Author’s response - *Chemical and U-Sr isotopic variations in stream and source waters of the Strengbach watershed (Vosges mountains; France)* - Pierret M.C., Stille P., Prunier J., Viville D. and Chabaux F.

Responses to Anonymous referee (in blue in the text).

General comments

The authors presented a very comprehensive geochemical and isotopic dataset for stream and spring waters in the small Strengbach catchment in France. The reviewer was amazed by the amount of time and work involved in sample collections (~10 springs and streams for over two years) and measurements (general water chemistry, major elements, and U and Sr isotope ratios). The authors provided a sound and rea- sonable interpretation on the variability of geochemical and isotopic signatures of the source waters in this small catchment. The authors suggested that the different flow paths, intensity of water-rock interactions, and involvement of secondary minerals/clay minerals are the main controlling factors for stream and spring water chemistry in the Strengbach catchment. Furthermore, the new U isotope data show great promise in tracking water flow path/residence time in the subsurface, as compared to other tradi- tional solute tracers (major elements and Sr isotopes). This work highlights the use of multi-tracer approaches in catchment studies. The manuscript is generally well written. The length of the paper (e.g. number of figures/tables) may be reduced. Below the reviewers indicates some specific comments for the authors to consider.
Overall, the manuscript will be of great interest to the readers of HESS and should be considered for publication by HESS.

Specific comments:
1) Abstract/introduction: although this study is intended to be a case study, the reviewer would like to see how the gained insights from this study help to understand the impact of such as vegetation cover and soils on evolution of surface waters at a small catchment scale and what are the global implications of these findings.

The vegetation cover and soils have a great influence on the chemistry of soil solutions. However, on the base of chemical mass balance this study show that the chemistry of the first meter soil solution didn’t control strongly the signature of spring and stream waters at the catchment scale. Our study seems to show that the mineralogy, the secondary phases and the water pathways are the main factors explaining the signatures of stream waters.
The global implications are that the water pathways and the secondary phases, especially clays have to be taken into account more deeply at the watershed scale. 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 within deep horizon along the specific water pathways.

2) Chemistry comparison of northern vs. southern slopes: in addition to the difference in

mineralogy/hydrothermal alternation of the bedrock, the reviewer wonders whether the landscape positions (e.g., sun-facing vs. shade-facing) play a role in the soil development and water chemistry evolution. The effects of landscape aspect on micro-climate conditions at the catchment scale have been commonly observed and may be relevant here. For example, it has been shown that for mid-latitude regions, different soil temperature and moisture content could be generated by aspect through controls on the amount of solar radiation at the catchment scale [e.g., Cooper, 1960, Soil Sci., 90, 109–120; Churchill, 1982, Earth Surf. Processes Landforms, 7, 171–182.; Carter and Ciolkosz, 1991, Geoderma, 49, 199–213; Egli et al., 2007, Clay Minerals, 42, 373–398; 2010; Geomorphology, 114, 466–482.]

Line 25, p 3546 to line 4 p 3547 – has be change to:

In addition, the northern sun-facing slope is characterized 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 meter 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 characterized 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 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).

3) The reviewer would also like to see some saturation index (SI) values calculated based on the measured chemistry data of the streams and springs to back up the arguments of processes involved clay mineral precipitation/dissolution. Also, it may be necessary to present the mineralogy of the soils and bedrock and to compare/discuss with the SI values of the waters. The SI values may help to elucidate the water-rock interaction processes

Recent numerical modelings of superficial waters have shown that only primary mineral weathering is not able to explained the chemical signature of river waters.

Thus, the role of secondary phases, especially dissolution/precipitation of clay minerals, on the chemical composition of soil solution and river water have been explored and proposed in several studies using thermodynamic approach (Price et al., 2005; Goddéris et al., 2006; Maher et al., 2009; Violette et al., 2010; Beaulieu et al., 2011).

However, significant uncertainties affect the prediction of thermodynamic properties of clay minerals. DG°f values are only available for ideal structures whereas clay minerals can present large quality variations in term of cristallinity or composition (Al, Fe contents). As an illustration, field smectites can be a complex mixing of ideal end-members as Ca-, Mg-, Na- or K-montmorillonites.

In addition, several papers have highlighted the differences between thermodynamic and kinetic constants determined under experimental conditions with them in natural systems (White and Brantley, 1995; White and Brantley, 2003, Daval et al., 2011).

That's why, the solubility products of clay minerals as montmorillonite or kaolinite have to be artificially increased (by a factor range from 8 to 15) to account for the Mg, Ca and aqueous silica concentrations in waters (Godderis et al., 2006; Violette et al., 2010; Beaulieu et al., 2011). Poorly crystallized clays have typically higher pK than theoretical idealized clays, and clays from recent soils or in active fractures are typically not perfectly crystallized. This was confirmed in the Strengbach case with SEM study of soils and rocks (not shown here). Furthermore, clay hydratation imply also variations of ΔH and then of pKeq. So, considerable uncertainties surrounding the use of pKeq for minerals like clays.

In addition, during the water circulation through soils first and then more or less weathered and fractured bedrock, the saturation index in solution changes because the water becomes more concentrated and less acidic due to water/rock interactions. Then even when river water is oversaturated in respect to a mineral, the chemical elements in this water can come from the earlier dissolution of this same mineral.

As suggested by the two reviewers, we calculated some saturation index in the different springs and stream of the Strengbach catchment (Figs. 1 and 2).

The questions concerning mainly clays, we will discuss the saturation index of some of them: Ca-smectite, Mg-smectite (similar to Ca-smectite), Illite, kaolinite and chlorite.

Using the theorical pKeq of ideal structures (see Godderis et al., 2006) we obtained that all the waters are oversaturated with respect to Ca- and Mg-smectite and illite. All spring except SH are oversaturated with respect to kaolinite. All springs are undersaturated with respect to chlorite.

On the base of this first approach we can proposed that Mg in waters can be explained by a contribution of chlorite dissolution, which confirm the contribution of clay mineral dissolution in the chemical signatures of waters.

However, smectite is an important component of the clay fraction from several weathering profiles at the Strengbach watershed whereas chlorite has been more rarely identified (Fichter et al., 1997; Prunier, 2008; Table 4).

That's why the saturation index of Ca- and Mg-smectite have been calculated versus a large range of pK (figure below). Increasing the pK by a factor of 2 to 3 for the both smectite allowed to obtain $\text{Log}(Q/K) < 0$ for all springs (Fig. 1). Using the same factor imply that all the springs became undersaturated in respect to muscovite and illite.

Then, this approach suggests that the contribution of clays can explained the chemical signature of Strengbach superficial waters.

This is consistent with numerical model studies proposing a increase of the solubility products of smectite to obtain a correct prediction of Si, Ca and Mg concentrations in waters (Godderis et al., 2006; Violette et al., 2010; Beaulieu et al., 2011). Thus, saturation index calculations, based on theorical solubility products are probably not the best way to discuss the origin of chemical element in water.

Finally, the Sr isotopic compositions and chemical signature of spring waters highlight the necessity to take into account the clay mineral as a source of element to explain the signature of waters (cf. figure 9 / this paper).

Compared to these issues, we propose to not discuss these aspects of saturation index determination in the script because the document is already long. We added the reference Violette et al. (2010) that propose also the role of secondary minerals as clays (especially kaolinite and smectite) to explain the chemical composition of stream water in a watershed in India.

Unfortunately, because of the large gap between theoretical and probably real saturation index values for clays the SI values will not really help to elucidate water/rock interactions processes.

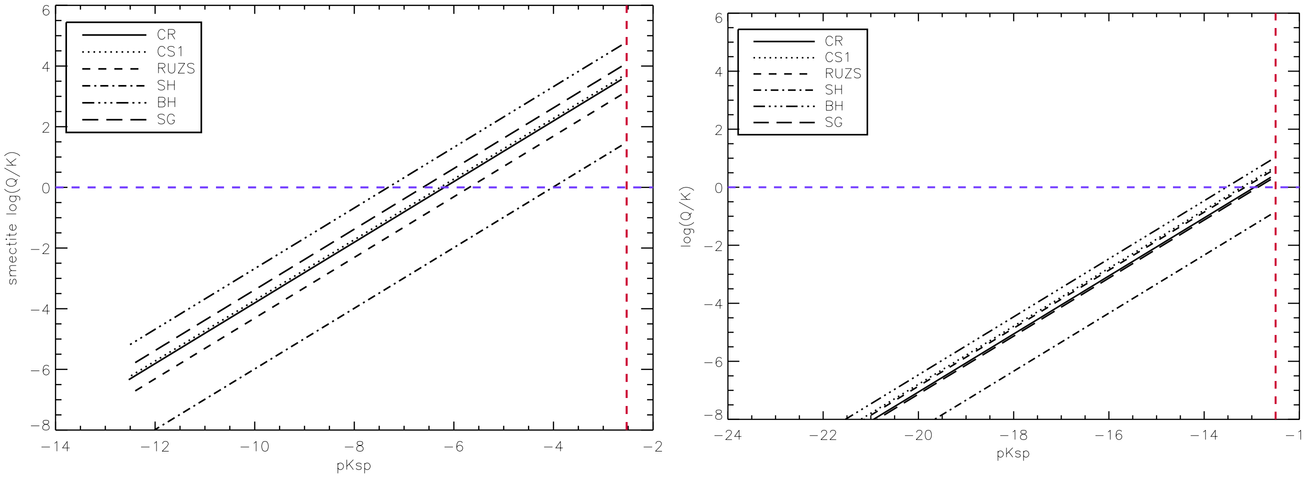

Fig. 1: Log (Q/K) vs different values of pKeq for Ca-smectite (left) and illite (right) for several springs of the Strengbach watershed. The red line corresponds to the theoretical value for idealized structure. Godderis (pers. com.).

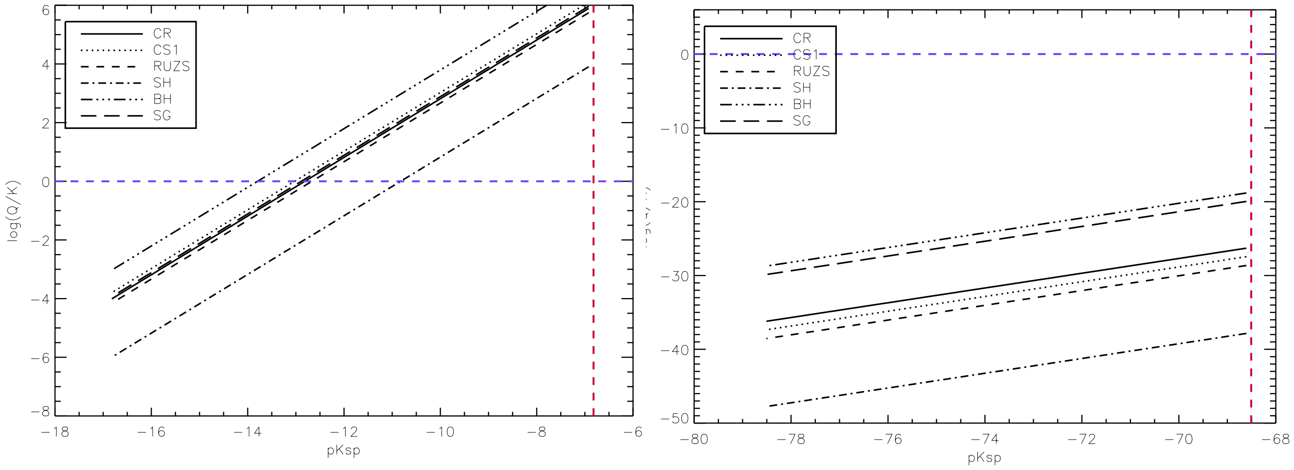

Fig. 2: Log (Q/K) vs different values of pKeq for kaolinite (left) and chlorite (right) for several springs of the Strengbach watershed. The red line corresponds to the theoretical value for idealized structure. Godderis (pers. com.).

Ref :

Daval D., Sissmann O., Menguy N., Saldi G.D., Martinez I., Corvisier J., Garcia B., Machouk I., Knauss K.G. and Hellmann R., 2011. Influence of amorphous silica layer formation on the dissolution rate of olivine at 90°C and elec-vated pCO_2. Chemical Geology 284, 193-209

Maher, K., Steefel, C.I., White, A.F., Stonestrom, D.A., 2009. The role of reaction affinity and secondary minerals in regulating chemical weathering rates at the Santa Cruz Soil Chronosequence, California. Geochimica et Cosmochimica Acta 73, 2804–2831

Price J.R., Velbel M.A. and Patino L.C., 2005. Rate and time scales of clay mineral formation by weathering in saprolitic regoliths of the southern Appalachians from geochemical mass balance. Geol Soc. Am. Bull. 117, 783-794.

White, A.F., Brantley, S.L., 1995. Chemical weathering rates of silicate minerals: an overview. : Chemical Weathering Rates of Silicate Minerals, Vol. 31. Mineralogical Soc America, Washington, pp. 1-22

White, A.F., Brantley, S.L., 2003. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? Chem. Geol. 202, 479–506

Violette A., Godderis Y., Maréchal J.C., Riotte J., Oliva P., Mohan Kuma M.S., Sekhar M. and Braun J.J., 2010. Modelling the chemical weathering fluxes at the watershed scale in the Tropics (Mule Hole, South India) : Relative contribution of the smectite/kaolinite assemblage versus primary minerals. Chemical Geology 277. 42-60.

4) The correlation presented in Figs. 4a and 4b, is somehow subjective.
That’s right because the correlations exist only for some springs. U and DOC are correlated for DOC-rich spring. But, DOC-poor spring can also have high U concentrations.
As the speciation of U is not really a main subject here, we propose to skip all the discussion about relation between U, DOC and Fe concentrations.
The speciation and behavior of U in springs, more or less concentrated in COD or more or less enriched in mineral or organic colloids can be a subject of another publication.

The information presented in Figs. 6 is not very clear.
The objective of this figure is to show the lack of correlation between Sr isotopes and U AR. This lack implies that the U activity ratios are not linked to lithology or geographical location, in contrast to Sr isotopic signature. Therefore the U AR have to be explained by other processes than those explaining the Sr isotopes. That’s why we have written in the legend: *“In contrast to Sr isotopic compositions, the U AR of springs do not allow to distinguish between the northern and southern slopes*”.

Technical corrections: Page 3544 line 24-27: please be specific on how 234U/238U ratios changes along river flows and hydrological mixing.

Text has been changed to :

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 in function of hydrological mixing (e.g., Chabaux et al., 2001; Durand et al., 2005; Maher et al., 2006; Osmond and 1982; Paces et al., 2002; Riotte et Chabaux, 1999).

Page 3535 line 4-6: this sentence is not very clear to the reviewer. Supposedly p. 3545

Text has been changed to:

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.

Page 3535 line 15-18: again, this sentence is not clear to the reviewer, what are the controlling factors?

Text has been changed to:

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.*

Page 3545 line 26: 80 ha: please use SI units

80 ha was changed to 0,8 km^2

Page 3547 line 19-25: the description on spring locations is confusing: are CS3 and CS4 on southern side or northern side?

The reviewer is right. Text is confusing because the waters of the 4 springs (CS1 to CS4), located on different slopes, finally arrived at the same place (a drinking water reservoir) where each of them has been collected.
We therefore propose to simplify the description.

The text has been changed to:

The springs SG, ARG, RH, BH, CS_3 *and* CS_4 *are located on the northern slope and the springs* CS_1*,* CS_2*, SH and RUZS emerge at the southern slope (Fig. 1).*

Page 3553 line 3-18: is the difference caused by different bedrock mineralogy (including different types of bedrock and hydrothermal alteration), or different degrees of water-rock interactions, or N. vs. S landscape locations?

The paragraph mentioned by the reviewer concerns the explanation of chemical signature of SG spring, which is characterized by the highest Ca and Mg concentrations.

The chemical differences among the different springs from the Strengbach watershed can be generally related to the different bedrock mineralogy, which is due to the fact that the granite from the northern slope has been stronger hydrothermally altered than that of the southern slope. In addition, the banded gneiss located at the top of the northern slope has a different mineralogy than the granites. The spring SG, emerging in the gneiss is a good illustration of the relation between lithology and geochemistry of water. SG is characterized by the highest Mg concentration linked with the gneiss mineralogy (more chlorite). In addition, among the springs circulating through a same lithology, the differences can be explained by intensity of water-rock interactions (recorded by pH, Alk or TDS).

Text has been changed to:

The geochemical signature of springs can generally be linked to specific lithological and mineralogical differences existing for the two hillsides of the Strengbach catchment. This is particularly obvious for the SG spring, which emerges near the top of the catchment, just under the banded gneiss, whereas the other sources emerge within the granitic environment (Fig. 1).

Page 3554: line 26-27: the northern slope samples are more radiogenic?? Typo here?

Text is confusing and has been changed to:

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.*

Page 3556 line 18-21: it is not clear to the reviewer that why this argument is supportive or against that U < 1 ratios are or not derived from the weathering of soils? Please elaborate.

The objective of this paragraph is to demonstrate that U coming from the upper soil horizons cannot explain the U AR in spring waters. We presented three arguments: 1) U mass balance calculation, 2) U concentration and 3) U AR.

The text has been changed to:

One might simply suggest that the U AR < 1 in the Strengbach source waters are the results of circulation through already weathered soils, supposedly having U AR<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 3). At the same time, the 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 2). 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.*

Page 3558 line 21-24: SI values may reveal more information about the evolution of water chemistry here.

The modeling of chemical composition of the waters from the Ringelbach catchment implies dissolution of primary minerals of granite and precipitation of secondary phases such as clays but no dissolution of clays (Schaffauser, 2013).
For the same reasons than explained in question 3, we propose to avoid discussion on SI values in this paper.

Ringelbach stream waters present higher alkalinity, pH and also conductivity, K, Mg, Si and Ca concentrations (not show) than spring and stream waters from Strengbach watershed, which is coherent with the fact that the U AR is correlated with intensity of weathering (Fig. 11).

The log (Q/K) for Ringelbach waters with respect to Ca- or Mg-montmorillonite will be higher than those for Strengbach waters.

Page 3559 line 10-12: why smectite? What about the SI values for smectite in these waters.

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. In addition BH is characterized by high Mg and Si concentrations. Numerical modeling proposed that Si and Mg fluxes in superficial waters are explained by dissolution of Mg-smectite (Godderis et al., 2006; 2009; Violette et al., 2011). Thus, we proposed that BH is characterized by higher dissolution rate of smectite along the pathway of this source water.
See also explanation to question N°3 of anonymous reviewer.

Page 3560 line 1-3: samples plotted in Fig 3 are not grouped with time, so it is hard to assess the temporal variations.

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 chemical concentrations of RUZS are given in table 1b and show the largest variations. In addition, in figure 3 the RUZS data (black circle with white ring) show the largest variations among the plotted data. It’s not possible to grouped with time the data.

Page 3563: line 5 to 12: all of these factors are related to the parent material/bedrock mineralogy. They can be combined as in one factor rather than the three factors here.

As proposed, we reduced the three first factors to one.

The text has been changed to:

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-, pH values, higher Ca, K, Mg concentrations and lower* $^{87}Sr/^{86}Sr$ *ratios than sources draining the southern slope.*

Responses to S.J.K. Köhler referee (in red in the text).

Chemical and U-Sr isotopic variations of stream and source waters at a small catchment scale (the Strengbach case; Vosges mountains; France By Pierret et al.
This very comprehensive manuscript describes geochemical measurements of both element concentrations and isotope ratios in a small French catchment. The authors use these tracers to identify water sources and dominating geochemical processes.
The paper is generally well written and I have made a number of suggestions in the attached pdf file

I have a few general comments:
1) I would wish that the authors add some overview of the quantitative mineralogy of some of the soil plots. This new table could even contain data on CEC (see my comment in line 142).

We added table 4 with mineralogical and pedological data.

2) I do not understand why the authors do not display isotopic data for the chlorite and biotite in figure 9. Please comment !

The Sr concentrations of biotite and muscovite are respectively 4.3 and 3.1 ppm and their Sr isotopic composition are respectively 5.86 and 5.36 (Aubert et al., 2001). For comparison the Sr concentrations of apatite, plagioclase, orthose are 790, 74 and 77 ppm respectively.
Because of their low Sr concentrations, the dissolution of biotite and muscovite do not contribute mainly to the Sr budget of spring and stream waters.
In addition, the occurrence of significant Sr from biotite or muscovite has to increase strongly the Sr isotopic ratios of waters because of their very high $^{87}Sr/^{86}Sr$. The Sr isotopic compositions of stream and spring waters range from 0.72 to 0.73. Aubert et al. (2001), on the base of Sr and Nd isotopic signatures, already suggest that the most important source for Sr in stream water were apatite, plagioclase and to a lesser extent K-Felspar (see text p. 3554, l 20).

Biotite and muscovite cannot be represented in the figure 9 because they are largely out of scale of the axes (max at 0.95 for the $^{87}Sr/^{86}Sr$; figure 9).
In addition in comparison to southern slope granite, biotite mainly disappeared during hydrothermalism (cf site description) in northern slope granite. This confirms that the higher Mg concentration and Mg/Ca ratios in springs from the northern slope cannot be explained by a higher contribution of biotite dissolution.
The isotopic composition of chlorite has not been determined because it's difficult to enriched this phase. The clay fraction is a mixture of different clay minerals and also includes chlorite if this mineral phase occurs in sample. One might therefore suggest that the chlorite Sr isotopic composition is included in that of the clay fractions.

3) In the current version of the manuscript I find it difficult understanding whether the clays precipitate or dissolve and what the effect of this process is on K, Mg and Ca. (see comment in 338, 343)

Cf. explanation to question N°3 of anonymous reviewer.

4) The Mg-Smectite that is present could either have been formed during the hydrothermal activity, may have formed after that os may still be precipitating (which I thought it would according to Godderis et al.). Please clarify this

Cf. explanation to question N°3 of anonymous reviewer.

Thermodynamical calculation using theorical smectite pKe proposes that Mg-smectite precipitating. But Godderis et al (2006) has shown that the solubility products of all smectites have to be artificially increased (factor 8) to yield an accurate prediction of Mg, Ca and Si in Strengbach spring waters.

In the same way, Violette et al (2010) increase the pK for Ca- and Mg-smectite from 2.53 and 2.49 respectively until 11.53 and 11.49 respectively in order to modeling the chemical signature of stream in Mule Hole watershed.

So, despite the fact that smectite or other clay minerals are supposedly oversaturated following theoric thermodynamic constant, we proposed that they contribute to the water chemical fluxes.

5) What is the role of ion-exchange and organic matter for the isotopic signal of U? (see comment in line 233)

The speciation of U will not be discussed in detail here. Cf response N°4 to anonymous reviewer.

OM :

Complexation of U with organic matter is not supposed to fractionate the ^{234}U and ^{238}U. Therefore, the organic matter (mainly present in soils and soil solution and in weak concentrations in spring and stream waters) has only a small influence on the isotopic U signal.

CEC : The contribution of U from Ion exchange is low because the U concentration in exchangeable fractions is low (Prunier, 2008). The U from exchangeable pool in spring water comes mainly from soil because the CEC in granite is very low.

In addition, U coming from soil and present in soil solutions does not explain the U AR in spring and stream waters (cf response to reviewer 1 : copy below) :

One might simply suggest that the U AR < 1 in the Strengbach source waters are the results of circulation through already weathered soils, supposedly having U AR<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 3). At the same time, the 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 2). 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.

Finally, the U in the exchangeable phases corresponds to already weathered U and should have activity ratio similar to that of the solution. So the exchangeable U does not explain the variation of U activity ratios in spring or stream waters.

6) With regards to acid rain that effected the catchment in the 1970-1990 I am wondering if the catchment currently at steady-state with respect to ion-exchange. It is my experience that modeling results indicate that the process of cation recharge after depletion by acid rain may take 30-40 years. This could have an effect on the mass balance in table 2.

That's right. Therefore, we calculated the mass balance using the database of two successive hydrological years. Probably the catchment is not at steady-state with respect to ion-exchange because the rain pH continue to increase whereas the soils continue to acidify. The long-term series records of the chemical concentration of stream water at the outlet since 1986 show a continuous decrease of Mg and Ca concentrations and acidity. However, ion exchange in the soil can not explained the chemical signature of stream (see chemical balance, table 2 and response to question 5)

7) There are large number of French references on catchment work in the text. I appreciate that a lot of the isotope work is done in France but the authors seem to neglect the exhaustive work done by researchers in Northern America, Northern Europe including England, Finland and Sweden. (see my comment line 59)

That is right. We added some new references.

8) The Conclusions section is much too long

We reduced the conclusion

9) I propose to reduce the number of figures. Why not skip figures 2,3,14. Also Figure 5a and 8 could be combined and in figure 14 the pH, alk and H4SiO4) do not really show anything

In order to reduce the size of the publication we considered the comments of the reviewers.

We propose to skip the figure 2c and 2d. We keep the figure 2a and 2b because they are important to show the relationship between pH, TDS and alkalinity. These relations highlight the fact that the less acidic springs correspond to higher water/rock interaction and to the most intense weathering processes (see p. 3559, l9-12 :" The high pH and alkalinity observed for the BH source are in this case consistent with the fact that its water interacted with fresher bedrock; this further implies a stronger weathering intensity").

We propose to skip the figure 3b and 3c. We keep the figures 3a and 3d because they are a very good and necessary illustration of the differences between the springs from the two slopes. The 3b and 3c can be described in the text without showing them.

As suggested by anonymous reviewer, we decided to skip the figure 4 and to avoid discussion about U speciation (cf response N°4 to anonymous reviewer).

It’s difficult to combine figure 5a and 8 because of scale problems. Reporting all waters and soils in the same figure would minimize and reduce the differences, which exist between the spring waters from the two different slopes.

The objective of figures 13a,b,c was to show that at low discharge the geochemical signature of the stream at the outlet tends to the BH and at high discharge to RUZS signature. The elemental chemical concentrations confirm the isotopic (U and Sr) data. These observations are of importance and elucidate the hydrological dynamic in the catchment. But these figures (13a,b,c) can also be removed if it’s necessary.