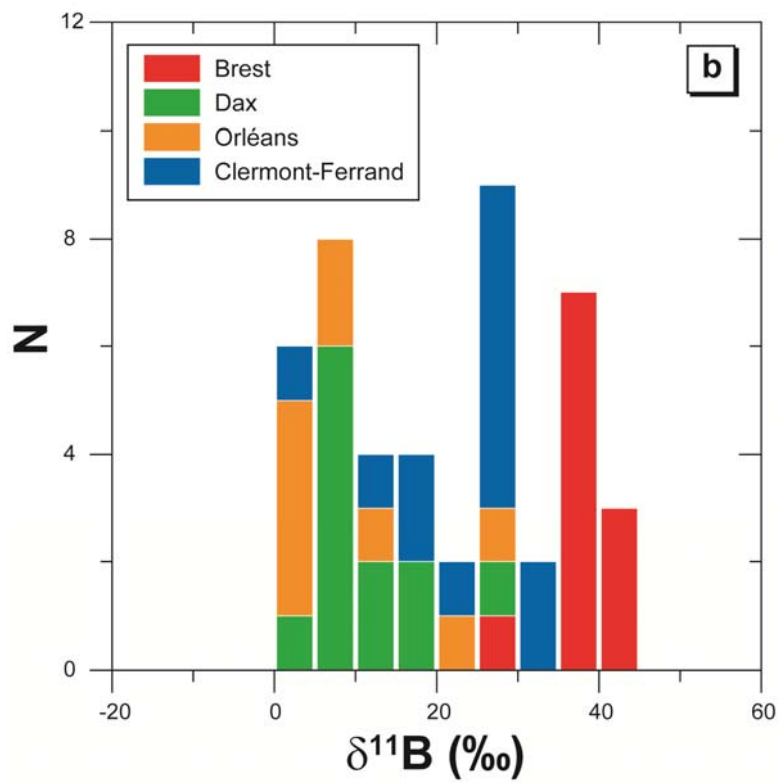
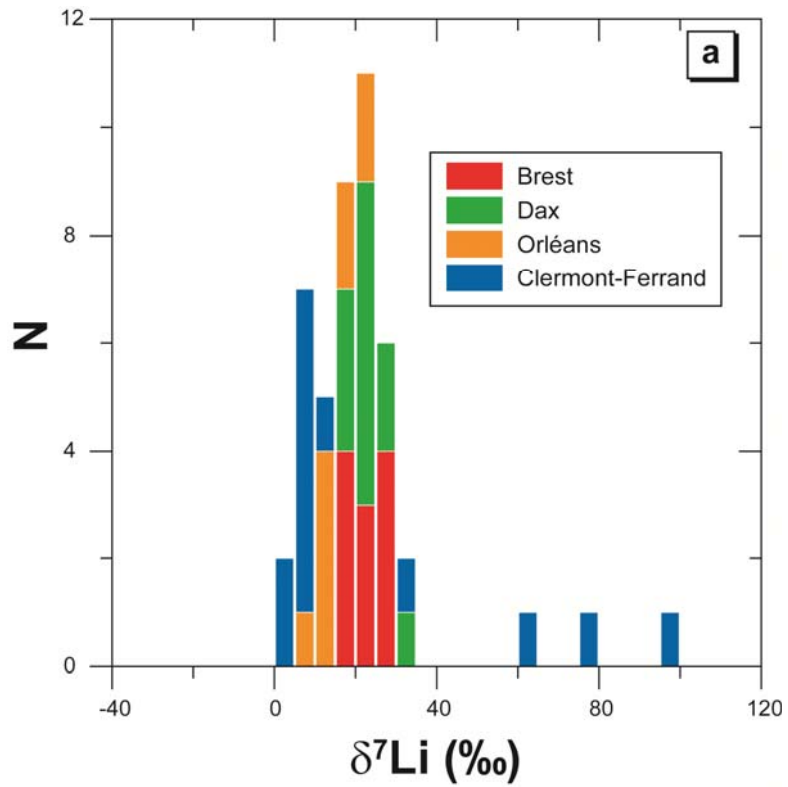
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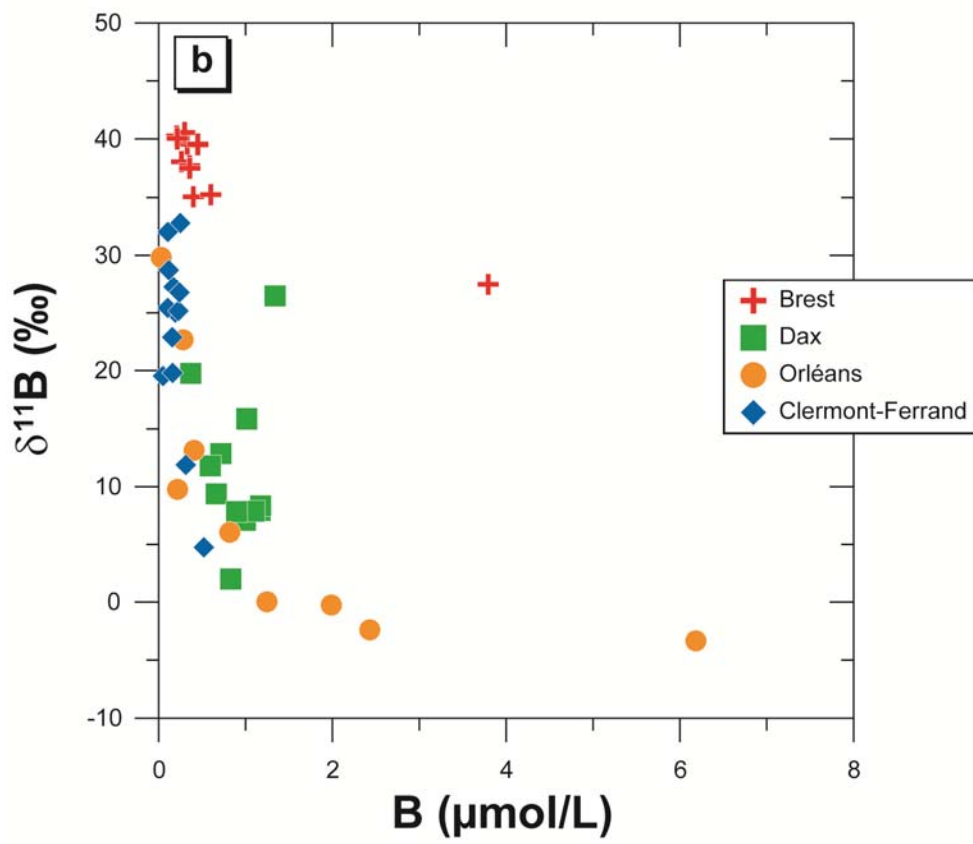
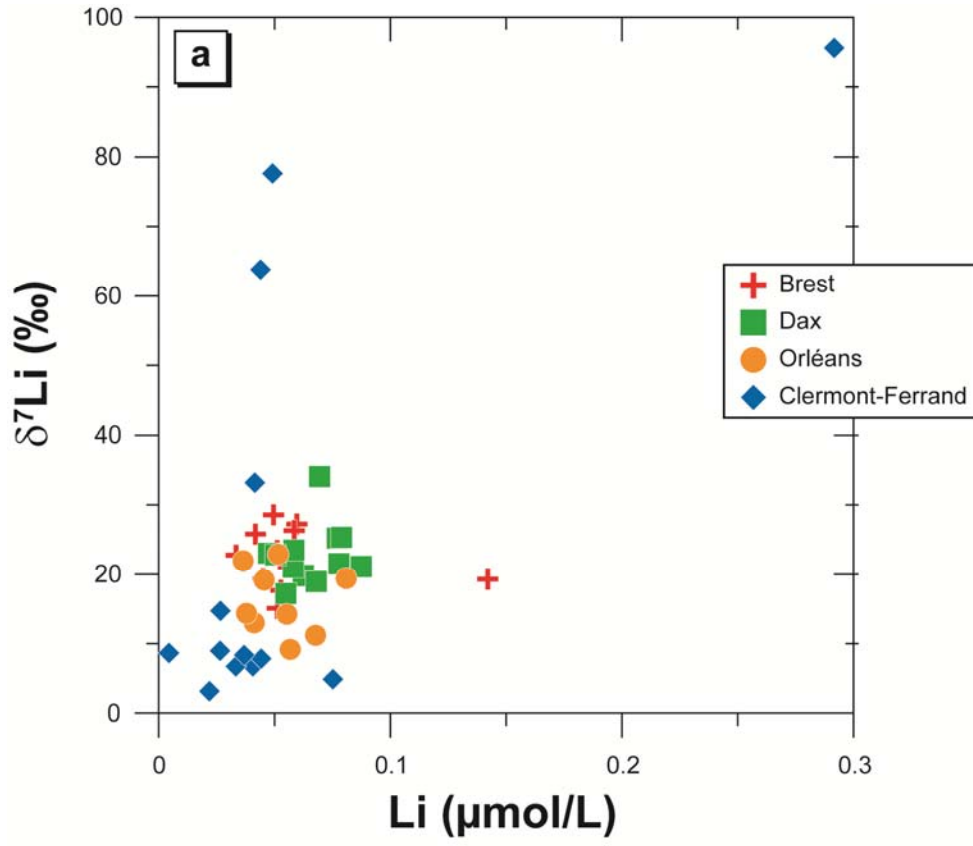
Figure 5



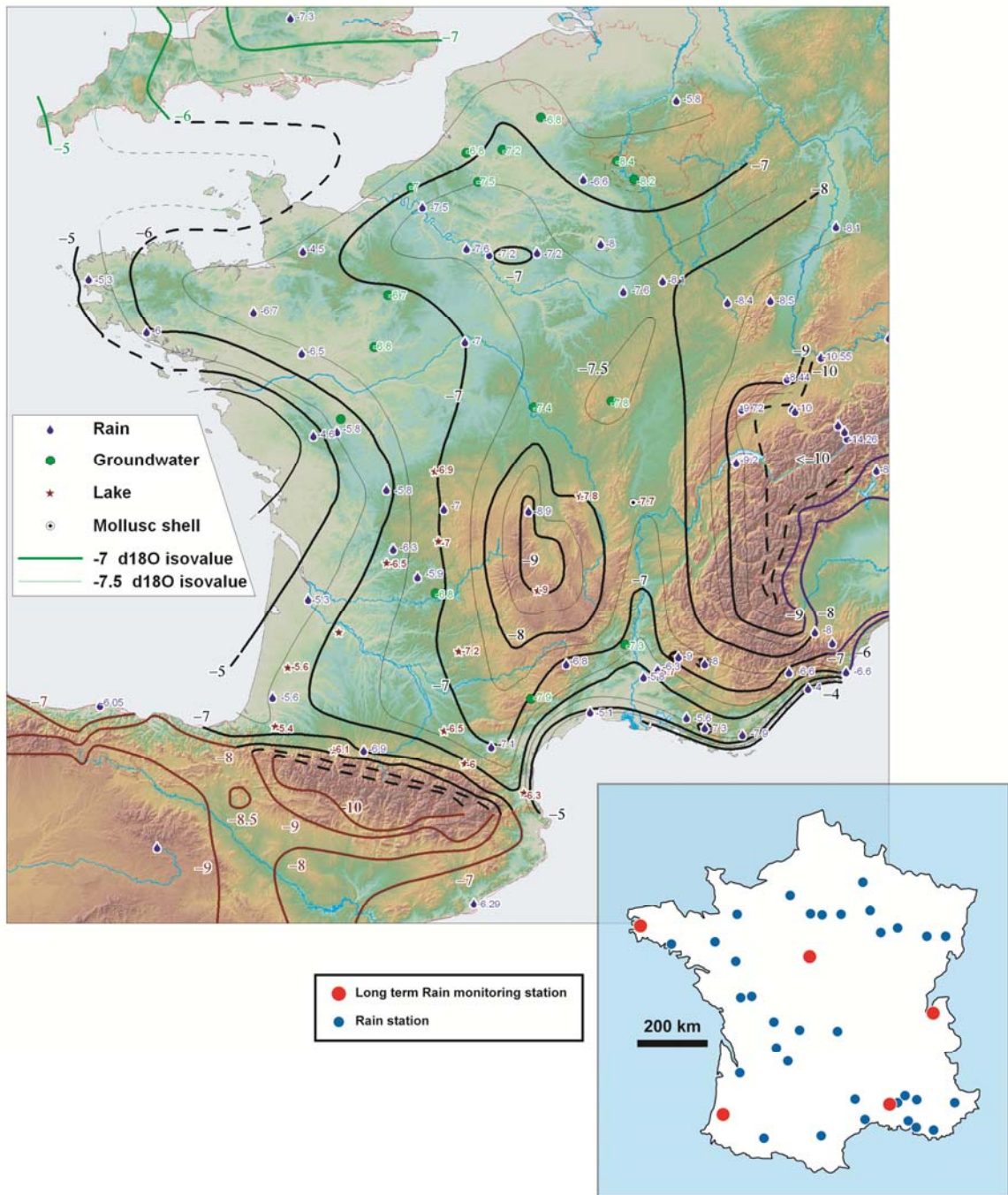
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990 **Figure 7**

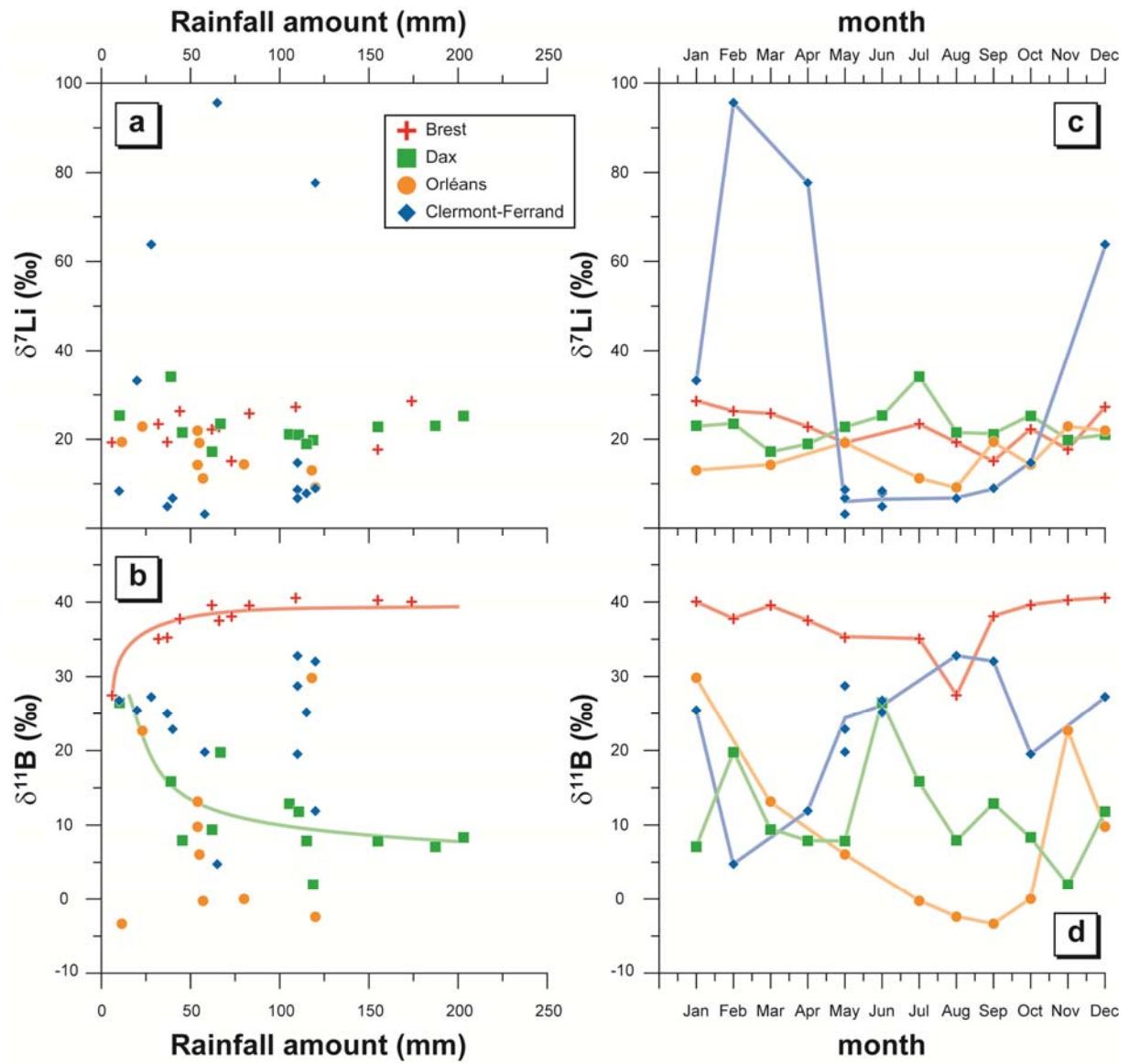


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Figure 9

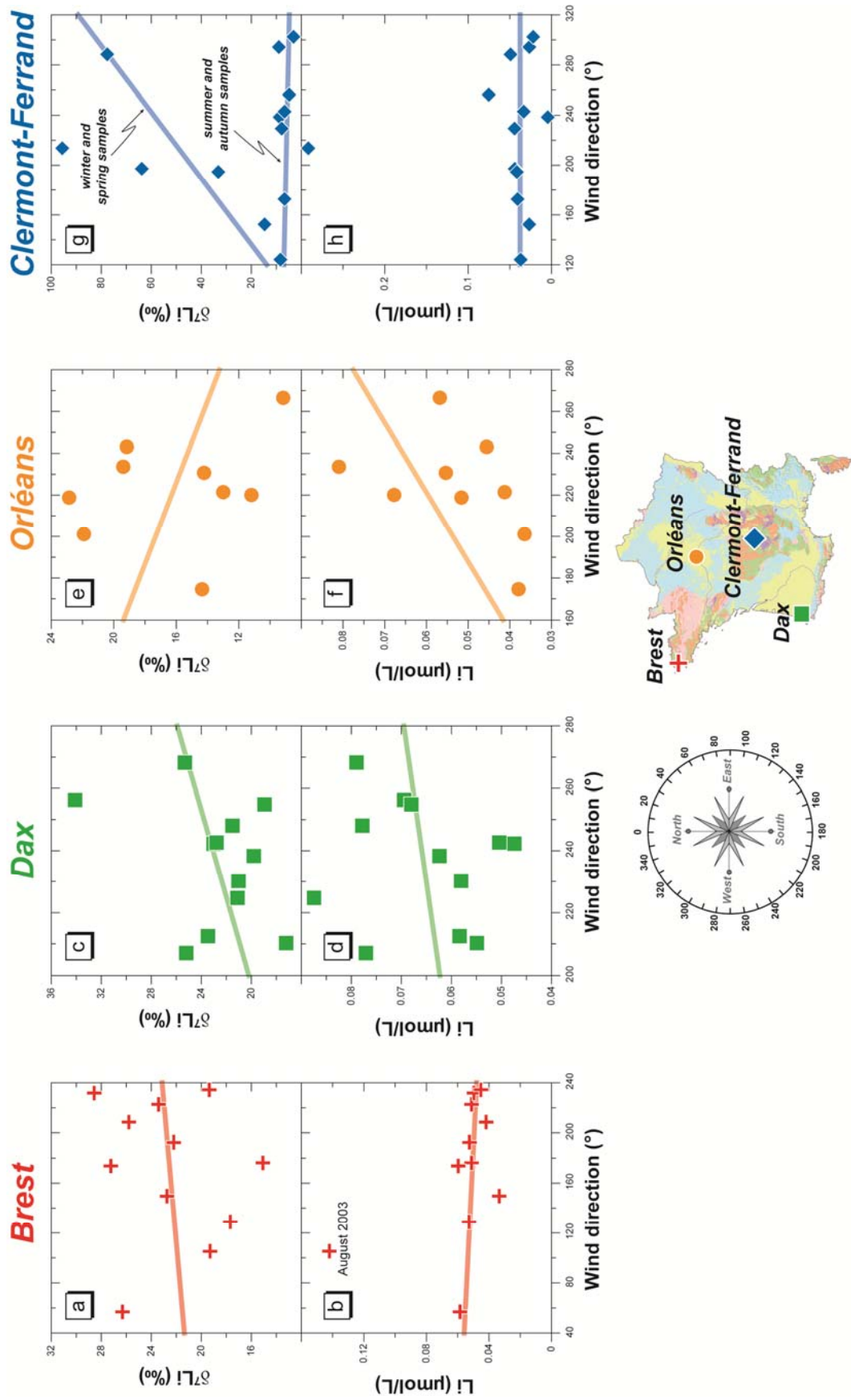


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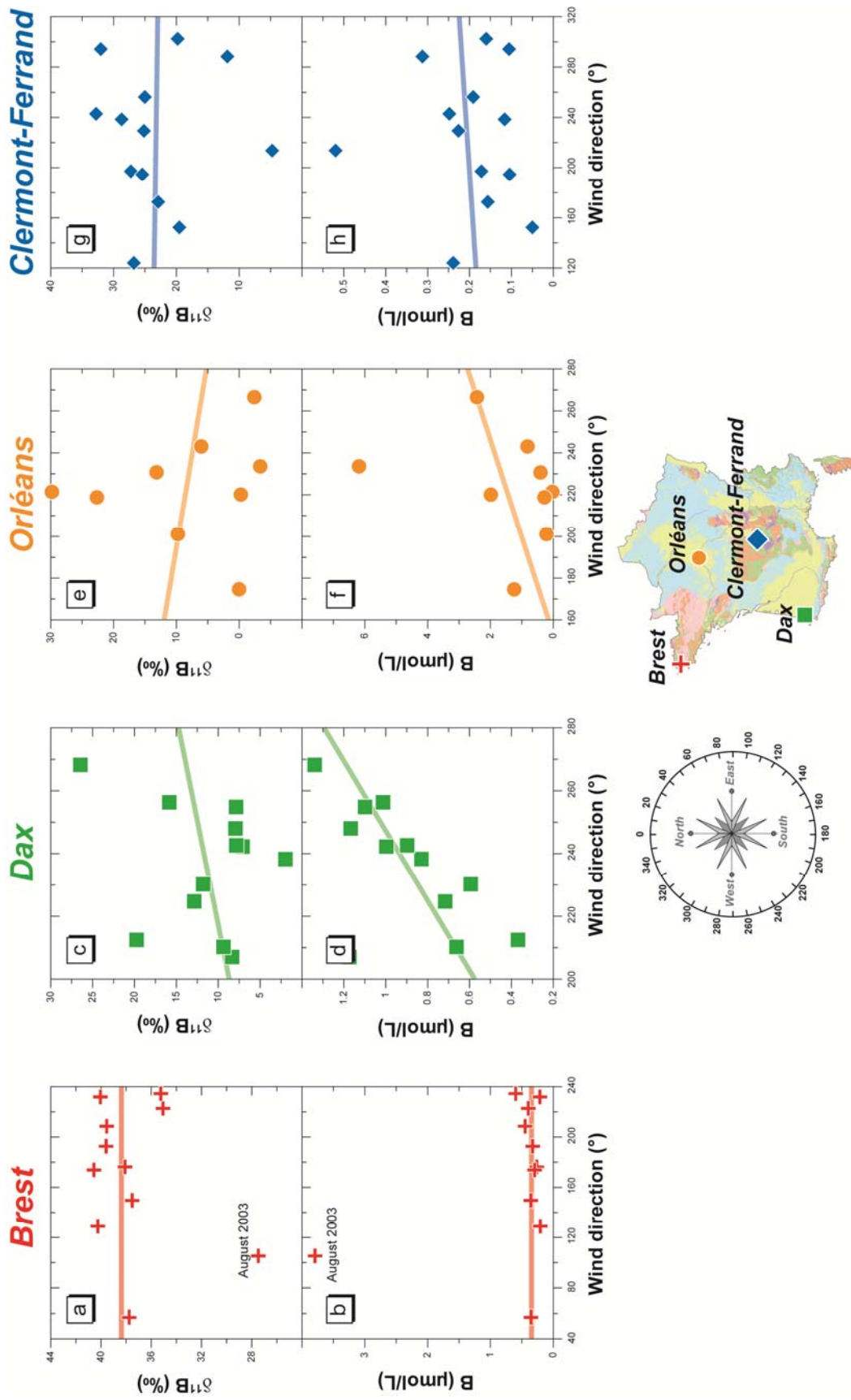
Figure 10



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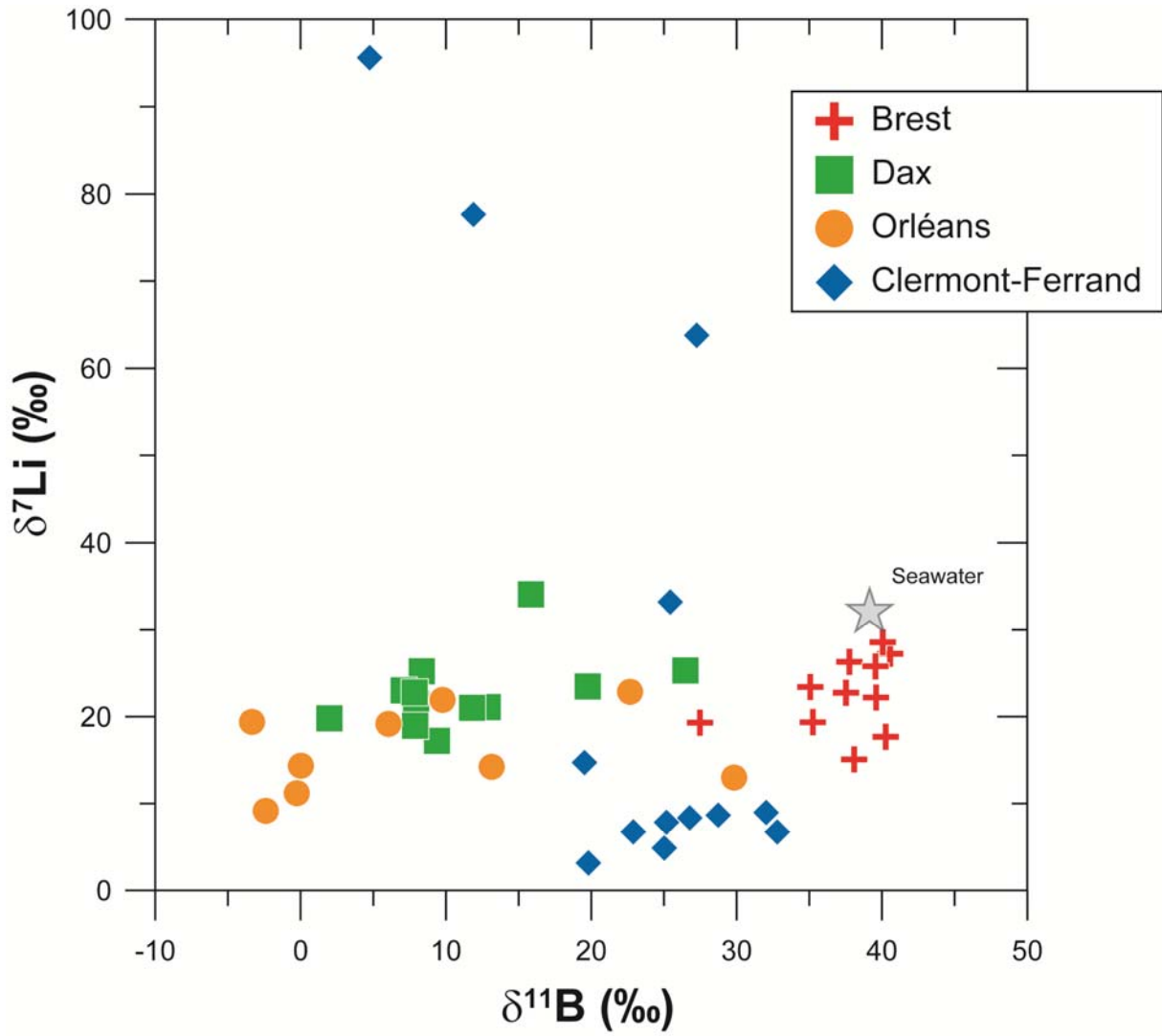
Figure 11



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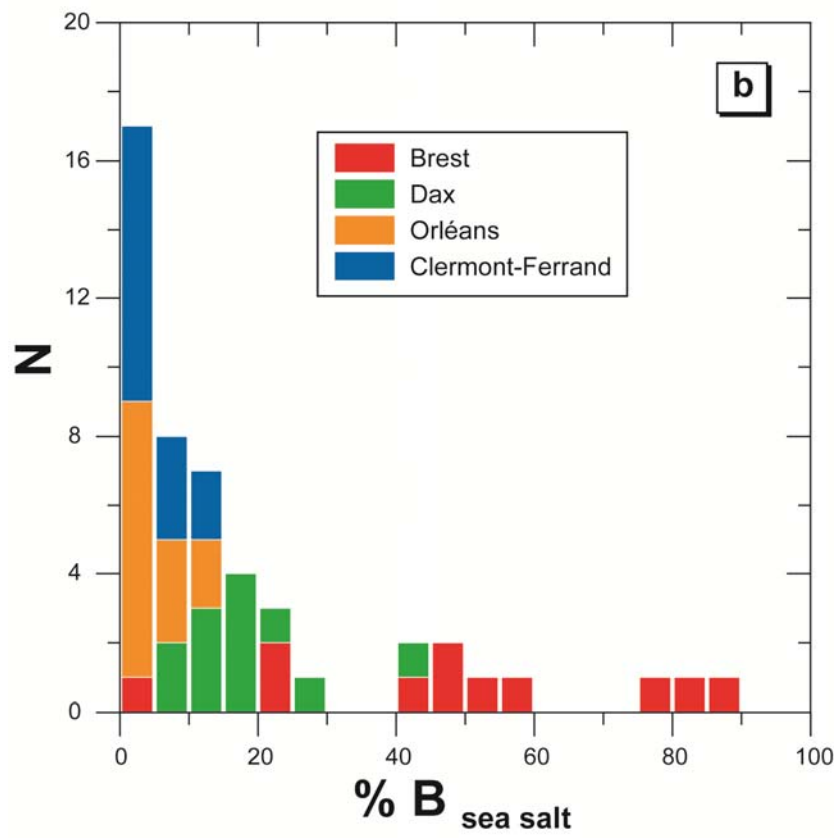
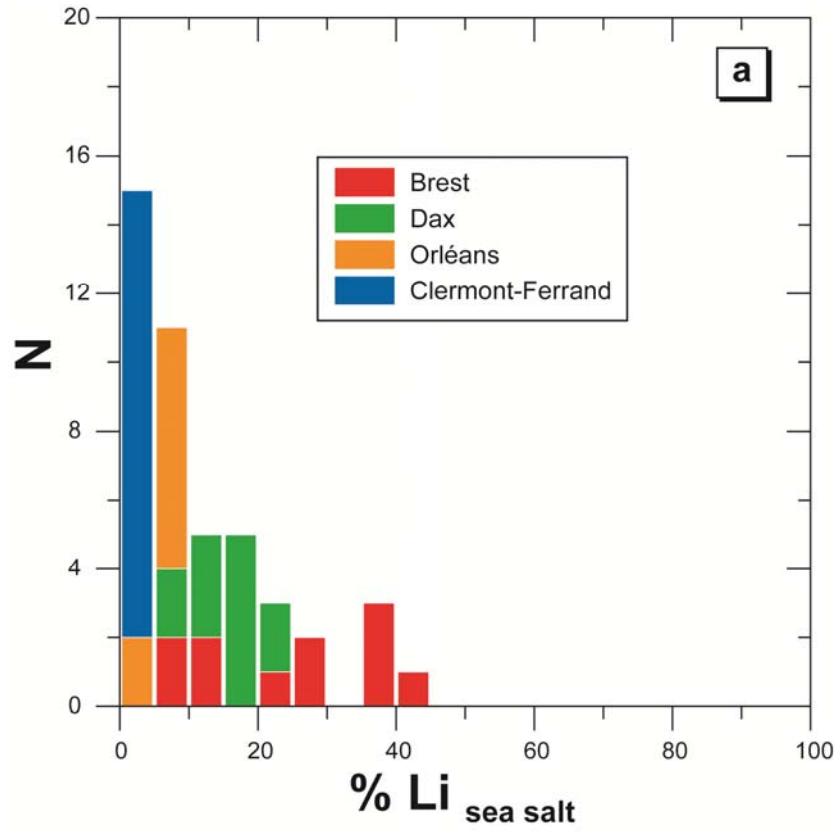
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Figure 12



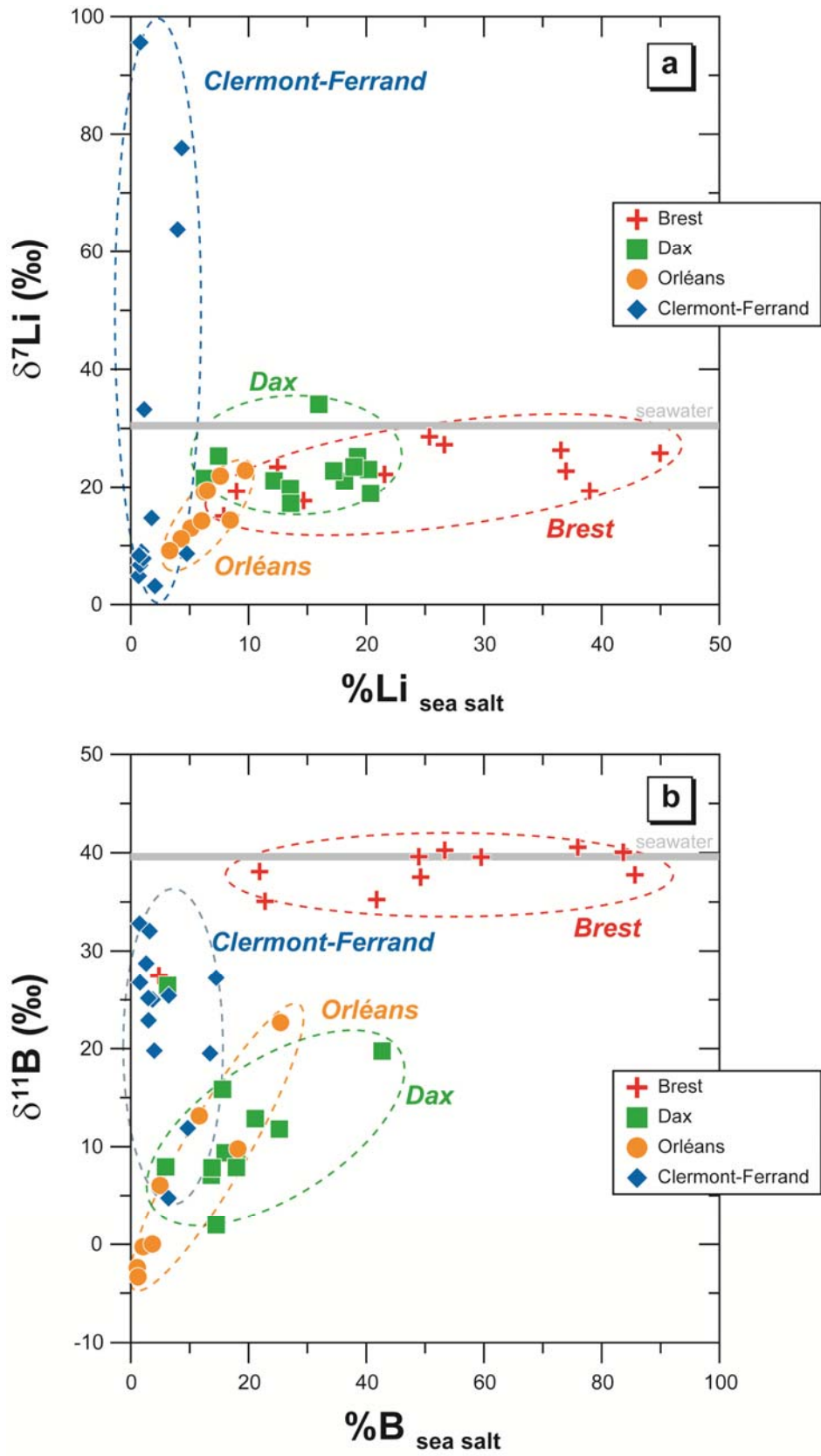
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1023 **Figure 13**



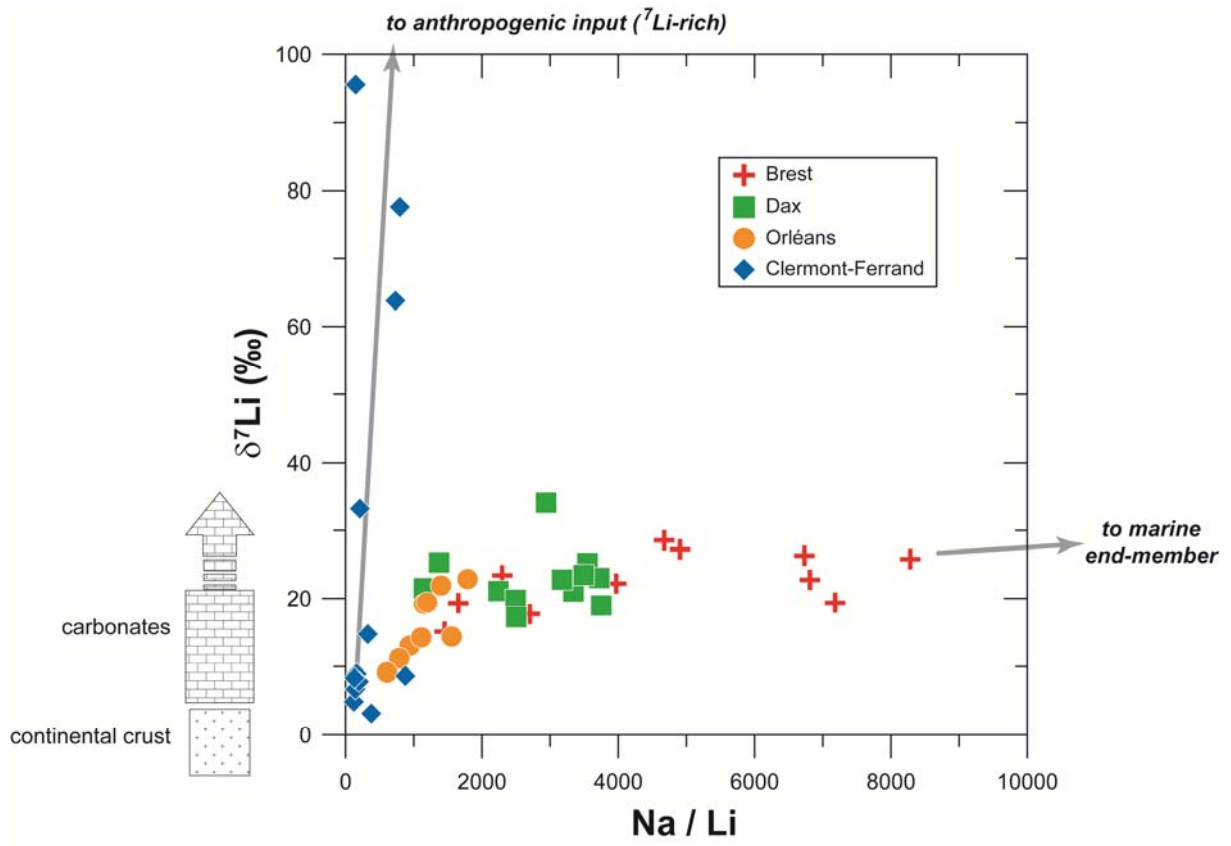
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1026 **Figure 14**  
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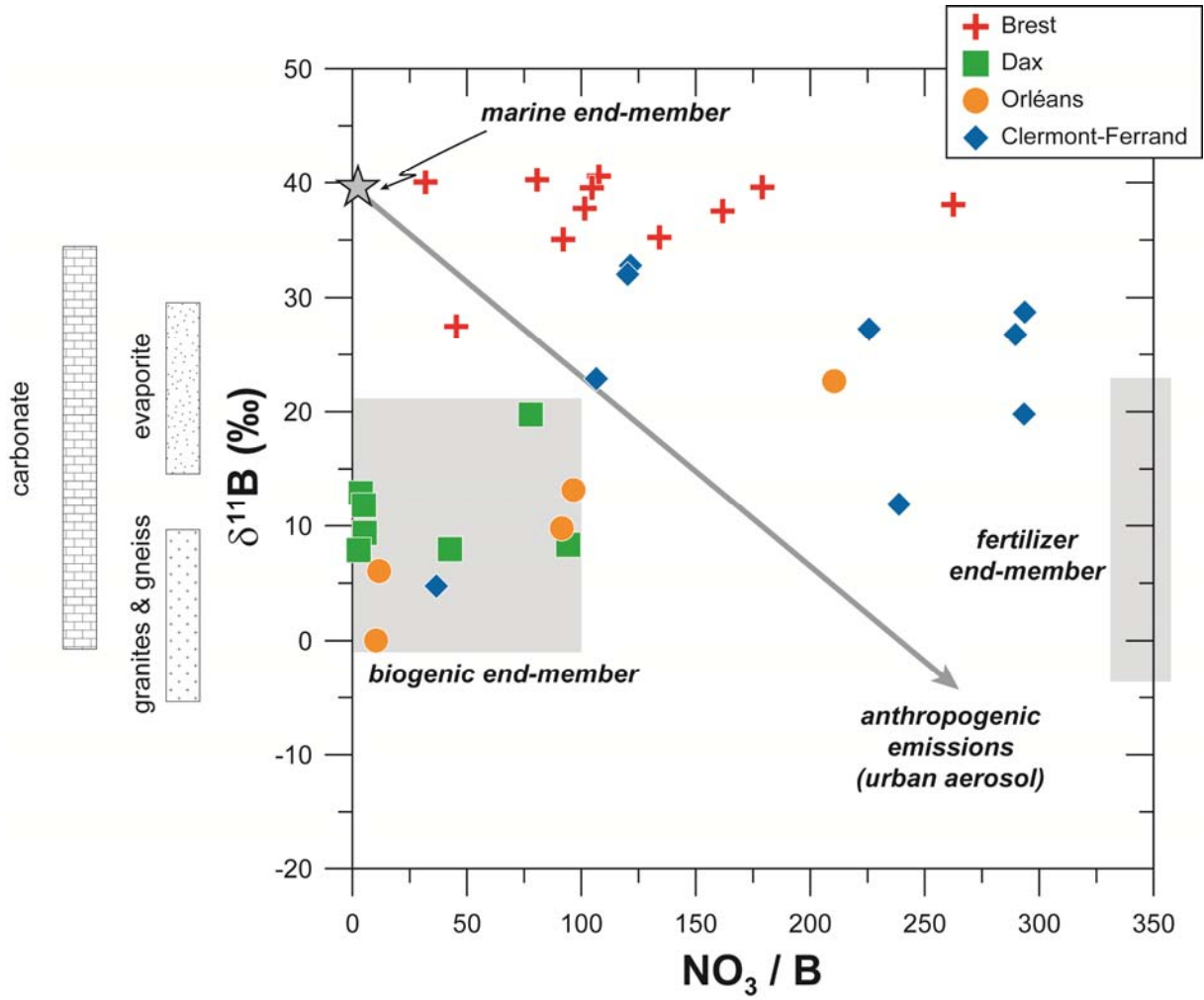
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1029 **Figure 15**  
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1039 **Figure 16**  
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