

1 **Chemical and U-Sr isotopic variations of stream and source waters at a small catchment scale**
2 **(the Strengbach case; Vosges mountains; France)**

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12

13 **Abstract**

14 This is the first comprehensive study dealing with major and trace element data as well as $^{87}\text{Sr}/^{86}\text{Sr}$
15 isotope and ($^{234}\text{U}/^{238}\text{U}$) activity ratios (AR) determined on the totality of springs and brooks of the
16 Strengbach catchment. It shows that the small and more or less monolithic catchment drains
17 different sources and streamlets with very different isotopic and geochemical signatures. Different
18 parameters control the diversity of the source characteristics. Of importance is especially the
19 **hydrothermal overprint** of the granitic bedrock, which was stronger for the granite from the northern
20 than from the southern slope; also significant are the different meteoric alteration processes of the
21 bedrock causing the formation of 0.5 to 9 meter thick saprolite and above the formation of an up to
22 1m thick soil system. These processes mainly account for springs and brooks from the northern
23 slope having higher Ca/Na, Mg/Na, Sr/Na ratios but lower $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios than those from
24 the southern slope. The chemical compositions of the source waters in the Strengbach catchment
25 are only to a small extent the result of alteration of primary bedrock minerals and rather reflect
26 dissolution/precipitation processes of secondary mineral phases like clay minerals.
27 The ($^{234}\text{U}/^{238}\text{U}$) AR, however, are decoupled from the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope system and reflect to some
28 extent the level of altitude of the source and, thus, the degree of alteration of the bedrock. The
29 sources emerging at high altitudes have circulated through already weathered materials (saprolite
30 and fractured rock depleted in ^{234}U) implying ($^{234}\text{U}/^{238}\text{U}$) AR <1, which is uncommon for surface
31 waters. Preferential flow paths along constant fractures in the bedrocks might explain the over time
32 homogeneous U AR of the different spring waters. However, the geochemical and isotopic
33 variations of stream waters at the outlet of the catchment are controlled by variable contributions of
34 different springs depending on the hydrological conditions.
35 It appears that the ($^{234}\text{U}/^{238}\text{U}$) AR is an appropriate very important tracer for studying and
36 deciphering the contribution of the different source fluxes at the catchment scale because this
37 unique geochemical parameter is different for each individual spring and at the same time remains
38 unchanged for each of the springs with changing discharge and fluctuating hydrological conditions.

39 This study further highlights the important impact of different and independent water pathways in
40 fractured granite controlling the different geochemical and isotopic signatures of the waters.

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42 Keywords: U activity ratios, Sr isotopes, spring and stream water chemistry, weathering,
43 Strengbach catchment.

44

45 **1. Introduction**

46 Large rivers carry erosion products from the different drainage areas and, therefore, are pathways of
47 continental weathering products that finally enter the oceans. Thus, they fetch the various chemical
48 and isotopical characteristics of the different drainage basins and therefore allow to elucidate
49 erosion processes, derive erosion rates and to illustrate biogeochemical cycling of elements.
50 ~~Actually~~ many of the major world rivers are well documented with major and trace element and
51 isotope data on dissolved and suspended phases, which provide the different factors controlling
52 chemical and physical denudation (Degens et al., 1991; Dupré et al., 2003; Gaillardet et al., 1999;
53 Martin and Meybeck, 1979 ; Négrel et al., 1993). At the large catchment scale, the stream waters
54 chemical composition is generally the result of mixing between phases derived from the different
55 main lithologies (e.g., Bickle et al., 2006; Blum et al., 1998; Chabaux et al., 2001; Millot et al.,
56 2003; Steinmann and Stille, 2009; Tipper et al., 2006; Zakharova et al., 2007). However, especially
57 at the small catchment scale, the impact and the role of vegetation cover and soils on the chemical
58 or isotopical evolution of erosion signals in waters have only seldom been observed and discussed
59 (Cenki-Tok et al., 2009; Cidivini et al., 2011; Lemarchand et al., 2010; Zakharova et al., 2007). In
60 addition, determination of parameters controlling the chemical composition of superficial waters is
61 important for a correct modeling of the future evolution of the ecosystems in response to external
62 natural or anthropogenic forcing such as climate evolution and atmospheric pollution (trace metal
63 depositions, acid rain etc.). Among these parameters water/rock interactions (including secondary
64 phases such as clays), hydrological processes and biological activities play an important role in



65 affecting mobilization, (re)cycling and fractionation of elements; their specific influences on
66 weathering processes at the watershed scale remains a matter of discussion (Brantley et al., 2008).
67 Because natural systems are subject to complex and multiple reactions, the combination of different
68 geochemical and isotopic tools is necessary to decipher the different natural processes. $^{87}\text{Sr}/^{86}\text{Sr}$
69 isotopic ratios and ($^{234}\text{U}/^{238}\text{U}$) AR have successfully been used in the discussion of hydrological and
70 hydrochemical processes at the catchment scale (e.g. Riotte and Chabaux, 1999; Tricca et al., 1999;
71 Aubert et al., 2002; Bagard et al., 2011; Bickle et al., 2005; Bonotto and Andrews, 2000; Chabaux
72 et al., 2011; Durand et al., 2005; Schaffhauser et al., in press). The Sr isotopic composition of e.g. a
73 source water mainly reflects its origin and, thus, is a tool to discuss water-rock interactions.
74 Alternatively, the value of the U activity ratios can reflect a strong constraint from minerals and
75 rocks involved in the water-rock interactions. Indeed, in the case that the U system has been closed
76 for approximately 1 million years, minerals and rocks are in secular equilibrium and activities of all
77 parents and daughters from ^{238}U decay chain are identical and the ($^{234}\text{U}/^{238}\text{U}$) AR is equal to 1.
78 However, this ratio can fractionate during chemical weathering when ^{234}U is more easily escaping
79 into solution by the combined effects of 1) direct recoil of ^{234}Th near grain boundaries out of
80 mineral and 2) preferential release from crystal lattices that are damaged by energetic α -decay (e.g.
81 Bourdon et al., 2009; Chabaux et al., 2003; 2008; DePaolo et al., 2006; 2012; Osmond and
82 Ivanovich, 1992 and reference therein). Therefore, natural waters (stream, spring, groundwaters,
83 seawaters) are generally in excess of ^{234}U and have a ($^{234}\text{U}/^{238}\text{U}$) AR >1 (Andrews and Kay, 1983;
84 Camacho et al., 2010; Chabaux et al., 2003, 2008; Dosseto et al., 2008, 2012; Gryzmko et al., 2007;
85 Osmond and Ivanovich, 1992; Paces et al., 2002; Pierret et al., 2012; Stromman et al., 2012; Vigier
86 et al., 2001, 2006). Consequently, ($^{234}\text{U}/^{238}\text{U}$) AR in superficial waters allow to trace river- flow
87 patterns, and hydrological mixing (e.g., Chabaux et al., 2001; Durand et al., 2005; Maher et al.,
88 2006; Osmond and 1982; Paces et al., 2002; Riotte et Chabaux, 1999).

89 In the present paper we focus on a small, more or less monolithic drainage basin, the experimental
90 Strengbach catchment (Vosges mountains, NE France). Several studies have shown that the

91 vegetation cover, the atmospheric deposition, the secondary minerals and the biological recycling
92 play an important role in controlling the geochemical signatures of soil solutions (Brioshi et al.,
93 2012; Lemarchand et al., 2010; Lemarchand et al., 2012; Prunier, 2008; Stille et al., 2006, 2009,
94 2011, 2012). However, soil solution contributions to the outlet can be variable; for instance, it
95 represents 5 to 20 % for the Ca, depending on the type of vegetation or soil (Cenki Tok et al.,
96 2009).

97 A previous U isotope study performed on waters from the Strengbach streamlet shows a decrease of
98 the ($^{234}\text{U}/^{238}\text{U}$) AR from 1.02 to 0.96 when the discharge of the stream increases (Riotte and
99 Chabaux, 1999). Such an isotopic evolution has been interpreted as mixing between a water body
100 enriched in ^{234}U which weathered the granitic bed rock at secular equilibrium, and waters with a
101 ($^{234}\text{U}/^{238}\text{U}$) AR below unity representing a mobilization of U from material that has already been
102 weathered. Similarly, the streamlets $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios collected during low flow periods have
103 less radiogenic Sr isotope ratios than during high water flow periods (Aubert et al., 2002). These
104 variations have been explained by important contributions of waters from the deep soil profile
105 during the recession stage but also by the relative importance of waters coming from distinct
106 distributive areas such as the opposite slopes or the saturated area of the catchment.

107 In order to define more precisely temporal and spatial variations of the hydrochemistry of the
108 streamlet and the different springs and to evaluate the major and trace element sources and the
109 processes controlling this element supply to the freshwaters, additional ($^{234}\text{U}/^{238}\text{U}$) AR, $^{87}\text{Sr}/^{86}\text{Sr}$
110 isotopic ratios and major and trace element concentrations were analyzed in the different source
111 waters collected during two different hydrological seasons (2004-2006) and compared to those of
112 the streamlet waters.

113

114 **2. Site description**

115 The Strengbach catchment is a small granitic watershed (80ha,) where meteorological, hydrological
116 and geochemical data are recorded since 1986 (Observatoire Hydro-Géochimique de



117 l'Environnement; OHGE ; <http://ohge.u-strasbg.fr>). The first studies were performed in order to
118 understand the impact of acid rain on the forested ecosystem (Dambrine et al. 1991, 1992; Probst et
119 al. 1990, 1992a, b;). The catchment is situated in the Vosges Mountains (NE France) at altitudes
120 between 880 and 1150 m (amsl) and has strongly inclined slopes (mean 15°; Fig. 1).

121 The climate is temperate oceanic mountainous (mean annual temperature of 6°C; mean monthly
122 temperature range from -2 to 14°C) with an average rainfall of 1400 mm/yr (ranging between 890
123 and 1630 mm/yr over the period 1986-2006) and with snowfall during 2-4 month/yr (Probst and
124 Viville, 1997; Viville et al., 2012; OHGE Data). The mean annual runoff for the same period is of
125 853 mm (26.9 Ls⁻¹km⁻²) and ranges from 525 to 1147 mm over 1986-2006 (Ladouche et al., 2001;
126 Probst and Vivile, 1997; OHGE data). The evapotranspiration (ETP) has been evaluated to be about
127 40% on the site (Aubert, 2001; Probst et al., 1992).

128 The bedrock is mainly composed of a Hercynian base-poor granite (332±2 Ma) (Boutin et al.,
129 1995), with low Ca and Mg contents (less than 1% for both); it suffered different degrees of
130 hydrothermal alteration some 180 Ma ago (Fichter et al., 1998). In addition to the granite, which is
131 strongly hydrothermally altered on the northern slope and comparatively weakly altered on the
132 southern slope, small microgranite and gneiss bodies outcrop at the southern and northern slopes
133 (Fig.1) (El Gh'mari, 1995; Fichter et al. 1998). The gneiss is enriched in Mg mainly because of the

134 presence of biotite and chlorite (El Gh'mari, 1995; Fichter, 1997). Hydrothermal processes caused
135 the alteration and transformation of albite, K-feldspar and muscovite into fine-grained illite and
136 quartz; biotite and albite disappeared to a large extent. The strongly altered granite (on the northern
137 slope) is characterized by larger amounts of quartz, clays and Fe-oxides, small amounts of apatite
138 (<1%), and by higher Mg but lower Ca, K and Na contents than the less altered granite at the
139 southern slope (El Gh'mari, 1995; Fichter et al., 1998). The soils are brown acidic to ochreous
140 brown podzolic and are generally about 1 meter thick. They are very coarse grained, sandy and rich
141 in gravel (Fichter et al., 1998). The brown acidic soils are mainly located on the northern slope and
142 are characterized by higher clay contents, lower K-feldspar, lower albite, higher cation exchange



143 capacity (CEC), lower pH and lower organic matter content than the ochreous brown podzolic soils,
144 which are mainly located on the southern slope (Fichter 1997; Fichter et al., 1998). A sandy
145 saprolite separates soil and granite. Its thickness varies between 1 and 9 meters; on the southern
146 slope it is generally thicker (El Gh'Mari, 1995) with the most important thickness in the depression
147 zone near the four springs CS1 to CS4. The forest covers 90% of the area and corresponds to about
148 80% spruce (mainly *Piceas Abies L.*) and 20% beech (*Fagus Sylvatica*). The catchment contains 10
149 different springs feeding the Strengbach streamlet (Fig.1).

150 The catchment is situated in a remote area lacking direct industrial activities. Nevertheless,
151 atmospheric pollution occurs in many forms (acidic deposition, O₃ pollution or as atmospheric dust
152 deposition). The forestry has increased the proportion of spruce with especially dense spruce plots
153 planted between 1890 and 1960. The site is well equipped for sampling of atmospheric depositions
154 and spring and stream waters at the whole catchment scale.

155 For this study, the stream and the different springs of the catchment were collected at various
156 hydrological periods with high and low water levels during a two years period (2004-2005) in order
157 to obtain a precise chemical and isotopic signature of the different sources in this hydrological
158 system (Fig. 1). Four springs were collected at the southern slope (CS₁, CS₂, CS₃ and CS₄). CS₁ and
159 CS₃ are the deepest (up to 4 meters depth) whereas CS₂ and CS₄ are both superficial springs. The
160 springs SG, ARG, RH, BH, CS₃ and CS₄ are located on the northern slope and the springs CS₁, CS₂,
161 SH and RUZS emerge at the southern slope. The spring RUZS is situated in the humid zone at the
162 bottom of the catchment near the outlet (saturated area, Fig.1) and covered by dense grass
163 vegetation. In addition rain (bulk precipitation) and throughfalls were collected using rain collectors
164 and gutters, respectively.

165

166 **3. Analytical procedures**

167 The different spring waters were collected every 6 weeks during 2 years unless the springs were dry
168 or under snow. The waters were collected in clean polyethylene (HDPE) bottles (250 ml for major

169 element analysis and 1 liter for isotope and trace element analysis) and filtered the same day
170 through a 0.45 μm pore diameter membrane (Millipore ester cellulose, 142 mm diameter). Before,
171 the HDPE bottles were washed with HCl 10% (24h contact) and then rinsed with MilliQ deionised
172 water. The filtrated waters for trace element and U-Sr isotopic composition determinations were
173 acidified with 250 μl of ultrapure HNO_3 13M and then stored in a cold room at 5°C.

174 The pH were measured just after filtration using a pHM210 MeterLab (Radiometer analytical) with
175 an Mettler HA405-DXKS8 electrode and calibrated with standard buffer solutions (pH 4.00 and
176 7.00 at 25°C). The precision of the pH measurement was ± 0.02 units. The electrical conductivity
177 and the alkalinity were determined respectively using a CDM210 MeterLab (radiometer analytical)
178 with an CDC 745-9 electrode (precision 0.1 $\mu\text{S}/\text{cm}$) and with 716DMS Titrino (Metrohm ; precision
179 of 0.01 meq/l – Acid/base titration, Gran method).

180 The major element contents were determined by Ionic chromatography, atomic absorption,
181 colorimetry and ICP-AES and the trace element concentrations were determined by ICP-MS
182 (Pierret et al., 2010, Chabaux et al., 2011). The analytical uncertainty of the determinations of the
183 major cations and anions in solution (by atomic absorption and ionic chromatography Dionex, 4000
184 I) is $\pm 2\%$. The uncertainty on the major element concentrations such as Fe, Al, Mn and Si (by ICP-
185 EAS, Jobin Yvon 124, at a precision of $\pm 2\%$) is 5%, and that of the trace element concentrations
186 (by ICP-MS, VG Plasma Quad; Thermo Electron) is $\pm 5\%$. The dissolved organic carbon (DOC)
187 was determined using an organic carbon analyser (Shimadzu TOC-5000A) with an uncertainty of 5
188 to 10 %. The accuracy of the analysis was assessed by regular analysis of the SLRS-4 riverine
189 standards.

190 The Sr isotopic ratios were determined by thermo-ionisation mass spectrometry on a multi-collector
191 VG-Sector mass spectrometer. Sr was extracted by standard procedures (Steinmann et Stille, 1997;
192 Lhad Geagea et al., 2008; Clauer et al., 2009; Pierret et al., 2010). The routinely measured NBS 987
193 standard yield an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71026 ± 0.00002 (2s) for 10 determinations during the
194 course of this study. The U isotope ratios were analysed on a TRITON Thermofinnigan mass



195 spectrometer after separation and purification of U by anionic exchange chromatography (resin
196 AG1X8, 200-400 mesh) following the classical technique used in the lab (e.g. Chabaux et al., 1997;
197 Pelt et al., 2008, Pierret et al., 2012). During this study (2006-2008) the reproducibility of the U
198 isotopic analyses was tested with the HU1 standard which yield an average value of 0.999 ± 0.004
199 (2σ) (n=27). The analytical error for the ($^{234}\text{U}/^{238}\text{U}$) activity ratio is $\pm 0.5\%$ (2σ).

200

201 **4. Results**

202 Previous studies performed on the Strengbach watershed mainly focused on the geochemical and
203 isotopic variations of dissolved loads of the stream waters collected at its outlet. The new results
204 (Tables 1 and 2) yield a first complete dataset of the spatial variability of major and trace element
205 concentrations as well as Sr and U isotope ratios of the spring and streamlet waters emerging on the
206 Strengbach watershed. The data also allow us to present the geochemical variability of the source as
207 well as stream waters at the outlet of the watershed over the period 2004-2006, that is to say during
208 two hydrologic cycles.

209

210 **4.1. The major and trace element data**

211 Among the spring and stream waters the pH, alkalinity, DOC, TDSw (total dissolved solids, table
212 1), TDS-Ca (total dissolved solids-cation; table 1) and conductivity are highly variable and range
213 respectively from 5 to 6.85, from 0 to 0.16 meq/L, from 0.42 to 11.6 ppm, from 10.3 to 26.8 mg/L,
214 from 3.87 to 9.05 mg/L, and from 13.2 to 60.3 $\mu\text{S}/\text{cm}$ (Table 1). The pH is well correlated with
215 alkalinity and TDS-Ca, Ca/Na and relatively well with Mg/Na (Fig. 2). The range of variations of
216 the major element concentrations at the watershed scale can be important but clearly depends on the
217 chemical elements and the physico-chemical parameters. For the cation concentrations the variation
218 at the watershed scale reaches about one order of magnitude for Mg, but only 20 to 30% for Na
219 concentrations. At the watershed scale, the most discriminating cation is Mg. SH and CS₁ sources
220 are marked by weakest Mg (and Ca) and the SG source by highest concentrations (Table 1). In



221 addition, as illustrated by Ca/Na, Mg/Na, K/Na, Sr/Na and H_4SiO_4/Ca concentration ratios, the
222 different springs are not only marked by different mean major element concentrations (2004-2006
223 period) but also by different elemental ratios (Fig.3).

224 The data points of the different sources define linear trends with slopes different from each other
225 (Fig.3). The variation of the Ca/Na and Mg/Na ratios are much larger at the watershed scale than at
226 the scale of a single spring. On the basis of the above data a clear distinction is possible between the
227 spring waters from the northern slope (SG, RH, ARG, CS₃, CS₄ and BH) and those from the
228 southern slope (CS₁, CS₂, SH and RUZS), the former being characterized by higher pH, alkalinity,
229 conductivity TDSw and Ca/Na, K/Na and Mg/Na ratios than the latter (Fig.2; Fig. 3). In addition to
230 the spatial variations, the chemical signatures of waters also show temporal variations. These are
231 strongest for the most DOC enriched sources (RUZS, SH) and for the stream at the outlet (RS).

232 The Fe, U and DOC concentrations vary strongly in the different spring waters (Fig.4). For some
233 springs with high DOC concentrations (SH, BH, RUZS), U concentrations are correlated with
234 dissolved organic carbon and Fe concentrations, whereas for the others (CS1, CS2, CS3, CS4, RH,
235 ARG) no clear correlation are recognizable. Nevertheless, the later are characterized by large
236 variations of U and Fe concentrations despite their low DOC contents (Fig.4).

237

238 4.2. Sr and U isotope data

239 The $^{87}Sr/^{86}Sr$ isotopic composition values of the different spring waters are highly variable and
240 range between 0.72206 (RH) and 0.72801 (SH) with an average Sr isotopic composition for the
241 stream at the outlet of 0.72573 (Fig.5, Table 1). The data show a clear relationship between the Sr
242 isotopic signature and the geographical location in the watershed; the springs from the northern
243 slope are characterized by lower $^{87}Sr/^{86}Sr$ ratios and higher Sr concentration (Fig 5).

244 As shown in Fig.6, the variation range of ($^{234}U/^{238}U$) AR in the source waters is much larger than
245 that of the streamlets waters at the outlet. The U AR range from 1.112 (BH) to 0.819 (CS3); the
246 average ($^{234}U/^{238}U$) AR for the stream at the outlet is 1.104. Among the 9 springs analyzed, 8 of



247 them have unusual low ($^{234}\text{U}/^{238}\text{U}$) AR <1. In addition, and to the best of our knowledge, these
248 values are the lowest ever published before for superficial waters. Indeed, the U AR measured in
249 world surface rivers or groundwaters have generally ($^{234}\text{U}/^{238}\text{U}$) >1 (see introduction and citations
250 therein).

251 In contrast to Sr isotopic compositions (Fig. 7) or chemical concentrations (Fig. 3) ($^{234}\text{U}/^{238}\text{U}$) AR
252 of a single source do not significantly vary over the period 2004-2006 (Fig 7). Finally, $^{87}\text{Sr}/^{86}\text{Sr}$ and
253 $^{234}\text{U}/^{238}\text{U}$ AR of the source waters are not correlated with each other and in contrast to the Sr
254 isotopic compositions or chemical concentrations (Fig 6) there is no clear distinction between the U
255 AR of the springs from the southern and northern slope. In the Strengbach watershed there is a clear
256 increase of the U activity ratio of the source waters when the altitude of the spring decreases in the
257 watershed, as also observed in another small granitic watershed in the Vosges Mountain, the
258 Ringelbach watershed (Schaffhauser et al., submitted). But at the difference of the Ringelbach
259 catchment, where the U activity ratios in the spring waters are above 1, in the Strengbach catchment
260 the U activity ratios of spring waters are ≤ 1 for all sources but one (i.e., BH).

261

262 **5. Discussion**

263

264 **5.1 Geochemical and Sr isotopic characteristics of the spring waters:**

265 As shown in the result section, the chemical characteristics of the sources are marked by an
266 important spatial variation with in particular a clear distinction between the springs from the
267 northern and the southern slope (Fig.3). It appears that the Ca/Na, Mg/Na, K/Na and Sr/Na
268 concentration ratios are neither rainwater nor throughfall controlled. Indeed rainwater and
269 throughfall show rather large variations of their Ca/Na, Mg/Na, K/Na or Sr/Na ratios (throughfall:
270 Ca/Na: 0.9-2.1; Mg/Na: 0.3-0.6; K/Na: 0.6-0.9; Sr/Na: 0.02-0.07) and do not plot at one of the
271 extremities of the correlations. Mass balance calculations show that the atmospheric input
272 (including rain and throughfalls) corresponds to various proportion of the exportation flux at the

273 watershed scale, depending on type of element, as for example 2%, 8% or 19 % for Si, U or Sr
274 respectively (Table 3).


275 Similarly, the observation of a clear increase of the Sr isotope ratios with increasing discharge
276 towards values different from those of rainwater and/or throughfall Sr isotopic composition values
277 ($^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.71110, 0.71327 and 0.71293 for rain, throughfall under spruces and throughfall
278 under beeches respectively) implies that rainwater or throughfall cannot be a significant source of
279 cation fluxes in the spring waters (Fig. 7a,c; Fig. 13).


280 Therefore, chemical differences among the sources of the Strengbach watershed have to be
281 interpreted in terms of variations in the nature or in the intensity of water-rock interactions
282 occurring from one source to another or in the intensity of the interactions between different water
283 reservoirs. This interpretation is entirely consistent with the correlations observed for the spring
284 waters at the scale of the watershed between the alkalinity, TDSw and their pH, since consumption
285 of H^+ during silicate weathering increases pH and alkalinity. Thus, from these data it appears, that
286 the spring waters from the northern slope with higher total dissolved solid contents, higher
287 alkalinity and pH values (SG, CS4, CS3, RH with BH having the highest values) are more involved
288 in weathering reactions, or are subject to more intense weathering processes than spring waters
289 from the southern slope (especially SH, RUZS and CS1).

290 The variation in the nature and/or intensity of the weathering fluxes carried by the different springs
291 can be linked to specific lithological and mineralogical differences existing for the two hillsides of
292 the Strengbach catchment. This is particularly obvious for the SG spring, which emerges near the
293 top of the catchment, just under the banded gneiss, whereas the other sources emerge within the
294 granitic environment (Fig. 1). In comparison with the granite, the gneiss has 4 to 5 times higher Mg
295 concentrations due to important occurrences of biotite and chlorite (El Gh'mari, 1995). The Mg/Na
296 and Mg/Ca elemental ratios are about 30 respectively 6 for the gneiss and range from 0.1 to 0.2
297 respectively 0.5 to 1 for the granite (El Gh'Mari, 1995; Fichter, 1997) (Table 1). Mg is also more
298 concentrated in the gneiss-derived soils (0.60 to 0.81 wt.%), than in other soil profiles of the

299 catchment (0.11 to 0.41 wt.%) (El Gh'Mari, 1995; Lefèvre, 1988). Similarly, the Ca/Na ratios of the
300 gneiss (4.8) and the corresponding soils (0.3 to 4.6) are higher than those of the granite (0.19 to
301 0.25) or of the corresponding soils (0.06 to 0.4) (El Gh'Mari, 1995; Fichter, 1997) (Table 1). All
302 these lithological and pedological characteristics ~~easily~~ explain why the SG spring waters are more
303 concentrated in Mg and have higher Mg/Ca, Mg/Na and Ca/Na ratios than the other springs (Fig. 3).
304 The variation of the chemical data of the other spring waters emerging within the granitic
305 environment might result from the specific characteristics of the two hillsides, which show different
306 types and thicknesses of soils and saprolite and different degrees of hydrothermal alteration of the
307 granitic bedrock (Lefèvre, 1988; Fichter, 1997, El Gh'Mari, 1998; see also geological setting).
308 Indeed, the study of 13 weathering profiles from the whole Strengbach catchment point to important
309 variations of the mineralogical composition of soils and bedrocks at the catchment scale (El
310 Gh'Mari, 1995; Fichter, 1997; Aubert, 2001; Stille et al, 2009; Prunier 2008). The soils from the
311 northern slope are brown acidic and overlay a 0.5 to 4 m thick saprolite. At the southern slope,
312 however, an ochreous podzolic soil type overlays a much thicker 4 to 9m deep saprolite (El
313 Gh'mari, 1995; Fichter et al., 1998). The bedrock from the northern slope was subjected to stronger
314 hydrothermal alteration, which caused disappearance of albite and biotite, diminution of K-feldspar
315 but an increase of quartz, clays and white mica contents and the occurrence of hematite (Bonneau,
316 1994; Fichter, 1997; El Gh'Mari, 1995). The hydrothermally strongly altered granite on the
317 northern slope is characterized by generally higher Mg and lower Ca and Na contents than observed
318 for the less altered granite on the southern slope (Fichter et al., 1998, El Gh'Mari, 1995). This could
319 account for the comparatively higher Mg concentrations and Mg/Na ratios of the sources from the
320 northern slope, but not for e.g. the higher Ca or K concentrations.

321 The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of springs from the southern slope (SH, CS₂, CS₁, RUZS) are, like the
322 corresponding rocks and soils (Aubert et al. 2002) (Fig. 8), more radiogenic with lower Sr
323 concentrations than those from the northern slope (BH, RH, SG, CS₃, CS₄) (Fig. 5). Thus, the Sr
324 isotopic compositions of springs can be directly related to the signatures of the weathering profile

325 and their geographical localization. But the mineral phases involved in the weathering processes
326 and causing the geochemical characteristics of these superficial waters are still matter of discussion.
327 Based on Sr and Nd isotope ratios, Aubert et al. (2001) explained the isotopic signature of the
328 Strengbach stream water by mixing of two isotopically different end-members: apatite and
329 plagioclase. However, the Mg/Sr and Mg/Ca ratios of the waters cannot simply be explained by
330 dissolution of apatite and plagioclase (Fig. 9a,b). In addition, biotite and muscovite have far too
331 high Sr isotopic ratios (respectively 5.8 and 5.4; Aubert et al., 2001) and thus their contribution can
332 be ignored. The clay fractions, extracted from the two weathering profiles at sites HP and VP
333 (Prunier, 2008) can represent an end-member able to explain the Sr isotopic composition as well as
334 the Mg/Ca and Mg/Sr ratios of springs. In addition, the northern slope contains twice as much clay
335 and especially more Mg-bearing smectite than those of the southern slope (Fichter et al., 1998; this
336 study) which can explained why the springs for the northern slope are more radiogenic (Fig 5a,b)
337 with comparatively higher Mg/Ca and Mg/Sr ratios (Fig 9 a,b) than those from southern slopes, 
338 confirming the role play by clays.

339 Such an interpretation is consistent with results of numerical modeling, which indicates that
340 precipitation/dissolution of more or less crystallized clay minerals (such as smectite) control the Mg
341 concentrations and possibly the high Mg/Ca ratios in the source waters of the Strengbach watershed
342 (Godderis et al. 2006; 2009). The same authors proposed that Mg^{2+} is controlled by smectites, Ca^{2+} 
343 by the dissolution of apatite and by smectite, and K^+ by smectite/illite precipitation and dissolution
344 of K-feldspar. Interaction with clays might occur all along the circulation pathway of waters in
345 soils, saprolite and in bedrock fractures. Recent studies in Mackenzie basin and Damma Glacier
346 catchment confirm the importance of secondary mineral formation, especially montmorillonite in
347 the control of chemical composition of stream at the watershed scale (Beaulieu et al., 2011;
348 Hindshaw et al., 2011).

349

350 Thus, the variation of the current chemical compositions of the source waters in the Strengbach
351 catchment possibly reflects dissolution/precipitation processes of secondary mineral phases like
352 clay minerals. In such a model the generally low apatite-like Sr isotopic composition values of the
353 source waters and comparatively high and not apatite-like Mg/Ca ratios can be explained by the fact
354 that the Sr has not been remobilized by alteration of primary apatite but by weathering of secondary
355 mineral phases, which integrated during an earlier stage of alteration and crystallization apatite-
356 derived Sr. At this point we therefore propose that the alteration flux controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ and
357 Mg/Ca (resp Mg/Sr) variation in the sources is imposed by secondary minerals.

358

359 **5.2. $^{234}\text{U}/^{238}\text{U}$ AR in spring waters**

360 Observation of ($^{234}\text{U}/^{238}\text{U}$) AR < 1 in most of the spring and stream waters of the Strengbach
361 catchment is unusual as river waters exhibit generally ^{234}U excess (e.g., Chabaux et al., 2003). Such
362 U AR < 1 have already been observed before for waters from the outlet of the Strengbach catchment
363 (0.963 to 1.023) with a decrease of the U AR in the dissolved load when the discharge increases
364 (Riotte et al., 1999). The authors explained this variation by the involvement of at least two
365 different weathered end-members: a water body enriched in ^{234}U which weathered the granitic
366 bedrock at secular equilibrium and a water with a U AR below unity representing mobilization of U
367 from material that has already been weathered. Our study shows an even larger range of variation of
368 the U AR among the different springs ranging from 0.819 (CS3) to 1.112 (BH) (table 2).

369 The lack of correlation between ($^{234}\text{U}/^{238}\text{U}$) AR and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition or chemical
370 values (Fig 6a, 6b) show that AR are not simply lithology controlled.

371 The mechanisms classically involved to explain ($^{234}\text{U}/^{238}\text{U}$) AR >1 in natural waters are linked to the
372 recoil process associated to the decay of ^{238}U : 1) due to alpha recoil when ^{238}U decays to ^{234}Th , it can
373 be ejected out of a grain into the fluid if the distance to the grain boundary is smaller than the recoil
374 range of ^{234}Th (~30 nm; DePaolo et al., 2006); the ^{234}Th decays then rapidly to ^{234}U (^{234}Th half-life is
375 24 days); (2) α - particles emitted during radioactive decay damage the crystal lattice of mineral

376 grains and the recoil nuclide is subsequently easily mobilized out of the damaged site. As a
377 consequence, the daughter nuclide ^{234}U is preferentially leached relative to the parent ^{238}U during
378 weathering. Thus, natural waters with $(^{234}\text{U}/^{238}\text{U}) \text{ AR} < 1$ most likely correspond to environments,
379 which have already experienced a loss of ^{234}U .

380 In a first and simple approach one might interpret the U AR <1 in the Strengbach source waters by
381 circulation through already weathered soils. However, chemical flux balance calculations show that
382 the annual U fluxes from the soils under spruces or beeches represent at maximum about 8% or
383 22%, respectively, of the annual U flux at the outlet (Table 3). At the same time, the U
384 concentrations in the different springs can reach in average 0.345 ppm whereas it ranges only
385 between 0.011 to 0.023 ppm (factor of 30 to 15 lower) in the deep soil solutions of the two
386 experimental plots (Table 2). These two observations indicate that the U in the springs originates
387 from circulations and interactions, which occurred below the soil horizons.

388 The relationship between the U AR and the altitude of the springs (Fig. 10) indicates that the
389 springs from both slopes with the lower U AR (CS1, CS2, CS3, CS4) are located at higher altitude
390 and circulate in zones where the saprolite reaches 7 to 9 m depth (El'Ghmari, 1995) than springs
391 with high U AR. The spring BH, with the highest U AR is located at the bottom of the watershed
392 where the saprolite layer reaches less than 1.5 m thickness (Fig. 1). Also RUZS was taken at low
393 altitude (950masl), but drains the whole wetland and, therefore, integrated an intermediate U AR.
394 Thus, a possible scenario explaining the $(^{234}\text{U}/^{238}\text{U}) \text{ AR}$ of the spring waters is that BH like sources
395 are closer to the “fresh” granite and reflect meteoric alteration of fresher rock material at secular
396 equilibrium. CS₁, CS₃, CS₂, CS₄ and SH sources, by contrast, drain thicker saprolite profiles and/or
397 less fresh granite and, therefore, their low AR may point to the mobilization of U from mineral
398 phases whose outermost surfaces have already been depleted in ^{234}U due to previous water-rock
399 interactions (old saprolite where the pool of excess ^{234}U has been exhausted). We therefore propose
400 that the $^{234}\text{U}/^{238}\text{U} \text{ AR}$ in the catchments spring waters can be interpreted as a function of water
401 pathways. The sources emerging at high altitude, with AR<1, have circulated through already

402 weathered horizons (saprolite, fractured bedrock depleted in ^{234}U , i.e., with U AR $\ll 1$), whereas the
403 springs emerging at the bottom of the watershed have U AR > 1 because of the interaction with
404 fresher mineral phases. Therefore, U disequilibrium ratios can be a powerful tool to study the water
405 pathways. These preferential flow paths cross more or less weathered materials implying various
406 ($^{234}\text{U}/^{238}\text{U}$) AR for the corresponding springs.

407 This interpretation is in agreement with a granite leaching experiment under continuous flow
408 through a reactor (Andersen et al., 2009). It is indeed shown that during the experiment (1200
409 hours) there is a clear trend of variation of the U activity ratios in the outflowing waters, with
410 ($^{234}\text{U}/^{238}\text{U}$) AR > 1 at the beginning of the experiment and a minimal value of 0.9 after 650 to 700
411 hours; then the AR increased up to 0.95. The values suggest that at the beginning of the experiment
412 high exposure of fresh material promotes direct recoil of ^{234}U into water and potentially enhances
413 preferential release of ^{234}U from damaged lattice sites. However, since there was no renewal of
414 material, because the excess ^{234}U constitutes a finite pool of easy leachable ^{234}U , the ($^{234}\text{U}/^{238}\text{U}$)
415 values become lower than unity when this pool is used up.

416 Similarly, the observed ($^{234}\text{U}/^{238}\text{U}$) AR < 1 in Strengbach springs might indicate that the rate of
417 production of ^{234}U excess (by direct recoil and preferential release) is lower than the rate of renewal
418 of material. This can be explained by continuous preferential water circulation along fractures (Le
419 Borgne et al., 2007), in an old weathered mineral surface where the production of ^{234}U excess is
420 supposed to be low.

421 However, the springs emerging at lower altitude (mainly BH and to a lesser extent RH), with
422 ($^{234}\text{U}/^{238}\text{U}$) > 1 , circulate through fresher granite where α -recoil tracks have direct contact with the
423 outer mineral surfaces and thus with fresh mineral phases (Andersen et al., 2009).

424 At this point it is interesting to note that in a neighbored granite catchment (Ringelbach watershed)
425 all the sources only display U AR > 1 (Schaffhauser, 2013; Schaffhauser et al., in press). This small
426 catchment located in the Vosges massif at altitudes between 750 and 1100m (0.36km²) also

427 consists of Hercynian granite capped in its upper part by residual Triassic sandstones (Schaffauser
428 et al., in press).

429 Plotting the U AR of springs of the both watersheds versus alkalinity and pH (Fig 11) one observes
430 a pretty good correlation where springs with highest U AR are characterized by highest alkalinity
431 and pH values. These two parameters can be considered to reflect the intensity of weathering and
432 water/rock interactions, meaning that the waters from the Ringelbach watershed are characterized
433 by more intense weathering. Only SG spring from the Strengbach catchment shows a slightly
434 different behavior because it originates from a gneiss and not a granite body (see section 5.1). The
435 modeling of chemical composition of the waters from the Ringelbach catchment implies dissolution
436 of primary minerals of granite and precipitation of secondary phases such as clays but no
437 dissolution of clays (Schaffauser, 2013); this is in contrast to Strengbach catchment. Thus, we
438 suggest that the waters with the lowest U AR correspond to less intense weathering in an already
439 rock altered system with only few fresh primary mineral phases whereas higher U AR correspond to
440 more intense weathering for waters circulating for example in fresher bedrock. In this way, the
441 weathering history can be older in the Strengbach watershed than in Ringelbach watershed, which is
442 consistent with the fact that Triassic sandstones still cover the granite in the Ringelbach catchment.
443 It is striking that the BH waters from Strengbach watershed plot in between the data from the
444 Strengbach and Ringelbach watershed (Fig 11a and b) and are characterized by the highest pH (6.7)
445 and alkalinity despite the relatively high DOC content (2.27 ppm), which usually increases the
446 acidity of solution. If we consider that the proton inputs due to atmospheric deposition or biological
447 activity are homogeneous at the watershed scale, then the variation of pH in the different springs
448 only reflects water/rock interactions and the consumption of protons by dissolution reactions. The
449 high pH and alkalinity observed for the BH source are in this case consistent with the fact that its
450 water has interacted with fresher bedrock; this further implies a stronger weathering intensity and
451 higher dissolution rate of smectite along the pathway of this source water.



452 In such a scenario, the relationship observed between ($^{234}\text{U}/^{238}\text{U}$) AR and Mg/Ca ratios (Fig. 12)
453 would indicate that the intensity or the nature of water reactions controlling the Ca-Mg budget of
454 these waters, namely the dissolution/precipitation reactions of Mg- or Ca-smectites (see discussion
455 in 5.1), would be clearly dependent on the weathering level of the saprolite/bedrock system. This is
456 consistent with the fact that 1) smectite occurs along the weathering profile and even in deep
457 weathering horizons (Fichter et al., 1998) and 2) the reactivity of secondary phases like smectite
458 control the chemistry of Mg and Ca in streamwater (this study, Godderis et al., 2006, 2009). In
459 addition, dissolution of clays implies an increase of Mg/Ca ratios in water (Fig 9b). Thus, the
460 relation between U AR and Ca/Mg ratios for the Strengbach springs reflects nothing else than the
461 degree of alteration of the source rock being in contact with the waters: at low altitude the material
462 is fresher, the weathering intensity is more important (higher pH and alkalinity) and thus causes
463 higher Ca/Mg and U AR ratios in the waters than at higher altitudes.

464

465

466 **5.3. Temporal variations of spring waters**

467 The data obtained during 2 hydrological years allow for the analysis of the temporal variations of
468 the springs (Fig. 3). The spring RUZS shows the largest variations, which can be explained by the
469 fact that this spring, drains wetland (10 to 15 % of the whole catchment area) with fluctuations in
470 the groundwater level and contributions.

471 The Sr isotopic compositions of single springs are correlated with discharge (Fig. 7a). In previous
472 studies these variations have been interpreted by mixing of superficial (soil solution type) and deep
473 (groundwater type) waters (Aubert et al., 2002). But, at the same time, the U AR show no temporal
474 variation and, therefore, no relation with discharge (Fig. 7b).

475 Consequently, the U AR and Sr isotopic compositions are not correlated. Similarly, there is no
476 correlation between U AR and geographical location and lithology (discussed in section 5.2). In
477 addition, the lack of temporal U AR variations indicates that the single springs are probably not the

478 result of mixing of different waters. In the same way, the lack of correlation between discharge and
479 DOC or NO_3 , but also the majority of major and trace element concentrations suggests that the
480 variation of chemical composition of spring waters cannot be explained by a simple variation of the
481 contribution between different types of waters or as mixing between superficial waters (with high
482 DOC, NO_3 concentrations for instance) and deep waters. At the same time, the lack of correlation
483 between Sr isotopic compositions and concentrations for individual springs (Fig 5a) confirms that
484 the temporal variations of spring waters cannot simply be explained by mixing between two end-
485 members (e.g. superficial and deep waters). The lack of variation of U AR of the individual springs
486 with changing discharge (figure 7) during 2 years further suggests that the water pathways are the
487 same whatever the hydrological conditions. Under these conditions, the water did not interact with
488 new fresh material but rather with minerals having experienced at their surface a prior loss of ^{234}U
489 from damaged lattice sites (Andersen et al., 2009). In such a fractured bedrock system, the water
490 flow is often reduced to only a few main flow paths that control most of the hydrological response
491 of the aquifer (Le Borgne et al., 2007). These preferential flow paths along constant fractures in the
492 bedrocks might explain the over time homogeneous ($^{234}\text{U}/^{238}\text{U}$) AR of the different analyzed spring
493 waters.

494 In contrast, there is a correlation between discharge and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for each single spring (Fig.
495 7b). When increasing discharge the Sr isotopic composition increases as well, whereas the Si
496 concentrations and alkalinity decrease (Fig. 13).

497 Different Si concentration-discharge relationships have been observed in several catchments and
498 three different types have been identified: type 1 when Si concentration decreases with discharge;
499 type 2 when Si concentration remains constant and type 3 when Si concentration remains constant
500 until a threshold in discharge is exceeded (Godsey et al., 2009; Maher 2011). The springs from the
501 Strengbach watershed belong to the type 1 which are explained by average residence times shorter
502 than required to approach chemical equilibrium. Thus, the chemistry of waters could vary entirely
503 as a function of the nature of subsurface flow paths and the global solute fluxes depend strongly on

504 the geometry, relief, runoff and permeability of basins (Maher, 2011). In addition, the variation of
505 the Sr isotopic compositions with discharge suggests that the source of Sr changes with changing
506 hydrological condition; this confirms again that the temporal variation cannot be explained by a
507 mixing process but possibly also by changing residence times of fluid and/or flow rate which
508 according to Maher (2010) have an important impact on the weathering rates. This is in accordance
509 with the hypothesis of preferential flow pathways through fractures for the water circulation in the
510 basin.

511 In addition, modeling studies have shown that precipitation/dissolution process of secondary phases
512 control the dissolved Si export in stream waters (Godderis et al., 2006; Beaulieu et al., 2011). Thus,
513 the decrease of Si concentration with increasing discharge can be explained by a change in the ratio
514 between dissolution and precipitation of clays (see also chapter 5.2). We propose that at high
515 discharge the water is undersaturated for clay precipitation (lower Si concentration) causing a more
516 important contribution by dissolution of clays as implied by the higher Mg/Ca (see chapter 5.1) and
517 Sr isotopic ratios (Fig 12c). Thus, in agreement with Maher (2011), our study confirms that
518 hydrological properties limit the solute fluxes carried by rivers and physico-chemical conditions.

519

520

521 **5.4. The chemical and isotopic signatures of the waters at the Strengbach outlet**

522 The stream at the catchments outlet shows with increasing discharge increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and
523 decreasing alkalinity, pH, H_4SiO_4 , and $(^{234}\text{U}/^{238}\text{U})$ AR (Fig. 14a-e). The important point is that the
524 variation of U AR observed at the outlet (Fig. 14e) can only be explained by a change in the
525 discharge contribution of the different springs because the U AR of single springs are constant with
526 time (Fig. 7). When the discharge increases, the U AR values tend towards 0.95, which is close to
527 the $(^{234}\text{U}/^{238}\text{U})$ AR of the spring from the saturated area (RUZS) (Fig. 6; Fig. 14). Previous papers
528 proposed that during storm event, the contribution of the small saturated zone could reach up to 30
529 % of the runoff (Idir et al., 1999; Ladouche et al., 2001). Similarly, the increase of the Sr isotopic

530 composition with increasing discharge points to the important contribution of RUZS to the
531 streamlet during high discharge events (Fig. 14d)
532 However, during the lowest discharge, the U AR of the stream at the outlet is > 1 (max. 1.023).
533 These higher values can only be explained by a more important contribution of the spring BH from
534 the northern slope which is the only one with a U AR>1 (average: 1.103; Table 1; Fig.14). Other
535 parameters such as H₄SiO₄, pH and alkalinity confirm the important contribution of the BH spring
536 to the streamlet during low discharge (Fig. 14). Similarly, the position of the RUZS spring with the
537 low pH, alkalinity and silica concentrations (Fig. 14) confirms its important contribution during
538 high discharge. But also the fact that the Sr isotopic composition of the stream at the outlet
539 decreases with decreasing discharge is in accordance with a more important contribution of the less
540 radiogenic springs from the northern (e.g. BH) (Fig. 14) than from the southern slope (Fig. 5).

541

542 **6. Conclusion :**

543

544 The study shows that the small and more or less “monolithic” Strengbach catchment drains different
545 sources and streams with very different isotopic and geochemical signatures. This heterogeneity is
546 mainly linked up with :

- 547 - the nature of the bedrock (gneiss, more or less altered granite),
- 548 - the specific mineralogical composition and thickness of the substratum (soil, saprolite, bedrock),
- 549 - the degree of hydrothermal alteration: the bedrock granite from the northern slope is
550 hydrothermally much more altered (less biotite, apatite and albite, more clays) and, therefore, the
551 sources draining this slope have higher TDSw-, pH values, higher Ca, K, Mg concentrations and
552 lower ⁸⁷Sr/⁸⁶Sr ratios than sources draining the southern slope,
- 553 - the water flow is probably controlled by pathways through main fractures, as it is generally the
554 case in fractured granite systems.

555 This study has also shown, that there is an important decoupling between chemical composition on
556 the one hand and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ($^{234}\text{U}/^{238}\text{U}$) AR on the other hand. The Sr isotopic
557 compositions of the source waters are generally thought to be the result of alteration of primary
558 mineral phases such as apatite. However, the low apatite-like Sr isotopic composition but
559 comparatively high and not apatite-like Mg/Ca ratio cannot simply be derived from apatite
560 dissolution; nevertheless, they might originate from alteration of a secondary mineral phase like
561 clay minerals, which integrated during their formation an apatite-derived Sr isotopic composition
562 from the solution. The dissolution and precipitation dynamics of secondary phases, especially clays
563 such as montmorillonite, seem to control the mobility of Si, Ca or Mg and, therefore, emphasize the
564 key role of the clays reactivity in the biogeochemical transfer of especially nutrient elements like Ca
565 and Mg.

566 Different processes control the variation of the U AR. Springs at high altitude with U AR < 1, which
567 is uncommon for surface waters, have circulated through already weathered bedrock (thick saprolite
568 and fractured rock) and have interacted with already weathered surface minerals. These values are
569 due to strong ^{234}U depletion during predating alteration processes of the bedrock granite. At the
570 opposite, springs emerging at the bottom of the watershed have U AR > 1 because of interaction
571 with fresher materials.

572 The lack of variation of U AR of the individual springs with changing discharge during 2 years
573 suggests that the water pathways are the same whatever the hydrological conditions and that there is
574 no interaction between the different source waters.

575 It appears that the ($^{234}\text{U}/^{238}\text{U}$) AR is a very important tracer for studying and deciphering the
576 contribution of the different source fluxes at the catchment scale because this unique geochemical
577 parameter is different for each individual spring and at the same time remains unchanged for each
578 of the springs with changing discharge and fluctuating hydrological conditions. Without this
579 parameter it would not have been possible to decipher the real contribution of the different water
580 masses, especially that of the BH spring at low discharge conditions.

581 Thus all these observations converge toward the same functioning:

582 - The proportion of the contributions of the different springs to the stream at the outlet varies in
583 function of the hydrological conditions; the variable contributions of the different sources carrying
584 different geochemical signatures define the signature of the waters at the Strengbach outlet.

585 - During high flow events, the contribution of the saturated area (RUZS) to the streamlet increases.

586 - At low discharge, the contributions of springs from the northern slope become important (e.g.
587 BH).

588 The U-Sr isotope study, combined with physico-chemical investigations of the waters offered the
589 opportunity to better understand the processes causing the hydrochemical signature and its temporal
590 variation in each of the individual springs and in the stream waters at the outlet of the small
591 catchment. Indeed, this work points not only to the importance of investigate larger time intervals
592 including one total or even two hydrological cycles but also the interest of geographically enlarged
593 studies including several springs; punctual or only outlet observations will not allow for
594 understanding of the complex functioning of a watershed.

595 The study further highlights the important impact of different and independent water pathways in
596 fractured granite controlling the different geochemical and isotopic signatures of the waters.

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599

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606

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608 **References:**

609

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867 **Table captions**

868 Table 1: Chemical compositions of spring and stream waters, open field precipitation, throughfalls
869 under spruces (PL5) and beeches (PLH). The total dissolved solids (TDS_w) have been calculated
870 from the concentrations of the major dissolved elements (cations, anions and silica) and are
871 expressed in mg/L, as calculated for several watersheds (e.g., Gaillardet et al., 1999). Another
872 parameter, called here TDS-Ca ($=Ca+Mg+Na+K+SiO_2+Fe$) has been calculated as proposed by
873 Zakharova et al. (2007) and reflects the silicate weathering.

874 Table 2: Sr isotopic compositions and U activity ratios for spring waters, outlet, rain, throughfalls
875 and clays (Prunier, 2008) from the Strengbach watershed. Clays SS: clays from a soil profile
876 located in the southern slope and under beeches, and clays NS: clays from a soil profile located in
877 the northern slope and under spruces.

878 Table 3: Elementary fluxes for rain, throughfalls and outlet in the Strengbach catchments. The rain
879 corresponds to open field precipitations, the throughfalls have been collected under spruces (80% of
880 the forest cover) and beeches (20% of the forest cover). The chemical composition of throughfalls
881 results of (wet and dry atmospheric deposition) + (biological excretion = biological leaching). In
882 order to estimate the atmosphere-derived fluxes (input fluxes) we applied for every element a
883 specific corrective factor C_b (1)Ulrich et al, 1983; (2)Dambrine et al., 1998; (3)Thimonier et al.,
884 2008, (4)Berger et al., 2008. The global atmospheric input has been calculated considering the
885 catchment area as 15% of clearing and 85% of forest, the formula is then : $F_{atm} = 0,15 \cdot F_{rain} + 0,85$
886 $F_{throughfall(corrected)}$. The outlet fluxes correspond to the catchment export fluxes (b).

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891 **Figure captions**

892 Fig. 1: Map of the Strengbach catchment showing the principal lithological units and the location of
893 the 10 studied springs (SG, RH, ARG, BH, CS1, CS2, CS3, CS4, SH, RUZS). RS corresponds to
894 the Strengbach stream at the outlet of the studied catchment.

895 Fig. 2: Physico-chemical characteristics of the different source waters of the Strengbach watershed
896 (average values of period 2004-2006). a) pH vs TDSw; b) pH vs Mg/Na, c) pH vs Alk and d) pH vs
897 Ca/Na.

898 Fig. 3: Major element concentration ratios of the 9 different individual source waters of the
899 Strengbach watershed. a) Ca/Na vs Mg/Na; b) Ca/Na vs K/Na; c) Ca/Na vs Sr/Na and d) Ca/Na vs
900 $\text{Si(OH)}_4/\text{Ca}$. In each diagram the spring waters from the southern slope show different compositions
901 than those from the northern slope.

902 Fig. 4: Relationships between a) DOC (ppm) vs Fe (ppm), b) Alk (meq/l) vs U (ppb) and c) DOC
903 (ppm) and U (ppb). DOC: dissolved organic carbon. Some springs (BH, SH, RUZS, SG) show
904 relationship between Fe, DOC and U concentrations whereas for the others (CS1, CS2, CS3, CS4,
905 RH) the U concentrations show a large variation whereas the DOC concentrations remain low.

906 Fig. 5: Relationships between $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios and a) $1/\text{Sr}$ (ppb), b) Ca/Sr (ppb/ppb), The
907 isotope ratios allow a clear distinction between northern and southern slope sources.

908 Fig. 6: Relationship between $(^{234}\text{U}/^{238}\text{U})$ AR and a) $1/\text{U}$ and, b) $^{87}\text{Sr}/^{86}\text{Sr}$. In contrast to Sr isotopic
909 compositions, the U AR of springs do not allow to distinguish between the northern and southern
910 slopes.

911 Fig. 7: $^{87}\text{Sr}/^{86}\text{Sr}$ versus discharge and $(^{234}\text{U}/^{238}\text{U})$ AR versus discharge for respectively BH spring (a
912 and b) and for 3 other springs (CS1, RH3 and CS4; c and d) from the Strengbach watershed.

913 Fig. 8: Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ for the soil and saprolite samples from the Strengbach
914 watershed. The data show a clear difference between the samples from the northern slope and those
915 from the southern slope (Aubert, 2001; Stille et al, 2009 , Prunier, 2008).

916 Fig. 9: a) $^{87}\text{Sr}/^{86}\text{Sr}$ versus Mg/Ca and b) $^{87}\text{Sr}/^{86}\text{Sr}$ versus Mg/Si for the spring waters (NS = northern
917 slope and SS=southern slope), primary minerals of the granite (Aubert et al., 2001) and clays from
918 soils (Prunier, 2008).

919 Fig. 10: Variations of ($^{234}\text{U}/^{238}\text{U}$) activity ratios vs elevation in the springs from the Strengbach
920 watershed. At catchment scale we observe relation between U AR and the altitude of source of the
921 springs.

922 Fig. 11: Variations of ($^{234}\text{U}/^{238}\text{U}$) activity ratios vs Mg/Ca ratio in the springs from the Strengbach
923 watershed. At catchment scale we observe a clear relation between U AR and the Mg/Ca ratio of the
924 springs.

925 Fig.12: Variations of ($^{234}\text{U}/^{238}\text{U}$) activity ratios vs a) alkalinity and b) pH in the springs from the
926 Strengbach and Ringelbach (Shaffauser et al., in press) watersheds.

927 Fig. 13: Variations of $^{87}\text{Sr}/^{86}\text{Sr}$ versus a) alkalinity and b) Si concentration for the springs from the
928 Strengbach watershed. For each individual spring we observe a relation between $^{87}\text{Sr}/^{86}\text{Sr}$ and
929 alkalinity or Si content.

930 Fig. 14: Variation of a) H_4SiO_4 concentration, b) alkalinity, c) pH, d) ($^{234}\text{U}/^{238}\text{U}$) AR and e) $^{87}\text{Sr}/^{86}\text{Sr}$
931 versus discharge for the Strengbach stream at the outlet, for the 2004-2006 studied period
932 (additional data from Riotte et al. (1999) and Aubert et al., (2002) for respectively U AR and Sr
933 isotopic compositions).

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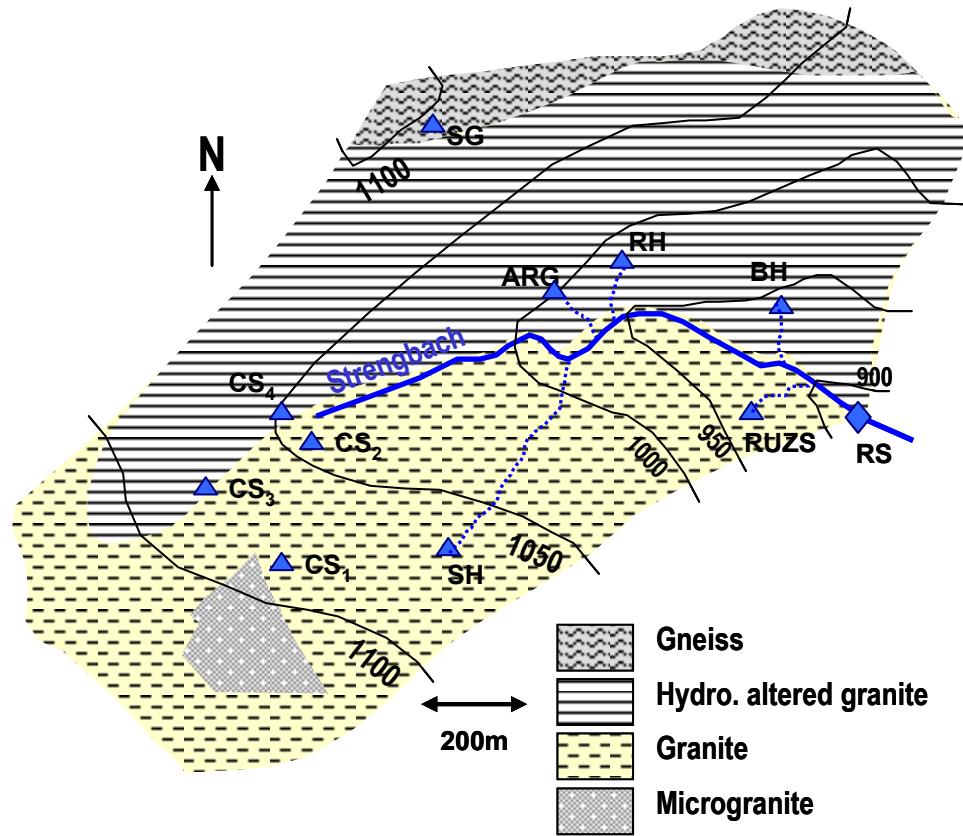


Fig.1

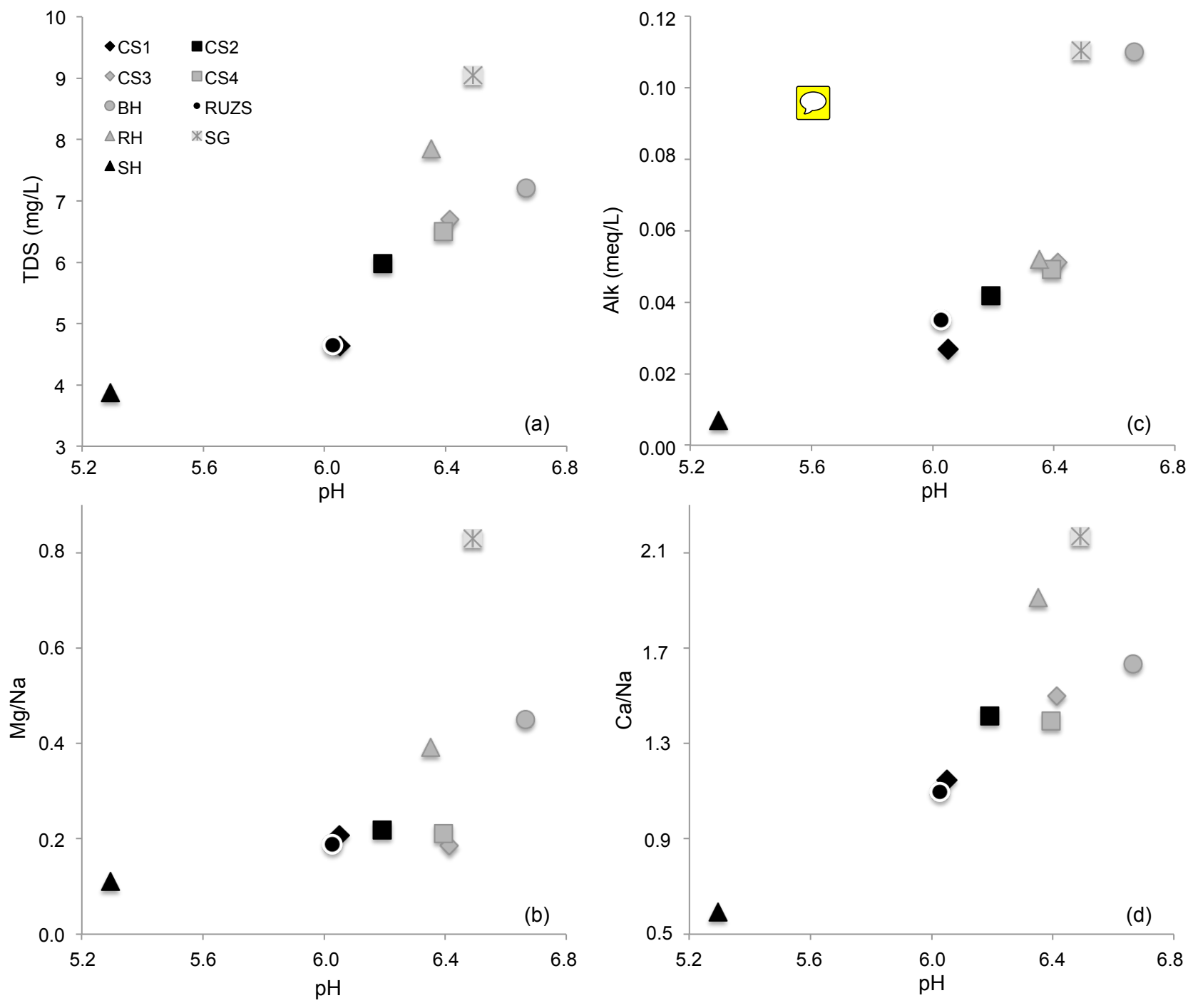


Fig.2

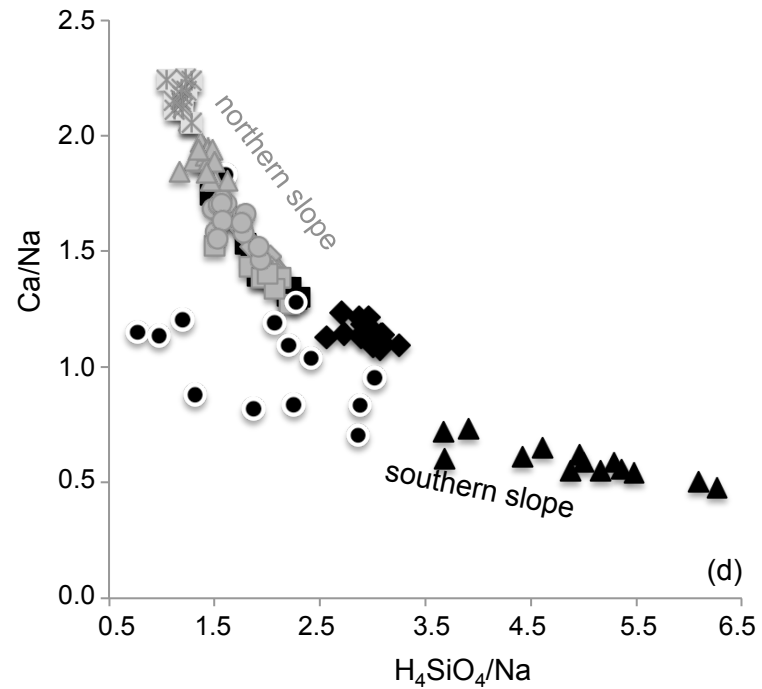
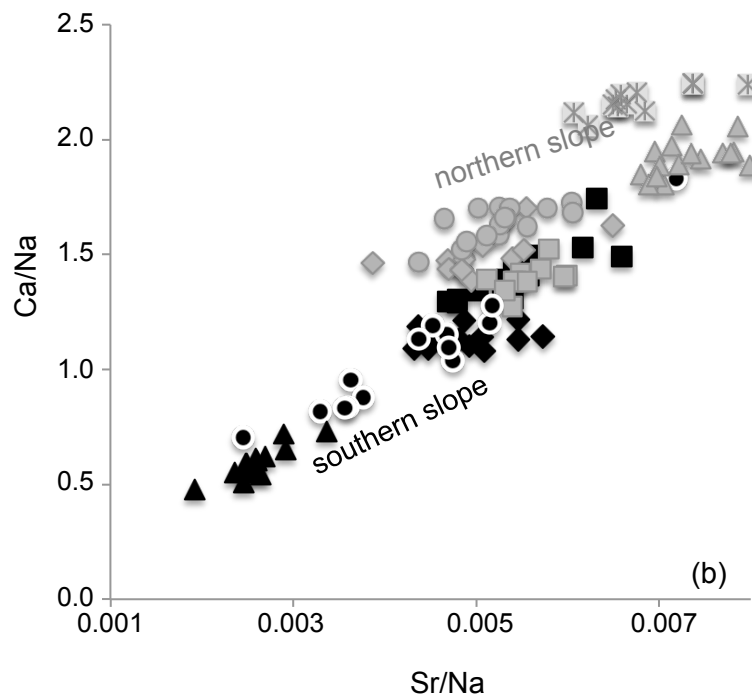
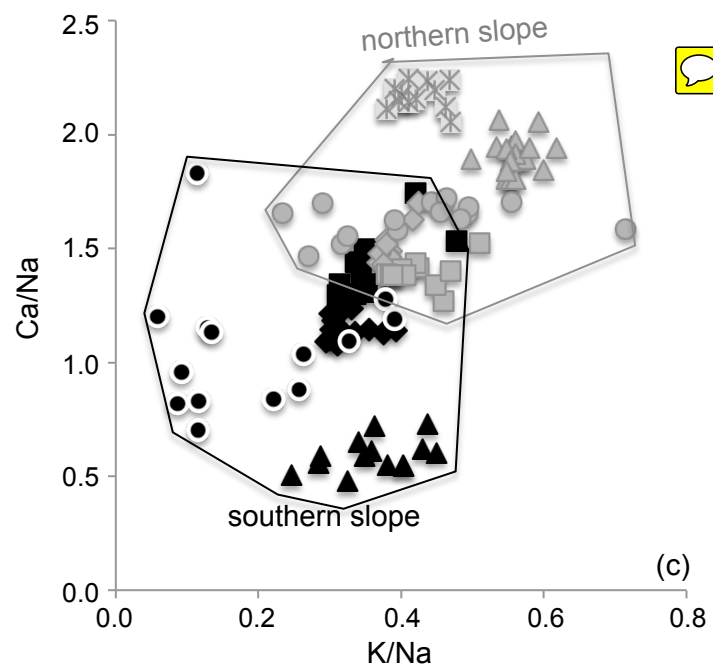
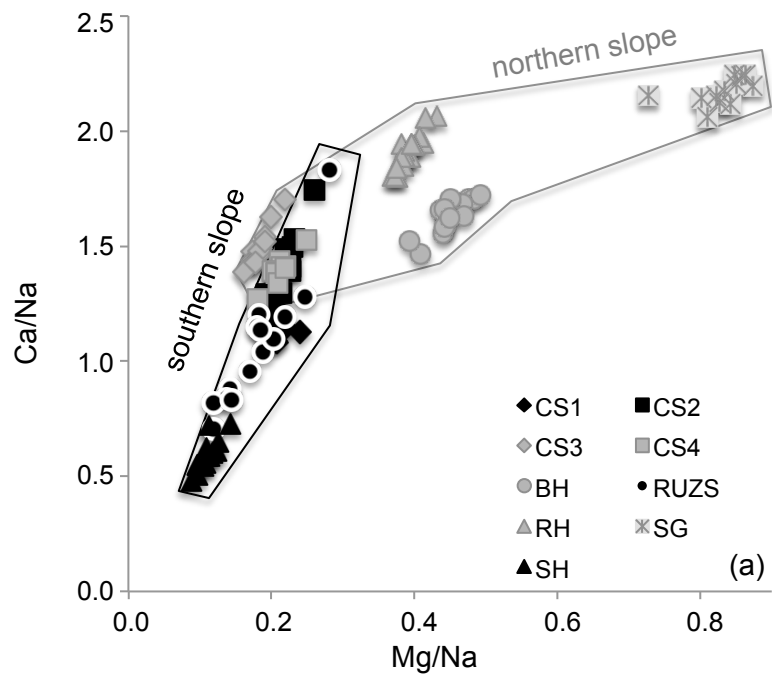
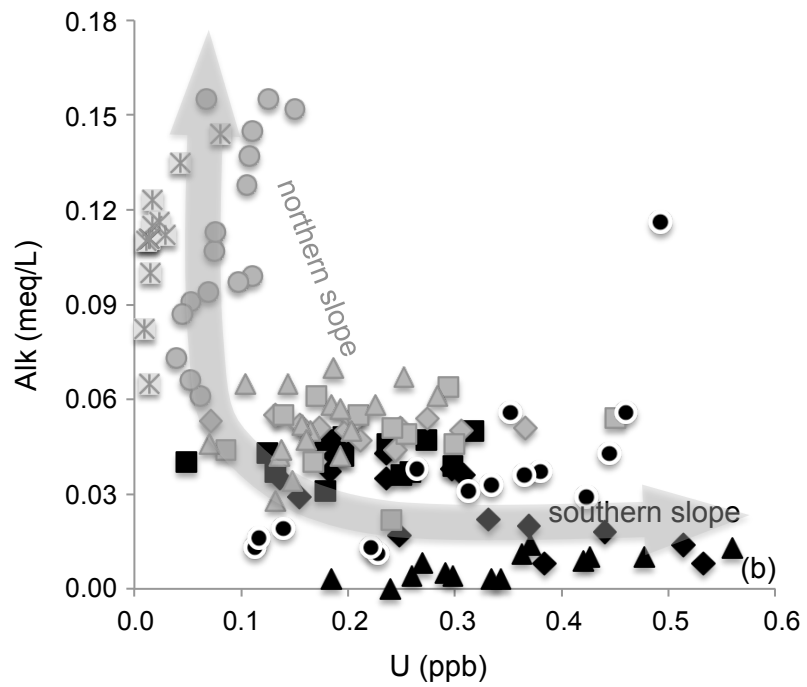
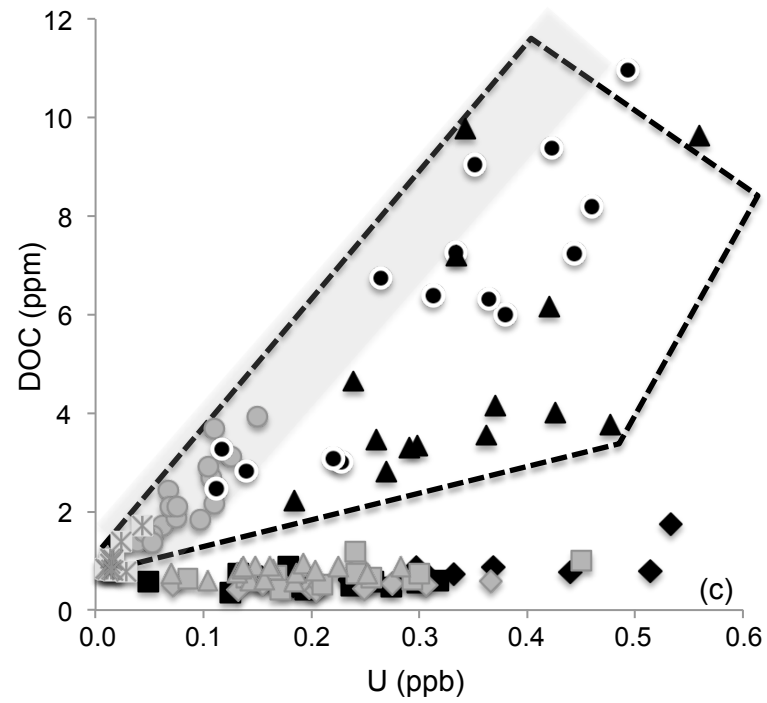
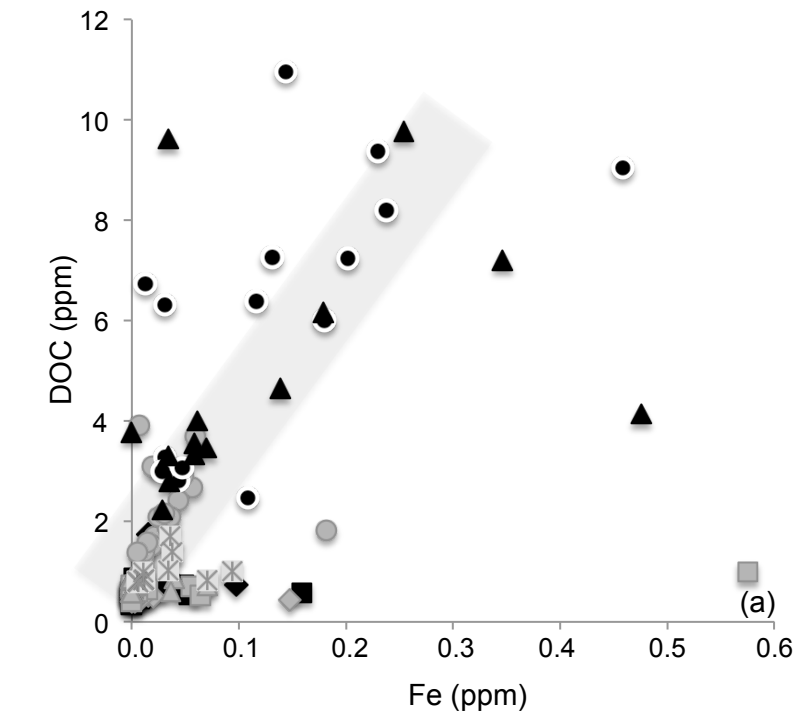


Fig.3



- ◆ CS1
- ◆ CS3
- BH
- ▲ RH
- ▲ SH
- CS2
- CS4
- RUZS
- * SG



Fig.4

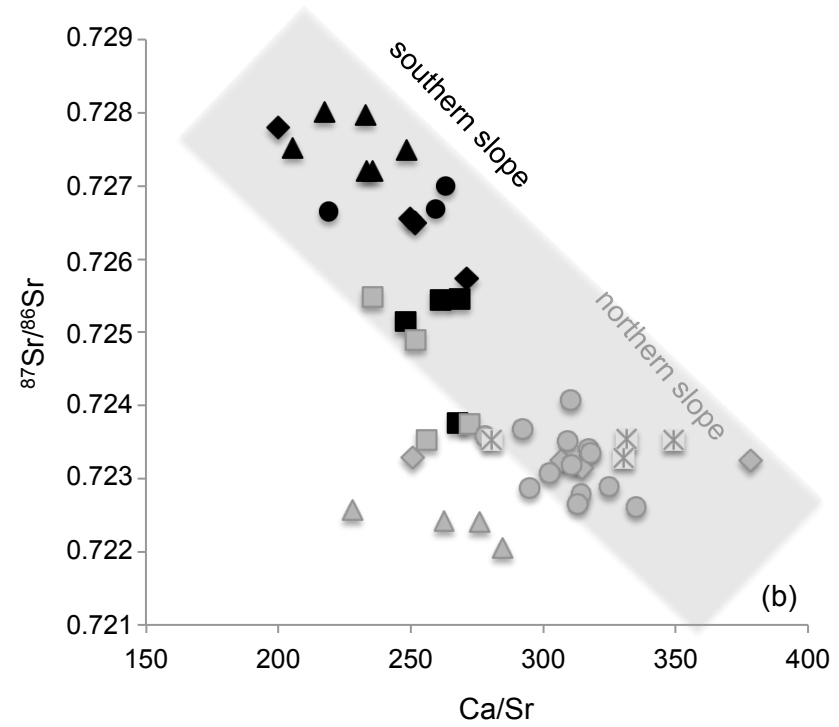
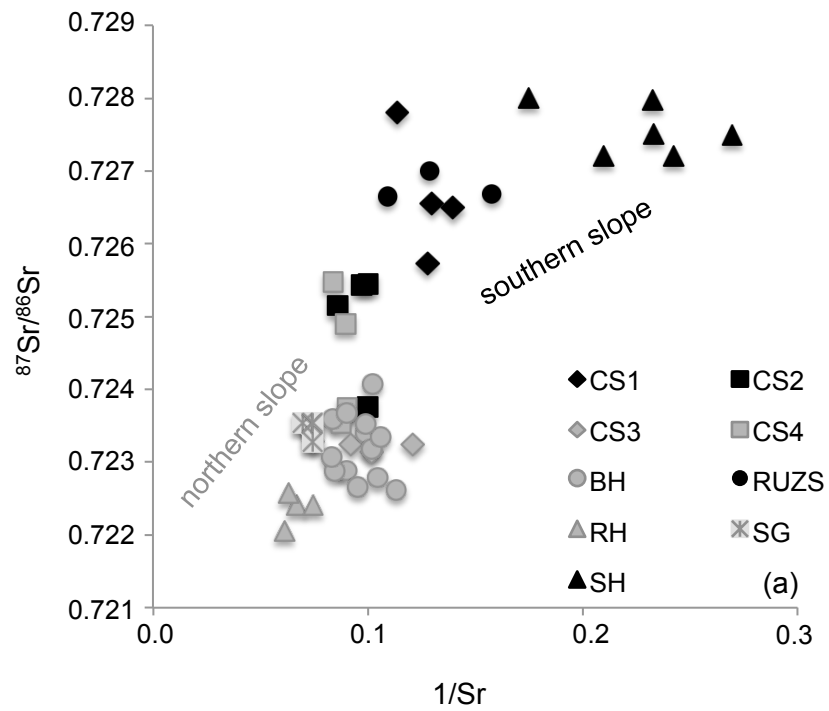


Fig.5

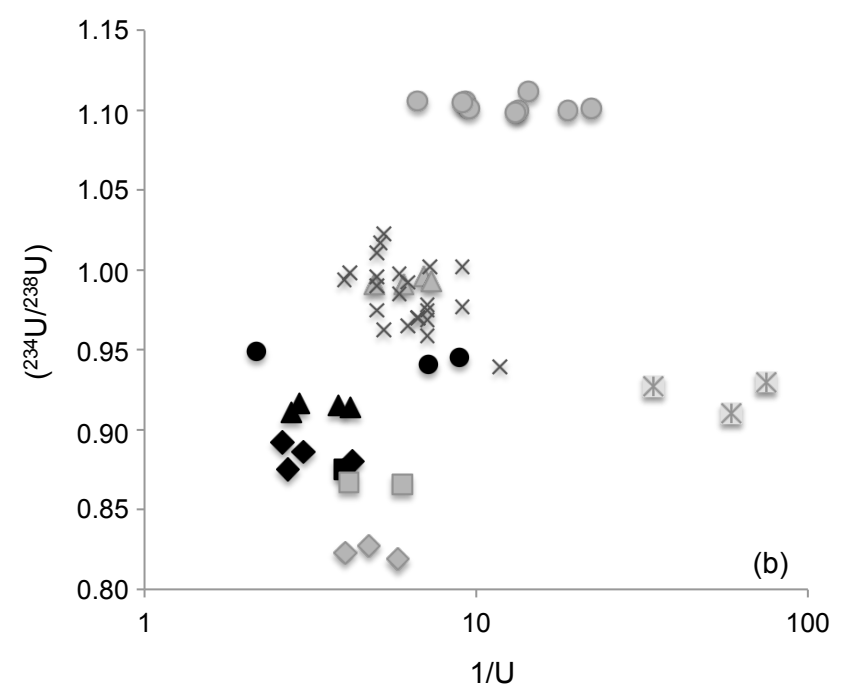
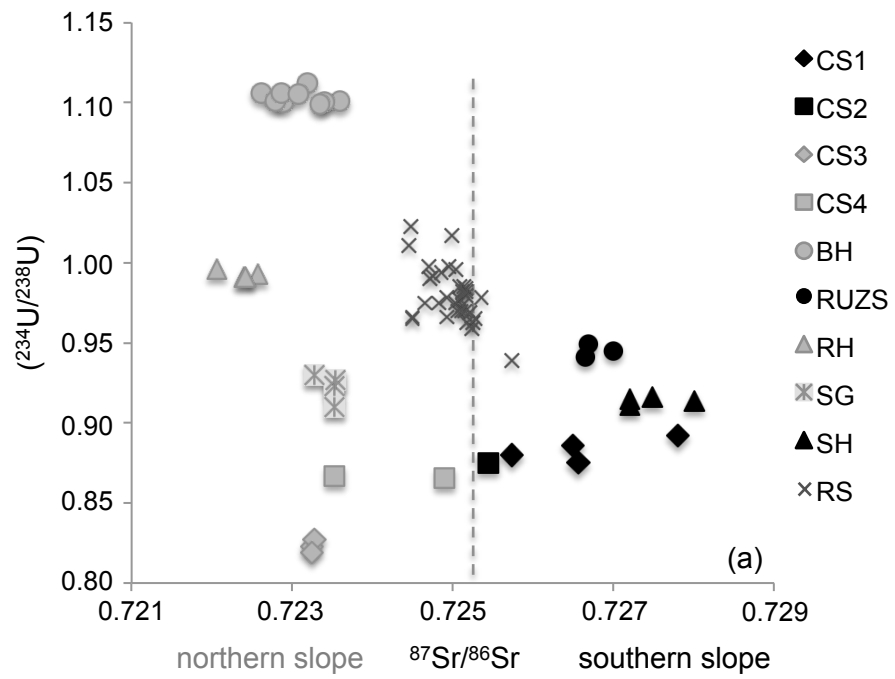


Fig.6



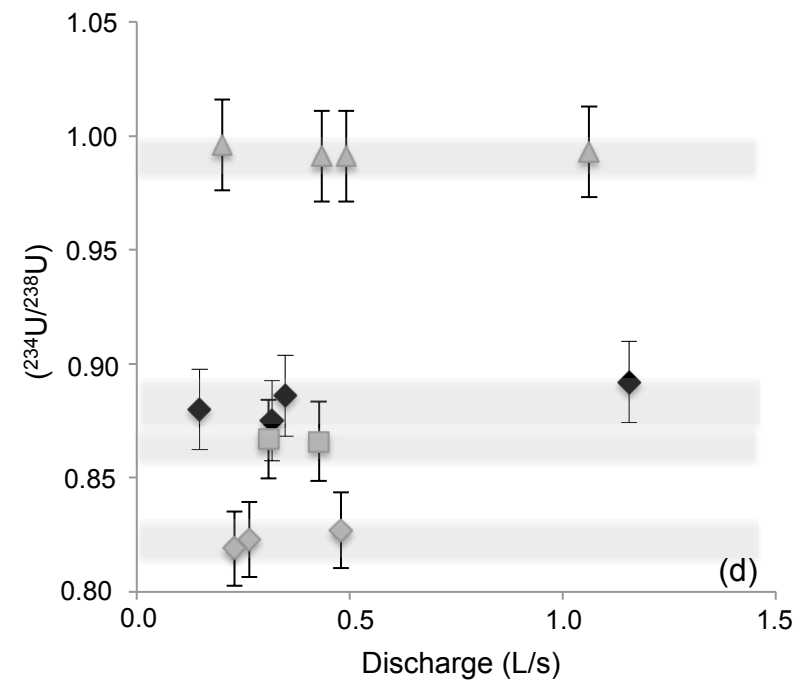
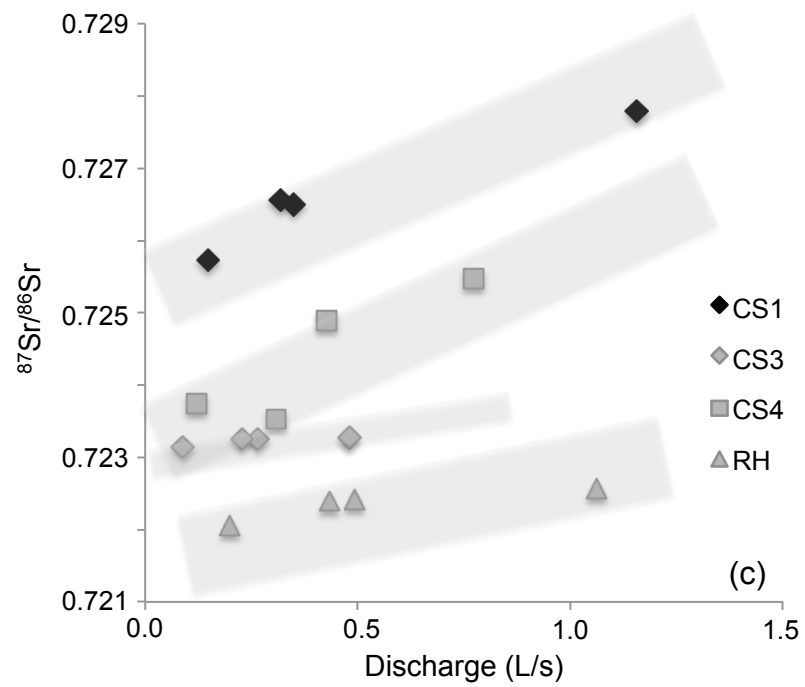
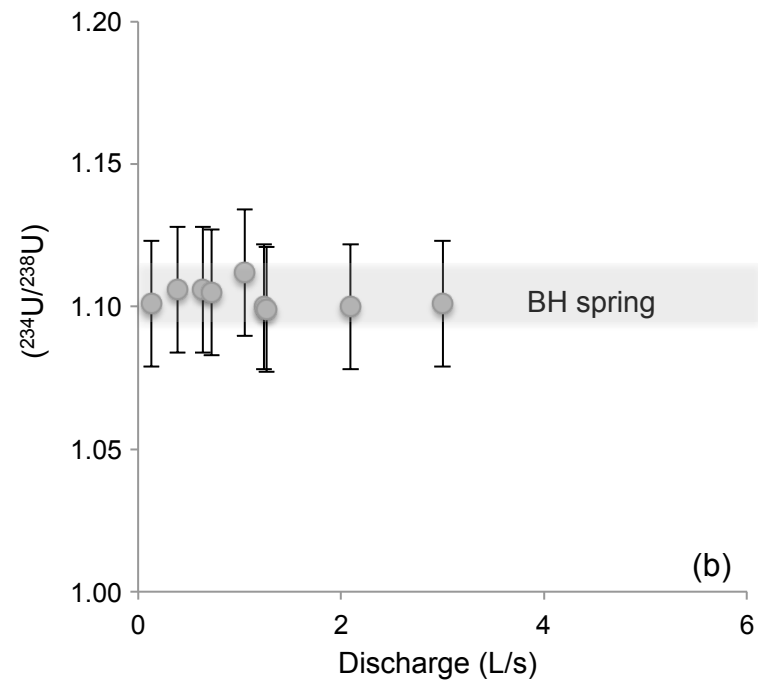
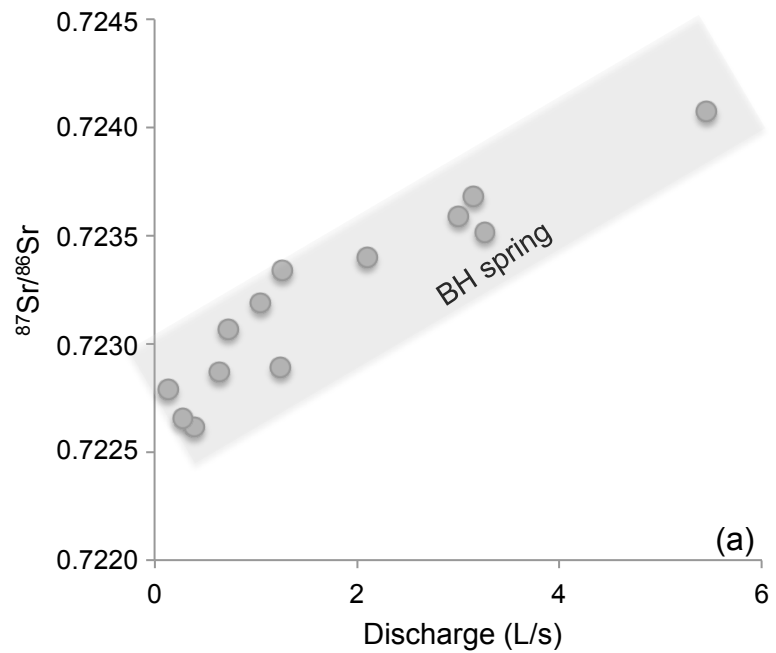


Fig.7

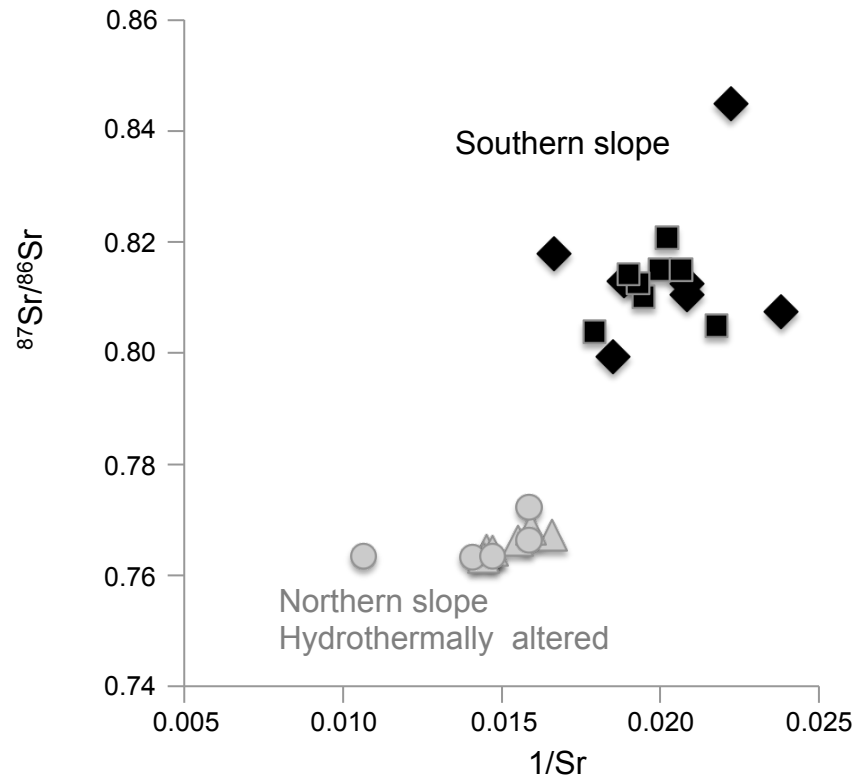


Fig.8

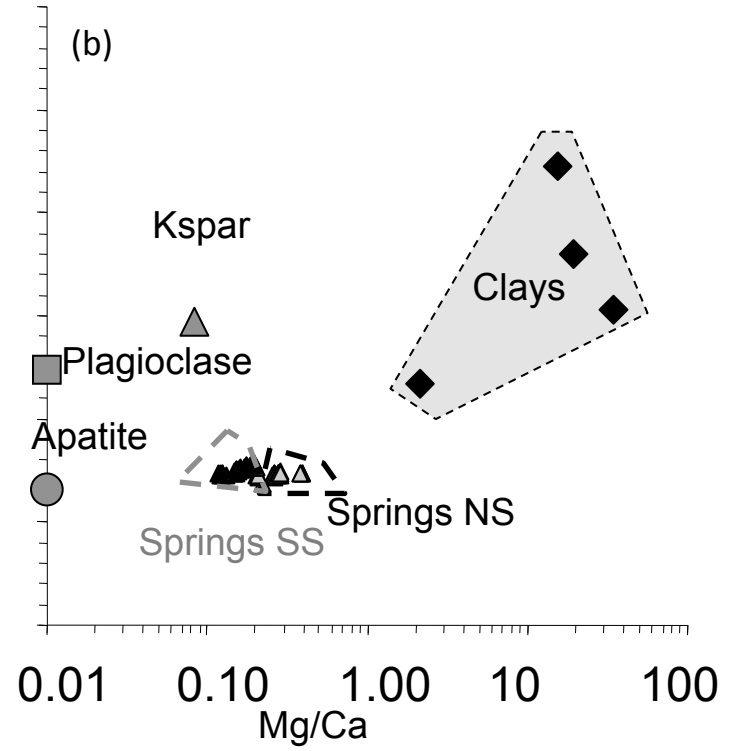
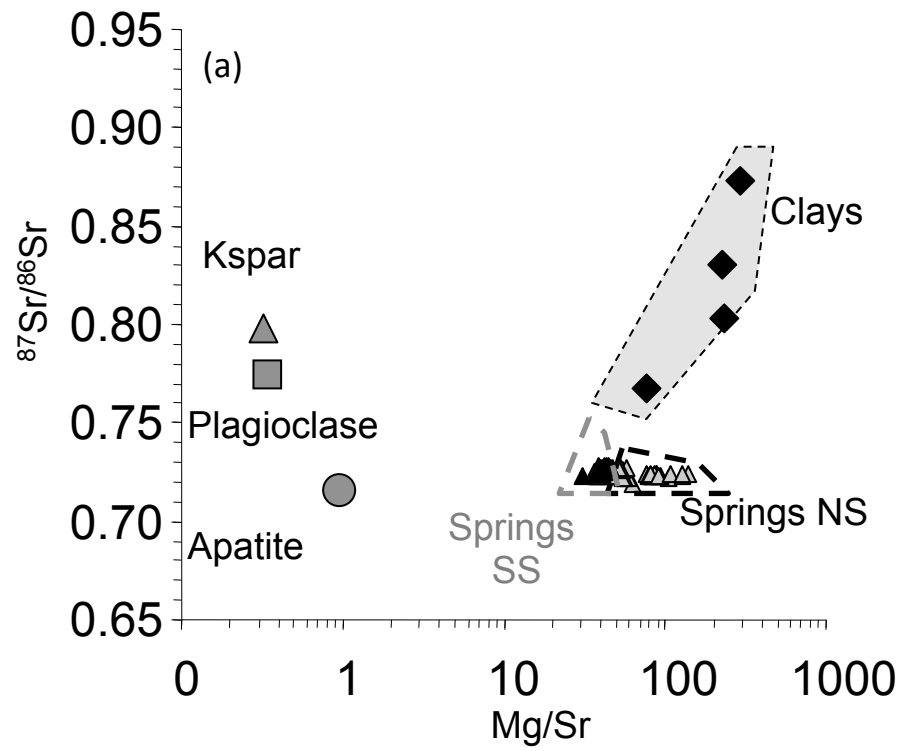


Fig.9

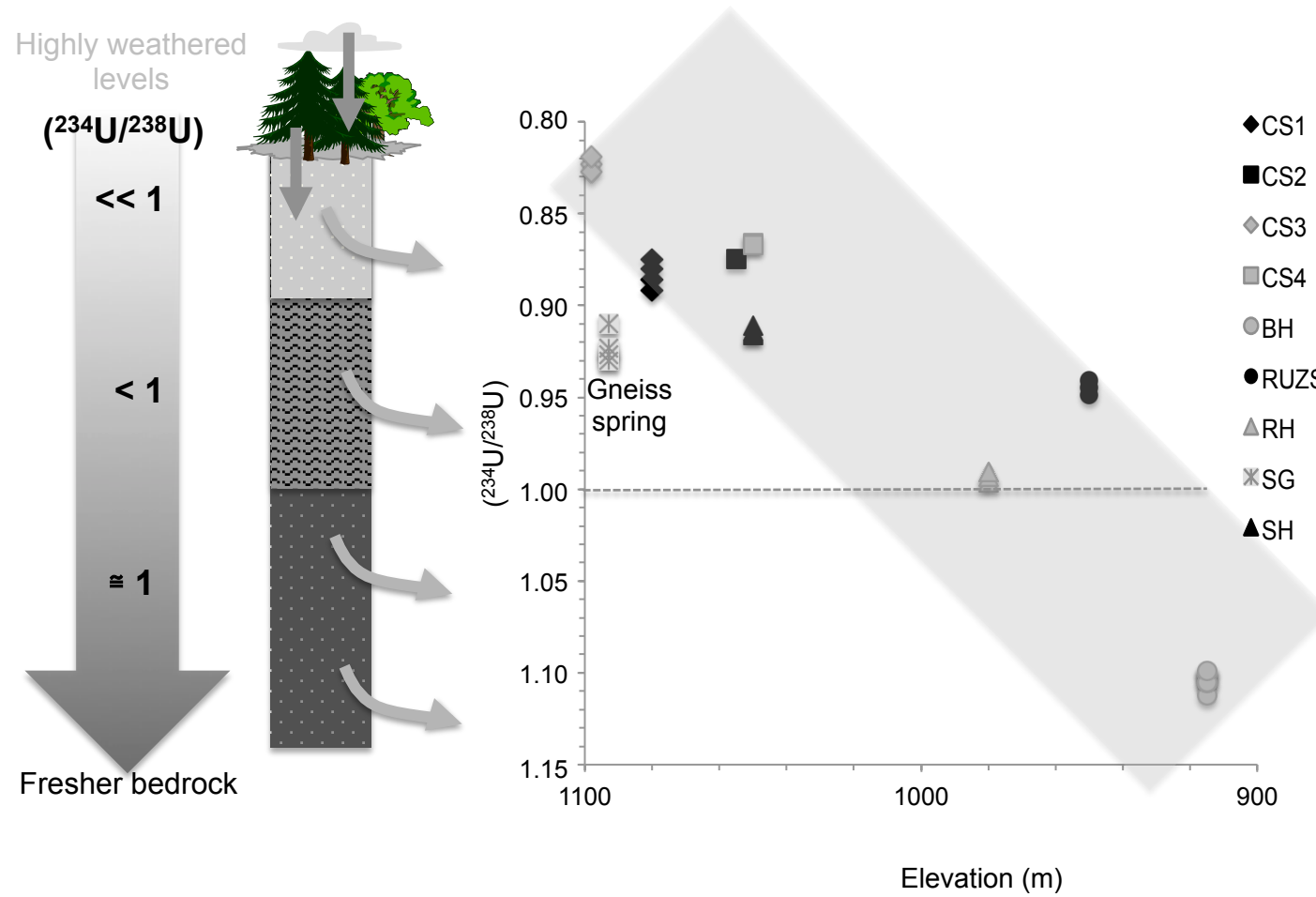


Fig.10

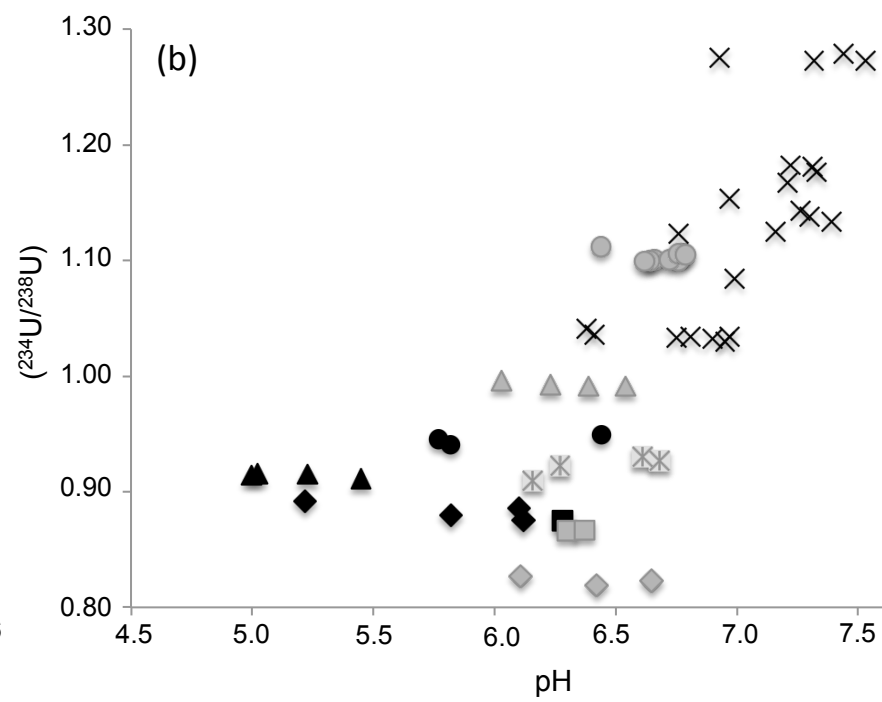
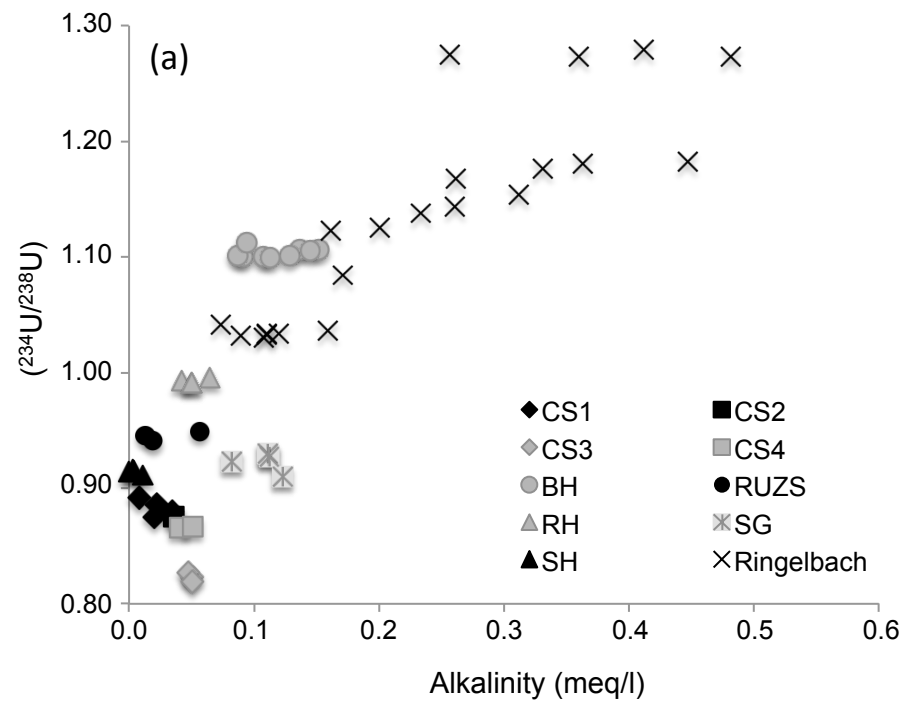


Fig.11

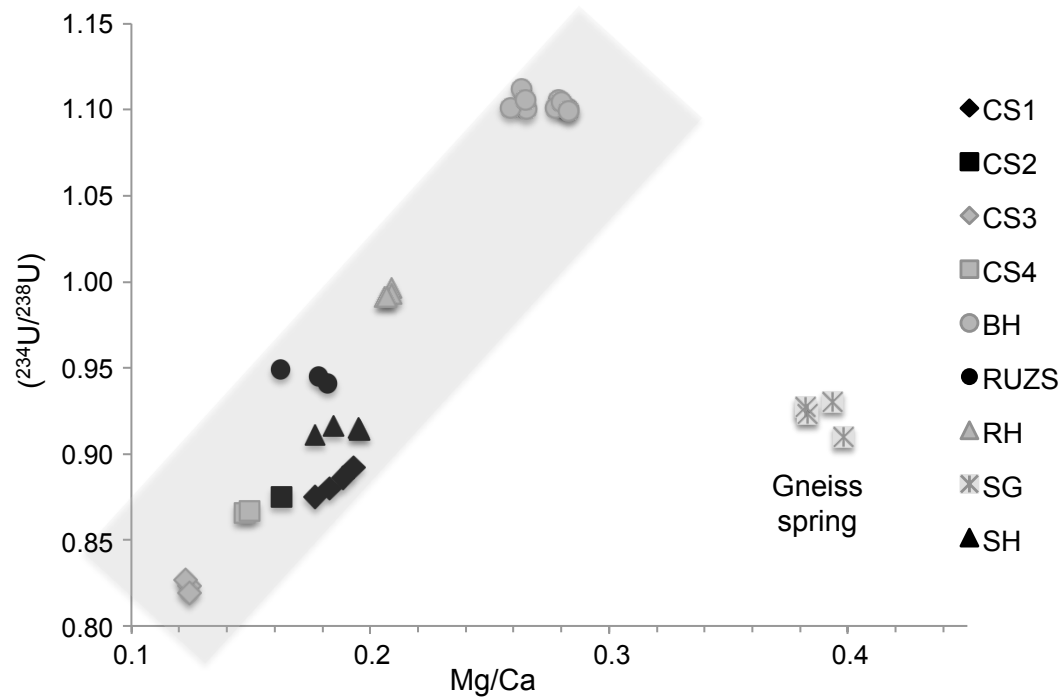


Fig.12

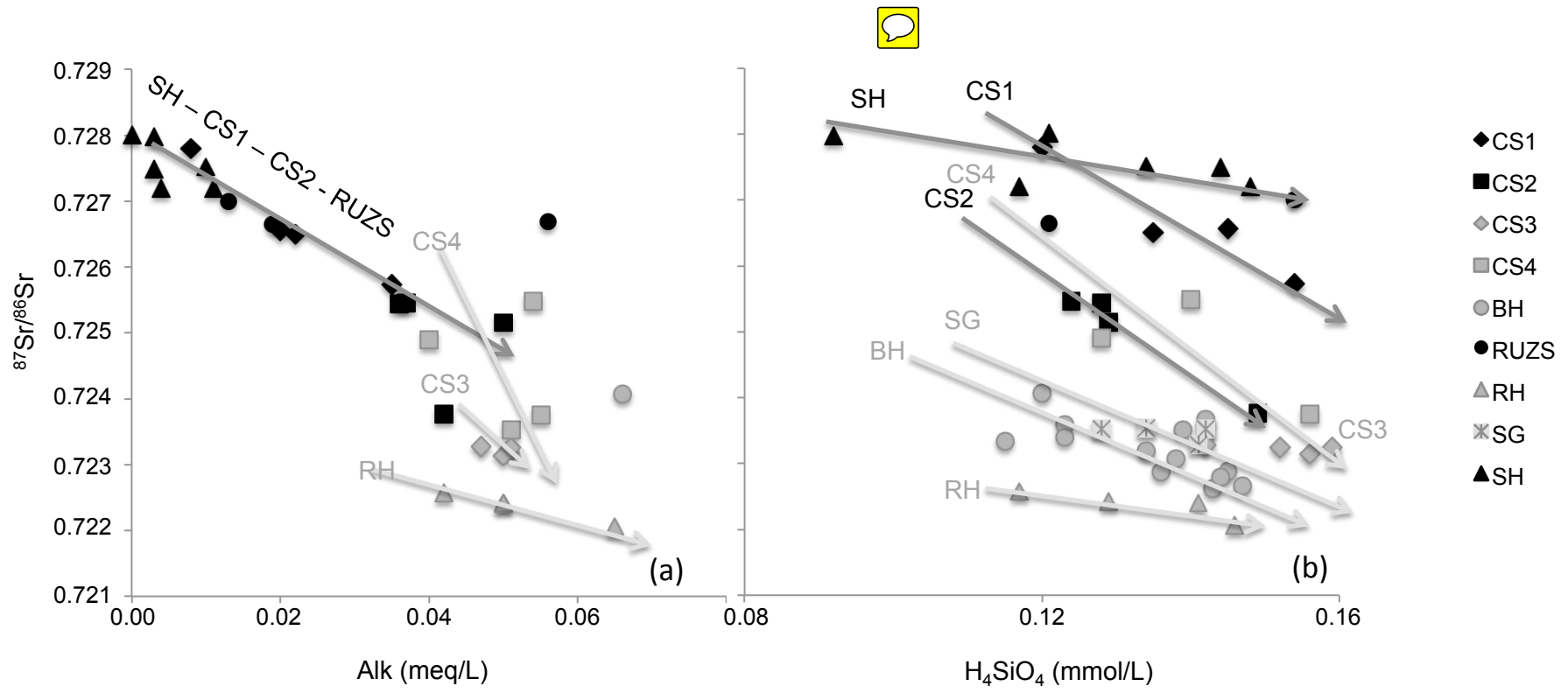


Fig.13

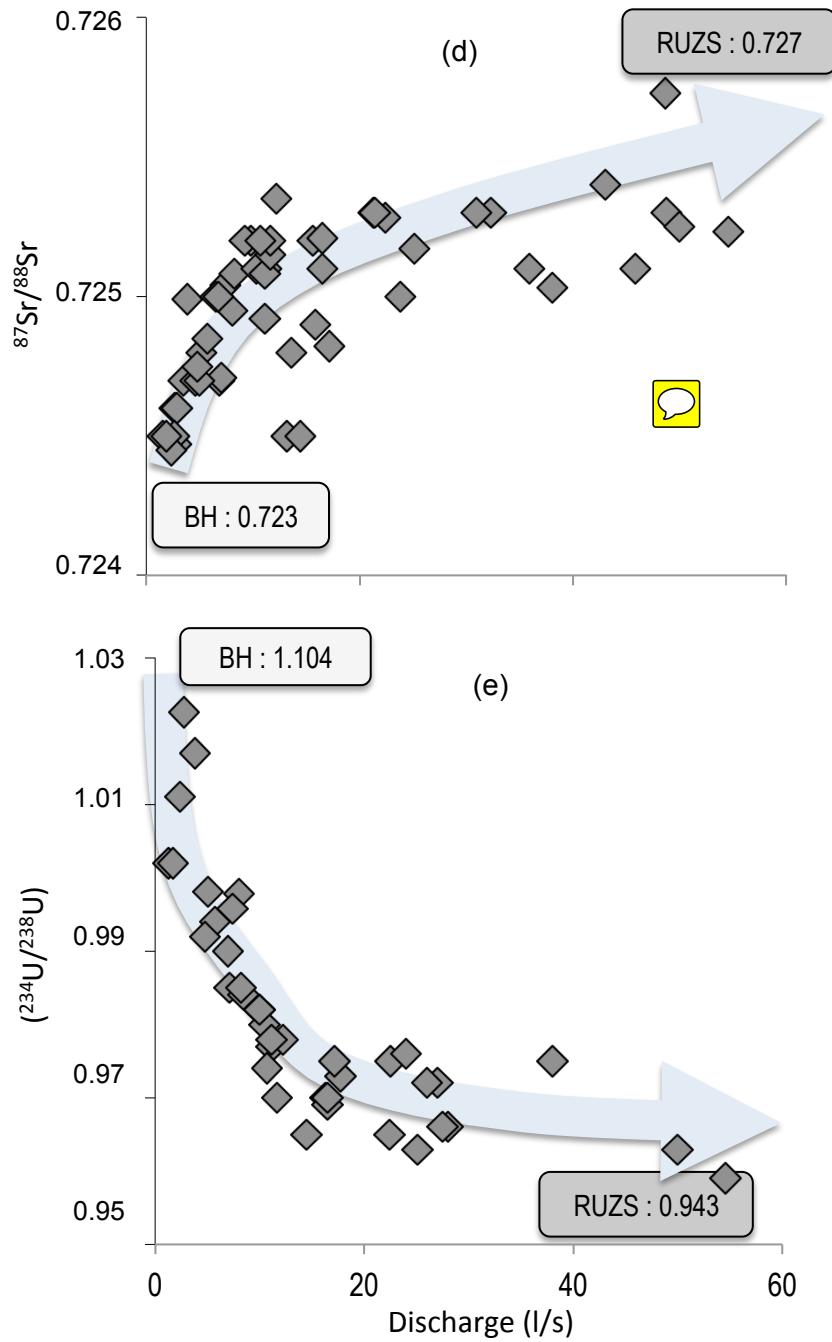
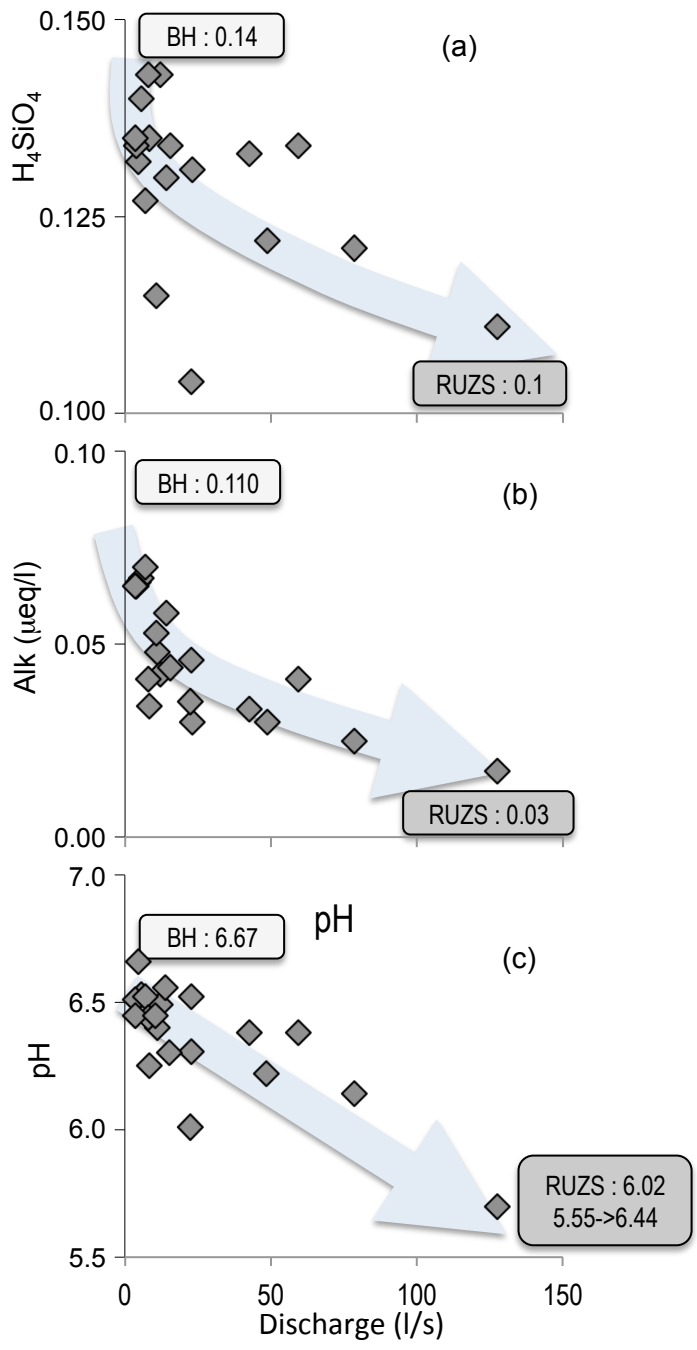


Fig.14

SH	21/08/06	0.554	5.60	15.40	0.077	0.013	0.008	0.026	0.01	0.045	0.005	0.042	4.01	0.130	0.25	0.03	0.06	20.56	2.97	4.39	0.43	10.18	3.66
SH	02/10/06	0.883	5.61	18.50	0.076	0.011	0.007	0.022	0.01	0.051	0.004	0.040	3.77	0.134	0.24	0.02	0.00	20.60	2.95	4.29	0.48	9.86	3.31
SH	Average		5.29	20.11	0.077	0.02	0.008	0.026	0.01	0.05	0.01	0.04	4.86	0.13	0.24	0.08	0.13	20.60	3.99	4.61	0.35	10.32	3.87
Outlet RS	02/02/04	nd	6.19	30.10	0.083	0.020	0.024	0.069	0.03	0.056	0.059	0.068	1.85	0.131	0.05	0.01	0.02	67.31	2.41	10.46	0.14	19.99	6.15
RS	12/07/04	4.58	6.66	29.20	0.081	0.016	0.020	0.060	0.07	0.044	0.026	0.059	1.99	0.132	0.02	0.01	0.05	57.08	1.76	9.07	0.19	18.29	5.52
RS	28/09/04	5.45	6.53	32.60	0.090	0.018	0.024	0.070	0.07	0.053	0.044	0.061	1.80	0.140	0.06	0.01	0.04	69.00	2.96	11.50	0.15	20.77	6.29
RS	02/11/04	59.30	6.38	30.10	0.084	0.020	0.025	0.073	0.04	0.057	0.068	0.063	1.55	0.134	0.05	0.01	0.02	71.65	3.19	11.05	0.12	21.07	6.35
RS	13/12/04	12.00	6.49	34.30	0.088	0.019	0.025	0.075	0.04	0.061	0.061	0.062	1.13	0.143	0.03	0.01	0.02	68.76	2.59	11.10	0.08	20.90	6.49
RS	24/01/05	42.60	6.38	33.10	0.083	0.021	0.025	0.073	0.03	0.057	0.068	0.067	1.30	0.133	0.03	0.00	0.01	78.96	2.64	12.29	0.08	20.96	6.36
RS	07/03/05	8.37	6.25	32.40	0.085	0.019	0.023	0.070	0.03	0.057	0.059	0.068	1.10	0.135	0.02	0.00	0.02	69.00	2.43	13.16	0.07	20.36	6.16
RS	21/03/05	78.50	6.14	32.40	0.079	0.022	0.024	0.071	0.03	0.055	0.075	0.063	1.63	0.121	nd	nd	nd	nd	nd	nd	nd	20.29	6.18
RS	29/03/05	48.70	6.22	31.90	0.079	0.020	0.022	0.068	0.03	0.056	0.059	0.065	1.28	0.122	0.03	0.00	0.01	74.63	2.74	12.00	0.08	19.58	5.94
RS	03/05/05	22.70	6.31	28.00	0.076	0.015	0.021	0.063	0.05	0.044	0.038	0.060	1.99	0.104	< 0.01	0.02	0.05	70.27	2.08	10.03	0.13	17.84	5.48
RS	31/05/05	11.10	6.40	28.60	0.078	0.013	0.021	0.065	0.05	0.044	0.038	0.058	1.78	0.119	< 0.01	0.01	0.03	68.14	1.95	13.35	0.12	17.60	5.45
RS	11/07/05	3.85	6.51	28.20	0.080	0.014	0.020	0.063	0.07	0.041	0.028	0.056	1.85	0.134	< 0.01	0.03	0.04	70.27	2.35	10.65	0.18	17.99	5.52
RS	22/08/05	6.88	6.52	29.00	0.089	0.020	0.023	0.069	0.07	0.056	0.032	0.057	2.92	0.127	0.06	0.07	0.01	68.03	3.14	10.04	0.22	19.91	6.24
RS	03/10/05	14.00	6.56	29.10	0.085	0.022	0.022	0.065	0.06	0.057	0.035	0.057	2.73	0.130	0.07	0.00	0.04	69.48	3.37	11.16	0.23	19.21	6.07
RS	28/11/05	4.70	6.16	32.20	0.089	0.020	0.024	0.070	0.06	0.059	0.049	0.067	1.20	0.143	nd	nd	nd	nd	nd	nd	nd	21.08	6.21
RS	07/02/06	8.05	6.44	33.20	0.089	0.021	0.024	0.075	0.04	0.057	0.059	0.071	1.20	0.143	0.03	0.00	0.02	74.11	2.66	11.50	0.08	21.48	6.55
RS	20/03/06	22.97	6.52	32.10	0.084	0.022	0.023	0.068	0.03	0.056	0.060	0.067	1.22	0.131	nd	nd	nd	nd	nd	nd	nd	20.06	6.16
RS	03/04/06	127.50	5.70	30.50	0.076	0.024	0.020	0.064	0.02	0.052	0.072	0.061	1.64	0.111	0.09	0.02	0.01	73.05	2.96	10.86	0.14	18.93	5.82
RS	22/05/06	10.70	6.45	28.00	0.082	0.017	0.022	0.064	0.05	0.045	0.041	0.062	1.72	0.115	0.07	0.01	0.03	65.82	2.80	10.44	0.15	18.97	5.75
RS	10/07/06	3.60	6.45	30.10	0.084	0.017	0.021	0.064	0.07	0.046	0.033	0.057	1.59	0.135	0.03	0.01	0.03	59.80	2.59	9.68	0.17	18.85	5.79
RS	21/08/06	22.40	6.01	22.90	0.098	0.005	0.012	0.047	0.04	0.030	0.001	0.056	7.03	0.089	0.05	0.01	0.03	70.00	2.45	10.54	0.18	13.23	4.71
RS	02/10/06	15.50	6.30	31.60	0.083	0.019	0.022	0.067	0.04	0.052	0.057	0.059	1.59	0.134	0.05	0.01	0.00	71.59	2.59	10.62	0.17	19.65	5.96
RS	Average		6.34	30.44	0.084	0.018	0.022	0.067	0.05	0.05	0.05	0.06	1.91	0.128	0.04	0.01	0.03	69.31	2.61	11.03	0.14	19.41	5.96
atmpsheric inputs	Average data																						
Rain	2004-2006		5.21	15.73	0.011	0.004	0.002	0.005	0.01	0.012	0.038	0.016	1.01	0.000	0.01	0.01	0.01	3.77	1.47	0.85	0.01		
Throughfalls spruces	2004-2006		5.18	34.11	0.048	0.069	0.011	0.027	0.01	0.058	0.074	0.041	8.80	0.003	0.10	0.31	0.02	9.34	13.99	3.37	0.01		
Throughfalls beeches	2004-2006		5.75	23.14	0.026	0.074	0.006	0.010	0.04	0.029	0.033	0.022	6.42	0.005	0.02	0.02	0.03	11.41	28.70	1.02	0.00		

2004-2006	water fluxes	Na fluxes	K fluxes	Mg fluxes	Ca fluxes	Si fluxes	Sr fluxes	U fluxes
	(mm)	mg/m ² /yr	mg/m ² /yr	mg/m ² /yr	mg/m ² /yr	mg/m ² /yr	µg/m ² /yr	µg/m ² /yr
rain - F_{rain}	1247	306	219	56	256	5	1.1	7.6
throughfall - $F_{\text{throughfall}}$	1070	1041	3037	256	1034	101	2.4	12.6
<i>biological contribution to throughfalls C_b (1.2.3.4)</i>		0.2	0.9	0.3	0.25	0.1	nd	nd
Atmospheric contribution to throughfall - $F_{\text{throughfall(corrected)}}$		833	304	179	776	91	nd	nd
global atmospheric input (a)	1096	754	291	161	697	78	1.1 to 2.4	7.6 to 12.6
outlet fluxes (b)	850	1634	608	456	2276	3008	8.8	113
rain-corrected outlet fluxes (c)	850	1328	388	399	2019	3003	7.7	105
(wet+dry atmos. deposits)-corrected outlet fluxes (d)	850	880	317	295	1579	2929	7.7 to 6.6	105 to 101

Samples	date	⁸⁷ Sr/ ⁸⁶ Sr	2sigma	²³⁴ U/ ²³⁸ U	2sigma	altitude (m)
Spring CS1	28/09/04	0.72573	0.00002	0.880	0.001	1080
CS1	13/12/04	0.72656	0.00004	0.875	0.005	1080
CS1	29/03/05	0.72780	0.00001	0.892	0.003	1080
CS1	22/05/06	0.72650	0.00001	0.886	0.002	1080
CS1	Average	0.72665		0.883		
Spring CS2	03/05/05	0.72546	0.00001			1055
CS2	11/07/05	0.72376	0.00001			1055
CS2	22/05/06	0.72544	0.00001	0.875		1055
CS2	02/10/06	0.72515	0.00001			1055
CS2	Average	0.72495		0.875		
Spring CS3	13/12/04	0.72325	0.00002	0.823	0.003	1098
CS3	29/03/05	0.72328	0.00001	0.827	0.003	1098
CS3	11/07/05	0.72314	0.00002			1098
CS3	22/05/06	0.72325	0.00001	0.819	0.004	1098
CS3	Average	0.72323		0.823		
Spring CS4	03/05/05	0.72490	0.00002	0.866	0.003	1050
CS4	11/07/05	0.72375	0.00001			1050
CS4	22/05/06	0.72353	0.00001	0.867	0.002	1050
CS4	02/10/06	0.72548	0.00001			1050
CS4	Average	0.72442		0.867		
Spring BH	12/07/04	0.72262	0.00002	1.106	0.005	915
BH	13/12/04	0.72289	0.00002	1.1	0.003	915
BH	29/03/05	0.72359	0.00001	1.101	0.003	915
BH	03/05/05	0.72340	0.00001	1.1	0.003	915
BH	31/05/05	0.72319	0.00001	1.112	0.003	915
BH	11/07/05	0.72279	0.00001	1.101	0.003	915
BH	22/08/05	0.72287	0.00001	1.106	0.003	915
BH	03/10/05	0.72307	0.00001	1.105	0.003	915
BH	22/05/06	0.72334	0.00002	1.099	0.004	915
BH	Average	0.723084		1.103		
Spring RUZS	13/12/04	0.72700	0.00002	0.945	0.004	950
RUZS	29/03/05	0.72665	0.00001	0.941	0.003	950
RUZS	22/05/06	0.72669	0.00001	0.949	0.003	950
RUZS	Average	0.72678		0.945		
Spring RH	28/09/04	0.72206	0.00008	0.996	0.003	980
RH	13/12/04	0.72240	0.00002	0.991	0.004	980
RH	29/03/05	0.72257	0.00002	0.993	0.005	980
RH	22/05/06	0.72242	0.00001	0.991	0.004	980
RH	Average	0.72236		0.993		
Spring SG	28/09/04	0.72353	0.00002	0.91	0.004	1093
SG	13/12/04	0.72328	0.00007	0.93	0.003	1093
SG	29/03/05	0.72352	0.00002	0.923	0.004	1093
SG	22/05/06	0.72354	0.00002	0.927	0.002	1093
SG	Average	0.72347		0.923		
Spring SH	28/09/04	0.72749	0.00003	0.916	0.003	1050
SH	13/12/04	0.72720	0.00009	0.915	0.003	1050
SH	29/03/05	0.72801	0.00002	0.914	0.004	1050
SH	03/05/05	0.72798	0.00001			1050
SH	22/05/06	0.72720	0.00001	0.911	0.004	1050
SH	02/10/06	0.72752	0.00001			1050
SH	Average	0.72757		0.914		
Outlet RS	29/03/05	0.72573	0.00002	0.939	0.003	883
RS	22/05/06	0.72520	0.00001	0.974	0.004	883
RS	Average	0.72547		0.957		
atmospheric inputs	Average					
Rain	2004-2006	0.7111		1.175		
Throughfalls spruces	2004-2006	0.71290		1.079		
Throughfalls beeches	2004-2006	0.71620		0.953		
clays SS under beeches	35 cm depth	0.872847	0.00002	1.26	0.003	
clays SS under beeches	95 cm depth	0.767439	0.00001	1.074	0.002	
clays NS under spruces	35 cm depth	0.830034	0.00001	1.094	0.002	
clays NS under spruces	95 cm depth	0.802886	0.00001	nd		