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**Characterization of groundwater circulations in a headwater catchment from
an analysis of chemical concentrations, Sr-Nd-U isotope ratios, and CFC, SF₆
gas tracers (Strengbach CZO, France)**

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Abstract

In order to characterize the chemical composition and the age of the water circulating in the critical zone of the Strengbach catchment (Vosges mountains, France), water samples from springs, 10–15 m deep piezometers and 50–120 m deep boreholes were collected and analyzed in elementary concentrations, in Sr, Nd, and U isotopic ratios, and in chlorofluorocarbon (CFC) and sulfur hexafluoride (SF_6) concentrations. The results evidence a clear distinction between surface water (< ≈ 10 –15 m) and deeper water. The latter has much higher conductivity and cationic loads and is marked by lower Sr isotopic ratios and higher U activity ratios. Such a water typology suggests that the spring and piezometer water flows within the same shallow subsurface aquifer while deep borehole water belongs to a different circulation system, which flow path is controlled by the bedrock fracture network. The CFC data show that these two circulation systems are marked by contrasted residence times with a short residence time for the surface water and a longer residence time (water ages > 50 years) for the deep water. These results confirm different circulation histories for surface and deep water in the Strengbach catchment. They also suggest that the higher degree of chemical saturation of the deep water compared to the surface water is caused more by longer water residence times in the deep circulation systems than by differences in the primary minerals involved in each of the water-rock interaction systems. Our results also point that in the Strengbach granitic catchment, the SF_6 concentrations cannot be used for water dating due to their lithogenic production in granitic bedrocks.

1. Introduction

The identification of the main water circulation levels in the Critical Zone (CZ) and the determination of the characteristic times of these circulations are among key parameters controlling the CZ functioning and its vertical extension (i.e., Riebe et al., 2017). These parameters also control its future evolution in response to environmental modifications, whether related to global climate change or to human activities of more local impact. This information, in particular, the partitioning between deep and subsurface circulations, is also important to achieve a sustainable management of the world's water resources and to model their future evolution in response to ongoing climate change (e.g., Gleeson et al., 2016; Ameli et al., 2017; Liu et al., 2017; O'Geen et al., 2018; Weill et al., 2019; Ackerer et al., 2020a).

Surface and subsurface water circulations, especially in small headwater watersheds, are studied more than deep water circulations occurring in fractured bedrock (e.g., Viville et al., 2012; Brantley et al., 2017). The relatively recent setting up of several tens of meters-deep boreholes on such watersheds, especially those belonging to the so-called Critical Zone Observatories, is now allowing a much better exploration of water circulations and weathering processes in the deeper parts of the CZ (e.g., Brantley et al., 2013; Buss et al., 2013; Chabaux et al., 2017; Hahm et al., 2019; Holbrook et al., 2019; Ranchoux, 2020). These latter studies have systematically evidenced water circulation at great depths in the various explored sites. The hydrogeochemical characteristics of these waters, in particular, their specificity compared to surface waters, should be further clarified to better identify the water-rock interaction processes occurring in the deep CZ and the water circulation residence times in these deep levels.

The purpose of this study, conducted on the Strengbach CZO, France, is to determine the nature and residence time of the various waters circulating in the bedrock of the Strengbach catchment from the surface to ≈ 100 m depth. The Strengbach basin has been the subject of relatively extensive hydrogeochemical studies in the past for surface waters (springs, soil solutions, streams),

which today allows us to have a fairly good knowledge of their geochemical composition in major elements as well as Sr, Nd, and U isotopic ratios. These elements and ratios are relevant tracers when we seek to decipher the main water-rock interactions involved in biogeochemical and hydrogeochemical cycles (e.g., Aubert et al., 2001; Riotte and Chabaux, 1999; Tricca et al., 1999; Chabaux et al., 2011, 2013, 2019; Durand et al., 2005; Schaffhauser et al., 2014; Pierret et al., 2014, and references therein). All these data have led us to propose a first order relatively solid interpretative framework on the nature of water-rock interactions controlling the geochemical composition of surface waters in the Strengbach catchment.

In the current study, we propose to establish the hydrogeochemical typology of the deeper waters of the Strengbach CZO by a multi-method geochemical approach that combines the analysis of the above tracers (i.e., major and trace elements, Sr, Nd, and U isotope ratios) with the analysis of anthropogenic gases, namely, chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF₆). These latter elements are indeed suitable for determining the water ages and/or residence times in aquifers for relatively recent periods, 0-70 years or a little more, depending on the interpretative models used (e.g., Busenberg and Plummer, 1992; Corcho Alvarado et al., 2005; Plummer et al., 1998; Jankovec et al., 2017; De Montety et al., 2018; Cao et al., 2020). In particular, anthropogenic gases were successfully applied to estimate mean water transit time in fractured aquifers (Cook et al., 1996, 2005; Plummer et al., 2000; Bockgard et al., 2004; Ayraud et al., 2008; Jaunat et al., 2012; Roques et al., 2014a, b; Marçais et al., 2018). The results presented here on the Strengbach CZO highlight the interest of combining these different geochemical tracers to explore the hydrological functioning of the deep CZ.

2. Site presentation

The Strengbach catchment is a small 0.8 km² granitic catchment in the Vosges mountains (northeastern France) at an altitude ranging between 880 and 1150 m a.s.l. with fairly steep slopes (mean slope of 15°) (Fig. 1). It is an equipped environmental observatory where meteorological, hydrological, and geochemical data have been recorded since 1986 (Observatoire Hydrologique et Géochimique de l'Environnement/Hydrological and Geochemical Environmental Observatory, OHGE; <http://ohge.unistra.fr>) and is one of the reference headwater sites of the French critical zone observatory network OZCAR (Observatoire de la Zone Critique: Application et Recherche/ Critical Zone Observatories: Research and Application, <https://www.ozcar-ri.org>). The climate is temperate oceanic mountainous with a mean annual temperature of 7 °C (mean monthly from -2 to 14 °C). Annual precipitation is between 890 to 1630 mm.yr⁻¹ (mean 1400 mm.yr⁻¹) with snow cover for 2-4 months.yr⁻¹ (Viville et al., 2012; Pierret et al., 2014). The mean runoff of the catchment is 853 mm and varies from 525 to 1147 mm (Ladouche et al., 2001; Viville et al., 2012). Forest covers 90% of the surface area (Azaël, 1990) and is essentially composed of 80% spruce trees and 20% beech trees.

The bedrock is mainly constituted by a Hercynian leucogranite affected by hydrothermal alteration (e.g., Fichter et al., 1998a, b; Chabaux et al., 2019). The hydrothermal events caused the alteration and transformation of primary minerals (albite, K-feldspars, muscovite) into fine-grained illite and quartz. There is an occurrence of gneiss in the upper part of the northern slope of the basin (El Gh'mari, 1995; Fichter, 1997; Fichter et al., 1998; Chabaux et al., 2019). Compared to granitic bedrocks, gneiss is enriched in Mg due to the presence of biotite and chlorite (El Gh'mari, 1995; Fichter, 1997). The soils are 80–100 cm deep and vary from Dystric Cambisol (southern slope) to Albic Podzol (northern slope). The soils are usually developed on a sandy saprolite, 1 to 9 m thick, the thickest saprolite being located on the downstream part of the southern slope (El Gh'mari, 1995). Several springs are emerging in the catchment on both slopes. Some of them (Cs1, Cs2, Cs3, Cs4, ARG, RH3) were sampled for the present study (location on Fig. 1).

For studying deep water circulation within the Strengbach watershed, the site was equipped, between 2012 and 2014, with 9 boreholes drilled along two transects, one along the south-facing slope, and one along the north-facing slope (Fig. 1c-d). This includes six deep boreholes (50 to 120 m depth — F1a,b, F5, F6, F7, F8) and three shallower ones of ≈ 15 m depth (pz3, pz5, pz7), named piezometers in the following text. The main equipment installed in each well is summarized in Supplementary Material Table 1 (SM Table1). Briefly, the three piezometers were equipped along their length with a PVC tube, cased for the first two meters and screened deeper. In the screened zones, gravel pack was introduced between the tube and the bedrock. Boreholes F6, F7, and F8, drilled in 2012, were entirely cased and equipped with multi-level screened sections (SM Table 1), in front of well-located fracture zones identified by the drilling company and considered as potential water circulation levels. A gravel pack was set up outside the screened sections to ensure proper water flow, and clay plugs of bentonite (compactonite) were used to tighten the cased sections. To limit the pollution risks of the chemical composition of the water by the gravel and bentonite used in the above wells, it was decided to equip the southern slope with uncased wells. Thus, boreholes F5 and F1, drilled in 2013 and 2014, are uncased holes throughout their depth, except for the first 8 m where a PVC casing and a cement sheath were installed.

3. Methodology

3.1 Water sampling procedure

For the present study, 10 sampling campaigns, covering the diversity of hydrological contexts encountered on the catchment, were conducted over the period 05/2015–10/2018 (Fig. 2) for collecting water from springs CS1, CS2, CS3, CS4, RH3, and ARG, piezometers pz3, pz5, and pz7, and deep boreholes F5, F6, F7, and F8. Piezometer and borehole water were sampled with a pump descended to the chosen depth after generally 10 min of pumping, which is the time required to renew the water in the well. Piezometers were sampled at a depth of between 10 to 14 m. For deep borehole water, the initial sampling depths corresponded to the depths at which more significant

fractures were noticed from acoustic and optical logging. The sampling depths were adapted during the course of the study based on the first conductivity logging obtained in the wells as explained in Ranchoux (2020) (see Table 1 for sampling dates, sample depths, and the analyses performed on each sample).

Samples collected for major and trace element concentrations and Sr-Nd-U isotopic analyses were stored in 2 L polypropylene bottles, which were previously cleaned with ultra-pure HCl and ultra-pure water (18.2 MΩ.cm). For some Nd analyses requiring larger water volumes (up to 10 to 15 L), water was stored in large food-grade PVC water tanks. For analysis of dissolved gas concentrations (Ar, Ne, N₂, O₂) and CFC and SF₆ concentrations in water, samples were collected following the procedure described in Labasque et al. (2004, 2014). Water samples were stored in 500 mL glass bottles for Ar, Ne, N₂, and O₂ measurements and in steel ampoules of 40 ml and 300 ml for CFC and SF₆ analyses, respectively.

3.2 Analysis of major element concentrations and Sr-Nd-U isotope ratios

Determination of major and trace element concentrations, Sr-Nd isotope ratios, and U activity ratios were performed at LHyGeS, Strasbourg, France. Water samples were filtered through a 0.45 µm cellulose acetate membrane filter. Each water sample was divided into two aliquots. One aliquot was acidified with bidistilled 13.5 N HNO₃ to pH≈1 for trace element and isotopic analyses. The other aliquot was not acidified, measured pH and conductivity, and analyzed major element and Dissolved Organic Carbon (DOC) concentrations, following the standard procedures used in the laboratory (e.g., Lucas et al., 2010; Schaffhauser et al., 2014; Gangloff et al., 2014; Prunier et al., 2015). The pH was determined using a Meterlab® PHM210 pH-meter with a precision of ±0.02 units and the conductivity using a Meterlab® CDM210 conductometer with an uncertainty from 1 to 2%. The DOC was measured by the thermal method (Shimadzu TOC VPH) with an uncertainty of 2% and a detection limit of 0.3 mgC L⁻¹. Cation (Na⁺, K⁺, NH₄⁺, Ca²⁺, and Mg²⁺) and anion (Cl⁻, SO₄²⁻, and NO₃⁻) concentrations were analyzed by ionic chromatography (ICS 5000 Thermo Scientific) with

uncertainties of 2% and a detection limit of $5\mu\text{mol.L}^{-1}$. The Al, Mn, P, Si, and Fe concentrations were measured by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) with a Thermo ICAP 6500, a detection limit of $1\mu\text{g/l}$, and a measurement uncertainty of $\approx 5\%$. Trace element concentrations were analyzed by ICP-MS (Inductively Coupled Plasma Mass Spectrometer) Thermo XseriesII with an uncertainty of $\approx 5\%$ and detection limits between 1–10 ppt, depending on the elements.

$(^{234}\text{U}/^{238}\text{U})$ activity ratios were analyzed by mass spectrometry on a Neptune Thermo-Scientific multi-collector (MC-ICP-MS). U was first separated and purified by anionic exchange chromatography following procedures developed at the LHyGeS (e.g., Chabaux et al., 1995; Riotte and Chabaux, 1999). The procedure blanks were <10 pg, negligible compared to the U amount processed. The reproducibility and reliability of the U isotopic analysis were tested by the regular measurement of the HU1 standard, assumed to be in secular equilibrium, which for the analysis period 2015–2018 gave a $(^{234}\text{U}/^{238}\text{U})$ activity ratio of 0.999 ± 0.003 (2SD, $n = 71$).

For Sr and Nd isotope measurements, Sr and Nd were extracted and purified following the chromatography procedures used in the laboratory (Geagea et al., 2007; Guéguen et al., 2012). For Nd analysis on large water volume ($>1\text{L}$), Nd was first extracted from the water by coprecipitation with $\text{Fe}(\text{OH})_3$, followed by iron removal on cation exchange resins (Chauvel et al., 2011; Pelt et al., 2013). $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{144}\text{Nd}/^{143}\text{Nd}$ isotope ratios were measured on a Neptune Thermo-Scientific multicollector (MC-ICP-MS) and Thermo-Scientific Triton Thermal Ionisation Mass Spectrometry (TIMS), respectively. Blanks were $<1\text{ng}$ for Sr, i.e., negligible compared to the Sr amount analyzed in the samples. For Nd they reached 130 pg for samples processed with a coprecipitation stage, which represented a maximum contribution of 2-3% of the Nd used for the analysis in the few samples where the Nd amount processed was between 5 and 10 ng. The regular analysis of SRM 987 standard for the analysis period 2015-2018 gave a $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio 0.71026 ± 0.00003 (2SD, $n = 41$). Analysis of the La Jolla standard gave a $^{144}\text{Nd}/^{143}\text{Nd}$ isotope ratio of 0.511846 ± 0.00002 (2SD, $n = 39$).

for a Nd amount processed > 10 ng and a ratio of 0.511846 ± 0.00004 (2SD, $n = 8$) for a Nd amount between 2 and 10 ng.

3.3 Analysis of CFC, SF₆, and noble gas concentrations

The CFC, SF₆, and dissolved gas were analyzed at the Condé Eau platform (OSUR, University of Rennes, France). CFC and SF₆ were extracted by purge and trap and measured by gas chromatography with electron capture detection (Labasque, 2004), modified from Busenberg and Plummer methodology (1992, 2000). An uncertainty of 4% applies for high concentrations (above 0.1 pmol/kg for CFC and 0.1 fmol/kg for SF₆) and rises to 20% for lower values, next to the detection limit (between 0.01 to 0.05 pmol/L for CFC and 0.06 fmol/L for SF₆) (Labasque et al., 2006; Labasque et al., 2014). Samples for dissolved gases (Ar, Ne, N₂, O₂) were analyzed by gas chromatography following the Sugisaki method (Sugisaki and Taki, 1987) at the Condé Eau platform with uncertainties of around 3% for minor gases (< 100 ppm) and 1% for others.

3.4 Residence time and ages estimation model

CFC and SF₆ water concentrations were converted to atmospheric partial pressure (pptv) to be interpreted in terms of residence time by comparing these atmospheric concentrations with theoretical values obtained in simple hydrological models classically used for dating purposes. The conversion was done using the solubility functions for CFC-11, CFC-12, CFC-113, and SF₆ provided by Warner and Weiss (1985), Bu and Warner (1995) and Bullister, et al. (2002), respectively. Results obtained in such conversion depend on recharge temperature, altitude, and excess air (Darling et al., 2012). For the present study, the excess air was calculated using Ne concentrations, following the approach given in Heaton and Vogel (1981). The mean recharge temperature was fixed at 7 °C, the mean annual temperature measured at the meteorological station located at one of the summits of the Strengbach watershed (Fig. 1 for location). The recharge altitude used was consequently taken to 1100 m, the $\approx$ altitude of the meteorological station. The dependence of the results on the selected

recharge altitude and temperature is about 1.3%/100 m and 5%/°C (e.g., De Montety et al., 2018; Busenberg and Plummer, 1992).

The overall principle of CFC-SF₆ dating is that a given concentration of CFC-SF₆ in water, converted into atmospheric pressure (pptv) and associated to the atmospheric chronicle, provides an indication of the residence time. The CFC and SF₆ concentrations data for the northern hemisphere given by the software TRACER LPM (<https://www.usgs.gov/software/tracerlpm> – Jurgens et al., 2012) were used as an input parameter. The estimation of the residence time is linked to the conditions of infiltration in the soil and the water flow dynamics in the aquifer. A lumped parameter approach (Maloszewski and Zuber, 1982; Jurgens et al., 2012) can be used to compare the CFC and SF₆ measurements to the distribution of theoretical concentrations and thus correlate the measurements to the age of the groundwater in the system investigated. For the present study, we have used three classical models (Maloszewski and Zuber, 1982): the Piston flow model (PFM), the Exponential Mixing Model (EMM), and the Binary Mixing Model (BMM) represented in Fig. 3. The PFM model considers the system as a continuously flowing system in a tube where recent water compels older water (Fig. 3a). CFC data, in this case, leads to determination of “groundwater age.” The EMM corresponds to a vertical stratification of groundwater flow with a similar distribution of transit times, which increases logarithmically (Jurgens et al., 2012; Fig. 3b). The water sample is then an average of all the streamlines, and the obtained residence time corresponds to the “characteristic time,” which is in fact the mean of the residence time of all the streamlines. The BMM is a mixture of two components, which have evolved hydrologically independently and are mixed (Fig. 3c, d). We can thus provide one age for the two-components and a mixing proportion between these two components.

4. Results

4.1 Major element concentrations

Major element data for spring, piezometer, and borehole water analyzed for this study are presented in Supplementary Materials (SM Tables 2a, 2b; 3a, 3b; 4a, 4b).

4.1.1 Spring and piezometer water

As apparent in Fig. 4, the data obtained from the springs sampled for this study from 2015–2018 are consistent with previously published data for the period 1986–2010. More importantly, our data suggests that piezometer water, when excluding the deepest waters, has geochemical characteristics very similar to those of spring water (Fig. 5, 6 and SM Fig 1 for the piper diagram). Both are marked by low conductivities, alkalinity, and pH values, ranging from 30–50 $\mu\text{S}/\text{cm}$, 0.04 to 0.44 meq/L, and 5.46 to 7.84, respectively. The Si concentrations vary from 3.7 ppm to 6.4 ppm for piezometer water and from 3.3 ppm to 5.1 ppm for spring water. The concentrations of major cations Ca^{2+} , Mg^{2+} , Na^+ , and K^+ in spring water range from 1.3 to 3.7 ppm, 0.3 to 0.9 ppm, 1.5 to 2.4 ppm, and 0.2 to 1.1 ppm, respectively. For piezometer water, the concentrations range from 1.3 to 4.0 ppm, 0.2 to 0.7 ppm, 1.7 to 3.1 ppm, and 0.5 to 1.5 ppm, respectively (Fig. 5). Slightly higher Si and Na^+ concentrations in some Pz3 and Pz7 samples are, however, observed (Fig. 5d, e). The NO_3^- and SO_4^{2-} concentrations of piezometer water are also close to those of spring water. Some of the deepest Pz3 and Pz5 samples can have much higher conductivities than the other piezometer samples (SM Table3a,b). For three different sampling periods, Pz3 deep water was analyzed in major elements. The data indicate that such water, in addition to being more conductive, has higher alkalinity and higher pH values than the other piezometer water as well as much higher major cations and anions concentrations (SM Table 3a).

4.1.2 Boreholes water

Compared to the spring and piezometer water, samples collected in the boreholes have higher pH, conductivities, and alkalinity values, with pH from 6.98 to 8.32, conductivity between 150 and 270 $\mu\text{S}/\text{cm}$, and alkalinity between 0,3 meq/L and 2,7 meq/L (Fig. 5a). Their concentrations in the main cations and anions are also different (Fig 5, Fig 6, SM Fig 1), with Ca^{2+} and Mg^{2+} concentrations four to eight times higher in deep water than in spring and piezometer water, and Na^+ and K^+ concentrations up to one to four times higher. Si concentrations are more concentrated, usually by about twice the maximum. NO_3^- concentrations usually have lower values in deep borehole water with values close to zero in some of them (Fig. 6e). Finally, Cl^- and SO_4^{2-} concentrations for all groups of water (spring, piezometer, and deep borehole water) are in the same range of variations (Fig. 6). The data also show that the geochemical characteristics of the borehole water are quite different from one borehole to another and also within the same borehole.

- Borehole F5

The water column of borehole F5, when not perturbed for a long time and hence at a steady state of hydrological functioning, is divided into two conductivity zones, with a surface zone marked by low conductivity values closed to those observed in spring and piezometer water ($\approx 30 \mu\text{S}/\text{cm}$) and a deeper zone of several 10 m thick characterized by high conductivity values ($\approx 250 \mu\text{S}/\text{cm}$) (Fig. 7). The transition between the two zones is narrow and takes place over less than 1 m. Its depth depends on the sampling period: the higher the water level (i.e., high flow period in the catchment) the deeper the transition zone (Fig. 7). Geochemical data obtained on water samples collected in such hydrological steady-state boreholes point out that water sampled around 43 m deep has high concentrations in major cations, HCO_3^- , and Si, and low to zero concentrations in NO_3^- (Fig. 6). Water samples from 13–14 m deep during periods of high water, i.e., not in the vicinity of the conductivity transition zone (see Fig. 7), have much lower concentrations of major cations, HCO_3^- , Si, and higher concentrations of NO_3^- . This F5 surface water has the same geochemical characteristics as those of Pz5 water, located a few meters away from the F5 borehole, and defines the same range of

variability in all the binary diagrams studied (Fig. 5 and 6) and in the Piper diagrams (SM Fig. 1). The other samples, i.e., the 13 m deep water taken during the lower water period and thus in the vicinity near the conductivity transition zone in the water column (see Fig. 7), as well as the water sampled at 23-27 m deep, define in all these diagrams (Fig. 5 and 6) an alignment between the above two water types.

In 2015, three pumping tests of a few hours, with the pump at the bottom of the borehole, were performed in borehole F5. As illustrated in Fig. 7b, the electrical conductivity profile of the water column was significantly modified, especially in its deeper part, with conductivity decreasing to 50 to 90 $\mu\text{S}/\text{cm}$, depending on the pumping dates. After the pumping, a slightly higher conductivity level around 21 m depth can be observed on some profiles (Fig. 7b). The data also highlights that the water column recovers its stationary profile with two contrasted conductivity zones in a few days (Fig. 7c). Several samples, collected along the water column a few hours after pumping or one or two days later when the profile was returning to equilibrium (Fig. 7 b, c), were analyzed in major elements. All these samples, including the samples collected at ≈ 23 m and ≈ 45 m, plot in Fig. 5 and 6 along the linear trends defined between the unperturbed deep end-member and piezometer Pz5 end-member.

- Boreholes F6-F7-F8

The concentrations of major elements in F6, F7, and F8 boreholes, located on the northern slope, show that the deep water of the different boreholes has geochemical characteristics specific to each of them and different from those of borehole F5 (Fig. 5, 6). Deep water from the F6 borehole has relatively stable major element concentrations over time. This water has the highest conductivity, alkalinity, Mg^{2+} , and Cl^- concentrations of all the deep water sampled in the Strengbach catchment and the lowest Si and Na^+ concentrations (Fig. 5). It has also high Ca^{2+} and SO_4^{2-} concentrations, similar to those analyzed in F5 deep water, and as for this water, no NO_3^- (Fig. 6). Compared to borehole F6, the F7 and F8 deep water have lower alkalinity, conductivity, Cl^- , Ca^{2+} , and Mg^{2+} concentrations, but higher Si, Na^+ , and NO_3^- concentrations, and similar K^+ concentrations. F8

water has lower Mg^{2+} , Cl^- , and SO_4^{2-} concentrations compared to F7 water. In addition, in the SO_4^{2-} vs. Mg^{2+} (Fig. 6d) or vs. Ca^{2+} (Fig. 6c) concentrations diagrams, all deep water samples define a single linear and positive trend except for the F8 borehole, which plots in a different and negative trend. Compared to F6 and F5 deep water, the F7 and F8 deep water is marked by a higher range of variations in nearly all the major anion and cation concentrations, which, however, remain relatively small compared to the inter-borehole chemical variability described above.

4.2 Sr, U, and Nd isotopic ratios

The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratios and ($^{234}\text{U}/^{238}\text{U}$) activity ratios are given in Table 1. The data indicate that spring water samples collected in this study display U-Sr isotopic systematics very similar to the one observed for water collected in 2004-2006 (Prunier 2008; Pierret et al., 2014) with similar ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ and ($^{234}\text{U}/^{238}\text{U}$) variations for each studied spring (and similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variations with discharge (Figures in supplementary material SM Fig. 2a,b). The data also confirm the existence of small but possibly significant variations of ($^{234}\text{U}/^{238}\text{U}$) with discharge (Fig. SM Fig. 2b). The data also evidence similar $^{87}\text{Sr}/^{86}\text{Sr}$ and ($^{234}\text{U}/^{238}\text{U}$) ratios in piezometer and spring water (Fig. 8a,b) with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.72039 and 0.72627 in piezometer water and between 0.72117 to 0.72785 in spring water, and with ($^{234}\text{U}/^{238}\text{U}$) systematically < 1 in spring and piezometer water except in one Pz7 sample, which has a ($^{234}\text{U}/^{238}\text{U}$) ratio of 1.168 ± 0.003 (Fig. 8b). Compared to spring and piezometer water, deep borehole water has much less radiogenic Sr ratios, ranging between 0.71416 (F5) to 0.71898 (F6), and have U activity ratios systematically > 1 with values ranging between 1.071 and 1.103 in F7 and F8 borehole deep water, between 1.073 and 1.354 in F6 borehole water, and around 2.000 in F5 borehole water (Table 1 and Fig. 8). For F5 borehole water, while deep water is isotopically not very variable over time, the Sr and U ratio of surface and intermediate water show much higher variability. Surface water collected during high water periods, far from the conductivity transition zone (see above), has values close to those of the piezometer Pz5. On the other hand, surface water taken during low flow, i.e., intermediate water and water after

a long pumping test, have more variable values intermediate between the values of Pz5 water and F5 deep water. Compared to the variations of ($^{87}\text{Sr}/^{86}\text{Sr}$) and ($^{234}\text{U}/^{238}\text{U}$) ratios, the variations of ($^{143}\text{Nd}/^{144}\text{Nd}$) ratios are much less important with similar values in surface and deep water, with $^{143}\text{Nd}/^{144}\text{Nd}$ values ranging from 0.51214 to 0.51227 in spring water, from 0.51220 to 0.51227 in piezometer water, and from 0.51219 (F8) to 0.51224 (F5), in borehole deep water (Table 1).

4.3 CFC and SF₆ data

CFC and SF₆ data collected for this study are given in Table 2 with water concentrations given in pmol/L and atmospheric mixing concentrations in pptv. The data show that spring waters have high CFC concentrations: 155 to 272 pptv for CFC-11, 376 to 625 pptv for CFC-12, and 50 to 101 pptv for CFC-113. A few springs were also analyzed in 2006 and 2007 and data are given in Supplementary materials (SM Table 5). Are also given in supplementary materials the dissolved gas concentrations (Ne, Ar, N₂ and O₂) (SM Table 6). The CFC concentrations obtained in 2006 and 2007 are very consistent with the values obtained 10 years later at a similar season (Fig. 9). As observed with the elementary and isotopic geochemical characteristics, the CFC and SF₆ concentrations in the piezometer water (Pz3, Pz5, and Pz7) are similar to those of springs (Fig. 9). For spring and piezometer water, the data show lower CFC concentrations during low flow periods (August 2015) than during high flow periods (May 2006, 2007, and 2015). The data may also indicate a decrease of CFC concentration with the increase of Si concentration for spring water. This trend is less apparent when piezometer data are added (Fig. 10).

CFC data from boreholes lead to water typologies similar to those observed with elemental or isotopic geochemistry data. Surface water from F5 (13-15 m deep) plot within the same range of variation as spring and piezometer water (Fig. 9). For this water as for spring and piezometer water, CFC concentrations in samples collected during high flow periods (May 2015) are higher than during low flow periods (August 2015). F5 borehole water collected at 23-26 m has concentrations between F5 deep water and surface water concentrations (Pz5 and "surface" water from F5) (e.g., in Fig. 10b).

Deep water from boreholes F6, F7, F8, and F5 has lower concentrations than in spring and piezometer water, 16 to 124 pptv, 131 to 383 pptv, 12 to 48 pptv for CFC-11, CFC-12, and CFC-113, respectively. The distinction between surface and deep water, evidenced by the CFC concentrations, is clearly illustrated in the CFC-11 vs. CFC-113 or CFC-12 vs. CFC-113 binary diagrams (Fig. 9), despite the scattering of the data of each of these water types. Compared to CFC concentrations, SF_6 concentrations in Strengbach water do not show a systematic difference between spring/piezometer water and deep water. Only the amplitude of the variation range is different, with concentrations ranging from 6 to 24 pptv in spring and piezometer water and from 2 to 50 pptv in borehole deep water. The highest SF_6 concentrations are analyzed in the deep water of borehole F5, with values far above the maximum values measured in the atmosphere (9 pptv in 2016). When these samples are not considered, the variation range in SF_6 concentrations is more limited ($\approx 2 - 15$ pptv) and closer to that of surface water.

5. Discussion

Geochemical data, whether elementary concentrations, $^{87}\text{Sr}/^{86}\text{Sr}$ and $(^{234}\text{U}/^{238}\text{U})$ ratios, or tracer gases (CFC and SF_6), show a systematic distinction between the values measured in spring and piezometer water, on the one hand, and in deep borehole water, on the other hand. These data also show second-order variability between the different piezometers and between the different deep water sampled in the boreholes.

5.1. Influence of borehole building materials on water chemistry

As detailed in section 2, boreholes and piezometers have been equipped with various materials (SM Table 1 in Supplementary Materials), which can potentially impact the chemical composition of waters. The major and trace element concentrations of these different materials were analyzed and leaching was carried out on each of them for additional analysis. The protocol is presented in the Supplementary Materials 3 (leaching experiments), with the related table of results (Table SM3) and Figures (Fig. SM3a, b). The plot of the data in (Fig. SM 3a, b) clearly show that the

trends defined in each of these diagrams by deep borehole water (F5, F6, F7, and F8) cannot be explained by the contribution of a chemical flux with the characteristics of one of these materials or of their leachate into a surface-type water end-member. The trends defined by the data points in the diagrams never go towards one of such potential end-members. Similarly, the trends defined in Fig. SM 3a, b by the piezometer data points are very similar to those defined by the spring water and do not show any specific bias towards one of possible pollution end-members, except for the deep water of piezometer pz3. The latter water samples in Fig SM 3 define linear trends from the more surface waters of the piezometer to the domain defined by the leachates of the soda-lime glass beads used as filters in the piezometers. Based on such observations, it can be suspected that at the bottom of the pz3 piezometer, the bead filter has construction defects, which causes leaching of these beads and hence pollution of the deep pz3 waters. For this reason, the deep piezometer water samples are no longer discussed in the following sections.

5.2 Hydrological Implications from geochemical characteristics of spring and piezometer waters

As shown in the result section, the geochemical characteristics of spring water collected between 2015 and 2018 are consistent with those collected and analyzed over the 1986–2010 period, indicating similar hydrogeochemical contexts and processes at the origin of the geochemical signatures of spring water over these different periods. Hydrogeochemical modeling of the Strengbach spring water for the period 1986–2010 (Ackerer et al, 2018, 2020a) has made it possible (a) to better specify the nature of the water-rock interactions controlling the geochemical budget of this water, (b) to specify the origin of the chemostatic behavior of these sources (Ackerer et al., 2018, 2020a), and (c) to explain the decoupling that exists between the time evolution of the Si-Na concentrations and Ca-K concentrations in the Strengbach spring water over the past 30 years (Ackerer et al., 2018). Furthermore, the simulation results show that the rock interacting with the water feeding these springs is neither a fresh granitic bedrock nor a surface saprolite type rock but an already slightly weathered granite corresponding to fractured saprolite rocks located between one to

a few meters deep (Ackerer et al., 2018). This conclusion is not specific to the Strengbach case. It is also proposed for a neighboring granitic catchment, the Ringelbach catchment, based on the modeling of the geochemical composition of the Ringelbach spring water (Lucas et al., 2017; Schaffhauser et al., 2014). Such conclusions are consistent with the hydrological schemes deduced for the Strengbach catchment from hydrologic modellings, i.e., water circulating in a shallow subsurface aquifer constituted by the relatively thin (≈ 10 m) porous saprolite above the more compact bedrock (Ackerer et al., 2020a; Weill et al., 2019). Furthermore, as previously proposed (Riotte and Chabaux, 1999; Pierret et al., 2014; Prunier et al., 2015), water interactions with already weathered granites readily explain the occurrence of $(^{234}\text{U}/^{238}\text{U}) < 1$ in the stream and spring Strengbach water, including the spring water retained in the present study. Such an interpretation is consistent with $^{234}\text{U}/^{238}\text{U} < 1$ measured in soil horizons of the Strengbach catchment (Prunier et al., 2015; Ackerer et al., 2016). The geochemical modeling studies also explain the different behavior of Ca and the Si-Na system in the Strengbach spring water, whether because of their different long-term concentration trends or the greater spatial variability of Ca concentrations compared to the Si ones (Ackerer et al., 2018, 2020a). Both are related to the different nature of the main minerals controlling the budget of these elements in the Strengbach spring water. Dissolution of albite is the main mineral source of Na in solution; biotite and feldspars are the main source of Si. The Ca in solution is essentially derived from the dissolution of apatite with a small contribution of anorthite (5–10% of the Ca). The predominant role of apatite or its alteration products on the Ca budget of the Strengbach surface water was also proposed from the Sr-Nd isotope ratios of the Strengbach surface water (Aubert et al., 2001; Stille et al., 2009). It is confirmed by the new Sr-Nd results obtained in the present study, which plot within the domain of previous Sr-Nd data between the apatite and plagioclase domains (Fig. 11). Incidentally, such a similitude shows that for the spring water, the alteration system controlling the Sr-Nd budget of water circulating in the regolith has not been significantly modified over the past 20 years at the difference of what is observed for soil solutions (Prunier et al., 2015; Schmitt et al. 2017; Chabaux et al., 2019 for more details on soil solutions).

Altogether, these data, acquired over the last 15 to 30 years in the Strengbach basin, lead to a fairly well-defined hydrogeochemical framework for the spring water of this basin, with a geochemical signature of the water acquired in a shallow subsurface aquifer formed by the more or less altered saprolite levels.

The observation that piezometer water has on average similar geochemical and isotopic characteristics to those of surface water, which are very different from deep water, indicates that such water in the Strengbach catchment circulates in a reservoir similar to that of spring water, i.e., in porous fractured saprolite. This conclusion thus confirms the hypothesis made by Ackerer et al. (2020a) to model the geochemical composition of Strengbach piezometer waters.

5-3 Origin of the geochemical characteristics of deep borehole waters

5-3-1 Water mixing processes

As seen in the Results section, the deep water collected in boreholes has geochemical and isotopic characteristics quite different from those of surface water. The data also show significant geochemical variation between and within wells. This is particularly visible in borehole F5, which is characterized by two contrasting water samples highlighting at least two inflows of water (Fig. 7a) with a surface water end-member having geochemical characteristics of spring/piezometer water and a deep water end-member marked by high conductivity values and geochemical characteristics relatively stable over time. The results also show that the other F5 water samples, i.e., those collected at 23-26 m, after a long pumping test, or in the vicinity of the conductivity transition zone, plot along a mixing line between the two end-members in classical binary elementary diagrams (Fig. 5-6). The U, Sr, and Nd isotopic results, as well as CFC and SF₆ data, confirm such a mixing interpretation as, for instance, all data of F5 water plots along mixing lines in the $^{87}\text{Sr}/^{86}\text{Sr}$ vs $1/\text{Sr}$ diagram (Fig. 8a). The different mixing lines defined in this diagram are easily explained by the geochemical variations of the surface end-member over time, which are much more important than for the deep end-member. The anti-correlation defined by all F5 data points in the CFC-11 vs. SF₆

diagram (Fig. 10c) can also be explained by the proposed mixing scenario with low SF6 content in surface and a deep water end-member concentrated in SF6. Altogether, these data evidence that in borehole F5, waters of intermediate depths, water taken after pumping, and water collected at the vicinity of the conductivity transition represent mixing in variable proportions between surface and deep water end-members, which is potentially induced by the pumping protocols used in this study.

Compared to the deep water collected in borehole F5 or to the deep water in borehole F6, the waters collected in F7 at 42 m and 47 m and in F8 at 27 m are marked by relatively large geochemical variations in nearly all the major anion and cation concentrations (Fig. 5 and 6). As for intermediary waters of borehole F5, such variability could be a consequence of the water pumping procedure because in both boreholes F7 and F8 such pumping was performed in the vicinity of a level of conductivity change in the water column (in Ranchoux 2020). For borehole F7, the chemical variability of the samples at 47 m is higher than at 42 m, with chemical compositions approaching those of the 42 m water when the conductivity transition between the two zones is close to the 47 m depth. These variations could therefore be interpreted in terms of mixing in varying proportions of two distinct water supplies within the water column, one close to 42 m depth and another one to 47 m depth, implying that our sampling protocol allows a better sampling of water at 42 m depth than at 47 m depth. Overall, these different results illustrate the difficulty of precisely sampling the diversity of deep water in boreholes with the sampling protocols, which can induce mixing artifacts between the different water incomes supplying the water column. However, such a protocol is sufficient to geochemically identify one to two specific deep water end-members per borehole, the geochemical composition of which is discussed later. These deep water end-members can be systematically associated to fractured areas in the two cores recovered during borehole F5 and F6 drilling or in camera logging (Ranchoux, 2020). This certainly confirms a system of water circulation in the deep part of the substratum principally controlled by the fractures structuring it (Chabaux et al., 2017).

5-3-2 Mineralogical control

The different deep water identified in boreholes F5, F6, F7, and F8 have conductivities, alkalinities, and pH much higher than those in surface water. Such a characteristic, also seen for the Ringelbach catchment (Lucas et al., 2017; Schaffhauser et al., 2014), confirms a different hydrogeochemical context for the deep water compared to surface water. Each of these water samples has its own geochemical characteristics, which is consistent with the interpretation that deep water circulations in the Strengbach catchment are located along with different fractures, each of them having its own hydrophysical and mineralogical characteristics. Among the parameters that can be involved to explain the distinction between surface water and deep water and between the different deep water themselves, there is the nature of water-rock interactions (primary and secondary minerals) occurring along the water pathway.

Saturation tests were performed for all water types in the Strengbach catchment using the Hydrogeochemical KIRMAT code (Gérard et al., 1996), which was recently used to contribute to the understanding of different issues such as groundwater salinization (Lucas et al., 2010; M’Nassri et al., 2019), weathering processes (Lucas et al., 2017; Ackerer et al., 2018) and hydrothermal alteration (Ngo et al., 2016). The minerals tested are the granite minerals and granite alteration products (clay minerals, carbonates, Fe oxides) with the same characteristics as those used for Strengbach springs modeling (Ackerer et al., 2018; 2020a). Phosphate phases (apatite) recognized as mineral phases controlling the budget of Sr, Nd, and probably Ca of surface water, i.e., stream, springs, and soil solutions (Aubert et al., 2001, 2002; Prunier et al., 2015; Chabaux et al., 2019) have also been tested based on the P total concentrations as well as Ca sulfates. Based on major element characteristics, three piezometer water samples (pz3, pz5, and pz7) and four borehole water samples (F5 deep, F6, F7 42 m, and F8 27m) have been selected for the saturation test. Besides, an average spring water composition has been used for the saturation test. Data used for the calculation are given in Table 3 and the results of the saturation index are given in Table 4 and illustrated in Fig. 12.

The results confirm different water-rock interaction characteristics between surface (piezometer and spring water) and deep water from boreholes F5, F6, F7, and F8. In terms of primary

silicate minerals, the surface water is undersaturated in biotite and plagioclases (Ca and Na) and slightly in K-feldspars. They are also oversaturated in muscovite and quartz. Deep water is undersaturated in plagioclases only (especially Ca and slightly or not in Na plagioclases) and saturated in K-feldspars, muscovite, quartz, and most often in biotite. The differences between the two types of water signature are also found in secondary or minor minerals: surface and deep water are both saturated with kaolinite and illite, while only deep water is saturated with a montmorillonite-type clay mineral. Moreover, surface water is highly undersaturated with calcite or dolomite while deep water is undersaturated in dolomite and only slightly in calcite. These results highlight the very different saturation degree between these two types of water, confirming that surface water is mostly in a context of dissolution, involving a wide range of primary silicate minerals but also minor minerals such as apatite, and secondary minerals such as clay minerals (Ackerer et al., 2018, 2020a). The deep water is, by contrast, in a context of dissolution limited essentially to plagioclase and carbonates.

The observation that, in the $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic diagram (Fig. 11), spring and piezometer water is placed on or near the theoretical apatite-plagioclase mixing curve is consistent with the interpretation that in the Strengbach catchment, the surface water has a Sr-Nd budget controlled by the dissolution of these two minerals without significant Sr-Nd fractionation (Aubert et al., 2001). The offset of surface water with such a theoretical mixing curve has been proposed due to a contribution from a component of the atmospheric deposition type (Aubert et al., 2002). Compared to spring and piezometer water, borehole water is characterized by less radiogenic Sr isotope ratios. In the Sr-Nd isotopic diagram, the borehole water data thus defines a domain distinct from that of surface water (Fig. 11). Explaining the difference between the Sr-Nd systematic in surface and deep waters by a different atmospheric contribution in the two water types would imply a higher atmospheric contribution in the deep borehole water than in spring or piezometer water, which is difficult to consider. Thus, the deep-water data points in the Sr-Nd diagram, assuming for surface water a Sr-Nd budget essentially controlled by the phosphate-plagioclase minerals, would impose a

dissolution of these two minerals with a significant Sr-Nd fractionation at the difference of what we propose for surface water. An alternative explanation would be that the Sr and Nd chemical budget in deep water is controlled by an additional mineral phase and not only by the apatite plagioclase dissolution. Saturation tests indicate that deep water, in addition to being undersaturated in plagioclase, is also relatively undersaturated in carbonates. Carbonates are also observed as fracture minerals in cores (Ranchoux, 2020). We propose, therefore, that they can contribute to the Sr-Nd budget of deep water. Besides, if apatite dissolution in deep water-rock interaction is assumed not to fractionate Sr-Nd, as for surface water, the Sr and Nd isotope ratios of carbonates must have unradiogenic Sr and Nd to account for the deep water points in the Nd vs. Sr isotope ratio diagram. Observation of sulfate-rich water for boreholes F5, F6, and F7, and less rich for borehole F8, may also suggest a contribution of sulfate minerals in deep water-rock interactions in the Strengbach catchment. Sulfate minerals are observed in fractures (Lerouge pers. comm.), and their role is also invoked to explain some specific chemical characteristics of soil solutions (Prunier et al., 2015; Chabaux et al., 2019).

We, therefore, propose from the above geochemical and isotopic data that differences between surface and deep water in the Strengbach catchment are the consequence of two different water circulation contexts, with surface water circulating in a shallow subsurface aquifer or very fractured area and deep water circulating in a network of more or less independent fractures separated by fresh bedrock. The observation that borehole water at Strengbach has $^{234}\text{U}/^{238}\text{U}$ activity ratios systematically > 1 , whereas surface water (spring and piezometer water) has activity ratios < 1 , supports this pattern of different alteration contexts for the two types of water. For deep water, a ^{234}U - ^{238}U fractionation is classically expected in a fresh bedrock alteration context, i.e., at $^{234}\text{U}/^{238}\text{U}$ equilibrium. However, this pattern needs to be confirmed by ^{234}U - ^{238}U analysis of rocks and minerals in fractures, which is beyond the scope of this study. In the Ringelbach catchment, Lucas et al. (2017) proposed that the chemical differences between surface and deep water and between two deep water samples result from their different hydrodynamic characteristics, namely, from different water

velocity and/or residence times between the two systems with faster water flow for surface water than for deep water. The observation that in the Strengbach catchment the saturation index of deep water increases with decreasing altitude (Fig. 12) may support the assumption that the groundwater residence time potentially plays an important role in the geochemical diversity of the Strengbach water. The CFC analysis makes it possible to discuss this point for the Strengbach catchment.

5-4 Water age dating

5.4.1 SF₆ lithogenic production

As for the chemical and isotopic data, the CFC data indicate a systematic difference between surface and deep water, which is interpreted as two different water circulation systems for surface water and deep water. The data also define positive trends in binary CFC diagrams (Fig. 9a, c). By contrast, no global correlation is observed between CFC and SF₆. In almost all water samples, SF₆ concentrations are higher than the maximum SF₆ atmospheric concentrations with values as high as five times the maximum atmospheric values. A lithogenic production of SF₆ is often invoked to explain such high concentrations. SF₆ terrigenous flux was proposed, for instance, in diagenetic fluids (Busenberg and Plummer, 2000), basalt, or granitic rocks (Kranz 1966; Harnisch and Eisenhauer, 1998; Busenberg and Plummer, 2000; Koh et al., 2007). SF₆ lithogenic production requires a fluor source in rocks, which can be found in some minerals such as magmatic micas, fluorapatites or fluorites. It also requires an energy source, which is often assumed to be linked to energy produced by α decays of the U and Th series (Kranz, 1966). Fluorites or fluorapatites are observed in Vosges granites or fracture systems of the Vosges granites (Blanalt et al., 1972; Turpault et al., 1998). Occurrences of such minerals may thus provide a terrigenous SF₆ source in the Strengbach catchment, which prevents the use of SF₆ concentrations for water age estimation.

5.4.2 Age dating of spring and piezometer water

CFC data show similar values for spring and piezometer water consistent with the interpretation that these two water types circulate in a similar hydrological environment. The CFC values are relatively close to the current atmospheric values, both for the 2015–2018 or 2006–2007 data. This implies young ages for this water. The dispersion of the CFC data is relatively high (Fig. 9), much higher than the analytical uncertainty. The dispersion of data in the CFC binary diagrams is classical and has been explained by different processes, which, in addition to the possible variation of recharge T° , can be due to local atmospheric pollution leaks from landfills or agriculture (e.g., Oster et al., 1996; Ho et al., 1998; Hohener et al., 2003; Plummer et al., 2000; Spurlock et al., 2000; International Atomic Energy Agency, 2006; Darling et al., 2012) or to CFC microbial degradation in reductive context. Such microbial degradation affects CFC-11 much more than CFC-113 and, finally, CFC-12 (e.g., Cook et al., 1995; Plummer et al., 1998; Sebol et al., 2007; Horneman et al., 2008). In the Strengbach deep water, the correlation observed between CFC-11 and NO_3^- concentrations (Fig. 10b), associated with low values of dissolved oxygen (Table SMT1), likely indicates the occurrence of CFC microbial degradation. CFC microbial degradation does not occur in an oxidizing environment and thus cannot be invoked for CFC scattering of surface water.

The observation that the spring and piezometric water collected in August 2015 during periods of low flow have systematically lower values than water from periods of higher flow might indicate mean residence times of water greater during low flow periods than during high flow periods with a potential difference of several years. Such age might even be consistent with the preliminary estimate of surface water residence time made in the Strengbach catchment from oxygen isotopic data (Viville et al., 2006). The global anticorrelation observed between the CFC-113 concentrations and Si concentrations (Fig. 10a) might also reinforce such an interpretation if the Si concentrations of water were considered as a proxy of the water residence time within the aquifer (e.g., Marçais et al., 2018). However, a variation of water temperature recharge of $\approx 1^\circ\text{C}$ can entirely

account for the CFC concentration range of the spring and piezometer water. The noble gases concentrations vary following a similar trend as CFC, with higher concentrations in high flow (May) and lower in low flow (August) periods (SM Table 6 in Supplementary Material). Such variations can result from a variation of the equilibration temperature of these dissolved gases at the season scale in the context of a monthly circulation of the surface water in the Strengbach catchment. The hydrological modeling works, using the NIHM code (Pan et al., 2015; Weill et al., 2019) as well as the coupled hydrogeochemical NIHM-KIRMAT modeling (Ackerer et al., 2020a), evidence short water transfer times of a few months maximum for the spring and piezometer water in the Strengbach catchment, which is not very variable from one hydrological period to another. The hydrogeochemical modeling exercise also explains the origin of the SiO_2 concentration variations within the Strengbach surface water (Ackerer et al., 2020a). A seasonal variation of recharge temperature of the surface water in the Strengbach catchment is certainly the main cause of the observed CFC data dispersion. This implies that in such mid-mountain and headwater catchments where surface water circulates relatively quickly, the classical assumption of a constant recharge temperature to recalculate atmospheric concentrations of CFC is not applicable. The consequence is that in such a hydrogeological context, without an independent estimate of water recharge temperature, CFC can only be used as tracers of short residence time (less than a year to a few years) and cannot be used to infer more precise water ages.

5.4.3 Age dating of borehole deep water

As seen in section 4.4, deep water has lower CFC concentrations than surface water and the data define a linear trend in the CFC-12 vs. CFC-113 diagram (Fig. 9b). In this diagram, the data does not plot along the theoretical curve given by the Piston Flow (PF) Model but rather along the theoretical curves from Binary Mixing (BM) Model and Exponential Mixing (EM) Model. These observations imply that the CFC data of the Strengbach borehole water cannot be interpreted with

the PF model but rather with the other two. The CFC data alone do not allow one model to be favored over the other. Therefore, they are discussed for both models.

In the case of the EM model, the CFC data mean that the groundwater residence time is greater than 30 years for F6 water (Table 2) and up to 130 years in the case of the less concentrated water (F5 and F8 in Tables 2). If we consider vertical circulation, the water's apparent velocity varies between 0.18 and 2.03 m/yr (Table 5), which is the order of magnitude typically used in modeling this type of circulation (e.g., Lucas et al., 2017). If we consider circulation in a fracture network, then the distance can increase considerably, inducing higher velocity. For a maximal distance proposed as the distance from the top added to the sampling depth (considering no tortuosity), the velocity obtained would vary between 1.56 and 11.97 m/yr (Table 5).

In the case of the BMM model with a straight line between the recent water and a point without CFC, i.e., before 1940, the deep-water concentration would be due to a mixture between recent water and water older than 80 years. The estimation of the proportion of recent and deep water can be calculated with a CFC-12 concentration to provide information on flow dynamics, considering a PF Model for recent water from 2018 to $\approx$ 1995 and old water without CFC for the second end-member. The average values of the proportion of recent water obtained for each borehole are presented in Table 2. The proportion of recent water on deep water ranges from 70% to 27%, depending on the observed borehole and the sampling period. Similar values are obtained using O₂ values (Table 2) with values ranging from 60% to almost 0%. A relationship appears between the proportion of recent water and the location of the borehole along the watershed slope: when the borehole is located lower in the slope, the influence of recent water is lower. It is also observed that when the sampling is deeper in the borehole, the proportion of young water is lower. The comparison of data from a borehole with the nearby piezometer validates the mixing hypothesis. For the two pairs F5-Pz5 and F7-Pz7, in almost all cases for the same sampling period, the couple of

surface-deep samples aligns between a young/present day water component and a water end-member without CFC in the diagram CFC-12 vs. CFC-113.

In a context other than that of the Strengbach catchment, old deep saline fluids of several hundred thousand years have been observed at a few hundred meters deep in the fracture granitic basement (e.g., Bucher and Stober, 2010). Even not considering such depths, in the fracture granitic basement in Brittany, France, ancient water has also been seen at depths of ≈ 100 to 200 m (Roques et al., 2014a, b). These waters circulate slowly in circulation loops which can exceed the limits of surface watersheds. They can show mixing processes with surface water during high flow periods similar to those observed in the deep drillings of Strengbach (Roques et al., 2014a, b; Bochet et al., 2019). Within such systems, the slow deep circulation allows for partial equilibration of the water with the granitic matrix (micro-fracturation), which provides solutes with much higher residence times related to diffusion through the matrix (Aquilina et al., 2015; Aquilina and Dreuz, 2011). We propose that such a scenario could be invoked to explain the CFC systematic of the Strengbach deep water, i.e., the water flowing in fractures is a mixture between recent water circulating rapidly through fracture networks and old water (> 80 yrs) flowing either in secondary fractures or in the granitic matrix.

6. Conclusion

This study presents the water geochemical characteristic of the Strengbach catchment at different depths to bring better constraints of the deep alteration process, which occurs in a small granitic catchment. For this purpose, spring water (i.e., water circulating in the first meter of a saprolite aquifer), water from piezometers (i.e., from 10 to 15 m deep), and deep water (from 50 to 120 m-deep boreholes) were sampled and analyzed under different hydrological conditions (high, intermediate, and low flow).

Chemical data show contrasted characteristics between spring and piezometer water, on the one hand, and water sampled in front of the main fractured area, on the other. Deep water is characterized by concentrations of major elements generally higher than those of more superficial water. This, therefore, highlights the existence of at least two types of water with contrasting signatures. Analysis of major elements as well as Sr and Nd isotopes shows that all the geochemical and isotopic signatures of the water of the catchment can be explained at first order by the primary mineralogy of the granite in place, and in particular by the dissolution of the phosphate-plagioclase minerals. Besides, the saturation index shows that chemical variations in water can be explained by a more advanced degree of alteration of primary minerals for deep water where minerals such as albite, anorthite, or biotite are closer to equilibrium.

CFC data show that the two types of water have very different ages. CFC concentration in surface water indicates recent ages. The data also suggests that the variations of CFC concentrations in spring and piezometer water, between the periods of high and low water, can result from a seasonal variation of recharge temperature of surface water. Such an interpretation implies that in a hydrological context of rapid surface water circulation, as in the Strengbach catchment, without an independent estimate of water recharge temperature, CFC data can mainly be used as tracers of short residence time (less than a year to a few years) without being able to determine the water ages more precisely. For deep water, the low CFC concentrations can be explained by (1) water with ages between 50 to 200 years or (2) a mixing between recent water having high concentrations of CFC and older than 70 years water without CFC, depending on the interpretation of the CFC mode used. Relationships between the deep boreholes and piezometers at intermediate depth observed for CFC as well as oxygen might favor the mixing interpretation as already observed in other fractured systems.

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Table captions

Table 1: Isotopic $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, ($^{234}\text{U}/^{238}\text{U}$) activity, and Sr, Nd, and U concentrations of boreholes, piezometers, and spring waters.

Table 2: CFC-SF₆ gas concentration in water (pmol/l), corresponding atmospheric mixing ratio (pptv), and simulation results of the PFM mean age, EMM mean age, and mix fraction of the young component of the BMM using CFC-12 values and TracerLPM software.

Table 3: Average water concentrations of springs, piezometers, and boreholes used for the index saturation test.

Table 4: Saturation Index of main minerals for the different water signatures. Negative values are highlighted in grey.

Table 5: Minimum water velocity estimates based on sampling depths and residence time from the EMM model.

Figure captions

Figure 1: (a) and (b) localization and presentation of the Strengbach catchment with the position of springs (dark blue), piezometers (light blue), and deep boreholes (orange) in the basin; (b) and (c) simplified slope cross-sections with borehole localization.

Figure 2: Precipitation (dark histogram on top), stream discharge (light blue), and F5 borehole piezometric level (red line) from 2015 to 2019. Borehole, piezometer, and spring water (dark point), and CFCs-SF₆ (yellow point) sampling periods are highlighted.

Figure 3: schematic lumped parameter model used for the CFC-SF₆ interpretation of this study, with (a) Piston Flow Model (PFM), (b) Exponential Mixing Model (EMM), (c) and (d) Binary Mixing Model (BMM).

Figure 4: Time evolution of Na⁺, K⁺, Ca²⁺, Mg²⁺ and Si concentrations of spring water from 1990 to 2016 (data: Ackerer et al., 2018, 2020a; this study)

Figure 5: Concentration plots of water samples: (a) conductivity vs. pH, (b) Ca²⁺ vs. alkalinity, (c) Ca²⁺ vs. Mg²⁺, (d) Si vs. Na⁺, and (e) K⁺ vs. Na⁺.

Figure 6: Concentration plots of water samples: (a) Cl⁻ vs. alkalinity, (b) Cl⁻ vs. NPOC, (c) SO₄²⁻ vs. Ca²⁺, (d) SO₄²⁻ vs. Mg²⁺, and (e) SO₄²⁻ vs. NO₃⁻.

Figure 7: Borehole F5 conductivity profile evolution influenced by long pumping: (a) before pumping, (b) after pumping (around 5 hr), (c) coming back to equilibrium, and (d) acoustic scanner of borehole walls. The fractured area is highlighted in grey.

Figure 8: (a) $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio vs. 1/Sr (ppm) and (b) ($^{234}\text{U}/^{238}\text{U}$) activity ratio vs. 1/U (ppm) of Strengbach water samples. As an example, mixing lines of borehole F5 are represented with a full

line corresponding to the May 2015 sampling period, dashed lines for December 2015, and dotted lines for November 2016.

Figure 9: Plot of (a) CFC-11 vs. CFC-113, (b) CFC-12 vs. CFC-113, and (c) CFC-11 vs. SF₆ of spring, piezometer, and borehole water from the Strengbach catchment. Theoretical curve given by Piston Flow Model (PFM – Black curve), Exponential Mixing Model (EMM – Grey curve) and Binary Mixing Model (BMM – dotted line). Dates of recharge are indicated on the PFM curve as well as the mean residence times on the EMM. The BMM curves consider a mixing between actual water (2018) and old groundwater (older than 80 years).

Figure 10: Plot of (a) CFC-113 (pptv) vs. Si (mmol/l) of spring and piezometer water, and (b) CFC-11 (pptv) vs. NO₃⁻ (mmol/l) of boreholes and piezometer water.

Figure 11: ¹⁴⁴Nd/¹⁴³Nd vs. ⁸⁷Sr/⁸⁶Sr diagram. Previously analyzed minerals (Aubert et al., 2001, 2002; Bosia pers. comm.) are represented. Several mixing hyperboles are also represented:

Yellow curve: Apatite-plagioclase mixing hyperbole using Sr and Nd concentrations and isotopic ratios measured in the two mineral end-members, namely, for apatite ¹⁴⁴Nd/¹⁴³Nd = 0.5123, ⁸⁷Sr/⁸⁶Sr = 0.7112, [Nd] = 430 ppm, and [Sr] = 752 ppm, and for plagioclase ¹⁴⁴Nd/¹⁴³Nd = 0.5121, ⁸⁷Sr/⁸⁶Sr = 0.7365, [Nd] = 1 ppm, and [Sr] = 16 ppm. The percentages on the curve represent the contribution of apatite in apatite-plagioclase mixing.

Grey curve: Theoretical mixing hyperboles assuming a Nd-Sr fractionation during mineral dissolution. The full grey curve corresponds to a case with a very limited leaching of Nd from apatite ([Nd] = 4 ppm instead of 430 ppm); the dotted grey line corresponds to a very small dissolution of Sr from plagioclase ([Sr] = 0.1 ppm instead of 16 ppm).

Dashed black curves: Mixing hyperboles between atmospheric end-member and a lithogenic weathering end-member resulting from dissolution of a apatite-plagioclase mixing without Sr-Nd fractionation. Atmospheric end-member: ¹⁴⁴Nd/¹⁴³Nd = 0.5121, ⁸⁷Sr/⁸⁶Sr = 0.71096, [Nd] = 25 ppm, and [Sr] = 360 ppm.

Figure 12: Saturation Index (SI) of (a) quartz, (b) albite, (c) feldspath, (d) Muscovite, (e) biotite, (f) montmorillonite, (g) dolomite, and (h) illites for average values of spring, piezometer, and deep borehole waters from the Strengbach catchment.

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Table 1:

Type	Name	Depth (m)	Date	Sr	Nd	U	$^{87}\text{Sr}/^{86}\text{Sr}$			$(^{234}\text{U}/^{238}\text{U})$			$^{143}\text{Nd}/^{144}\text{Nd}$		
					ppb		(2SE)			(2SE)			(2SE+0,5*10 ⁻⁵)		
Borehole	F5	13	10/11/2015	70.90	0.006	22.50	0.714996	±	7	1.953	±	3	0.51223	±	3
		14	12/11/2015	26.40	0.019	4.30	0.716876	±	9	1.728	±	1	-	±	-
		15	05/05/2015	13.10	0.026	0.22	0.722504	±	12	0.873	±	2	0.51226	±	3
		15	26/08/2015	15.90	0.026	1.06	0.719441	±	11	1.364	±	2	0.51224	±	3
		15	02/12/2015	8.70	0.029	0.26	0.724714	±	13	0.938	±	1	0.51226	±	3
		15*	10/11/2015	19.30	0.022	3.03	0.718447	±	9	1.614	±	4	0.51224	±	3
		23	23/11/2016	20.91	0.009	3.87	0.717270	±	7	1.758	±	2	0.51220	±	1
		26	05/05/2015	20.90	0.024	2.04	0.718890	±	13	1.816	±	2	0.51226	±	3
		26	26/08/2015	31.50	0.004	3.92	0.715910	±	10	1.805	±	2	-	±	-
		26	10/11/2015	120.00	<l.d	46.50	0.714096	±	7	1.983	±	4	-	±	-
		26	12/11/2015	43.00	0.004	8.56	0.715163	±	8	1.842	±	1	-	±	-
		26	02/12/2015	84.78	0.001	31.50	0.714258	±	6	1.982	±	1	-	±	-
		26*	10/11/2015	36.40	0.004	8.31	0.716311	±	8	1.680	±	2	0.51227	±	3
		40	05/05/2015	121.00	0.004	52.30	0.714065	±	14	2.019	±	2	-	±	-
		40	26/08/2015	72.80	<l.d	23.10	0.714516	±	10	1.994	±	2	-	±	-
		40	10/11/2015	126.00	<l.d	47.90	0.713944	±	6	1.991	±	3	-	±	-
		40	12/11/2015	103.00	<l.d	37.90	0.714248	±	9	1.961	±	1	-	±	-
		40	02/12/2015	100.00	<l.d	38.80	0.714083	±	6	1.990	±	1	-	±	-
		40*	10/11/2015	34.70	0.006	7.87	0.716387	±	11	1.713	±	3	-	±	-
		43	23/11/2016	88.83	<l.d	33.20	0.714073	±	6	1.935	±	1	0.51222	±	4
		48	10/11/2015	124.00	<l.d	47.70	0.714051	±	5	1.981	±	3	-	±	-
		48	12/11/2015	94.00	<l.d	36.00	0.714319	±	7	1.932	±	1	-	±	-
		48*	10/11/2015	38.20	0.006	9.21	0.716213	±	6	1.748	±	2	-	±	-
		49*	02/12/2015	15.14	0.008	1.49	0.718959	±	10	1.697	±	1	-	±	-
	F6	63	27/10/2016	16.51	0.002	6.93	0.719292	±	7	1.354	±	1	-	±	-
		63	22/11/2016	12.11	0.003	3.86	0.718662	±	6	1.073	±	1	0.51220	±	3
	F7	45	26/08/2015	82.80	0.003	24.40	0.715566	±	7	1.071	±	1	-	±	-
		46	26/10/2016	81.97	0.003	29.60	0.715583	±	7	1.090	±	1	-	±	-

		42	22/11/2016	53.82	0.006	13.90	0.715593	± 8	1.079	± 1	0.51223	± 3
		47	22/11/2016	77.84	0.002	30.80	0.715588	± 7	1.099	± 1	0.51221	± 1
	F8	27	22/11/2016	114.00	0.005	79.90	0.715201	± 8	1.103	± 1	0.51219	± 2
		45	22/11/2016	110.00	0.002	87.60	0.715248	± 8	1.095	± 1	-	± -
Piezometer	Pz3	11	26/08/2015	7.96	0.074	0.53	0.724897	± 12	0.860	± 2	-	± -
		11	22/11/2016	5.88	0.101	0.69	0.724694	± 8	0.850	± 1	0.51227	± 1
		13	22/11/2016	20.99	0.007	0.73	0.720393	± 9	0.883	± 1	0.51220	± 1
	Pz5	13	23/11/2016	7.27	0.025	0.40	0.724958	± 8	0.897	± 1	0.51225	± 1
	Pz7	12	26/08/2015	9.90	0.133	1.06	0.726271	± 10	1.168	± 1	-	± -
		13	22/11/2016	8.09	0.099	1.15	0.724853	± 9	0.985	± 2	0.51220	± 2
Spring	ARG		05/05/2015	8.05	0.031	0.06	0.726939	± 9	0.929	± 4	0.51224	± 1
			26/08/2015	7.66	0.041	0.10	0.726212	± 12	0.910	± 5	0.51222	± 1
	CS1		05/05/2015	6.93	0.285	0.30	0.727848	± 3	0.881	± 2	0.51225	± 3
			26/08/2015	6.04	0.093	0.13	0.725587	± 9	0.868	± 2	0.51214	± 5
			10/11/2015	6.44	0.102	0.17	0.725475	± 6	0.872	± 1	-	± -
			02/12/2015	7.01	0.251	0.23	0.727235	± 7	0.877	± 2	-	± -
	CS2		05/05/2015	9.79	0.051	0.15	0.725390	± 7	0.877	± 1	0.51226	± 1
			26/08/2015	8.74	0.051	0.23	0.725260	± 9	0.874	± 2	0.51225	± 2
			10/11/2015	8.94	0.050	0.24	0.725265	± 3	0.877	± 1	-	± -
	CS3		05/05/2015	9.51	0.043	0.36	0.722197	± 6	0.829	± 1	0.51217	± 2
			26/08/2015	9.34	0.012	0.21	0.722333	± 10	0.824	± 1	0.51216	± 4
			10/11/2015	10.70	0.016	0.25	0.722138	± 7	0.825	± 1	-	± -
	CS4		05/05/2015	7.83	0.179	0.27	0.726496	± 10	0.882	± 1	0.51225	± 1
			26/08/2015	9.42	0.057	0.24	0.723438	± 10	0.856	± 1	0.51227	± 0
			10/11/2015	9.75	0.056	0.24	0.723208	± 7	0.854	± 1	-	± -
	RH3		26/08/2015	11.80	0.032	0.18	0.721422	± 12	0.986	± 1	0.51222	± 0
			10/11/2015	12.70	0.033	0.16	0.721169	± 6	0.979	± 1	-	± -

* Influence of pumping

Table 2:

Type	Name	Depth	Date	SF ₆ *	CFC-12				SF ₆ *	CFC-12	CFC-11	CFC-113	CFC-12					
					PFM		EMM						BMM					
					Mean age	±**	Mean age	±**					Mix fraction of young component		±**			
					yr	%	yr	%					% (O ₂ %***)	%				
		m		x 10 ³	pmol/L			pptv										
Borehole	F5	15	05/05/2015	2.49	3.12	5.53	0.59	6	565	255	87	13	3	5	6	> 99	4	
		15	26/08/2015	5.85	2.25	4.78	0.4	15	408	221	59	30	2	26	<1	75	<1	
											Average	22		16		87		
		23	23/11/2016	5.87	2.48	4.23	0.34	15	449	195	50	29	1	20	<1	82 (88)	<1	
		23	24/04/2018	14.56	0.99	0.34	0.08	16	538	189	53	10	<1	6	2	98 (91)	<1	
		26	26/08/2015	5.43	2.03	3.91	0.33	14	368	181	49	32	<1	32	<1	67	<1	
											Average	24		19		82		
		40	05/05/2015	16.89	1.05	0.97	0.23	43	190	45	34	42	3	86	<1	35	<1	
		40	26/08/2015	11.3	1.36	2.19	0.22	29	247	101	33	40	<1	61	<1	45	<1	
		43	23/11/2016	21.48	0.81	0.56	0.09	55	146	26	13	46	1	124	<1	27 (2)	<1	
	43	24/04/2018	3.61	2.03	0.93	0.2	39	186	16	12	45	5	95	<1	34 (<1)	<1		
										Average	43		92		35			
	F6	63	22/11/2016	5.29	1.35	2.26	0.33	14	244	104	48	41	1	64	<1	45 (60)	<1	
		64	25/04/2018	3.14	0.7	1.54	0.16	10	383	45	31	34	1	31	<1	70 (56)	<1	
											Average	38		48		57		
	F7	45	05/05/2015	1.77	1.03	1.88	0.22	5	187	87	33	42	4	88	<1	34	<1	
		45	26/08/2015	1.59	1.03	1.59	0.17	4	186	73	25	43	1	89	<1	34	<1	
		42	22/11/2016	2.82	1.46	2.69	0.23	7	264	124	34	40	1	57	<1	48 (54)	<1	
		47	22/11/2016	1.46	0.97	1.89	0.16	4	177	87	24	44	5	98	<1	32 (53)	<1	
		47	26/04/2018	5.11	2.58	4.51	0.39	4	253	91	26	42	1	63	<1	46 (53)	<1	
										Average	42		79		39			
	F8	27	22/11/2016	4.01	0.76	1.31	0.13	10	137	61	19	47	4	134	<1	25 (20)	<1	
		29	25/04/2018	1.71	1.34	1.89	0.17	8	131	74	25	49	5	145	<1	24 (21)	<1	
											Average	48		140		24		
Piezometer	Pz3	11	26/08/2015	5.74	2.31	4.59	0.47	15	419	212	69	29	1	24	<1	77	<1	
		11	22/11/2016	7.29	2.69	4.45	0.33	19	487	206	48	27	<1	15	<1	89 (75)	<1	
										Average	20		15		88			
	Pz5	11	05/05/2015	4.13	3.13	5.52	0.66	11	567	255	97	13	3	5	6	99	4	

Journal Pre-proof																
	13	23/11/2016	8.27	2.84	4.87	0.36	21	515	225	53	25	<1	11	<1	94 (97)	<1
	14	24/04/2018	5.98	2.85	3.91	0.34	14	486	218	60	29	1	16	<1	89 (92)	<1
										Average	22		11		94	
Pz7	10	05/05/2015	4.18	2.56	6.57	0.58	11	464	304	85	27	<1	18	<1	85	<1
	12	26/08/2015	5.65	2.01	3.66	0.39	15	365	169	57	32	1	32	<1	67	<1
	13	22/11/2016	5.34	2.44	4.33	0.28	14	442	200	41	30	2	21	<1	81 (93)	<1
										Average	30		24		78	
Spring	ARG	05/05/2015	4.12	2.75	5.15	0.67	11	497	238	98						
		26/08/2015	4.68	2.22	4.26	0.41	12	402	197	60						
	CS1	05/05/2015	2.88	2.83	5.45	0.61	7	513	252	89						
		26/08/2015	2.98	2.21	4.24	0.41	8	401	196	61						
	CS2	05/05/2015	6.9	2.99	5.58	0.62	18	541	258	91						
		26/08/2015	4.52	2.44	4.68	0.47	12	442	216	69						
		24/04/2018	-	3.31	5.21	0.45	-	625	252	69						
	CS3	05/05/2015	4.66	2.58	5.37	0.56	12	467	248	82						
		26/08/2015	4.15	2.07	4.11	0.39	11	376	190	58						
	CS4	05/05/2015	3.3	2.98	5.65	0.68	8	540	261	101						
		26/08/2015	4.71	2.31	4.55	0.46	12	418	210	68						
	RH3	26/08/2015	-	2.27	4.21	0.41	-	412	194	61						

* SF₆ corrected from air excess with Ne concentration (conc.).

** Relative Error (ABS(model conc. - obs conc.) / obs conc.) * 100.

*** The value in brackets represents the proportion of recent water estimated with the O₂ values measured in the water (SM Table 6). The maximum value measured in water (8.83mg/L) is used as the current atmospheric value.

Table 3:

Sample name	Number of samples	temperature	Field pH	Conductivity	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
		°C		20°C µS/cm				
Mean F5 deep*	9	6.6	7.8	214	0.319	0.043	0.385	0.776
Mean F6*	6	6.3	7.8	231	0.134	0.048	0.632	0.719
Mean F7 42m*	5	7.2	7.3	129	0.139	0.043	0.251	0.426
Mean F8 27m*	5	7.3	7.9	161	0.479	0.061	0.184	0.497
Mean Pz3**	10	6.3	5.7	26	0.107	0.016	0.012	0.049
Mean Pz5	9	6.3	5.7	27	0.085	0.015	0.018	0.055
Mean Pz7	10	7.4	5.9	35	0.099	0.032	0.022	0.069
Mean springs Cs	25	6.0	5.7	28	0.086	0.017	0.015	0.063

Sample name	Mn ²⁺	Fe ³⁺	Al ³⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	P total	Si
	mmol/l							
Mean F5 deep*	3.64E-03	6.07E-04	1.21E-04	0.045	0.004	0.065	0.000	0.317
Mean F6*	5.33E-04	1.76E-04	7.55E-05	0.06	0.01	0.063	0.000	0.16
Mean F7 42m*	1.02E-04	3.37E-04	1.19E-04	0.054	0.056	0.059	0.003	0.271
Mean F8 27m*	2.73E-05	1.22E-04	1.84E-04	0.048	0.027	0.036	0.001	0.306
Mean Pz3 surface**	1.30E-04	2.40E-04	1.73E-03	0.035	0.032	0.041	0.002	0.195
Mean Pz5	2.08E-04	4.45E-04	1.04E-03	0.039	0.037	0.05	0.001	0.159
Mean Pz7	2.58E-04	3.58E-04	2.59E-03	0.042	0.091	0.05	0.002	0.181
Mean springs Cs	0.000	4.01E-04	1.44E-03	0.040	0.072	0.042	0.002	0.156

* Average of concentration without the sample from 10/01/18

** Pz3 average concentration without the three deepest charged samples

Table 4:

Sample	Saturation index												
	Quartz	Albite	K-Feldspar	Anorthite	Apatite	Kaolinite	Illite	Muscovite	Montmorillonite	Calcite	Dolomite	Biotite	Andysrite
Mean F5 deep	0.862	0.571	3.041	-4.12	-9.957	4.687	4.35	5.037	3.161	-0.339	0.299	4.104	-3.342
Mean F6	0.572	-0.879	2.021	-5.153	-10.309	3.717	2.958	3.632	1.78	-0.337	0.545	1.364	-3.402
Mean F7 42m	0.782	-0.278	2.542	-4.996	-15.015	4.992	4.037	4.996	2.665	-1.335	-1.161	0.469	-3.571
Mean F8 27m	0.834	0.858	3.29	-3.929	-11.253	4.791	4.582	5.443	3.283	-0.537	-0.215	-8.643	-3.732
Mean Pz3	0.659	-2.472	0.049	-9.611	-33.426	4.54	1.014	2.309	-0.533	-5.139	-9.619	-17.544	-4.542
Mean Pz5	0.57	-3.058	-0.465	-10.18	-37.179	3.921	0.223	1.353	-1.223	-5.102	-9.42	-17.253	-4.408
Mean Pz7	0.603	-1.919	0.916	-8.024	-39.704	5.489	2.536	4.223	0.717	-4.757	-8.72	-15.455	-4.31
Mean spring	0.536	-2.713	-0.066	-9.25	-40.603	4.492	1.022	2.378	-0.591	-4.967	-9.221	-16.583	-4.392

Table 5:

Borehole	F6	F7	F8	F5
Sampling depth* (m)	63	42 - 47	26	45
Longest way**(m)	100	300	430	730
EMM mean age (yr)	31 - 64	57 - 98	134 - 145	61 - 124
Velocity vertical (m/yr)	0.98 - 2.03	0.42 – 0.82	0.18 – 0.19	0.36 – 0.74
Velocity longest way (m/yr)	1.56 - 3.23	3.06 – 5.26	2.97 – 3.21	5.89 – 11.97

* Corresponding to input area from fracture network

** Distance from the top added to the sampling depth

Figure 1:

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Highlights :

- Geochemical typology of deep water in the Strengbach critical zone observatory
- Specific chemical concentrations and Sr-U isotope ratios relative to surface water
- Evidence of longer residence times (water ages > 50 years) for the deep water
- Different circulation histories for surface and deep water in the Strengbach CZO

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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