Chemical and U–Sr isotopic variations in stream and source waters of the Strengbach watershed (Vosges mountains, France)

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Abstract. This is the first comprehensive study dealing with major and trace element data as well as ^{87}Sr/^{86}Sr isotope and (^{234}U/^{238}U) activity ratios (AR) determined on the totality of springs and brooks of the Strengbach catchment. It shows that the small and more or less monolithic catchment drains different sources and streamlets with very different isotopic and geochemical signatures. Different parameters control the diversity of the source characteristics. Of importance is especially the hydrothermal overprint of the granitic bedrock, which was stronger for the granite from the northern slope; also significant are the different meteoric alteration processes of the bedrock causing the formation of 0.5 to 9 m thick saprolite and above the formation of an up to 1m thick soil system. These processes mainly account for springs and brooks from the northern slope having higher Ca/Na, Mg/Na, and Sr/Na ratios, but lower ^{87}Sr/^{86}Sr isotopic ratios than those from the southern slope. The chemical compositions of the source waters in the Strengbach catchment are only to a small extent the result of alteration of primary bedrock minerals, and rather reflect dissolution/precipitation processes of secondary mineral phases like clay minerals.

The (^{234}U/^{238}U) AR, however, are decoupled from the ^{87}Sr/^{86}Sr isotope system, and reflect to some extent the level of altitude of the source and, thus, the degree of alteration of the bedrock. The sources emerging at high altitudes have circulated through already weathered materials (saprolite and fractured bedrock depleted in ^{234}U), implying (^{234}U/^{238}U) AR below 1, which is uncommon for surface waters. Preferential flow paths along constant fractures in the bedrocks might explain the – over time – homogeneous U AR of the different spring waters. However, the geochemical and isotopic variations of stream waters at the outlet of the catchment are controlled by variable contributions of different springs, depending on the hydrological conditions.

It appears that the (^{234}U/^{238}U) AR are a very appropriate, important tracer for studying and deciphering the contribution of the different source fluxes at the catchment scale, because this unique geochemical parameter is different for each individual spring and at the same time remains unchanged for each of the springs with changing discharge and fluctuating hydrological conditions. This study further highlights the important impact of different and independent water pathways on fractured granite controlling the different geochemical and isotopic signatures of the waters. Despite the fact that soils and vegetation cover have a great influence on the water cycle balance (evapotranspiration, drainage, runoff), the chemical compositions of waters are strongly modified by processes occurring in deep saprolite and bedrock rather than in soils along the specific water pathways.

1 Introduction

Large rivers carry erosion products from the different drainage areas and, therefore, are pathways of continental weathering products that finally enter the oceans. Thus, they fetch the various chemical and isotopical characteristics of the different drainage basins and, therefore, allow elucidation of erosion processes, derivation of erosion rates and illustration of the biogeochemical cycling of elements. Many

of the major world rivers are well documented with major and trace element and isotope data on dissolved and suspended phases, which provide the different factors controlling chemical and physical denudation (Degens et al., 1991; Dupré et al., 2003; Gaillardet et al., 1999; Martin and Meybeck, 1979; Négrel et al., 1993). At the large catchment scale, the stream waters' chemical composition is generally the result of mixing between phases derived from the different main lithologies (e.g. Bickle et al., 2006; Blum et al., 1998; Chabaux et al., 2001; Millot et al., 2003; Steinmann and Stille, 2009; Tipper et al., 2006; Zakharova et al., 2007). The impact and the role of vegetation cover and soils on the chemical or isotopical evolution of erosion signals in waters of small catchments have very recently been discussed (Laudon et al., 2004; Cenki-Tok et al., 2009; Cividini et al., 2010; Engstrom et al., 2010; Kohler et al., 2014; Lemarchand et al., 2010; Zakharova et al., 2007). Determination of parameters controlling the chemical composition of superficial waters is important for correct modelling of the future evolution of ecosystems in response to external natural or anthropogenic forcing such as climate evolution and atmospheric pollution (trace metal depositions, acid rain, etc.). Among these parameters, water–rock interactions (including secondary phases such as clays), hydrological processes and biological activities play an important role in affecting mobilisation, (re)cycling and fractionation of elements; their specific influences on weathering processes at the watershed scale remain a matter of discussion (Brantley et al., 2008).

Because natural systems are subject to complex and multiple reactions, the combination of different geochemical and isotopical tools is necessary to decipher the different natural processes. $^{87}Sr/^{86}Sr$ isotopic ratios and $(^{234}U/^{238}U)$ AR have successfully been used in the discussion of hydrological and hydrochemical processes at the catchment scale (e.g. Riotte and Chabaux, 1999; Tricca et al., 1999; Aubert et al., 2002; Bagard et al., 2011; Bickle et al., 2005; Bonotto and Andrews, 2000; Chabaux et al., 2011; Durand et al., 2005; Schaffhauser et al., 2014). Indeed, when the U system has been closed for approximately 1 million years, minerals and rocks are in secular equilibrium and activities of all parents and daughters from ^{238}U decay chain are identical and the $(^{234}U/^{238}U)$ AR is equal to 1. However, this ratio can fractionate during chemical weathering when ^{234}U is more easily released into solution by the combined effects of (1) direct recoil out of mineral of ^{234}Th near grain boundaries and (2) preferential release from crystal lattices that are damaged by energetic α decay (e.g. Bourdon et al., 2009; Chabaux et al., 2003, 2008; DePaolo et al., 2006, 2012; Osmond and Ivanovich, 1992, and references therein). Therefore, natural waters (stream, spring, groundwaters, seawaters) are generally in excess of ^{234}U, with $(^{234}U/^{238}U)$ AR above 1 (Andrews and Kay, 1983; Camacho et al., 2010; Chabaux et al., 2003, 2008; Dosseto et al., 2008, 2012; Gryzmko et al., 2007; Osmond and Ivanovich, 1992; Paces et al., 2002; Pierret et al., 2012; Vigier et al., 2001, 2006).

Consequently, $(^{234}U/^{238}U)$ AR in superficial waters allow to identify river-flow patterns, and hydrological mixing by tracing the sources of water and recording mixing between superficial and groundwaters characterized by different U AR. Thus, the $(^{234}U/^{238}U)$ AR change along river flows and as a function of hydrological mixing (e.g. Chabaux et al., 2001; Durand et al., 2005; Maher et al., 2006; Osmond and Cowart, 1982; Paces et al., 2002; Riotte and Chabaux, 1999).

In the present paper we focus on a small, more or less monolithic drainage basin, the experimental Strengbach catchment (Vosges mountains, northeastern France). Several studies have shown that the vegetation cover, the atmospheric deposition, the secondary minerals and the biological recycling play an important role in controlling the geochemical signatures of soil solutions (Brioshi et al., 2013; Lemarchand et al., 2010, 2012; Prunier, 2008; Stille et al., 2006, 2009, 2011, 2012). The impact of physico-chemical processes in soil on the chemical balance of waters at the outlet is rather weak. For instance, the mean annual flux of Ca in soil solution at 60 cm depth represents 5 to 20 % of the annual flux at the outlet, depending on the type of vegetation or soil (Cenki-Tok et al., 2009). Therefore, the chemical compositions of waters are mainly controlled by interactions occurring with the deep saprolite and bedrock rather than with soils.

A previous U isotope study performed on waters from the Strengbach streamlet shows a decrease in the $(^{234}U/^{238}U)$ AR from 1.02 to 0.96 when the discharge of the stream increases (Riotte and Chabaux, 1999). Such an isotopic evolution has been interpreted as mixing between a water body enriched in ^{234}U, which is supposed to have interacted with a granitic bed rock at secular equilibrium, and waters with a $(^{234}U/^{238}U)$ AR below unity pointing to mobilisation of U from material that has already been weathered. Similarly, the streamlets $^{87}Sr/^{86}Sr$ isotope ratios collected during low flow periods have low$^{87}Sr/^{86}Sr$ ratios than during high water flow events (Aubert et al., 2002). The Sr signature at low discharge has been explained by important contributions of waters from the deep soil profile during the recession stage, whereas higher $^{87}Sr/^{86}Sr$ isotope ratios at higher discharge are due to important contributions of waters from the saturated area of the catchment.

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

2 Site description

The Strengbach catchment is a small granitic watershed ($0.8\,km^2$) where meteorological, hydrological and geochemical data have been recorded since 1986 (Observatoire Hydro-Géochimique de l'Environnement; OHGE; http://ohge.u-strasbg.fr). The first studies were performed in order to understand the impact of acid rain on the forested ecosystem (Dambrine et al., 1991, 1992a, b; Probst et al., 1990, 1992a, b). The catchment is situated in the Vosges Mountains (northeastern France) at altitudes between 880 and 1150 m (a.m.s.l.), and has strongly inclined slopes (mean 15°; Fig. 1).

The climate is temperate oceanic mountainous (mean annual temperature of 6 °C; mean monthly temperature range from -2 to 14 °C) with an average rainfall of $1400\,mm\,yr^{-1}$ (ranging from 890 to $1630\,mm\,yr^{-1}$ over the period 1986–2006) and with snowfall during 2–$4\,month\,yr^{-1}$; Viville et al., 2012; OHGE data). The mean annual runoff for the same period is of 853 mm ($26.9\,L\,s^{-1}\,km^{-2}$) and ranges from 525 to 1147 mm over 1986–2006 (Ladouche et al., 2001; OHGE data). The evapotranspiration (ETP) has been evaluated to be about 40 % on the site (Aubert et al., 2001; Probst et al., 1992a, b).

The bedrock is mainly composed of a Hercynian base-poor granite ($332 \pm 2\,Ma$) (Boutin et al., 1995), with low Ca and Mg contents (less than 1 % for both); it suffered different degrees of hydrothermal alteration some 180 Ma ago (Fichter et al., 1998). In addition to the granite, which is strongly hydrothermally altered on the northern slope and comparatively weakly altered on the southern slope, small micrograni-te and gneiss bodies outcrop at the southern and northern slopes (Fig. 1) (El Gh'mari, 1995; Fichter et al., 1998). The gneiss is enriched in Mg mainly because of the presence of biotite and chlorite (El Gh'mari, 1995; Fichter, 1997). Hydrothermal processes caused the alteration and transformation of albite, K-feldspar and muscovite into fine-grained illite and quartz; biotite and albite disappeared to a large extend. The strongly altered granite (on the northern slope) is characterised by larger amounts of quartz, clays and Fe-oxides, small amounts of apatite ($< 1\,\%$), and by higher Mg but lower Ca, K and Na contents than the less altered granite at the southern slope (El Gh'mari, 1995; Fichter et al., 1998). In addition, the northern sun-facing slope is characterised by a drier and slightly warmer climate with 10 % less precipitation than observed for the southern slope. The soils are brown acidic to ochreous brown podzolic and are generally about 1 m thick. They are very coarse grained, sandy and rich in gravel (Fichter et al., 1998). The brown acidic soils are mainly located on the northern slope and are characterised by higher clay contents, lower K-feldspar, lower albite, higher cation exchange capacity (CEC), lower pH and lower organic matter content than the ochreous brown podzolic soils, which are mainly located on the southern slope (Fichter, 1997; Fichter et al., 1998). The pedological differences are due to the different mineralogical compositions of
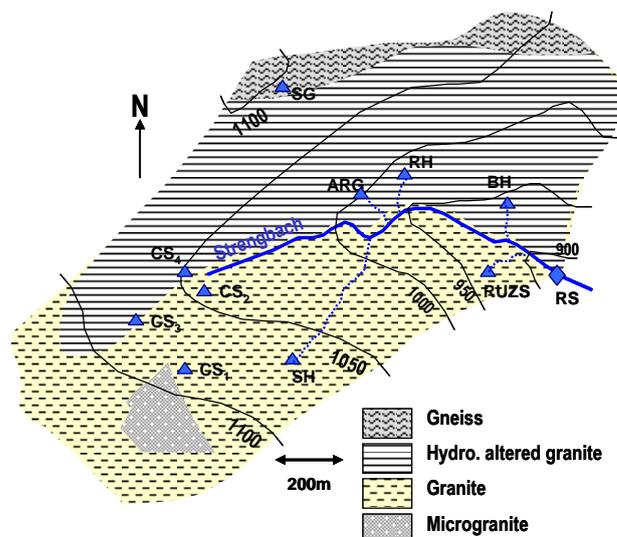
Figure 1. Map of the Strengbach catchment showing the principal lithological units and the location of the 10 studied springs (SG, RH, ARG, BH, CS1, CS2, CS3, CS4, SH, RUZS). RS corresponds to the Strengbach stream at the outlet of the studied catchment.

the northern and southern bedrocks, and the different types of vegetation but also the different orientations of the slopes. Indeed, exposure and consequently rainfall and temperature influence the chemical weathering of soils and organic matter, the soil acidity and processes of clay formation (Egli et al., 2007, 2010).

A sandy saprolite separates soil and granite. Its thickness varies between 1 and 9 m; on the southern slope it is generally thicker (El Gh'mari, 1995) with the most important thickness in the depression zone near the four springs CS1, CS2, CS3 and CS4. The forest covers 90 % of the area and corresponds to about 80 % spruce (mainly *Piceas Abies* L.) and 20 % beech (*Fagus Sylvatica*). The catchment contains 10 different springs feeding the Strengbach streamlet (Fig. 1).

The catchment is situated in a remote area lacking direct industrial activities. Nevertheless, atmospheric pollution occurs in many forms (acidic deposition, O_3 pollution or as atmospheric dust deposition). Anthropogenic Pb has been identified in the atmospheric dust depositions and soils (Lahd Geagea et al., 2008b; Stille et al., 2011). The forestry has increased the proportion of spruce with especially dense spruce plots planted between 1890 and 1960. The site is well equipped for sampling of atmospheric depositions and spring and stream waters at the whole catchment scale.

For this study, the stream and the different springs of the catchment were collected during various hydrological periods with high and low water levels during two hydrological years 2004/2005 and 2005/2006 in order to obtain a precise chemical and isotopic signature of the different sources in this hydrological system (Fig. 1). The springs SG, ARG, RH, BH, CS3 and CS4 are located on the northern slope and

the springs CS_1, CS_2, SH and RUZS emerge at the southern slope (Fig. 1). The spring RUZS is situated in the humid zone at the bottom of the catchment near the outlet (saturated area, Fig. 1) and covered by dense grass vegetation. In addition, rain (bulk precipitation) and throughfalls were collected using rain collectors and gutters, respectively.

3 Analytical procedures

The different spring waters were collected every 6 weeks for 2 years, unless the springs were dry or under snow. The waters were collected in clean polyethylene (HDPE) bottles (250 mL for major element analysis and 1 litre for isotope and trace element analysis) and filtered the same day through a 0.45 μm pore diameter membrane (Millipore ester cellulose, 142 mm diameter). Before, the HDPE bottles were washed with HCl 10 % (24 h contact) and then rinsed with MilliQ deionised water. The filtrated waters for trace element and U–Sr isotopic composition determinations were acidified with 250 μl of ultrapure HNO_3 13M and then stored in a cold room at 5 °C.

The pH were measured just after filtration using a pHM210 MeterLab (Radiometer analytical) with an Mettler HA405-DXKS8 electrode and calibrated with standard buffer solutions (pH 4.00 and 7.00 at 25 °C). The precision of the pH measurement was ±0.02 units. The electrical conductivity and the alkalinity were determined respectively using a CDM210 MeterLab (radiometer analytical) with an CDC 745-9 electrode (precision 0.1 μS cm⁻¹) and with 716DMS Titrino (Metrohm; precision of 0.01 meq L⁻¹ – Acid/base titration, Gran method).

The major element contents were determined by ionic chromatography, atomic absorption, colorimetry and ICP-AES and the trace element concentrations were determined by ICP-MS (Pierret et al., 2009; Chabaux et al., 2011). The analytical uncertainty of the major cation and anion determinations in solution (by atomic absorption and ionic chromatography Dionex, 4000 I) is ±2 %. The uncertainty on the major element concentrations such as Fe, Al, Mn and Si (by ICP-EAS, Jobin Yvon 124) is ±5 %, and that of the trace element concentrations (by ICP-MS, VG Plasma Quad; Thermo Electron) is ±5 %. The dissolved organic carbon (DOC) was determined using an organic carbon analyser (Shimadzu TOC-5000A) with an uncertainty of 5 to 10 %, The accuracy of the analysis was assessed by regular analysis of the SLRS-4 riverine standards,

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

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

4 Results

Previous studies performed on the Strengbach watershed mainly focused on the geochemical and isotopic variations of dissolved loads of the stream waters collected at its outlet. The new results (Tables S1 and S2 in the Supplement) yield a first complete data set of the spatial variability of major and trace element concentrations as well as Sr and U isotope ratios of the spring and streamlet waters emerging on the Strengbach watershed. The data also allow us to present the geochemical variability of the source as well as stream waters at the outlet of the watershed over the period 2004–2006, that is to say during two hydrologic cycles.

4.1 The major and trace element data

Among the spring and stream waters the pH, alkalinity, DOC, TDSw (total dissolved solids, Table S1 in the Supplement), TDS-Ca (total dissolved solids cation; Table S1 in the Supplement) and conductivity are highly variable and range respectively from 5 to 6.85, from 0 to 0.16 meq L⁻¹, from 0.42 to 11.6 ppm, from 10.3 to 26.8 mg L⁻¹, from 3.87 to 9.05 mg L⁻¹, and from 13.2 to 60.3 μS cm⁻¹ (Table S1 in the Supplement). The pH is well correlated with alkalinity and TDS-Ca (Fig. 2). The range of variations of the major element concentrations at the watershed scale can be important but clearly depends on the chemical elements and the physico-chemical parameters. For the cation concentrations the variation at the watershed scale reaches about one order of magnitude for Mg, but only 20 to 30 % for Na concentrations. At the watershed scale, the most discriminating cation is Mg. SH and CS_1 sources are marked by weakest Mg and Ca and the SG source by highest concentrations (Table S1 in the Supplement). In addition, as illustrated by the Ca/Na, Mg/Na and H_4SiO_4/Ca concentration ratios (Fig. 3), but also by the K/Na, Sr/Na, Mg/Ca ratios (not shown), the different springs are not only marked by different mean major element concentrations (2004–2006 period), but also by different elemental ratios.

The data points of the different sources define linear trends with slopes different from each other (Fig. 3). The variation of the Ca/Na and Mg/Na ratios are much larger at the watershed scale than at the scale of a single spring. On the basis of the above data a clear distinction is possible between the
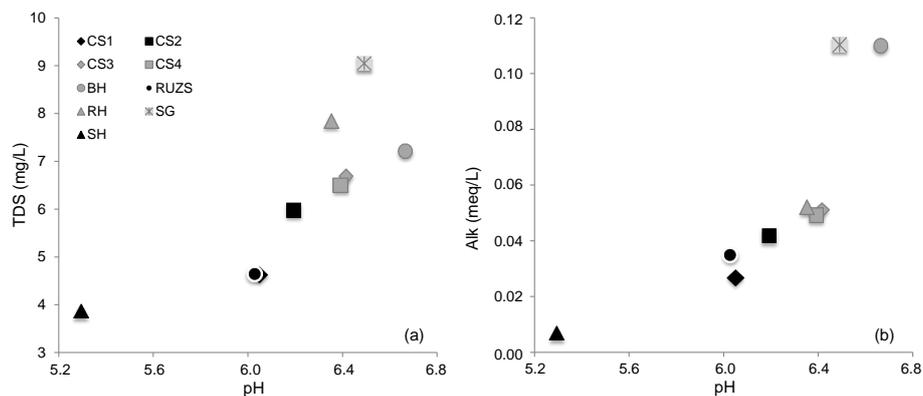
Figure 2. Physico-chemical characteristics of the different source waters of the Strengbach watershed (average values for the period 2004–2006). **(a)** pH vs. TDSw and **(b)** pH vs. Alk.
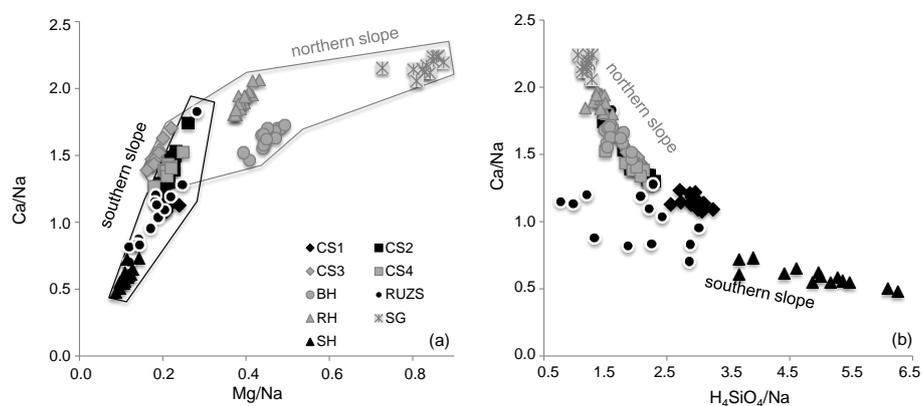
Figure 3. Major element concentration ratios of the 9 different individual source waters of the Strengbach watershed. **(a)** Ca/Na vs. Mg/Na and **(b)** Ca/Na vs. Si(OH)$_4$/Ca. In each diagram the spring waters from the southern slope show different compositions than those from the northern slope.

spring waters from the northern slope (SG, RH, ARG, CS$_3$, CS$_4$ and BH) and those from the southern slope (CS$_1$, CS$_2$, SH and RUZS), the former being characterised by higher pH, alkalinity, conductivity TDSw and Ca/Na, K/Na and Mg/Na ratios than the latter (Figs. 2 and 3; Table S1 in the Supplement). In addition to the spatial variations, the chemical signatures of waters also show temporal variations. These are strongest for the most DOC-enriched sources (RUZS, SH) and for the stream at the outlet (RS).

4.2 Sr and U isotope data

The ^{87}Sr/^{86}Sr isotopic composition values of the different spring waters are highly variable and range between 0.72206 (RH) and 0.72801 (SH) with an average Sr isotopic composition for the stream at the outlet of 0.72573 (Fig. 4, Table S1 in the Supplement). The data show a clear relationship between the Sr isotopic signature and the geographical location in the watershed; the springs from the northern slope are characterised by lower ^{87}Sr/^{86}Sr ratios and higher Sr concentrations (Fig. 4).

As shown in Fig. 6, the variation range of (^{234}U/^{238}U) AR in the source waters is much larger than that of the streamlets waters at the outlet. The U AR range from 1.112 (BH) to 0.819 (CS3); the average (^{234}U/^{238}U) AR for the stream at the outlet is 1.104. Of the nine springs analysed, eight of them have unusually low (^{234}U/^{238}U) AR below 1. In addition, and to the best of our knowledge, these values are the lowest ever published before for superficial waters. Indeed, the U AR measured in world surface rivers or groundwaters generally have (^{234}U/^{238}U) above 1 (see the introduction and citations therein).

In contrast to Sr isotopic compositions (Fig. 6) or chemical concentrations (Fig. 3) (^{234}U/^{238}U) AR of a single source do not significantly vary over the period 2004–2006 (Fig. 7). Finally, ^{87}Sr/^{86}Sr and ^{234}U/^{238}U AR of the source waters are not correlated with each other and in contrast to the Sr isotopic compositions or chemical concentrations (Fig. 6) there is no clear distinction between the U AR of the springs from the southern and northern slope. In the Strengbach watershed there is a clear increase of the U AR of the source
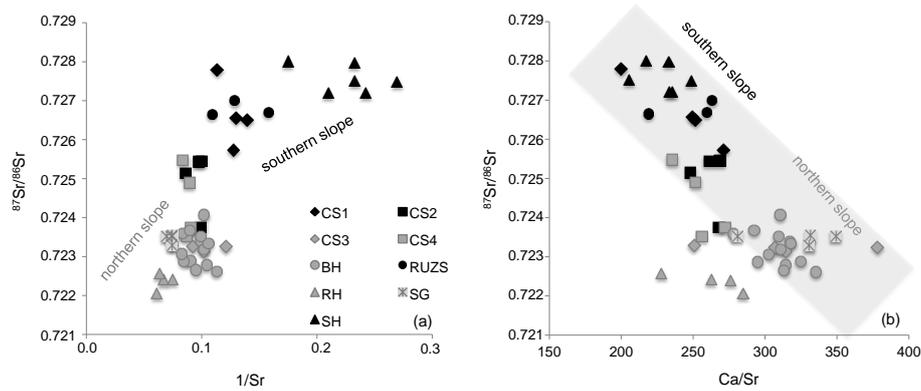
Figure 4. Relationships between $^{87}Sr/^{86}Sr$ isotope ratios and **(a)** $1/Sr$ (ppb); **(b)** Ca/Sr $(ppb\,ppb^{-1})$. The isotope ratios allow a clear distinction between northern and southern slope sources.

waters when the altitude of the spring decreases. A similar behaviour has been observed for waters from another small granitic watershed in the Vosges Mountains, the Ringelbach watershed (Schaffhauser et al., 2014). However, in contrast to the Ringelbach catchment, where the U AR in the spring waters are above 1, one observed for the spring waters of the Strengbach catchment U AR below or equal to 1, except for the BH source.

5 Discussion

5.1 Geochemical and Sr isotopic characteristics of the spring waters

As shown in the result section, the chemical characteristics of the sources are marked by an important spatial variation with in particular a clear distinction between the springs from the northern and the southern slope (Fig. 3), It appears that the Ca/Na, Mg/Na, and H_4SiO_4/Na concentration ratios are neither rainwater nor throughfall controlled. Indeed rainwater and throughfall show rather large variations of their Ca/Na or Mg/Na ratios (throughfall: Ca/Na: 0.9–2.1; Mg/Na: 0.3–0.6) and do not plot at one of the extremities of the correlations. Mass balance calculations show that the atmospheric input (including rain and througfalls) corresponds to various proportion of the exportation flux at the watershed scale, depending on type of element, as for example 2, 8 or 19 % for Si, U or Sr respectively (Table S3 in the Supplement).

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

Therefore, chemical differences between the sources of the Strengbach watershed have to be interpreted in terms of variations in the nature or in the intensity of water–rock interactions occurring from one source to another or in the intensity of the interactions between different water reservoirs. This interpretation is entirely consistent with the correlations observed for the spring waters at the watershed scale between the alkalinity, TDSw and their pH (Fig. 2; Table S1 in the Supplement), since consumption of H^+ during silicate weathering increases pH and alkalinity. Thus, from these data it appears that the spring waters from the northern slope with higher total dissolved solid contents, higher alkalinity and pH values (SG, CS4, CS3 and RH, with BH having the highest values) are more involved in weathering reactions, or are subject to more intense weathering processes than spring waters from the southern slope (especially SH, RUZS and CS1).

The geochemical signatures of the different springs can be generally linked to specific lithological and mineralogical differences existing for the two hillsides of the catchment. This is particularly obvious for the SG spring, which emerges near the top of the catchment, just below the gneiss, whereas the other sources emerge within the granitic environment (Fig. 1). In comparison with the granite, the gneiss has 4 to 5 times higher Mg concentrations due to important occurrences of biotite and chlorite (El Gh'mari, 1995; Table S4 in the Supplement). The Mg/Na and Mg/Ca elemental ratios are about 7.5 respectively 11 for the gneiss and range from 0.7 to 0.1 respectively 0.5 to 1.5 for the granite (El Gh'Mari, 1995; Fichter, 1997; Table S4 in the Supplement). Mg is also more concentrated in the gneiss-derived soils (MgO : 0.9 to 1.4 wt. %), than in other soil profiles of the catchment (0.4 to 0.7 wt. %) (El Gh'Mari, 1995; Lefèvre, 1988; Table S4 in the Supplement). Similarly, the Ca/Na ratios of the gneiss (0.71) and the corresponding soils (0.7 to 9.2) are higher than those of the granite (0.2 to 0.6) or of the corresponding soils (0.1 to 0.5) (El Gh'Mari, 1995; Fichter, 1997; Table S4 in the Supplement). All these lithological and pedological characteristics explain why the SG

spring waters are more enriched in Mg and have higher Mg/Ca, Mg/Na and Ca/Na ratios than the other springs (Fig. 3).

The variation of the chemical data of the other spring waters emerging from the granite might result from the specific characteristics of the two hillsides, which show different types and thicknesses of soils and saprolite and different degrees of hydrothermal alteration of the granitic bedrock (Lefèvre, 1988; Fichter, 1997; El Gh'Mari, 1995; see also geological setting). Indeed, the study of 13 weathering profiles from the whole Strengbach catchment points to important variations in the mineralogical composition of soils and bedrocks at the catchment scale (El Gh'Mari, 1995; Fichter, 1997; Aubert et al., 2001; Prunier, 2008; Stille et al., 2009). The soils from the northern slope are brown acidic and overlay a 0.5 to 4 m thick saprolite. At the southern slope, however, an ochreous podzolic soil type overlays a much thicker 4 to 9 m deep saprolite (El Gh'mari, 1995; Fichter et al., 1998). The bedrock from the northern slope was subjected to stronger hydrothermal alteration, which caused disappearance of albite and biotite, diminution of K-feldspar but an increase of quartz, clays and white mica contents and the occurrence of hematite (Fichter, 1997; El Gh'Mari, 1995). The hydrothermally strongly altered granite on the northern slope is characterised by generally higher Mg and lower Ca and Na contents than observed for the less altered granite on the southern slope (Fichter et al., 1998; El Gh'Mari, 1995; Table S4 in the Supplement). This could account for the comparatively higher Mg concentrations and Mg/Na ratios of the sources from the northern slope, but not for e.g. the higher Ca or K concentrations.

The $^{87}Sr/^{86}Sr$ ratios of springs from the southern slope (SH, CS$_2$, CS$_1$, RUZS) are, like the corresponding rocks and soils (Aubert et al., 2002) (Fig. 7), more radiogenic with lower Sr concentrations than those from the northern slope (BH, RH, SG, CS$_3$, CS$_4$) (Fig. 4). Thus, the Sr isotopic compositions of springs can be directly related to the signatures of the weathering profile and their geographical localisation. However, the mineral phases involved in the weathering processes and causing the geochemical characteristics of these superficial waters are still a matter of discussion.

Based on Sr and Nd isotope ratios, Aubert et al. (2001) explained the isotopic signature of the Strengbach stream water by mixing of two isotopically different end-members: apatite and plagioclase. However, the Mg/Sr and Mg/Ca ratios of the waters cannot simply be explained by dissolution of apatite and plagioclase (Fig. 8a and b). In addition, biotite and muscovite have far too high Sr isotopic ratios (respectively 5.8 and 5.4; Aubert et al., 2001) and thus their contribution can be ignored. The clay fractions, extracted from the two weathering profiles at sites HP and VP (Prunier, 2008) can represent an end-member able to explain the Sr isotopic composition as well as the Mg/Ca and Mg/Sr ratios of springs. The springs, bulk soils and clays from the southern slope show higher $^{87}Sr/^{86}Sr$ ratios than those from the

northern slope. Clay fraction contents in weathering profiles from northern slope are twice as big as those from the southern slope. This suggests that the impact of clay on the chemical composition of springs and streams is more important on the northern than the southern slope. This also explains why the springs from the northern slope are more radiogenic (Fig. 4a and b) with comparatively higher Mg/Ca and Mg/Sr ratios (Fig. 8a and b) than those from southern slope.

Such an interpretation is consistent with results of numerical modelling, which indicates that precipitation/dissolution of more or less crystallised clay minerals (such as smectite) control the Mg concentrations and possibly the high Mg/Ca ratios in the source waters of the Strengbach watershed (Godderis et al., 2006, 2009). The same authors proposed that Mg^{2+} is controlled by smectites, Ca^{2+} by the dissolution of apatite and by smectite, and K^+ by smectite/illite precipitation and dissolution of K-feldspar. Interaction with clays might occur all along the circulation pathway of waters in soils, saprolite and in bedrock fractures. Recent studies in the Mule Hole watershed, Mackenzie basin and Damma Glacier catchment confirm the importance of secondary mineral formation, especially montmorillonite in the control of chemical composition of stream water at the watershed scale (Violette et al., 2010; Beaulieu et al., 2011; Hindshaw et al., 2011).

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

5.2 234U/^{238}U AR in spring waters

Observation of ($^{234}U/^{238}U$) AR below 1 in most of the spring and stream waters of the Strengbach catchment is unusual, as river waters generally exhibit ^{234}U excess (e.g. Chabaux et al., 2003). U AR below 1 have already been observed for waters from the outlet of the Strengbach catchment (0.963 to 1.023), with a decrease in the U AR in the dissolved load when the discharge increases (Riotte and Chabaux, 1999). The authors explained this variation by the involvement of different weathered end-members: a water body enriched in ^{234}U which weathered the granitic bedrock at secular equilibrium and waters with a U AR below unity representing mobilisation of U from material that has already been weathered. Our study shows an even larger range of variation of the U AR among the different springs ranging from 0.819 (CS3) to 1.112 (BH) (Table S2 in the Supplement). The lack of
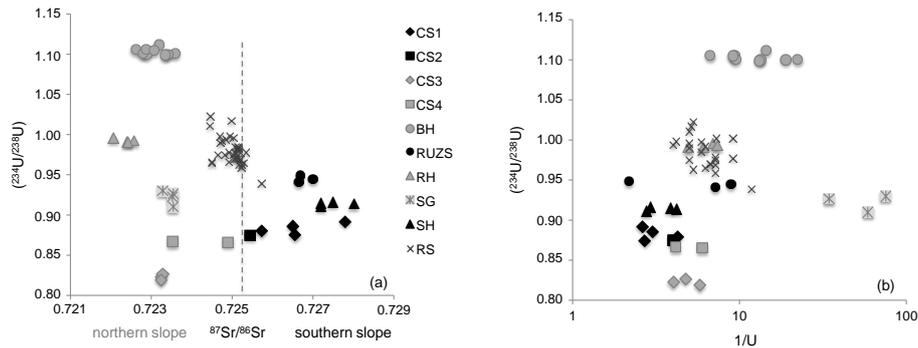
Figure 5. Relationship between $(^{234}U/^{238}U)$ AR and **(a)** $1/U$ and, **(b)** $^{87}Sr/^{86}Sr$. In contrast to Sr isotopic compositions, the U AR of springs do not allow to distinguish between the northern and southern slopes.
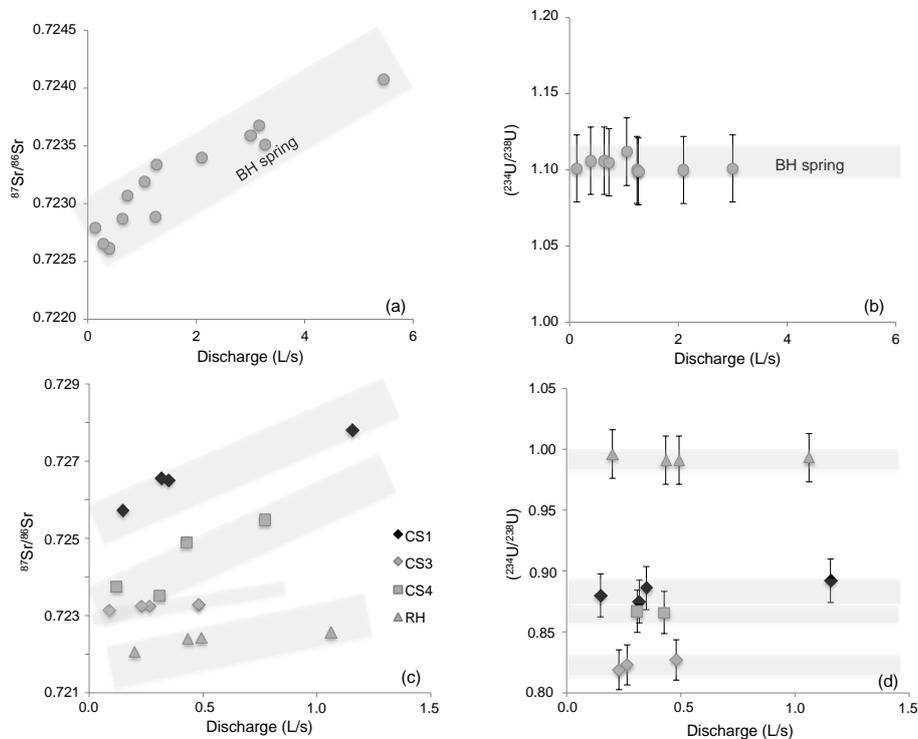

Figure 6. $^{87}Sr/^{86}Sr$ and $(^{234}U/^{238}U)$ AR vs. discharge for the springs BH, CS1, CS3, CS4 and RH from the Strengbach watershed.

correlation between $(^{234}U/^{238}U)$ AR and $^{87}Sr/^{86}Sr$ isotopic compositions or chemical values (Fig. 5a and b) show that AR are not simply lithology controlled.

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

mobilised out of the damaged site. As a consequence, the daughter nuclide ^{234}U is preferentially leached relative to the parent ^{238}U during weathering. Thus, natural waters with $(^{234}U/^{238}U)$ AR below 1 most likely correspond to environments which have already experienced a loss of ^{234}U.

One might simply suggest that the U AR below 1 in the Strengbach source waters are the results of circulation through already weathered soils supposedly having U AR below 1 due to previous weathering. However, chemical flux balance calculations show that the annual U fluxes from the soils under spruces or beech trees represent at maximum about 8 or 22 %, respectively, of the annual U flux at the outlet (Table S3 in the Supplement). At the same time, the
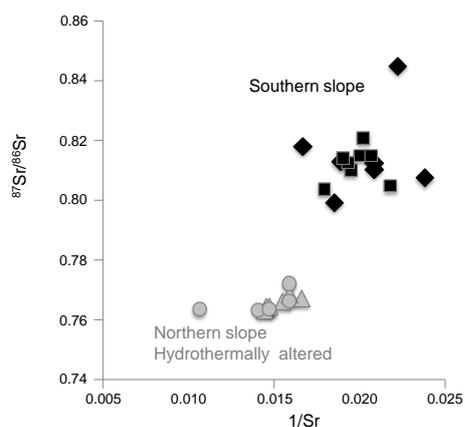
Figure 7. ^{87}Sr/^{86}Sr vs. 1/Sr for the soil and saprolite samples from the Strengbach watershed. The samples from the northern slope and those from the southern slope are clearly different (Aubert et al., 2001; Stille et al., 2009; Prunier, 2008).

U concentrations in the different springs can reach on average 0.345 ppb whereas they range only between 0.011 to 0.023 ppb (factor of 30 to 15 lower) in the deep soil solutions of the two experimental plots (Table S2 in the Supplement). In addition, (^{234}U/^{238}U) AR determined on soil solutions from depths between 5 and 70 cm, range from 0.899 and 0.945 under spruces and from 0.953 to 1.194 under beech trees (Prunier, 2008), whereas they are significantly low for some spring waters (0.82). This indicates that circulations and interactions in the saprolite and bedrock (below the soil) control the U isotopic signature in spring and stream waters.

The relationship between the U AR and the altitude of the springs (Fig. 9) indicates that the springs from both slopes with the lower U AR (CS1, CS2, CS3, CS4) are located at higher altitude and circulate in zones where the saprolite reaches 7 to 9 m depth (El'Ghmari, 1995) than springs with high U AR. The spring BH, with the highest U AR is located at the bottom of the watershed where the saprolite layer reaches less than 1.5 m in thickness (Fig. 1). RUZS was also taken at low altitude (950 m a.s.l.), but drains the whole wetland and, therefore, integrated an intermediate U AR. Thus, a possible scenario explaining the (^{234}U/^{238}U) AR of the spring waters is that BH-like sources are closer to the "fresh" granite, and reflect meteoric alteration of fresher rock material at secular equilibrium. CS_1, CS_3, CS_2, CS_4 and SH sources, by contrast, drain thicker saprolite profiles and/or less fresh granite and, therefore, their low AR may point to the mobilisation of U from mineral phases whose outermost surfaces have already been depleted in ^{234}U due to previous water–rock interactions (old saprolite where the pool of excess ^{234}U has been exhausted). We therefore propose that the ^{234}U/^{238}U AR in the catchments spring waters can be interpreted as a function of water pathways. The sources emerging at high altitudes, with AR below 1, have circulated through already weathered horizons (sapro-

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

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

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

However, the springs emerging at lower altitudes (mainly BH and to a lesser extend RH), with (^{234}U/^{238}U) above 1, circulate through fresher granite, where α recoil tracks have direct contact with the outer mineral surfaces and thus with fresh mineral phases (Andersen et al., 2009).

At this point it is interesting to note that in a neighboured granite catchment (the Ringelbach watershed), all the sources only display U AR above 1 (Schaffhauser, 2013; Schaffhauser et al., 2014). This small catchment located in the Vosges massif at altitudes between 750 and 1100 m (0.36 km^2) also consists of Hercynian granite capped in its upper part by residual Triassic sandstones (Schaffauser et al., 2014).

Plotting the U AR of springs of the both watersheds versus alkalinity and pH (Fig. 10) one observes a good correlation where springs with highest U AR are characterised by highest alkalinity and pH values. These two parameters can be considered to reflect the intensity of weathering and water–rock interactions, meaning that the waters from the Ringelbach watershed are characterised by more intense weathering. Only the SG spring from the Strengbach catchment shows a slightly different behaviour, because it originates from a gneiss and not a granite body (see Sect. 5.1). The modelling of chemical composition of the waters from the Ringelbach catchment implies mainly dissolution of primary granite minerals and precipitation of
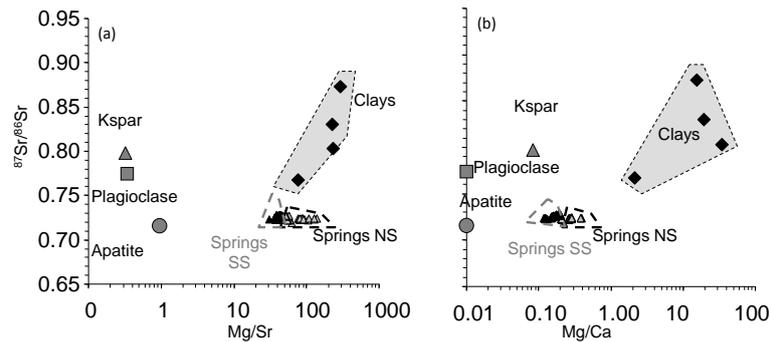
Figure 8. $^{87}Sr/^{86}Sr$ vs. Mg/Ca (**a**) and Mg/Si (**b**) for the spring waters (NS = northern slope and SS = southern slope), primary minerals of the granite (Aubert et al., 2001) and clays from soils (Prunier, 2008).
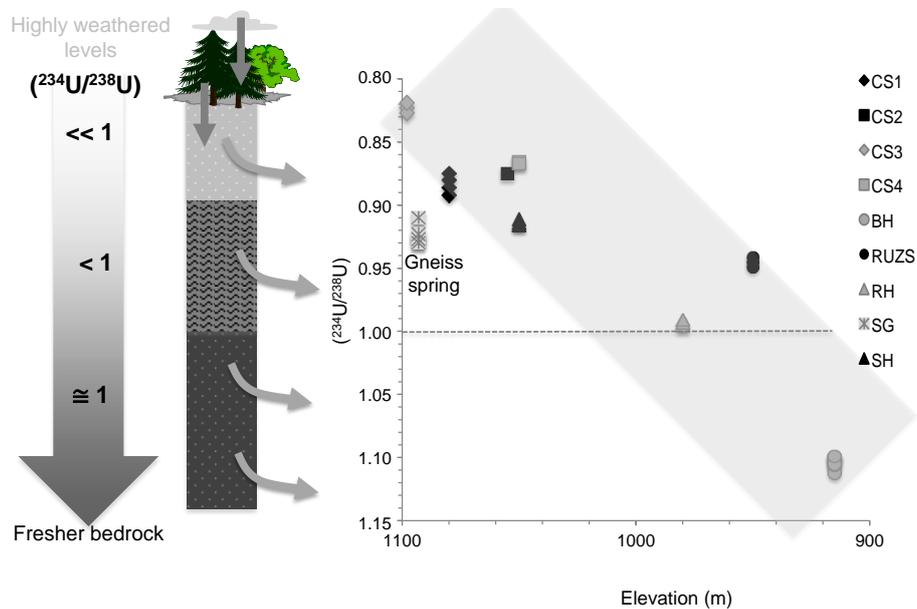

Figure 9. $(^{234}U/^{238}U)$ AR of springs vs. elevation. The U AR increase with decreasing altitude at the catchment scale.

secondary phases such as clays (Schaffauser, 2013). Ringelbach stream waters present higher alkalinity, pH (Fig. 10) and also conductivity, K, Mg, Si and Ca concentrations (not show) than spring and stream waters from Strengbach watershed, which might point to higher dissolution processes. Thus, we suggest that the waters with the lowest U AR correspond to less intense weathering in an already rock altered system with only a few fresh and primary mineral phases whereas higher U AR correspond to more intense weathering for waters circulating for example in fresher bedrock. In this way, the weathering history might be older for the Strengbach watershed than the Ringelbach watershed. This may be related to the fact that Triassic sandstones still cover the granite in the Ringelbach catchment.

It is striking that the BH waters from Strengbach watershed plot in between the data from the Strengbach and Ringelbach watershed (Fig. 10a and b) and are characterised

by the highest pH (6.7) and alkalinity despite the relatively high DOC content (2.27 ppm), which usually increases the acidity of solution. If we consider that the proton inputs due to atmospheric deposition or biological activity are homogeneous at the watershed scale, then the variations of pH in the different springs only reflect water–rock interactions and the consumption of protons by dissolution reactions. The high pH and alkalinity observed for the BH source are in this case consistent with the fact that its water has interacted with fresher bedrock; this further implies a stronger weathering intensity and higher dissolution rate of secondary phases such as smectite along the pathway of this source water.

In such a scenario, the relationship observed between $(^{234}U/^{238}U)$ AR and Mg/Ca ratios (Fig. 11) would indicate that the intensity or the nature of water reactions controlling the Ca–Mg budget of these waters, namely the dissolution/precipitation reactions of Mg- or Ca-smectites
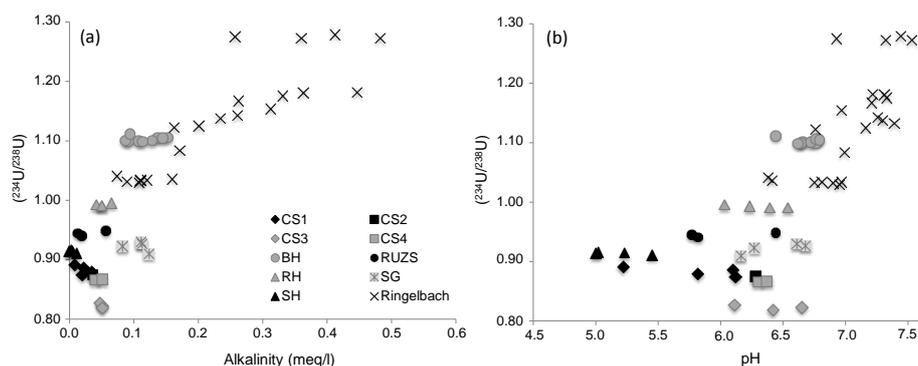
Figure 10. Variations of (^{234}U/^{238}U) AR vs. **(a)** alkalinity and **(b)** pH in the springs from the Strengbach and Ringelbach (Shaffauser et al., 2014) watersheds.
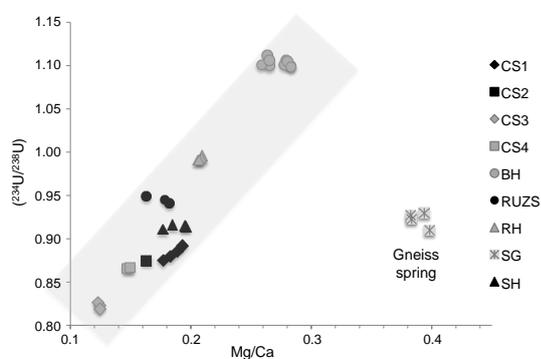
Figure 11. Variations of the (^{234}U/^{238}U) AR vs. Mg/Ca ratio in the springs. The U AR are positively correlated with the Mg/Ca ratios.

(see discussion in Sect. 5.1), would be clearly dependent on the weathering level of the saprolite/bedrock system. This is consistent with the fact that (1) smectite occurs along the weathering profile and even in deep weathering horizons (Fichter et al., 1998) and (2) the reactivity of secondary phases like smectite control the chemistry of Mg and Ca in streamwater (this study, Godderis et al., 2006, 2009). In addition, dissolution of clays implies an increase of Mg/Ca ratios in water (Fig. 8b). Thus, the relation between U AR and Mg/Ca ratios for the Strengbach springs reflects nothing else than the degree of alteration of the source rock being in contact with the waters: at low altitude the material is fresher, the weathering intensity is more important (higher pH and alkalinity) and, thus, causes higher Mg/Ca and U AR ratios in the waters than at higher altitudes.

5.3 Temporal variations of spring waters

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

The Sr isotopic compositions of single springs are correlated with discharge (Fig. 6a). In previous studies these variations have been interpreted by mixing of superficial (soil solution type) and deep (groundwater type) waters (Aubert et al., 2002). However, at the same time, the U AR show no temporal variation and, therefore, no relation with discharge (Fig. 6b).

Consequently, the U AR and Sr isotopic compositions are not correlated. Similarly, there is no correlation between U AR and geographical location and lithology (discussed in Sect. 5.2). In addition, the lack of temporal U AR variations indicates that the single springs are probably not the result of mixing of different waters. In the same way, the lack of correlation between discharge and DOC or NO$_3$, but also the majority of major and trace element concentrations suggests that the variation of chemical composition of spring waters cannot be explained by a simple variation in the contribution between different types of waters or as mixing between superficial waters (with high DOC, NO$_3$ concentrations for instance) and deep waters. At the same time, the lack of correlation between Sr isotopic compositions and concentrations for individual springs (Fig. 4a) confirms that the temporal variations of spring waters cannot simply be explained by mixing between two end-members (e.g. superficial and deep waters). The lack of variation of U AR in the individual springs with changing discharge (Fig. 6) during 2 years further suggests that the water pathways are the same whatever the hydrological conditions. Under these conditions, the water did not interact with new fresh material but rather with minerals having experienced at their surface a prior loss of ^{234}U from damaged lattice sites (Andersen et al., 2009). In

such a fractured bedrock system, the water flow is often reduced to only a few main flow paths that control most of the hydrological response of the aquifer (Le Borgne et al., 2007). These preferential flow paths along constant fractures in the bedrocks might explain the homogeneous (^{234}U/^{238}U) AR of the different spring waters with time.

In contrast, there is a correlation between discharge and ^{87}Sr/^{86}Sr ratios for each single spring (Fig. 6b). With increasing discharge the Sr isotopic composition increases as well, whereas the Si concentrations and alkalinity decrease (Fig. 12).

Different Si concentration–discharge relationships have been observed in several catchments and three different types have been identified: type 1 when Si concentration decreases with discharge; type 2 when Si concentration remains constant and type 3 when Si concentration remains constant until a threshold in discharge is exceeded (Godsey et al., 2009; Maher, 2011). The springs from the Strengbach watershed belong to the type 1 which are explained by average residence times shorter than required to approach chemical equilibrium. Thus, the chemistry of waters could vary entirely as a function of the nature of subsurface flow paths and the global solute fluxes depend strongly on the geometry, relief, runoff and permeability of basins (Maher, 2011). In addition, the variation of the Sr isotopic compositions with discharge suggests that the source of Sr changes with changing hydrological condition; this confirms again that the temporal variation cannot be explained by a mixing process but possibly by changing residence times of fluid and/or flow rate which according to Maher (2010) have an important impact on the weathering rates. This is in accordance with the hypothesis of preferential flow pathways through fractures for the water circulation in the basin.

In addition, modelling studies have shown that precipitation/dissolution process of secondary phases control the dissolved Si export in stream waters (Godderis et al., 2006; Violette et al., 2010; Beaulieu et al., 2011). Thus, the decrease of Si concentration with increasing discharge can be explained by a change in the ratio between dissolution and precipitation of clays (see also chapter 5.2). We propose that at high discharge the water is undersaturated for clay precipitation (lower Si concentration) causing a more important contribution by dissolution of clays as implied by the higher Mg/Ca (see Sect. 5.1) and Sr isotopic ratios (Fig. 11c). Thus, our study confirms that hydrological properties limit the solute fluxes carried by rivers and physico-chemical conditions.

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

The stream at the catchment outlet shows with increasing discharge increasing ^{87}Sr/^{86}Sr and decreasing alkalinity, pH, H$_4$SiO$_4$, and (^{234}U/^{238}U) AR (Fig. 13a–e). The important point is that the variation of U AR observed at the outlet (Fig. 13e) can only be explained by a change in the dis-

charge contribution of the different springs because the U AR of single springs are constant with time (Fig. 6). When the discharge increases, the U AR values tend towards 0.95, which is close to the (^{234}U/^{238}U) AR of the spring from the saturated area (RUZS) (Figs. 6 and 14). Previous papers proposed that during storm events, the contribution of the small saturated zone could reach up to 30 % of the runoff (Idir et al., 1999; Ladouche et al., 2001). Similarly, the increase in the Sr isotopic composition with increasing discharge points to the important contribution of RUZS to the streamlet during high discharge events (Fig. 13d).

However, during the lowest discharge, the U AR of the stream at the outlet is above 1 (maximum: 1.023). These higher values can only be explained by a more important contribution of the spring BH from the northern slope, which is the only one with U AR above 1 (average: 1.103; Table S1 in the Supplement; Fig. 13). Other parameters such as H$_4$SiO$_4$, pH and alkalinity confirm the important contribution of the BH spring to the streamlet during low discharge (Fig. 13). Similarly, the position of the RUZS spring with the low pH, alkalinity and silica concentrations (Fig. 13) confirms its important contribution during high discharge. However, the fact that the Sr isotopic composition of the stream at the outlet decreases with decreasing discharge is also in accordance with a more important contribution of the less radiogenic springs from the northern (e.g. BH) (Fig. 13) than from the southern slope (Fig. 4).

6 Conclusions

The study shows that the small Strengbach catchment drains different sources and streams with very different isotopic and geochemical signatures. This heterogeneity is mainly related to:

– The parent material (gneiss, more or less hydrothermally altered granite) and the degree of their weathering. This is confirmed by the fact that the sources draining the northern slope (hydrothermally much more altered) have higher TDSw and pH values, higher Ca, K, Mg concentrations and lower ^{87}Sr/^{86}Sr ratios than sources draining the southern slope.

– The water flow is probably controlled by pathways through main fractures, as it is generally the case in fractured granite systems.

This study has also shown, that there is an important decoupling between chemical composition on the one hand and the ^{87}Sr/^{86}Sr ratios and (^{234}U/^{238}U) AR on the other hand. The Sr isotopic compositions of the source waters are generally thought to be the result of alteration of primary mineral phases such as apatite. However, the low apatite-like Sr isotopic composition but comparatively high and not apatite-like Mg/Ca ratio cannot simply be derived from apatite dissolution; however, they might originate from alteration of
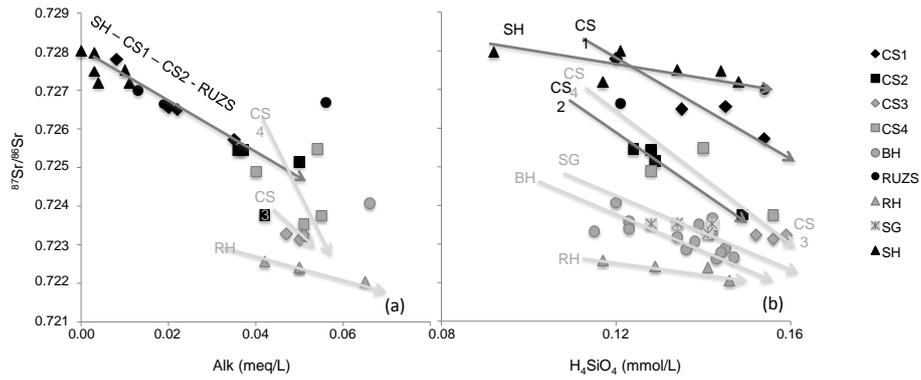
Figure 12. $^{87}Sr/^{86}Sr$ vs. alkalinity **(a)** and Si concentrations **(b)** for the springs from the Strengbach watershed. For each of the individual spring the $^{87}Sr/^{86}Sr$ ratios decrease with increasing alkalinity and Si content.
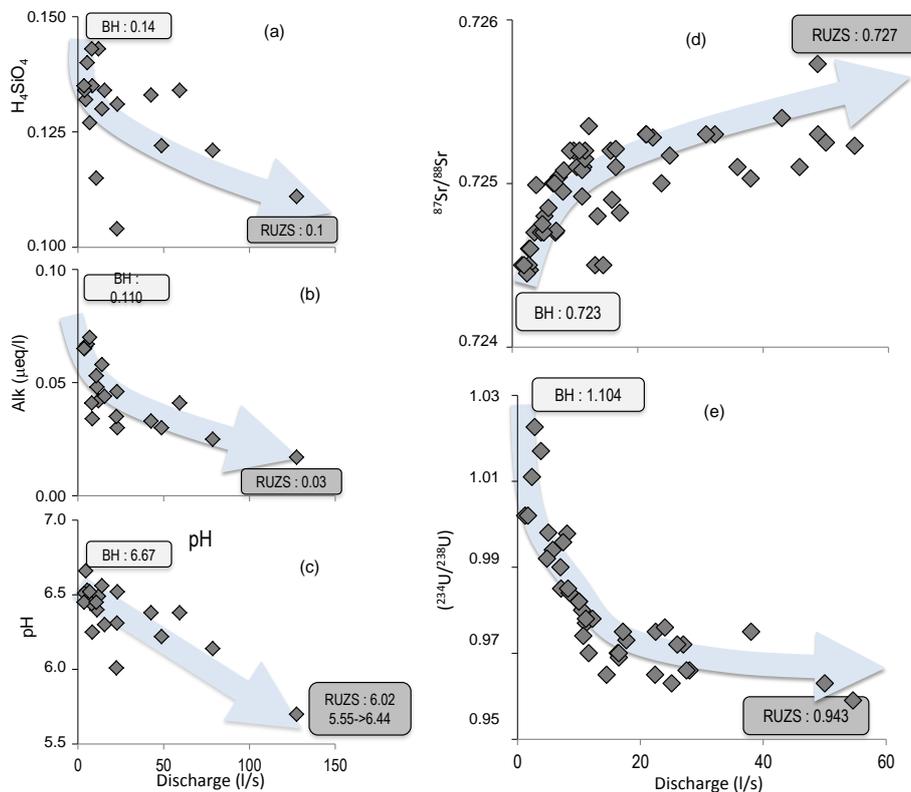
Figure 13. H_4SiO_4 concentration **(a)**, alkalinity **(b)**, pH **(c)**, ($^{234}U/^{238}U$) AR **(d)** and $^{87}Sr/^{86}Sr$ **(e)** vs. discharge at the outlet for the 2004–2006 period (additional data from Riotte and Chabaux, 1999 and Aubert et al., 2002).

secondary mineral phases like clay minerals, which integrated during their formation an apatite-derived Sr isotopic composition. The dissolution and precipitation dynamics of secondary phases, especially clays such as montmorillonite, seem to control the mobility of Si, Ca or Mg and, therefore, emphasise the key role of the clays reactivity in the biogeochemical transfer of especially nutrient elements like Ca and Mg.

Different processes control the variation of the U AR. Springs at high altitudes with U AR below 1 have circulated

through already weathered bedrock (thick saprolite and fractured rock), and have interacted with already weathered surface minerals. These uncommon values for surface waters are due to strong ^{234}U depletion during predating alteration processes of the bedrock granite. At the opposite end, springs emerging at the bottom of the watershed have U AR above 1, because of interaction with fresher materials.

The lack of variation of U AR in the individual springs with changing discharge during 2 years suggests that the water pathways are the same whatever the hydrological

conditions and that there is no interaction between the different source waters.

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

Thus, all these observations converge toward the same functioning:

– The proportion of the contributions of the different springs to the stream at the outlet varies as a function of the hydrological conditions; the variable contributions of the different sources carrying different geochemical signatures define the signature of the waters at the Strengbach outlet.

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

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

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

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

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