

Interactive comment on “Chemical and U-Sr isotopic variations of stream and source waters at a small catchment scale (the Strengbach case; Vosges mountains; France)” by M. C. Pierret et al.

M. C. Pierret et al.

marie-claire.pierret@unistra.fr

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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

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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 $^{87}\text{Sr}/^{86}\text{Sr}$. 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 $^{87}\text{Sr}/^{86}\text{Sr}$; 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.

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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 as 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 theoretical 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 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 to 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 theoretic 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 also 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.

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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, ($^{234}\text{U}/^{238}\text{U}$) 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

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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, 19-12 :” 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).

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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. We proposed a revised version, which takes account of the changes and responses to the two reviewers.

Please also note the supplement to this comment:

<http://www.hydrol-earth-syst-sci-discuss.net/11/C2631/2014/hessd-11-C2631-2014-supplement.pdf>

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 11, 3541, 2014.

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Soils under spruce - Northern slope [1]																										
depth	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	K2O	Na2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	mmucovite	Quartz	K-Feld	plagiocl	apophite	Smectite	amorph	amucicite (%)	OM	pH	Clays	CEC	
cm	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	
5	52.14	17.82	0.91	0.08	1.02	0.04	0.24	0.02	0.70	0.23	1.52	0.14	0.13	0.21	33.6	10.9	5.4	0.02	0.2	0.66	18.2	7.2	5.2	22.2	15.68	
10	54.82	20.71	0.88	0.15	2.43	0.04	0.32	0.02	0.80	0.43	1.65	1.27	0.15	50.1	27.3	3.6	7.5	0.21	1.3	1.09	19.8	8.2	4.4	25.3	11.98	
15	56.50	23.50	1.02	0.28	2.72	0.07	0.27	0.02	0.88	0.50	1.70	1.07	0.05	49.5	29.8	9	8.7	0.42	0	1.11	19.2	8.2	4.4	15.8	10.57	
20	59.10	25.41	0.72	0.18	2.54	0.02	0.40	0.02	0.62	0.71	0.43	2.10	1.24	41.4	27.4	8.9	8.1	0.41	1.1	0.89		6.3	4.5	12.5	9.18	
110	61.17	28.81	0.57	0.20	2.42	0.02	0.20	0.02	0.20	0.20	0.20	0.20	0.20	40.1	27.2	10.8	0.42	0.1	0.7	2.11	10.1	6.1	4.0	6.1	9.03	
120	59.25	21.10	0.58	0.19	1.82	0.02	0.22	0.02	1.87	0.81	0.49	1.22	0.52	42.5	22.1	10.7	10.4	0.54	1.1	0.97		5.9	2.9	8.9	9.23	
130	60.68	21.22	0.59	0.12	1.86	0.02	0.26	0.02	1.89	0.42	0.22	1.47	0.41	46.1	21.0	7.2	17.6	0.42	1.1	0.7		5.2	4.1	6.1	8.60	
140	60.31	20.15	0.80	0.31	1.50	0.03	0.17	0.01	1.81	0.77	0.35	1.64	0.54	39.4	20.9	12.6	15.9	0.41	0.4	0.54		3.8	4.7	4.2	6.76	
200	61.14	20.22	0.29	0.08	1.42	0.01	0.24	0.02	1.33	0.31	0.32	1.30	0.30	34.7	20.9	10.9	11.6	0.22	0.2	0.26		4.7	6.2	4.8	5.2	10.10
210	60.24	18.61	0.84																							
Soils under birches - Southern slope [1]																										
depth	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	K2O	Na2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	mmucovite	Quartz	K-Feld	plagiocl	apophite	Smectite	amorph	amucicite (%)	OM	pH	Clays	CEC	
cm	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	
4	72.95	14.27	0.31	0.18	1.13	0.01	0.33	1.50	4.77	0.25	2.54	0.28	0.38	18.9	39.5	18.9	14.9	0.15	4.4	0.54	14.4	15	4.0	15.3	7.85	
5	72.52	13.97	0.34	0.13	1.27	0.01	0.31	1.45	3.41	0.21	2.21	0.30	0.31	21.9	38.4	20	13.6	0.1	3.9	0.44		4.1	11.6	7.7		
6	68.10	15.80	0.35	0.10	2.10	0.04	0.29	1.20	4.36	0.40	2.59	0.34	0.31	21.1	35.1	17.8	13.2	0.05	4.3	0.14		12.3	4.8	10.7	8.60	
10	65.96	17.21	0.40	0.11	2.25	0.02	0.21	1.45	3.98	0.29	2.05	0.30	0.24	26.1	37.9	15.9	12.4	0.1	3.7	0.2	10.2	11.9	4.8	8.7	9.50	
17.5	65.03	18.67	0.47	0.16	2.80	0.06	0.30	1.55	4.96	0.37	2.48	0.40	0.38	28.7	38.6	14.4	14.3	0.12	6.1	0.39		10.9	4.8	6.3	4.24	
190	66.51	18.82	0.51	0.21	3.30	0.08	0.39	1.65	3.34	0.40	2.44	0.53	0.34	31	39.5	14.7	11.8	0.21	5.6	0.51	1.63	17.1	7.3	4.8	6.2	4.88
122.5	65.15	19.48	0.56	0.26	3.08	0.08	0.29	1.83	3.34	0.42	1.83	0.50	0.27	31.4	27.3	13.9	11.1	0.31	7.4	1.32		7.3	4.8	3.1	3.6	
180	64.14	20.46	0.51	0.21	2.72	0.11	0.28	2.12	3.32	0.45	1.40	0.40	0.28	33.8	22.7	14.8	10.6	0.4	7.1	1.61		6	4.8	2.8	2.6	
177.5	64.82	19.35	0.48	0.25	2.85	0.10	0.24	2.47	3.48	0.41	1.56	0.32	0.29	26.1	23.3	17.9	19.1	0.28	6.5	1.17		5.2	4.9	1.8	2.12	
122.5	65.49	18.16	0.48	0.22	2.81	0.10	0.28	2.46	3.36	0.40	1.20	0.24	0.28	25.2	20.2	14	13.2	0.22	6.1	1.0		5.2	1.8	1.82		
200	62.25	20.22	0.55	0.31	3.72	0.15	0.31	2.10	3.04	0.52	1.82	0.34	0.24	37.9	20.9	12.2	20.2	0.39	4	1.82	19.8	8.2	4.8	2.1	1.02	
Soils - Onies [2]																										
depth	SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	K2O	Na2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	mmucovite	Quartz	K-Feld	plagiocl	apophite								
cm	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%								
50	62.84	15.25	1.00	0.20	0.72	0.15	0.77	0.42	0.44	0.43	4.22	0.87	0.52	nd	nd	nd	nd	nd								
60	66.01	15.20	1.05	0.13	0.25	0.02	0.71	0.38	0.32	0.24	8.77	0.77	0.66	nd	nd	nd	nd	nd								
120	69.00	14.41	1.22	0.02	0.50	0.02	0.70	0.28	0.23	0.23	13.68	0.93	0.80	nd	nd	nd	nd	nd								
170	71.88	13.61	1.02	0.24	0.15	0.04	0.68	0.05	0.71	0.23	3.95	0.18	0.44	nd	nd	nd	nd	nd								
220	64.97	16.11	0.88	0.12	0.28	0.16	0.59	0.10	0.89	0.19	6.05	11.98	2.31	nd	nd	nd	nd	nd								
bedrock - average value [2], 0-10 m above																										
SiO2	Al2O3	MgO	CaO	Fe2O3	MnO	TiO2	K2O	Na2O	P2O5	Mg/Ca	Mg/Na	Ca/Na	mmucovite	Quartz	K-Feld	plagiocl	apophite									
%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%								
64.00	14.00	1.40	0.20	0.40	0.02	0.60	0.10	0.20	0.20	1.10	0.70	0.40	0.20	22	28	30	2	0.20								
Southern slope	14.13	1.43	0.20	0.38	0.02	0.38	0.10	2.49	5.70	0.10	0.15	0.14	31	34	30	22	0.15									
Onies	64.00	17.00	2.00	0.20	7.00	0.01	0.60	0.04	4.10	0.20	10.60	0.54	0.40	nd	nd	nd	nd	nd								

Fig. 1.

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