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1 **Investigating the role of deep weathering in critical zone evolution by reactive transport**  
2 **modeling of the geochemical composition of deep fracture water**

3

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20 **Abstract**

21 Relatively little is known about the deep water circulation and the role of deep weathering  
22 processes on the Critical Zone (CZ) evolution. In this study, major fractures from four deep  
23 boreholes and water collected from these fractures (20-60 m of depth) were studied to  
24 improve our understanding of the deep CZ in a granitic headwater watershed (Strengbach  
25 watershed, France). Geochemical analysis indicates that chemical composition of deep water  
26 (20-60 m) is clearly different than shallow subsurface waters (0-15 m), with higher mean  
27 concentrations and a stronger spatial variability across the watershed. Reactive-transport  
28 modeling performed with the 1D KIRMAT code (Kinetic of Reaction and MAss Transport)  
29 highlights the role of minor mineral dissolution (i.e. dolomite) and of longer mean transit time  
30 (100-597 yr) along fractures for explaining these differences. The obtained results also shed  
31 light on the difference of hydrogeochemical functioning between shallow subsurface system  
32 (water sampled from springs and piezometers) and deep system (deep water from borehole  
33 fractures). The shallow subsurface system (0-15 m) is characterized by a spatially relatively  
34 homogeneous water flow, high mean pore velocities, and water-rock interactions in a porous  
35 regolith, while the deep water circulation (20-60 m) behaves much more as independent  
36 systems along fractures, with low mean pore velocities, and variable mineralogy and  
37 hydrodynamic conditions. A state of chemical equilibrium can also be reached along fractures  
38 in the deep CZ for some primary minerals (biotite and K-feldspar), a feature never observed  
39 so far in the simulations of shallow subsurface water chemical composition in the Strengbach  
40 watershed. Even if the deep water exhibits higher solute concentrations, significantly lower  
41 mean pore velocities inferred in the fractured zones imply that the deep water is responsible  
42 for a very small part of the total hydrologic and weathering fluxes in the watershed. The  
43 limited role of the deep weathering processes (20-60 m) compared to the shallow subsurface

44 processes (0-15 m) suggests an up to bottom control of the CZ evolution at a millennial  
45 timescale. Our results also indicate that the majority of fresh water available for water supply  
46 at a human timescale originates from shallow subsurface waters, as the deep water  
47 circulation is too low for being critical at a timescale relevant for societal needs in this type of  
48 geological context.

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## 64 **1. Introduction**

65 To improve our understanding of the critical zone (CZ), defined as the uppermost layer of  
66 Earth where rock, water, air, and life meet dynamically, is a key issue for predicting future soil  
67 and water resources (Bales et al., 2006; Brantley et al., 2007; Chorover et al., 2011). Most of  
68 the supply of fresh water to human activities depends on several meters of soil, saprolite, and  
69 fractured rock across the landscape (Gleeson et al., 2016). These different vertical  
70 compartments of the CZ have distinct physical, geochemical, and hydrologic properties.  
71 Water can flow vertically through soil, saprolite, and fractured bedrock, and laterally  
72 depending on the permeability architecture of the CZ (Brantley et al., 2017). Hydrologic  
73 processes have been studied in soils for decades, but much less is known about deep  
74 groundwater and its control on CZ evolution (Chabaux et al., 2017; Lucas et al., 2017). This  
75 gap of knowledge is primarily due to the challenges of sampling and gathering information  
76 from the base of the CZ shielded by many meters of weathered materials (Riebe et al., 2017;  
77 Holbrook et al., 2019).

78 Motivated by several scientific questions and societal needs, study of deep water circulation  
79 and associated weathering processes recently received more attention from the scientific  
80 community (e.g. West, 2012; Holbrook et al., 2014; Lucas et al., 2017; O'Geen et al., 2018).  
81 Rock moisture represents a water reserve that is distinct from soil moisture, and there is a  
82 growing recognition that rock moisture is an important but yet poorly understood component  
83 of the hydrological cycle (Salve et al., 2012; Dralle et al., 2018; Rempe and Dietrich, 2018).  
84 There is also an increasing demand for accurate estimates of water storage capacity and water  
85 transit time in watersheds, which are partially controlled by the diversity of flow paths, and  
86 central to predicting water availability in the environment (O'Geen et al., 2018; Weill et al.,

87 2019; Ackerer et al., 2020b). The role of groundwater storage on vegetation, plant rooting  
88 depth, and on the resilience of forest ecosystem to drought similarly encouraged the study of  
89 the deep water in the saprolite and in the fractured bedrock (Fan et al., 2017; Klos et al.,  
90 2018). Investigating the deep water circulation is equally important to evaluate the  
91 dominance of surface, shallow subsurface or deep water sources for rivers, which is necessary  
92 to understand the role of mixing processes in shaping concentration-discharge relations (C-Q  
93 relations; e.g. Kim et al., 2017; Liu et al., 2017; Zhi et al., 2019).

94 Among the recent advances, sampling of boreholes played a major role in improving our  
95 knowledge of the deep weathering processes and provided new opportunities to sample  
96 water from the deep CZ (e.g. Brantley et al., 2013; Buss et al., 2013; Chabaux et al., 2017;  
97 Hahm et al., 2019; Holbrook et al., 2019). Boreholes and deep cores allow for exploration of  
98 deep water chemistry (Chabaux et al., 2017; Ranchoux et al., 2021), mineralogical  
99 assemblages along fractures (Holbrook et al., 2019), and the role of deep water in water  
100 storage capacity (Hahm et al., 2019). These studies demonstrated that deep water chemistry  
101 can be distinct from surface or shallow subsurface water chemistry, and that fractures  
102 primarily control the water flow in the deep CZ. Reports also indicate that the mineralogy of  
103 fractures usually contrasts with the unweathered surrounding bedrock (protolith; Holbrook  
104 et al., 2019), implying specific water-rock interactions along fractures. Despite these recent  
105 advances, several questions remain open concerning the deep water circulation in the CZ. For  
106 example, to what extent is the hydrogeochemical functioning of the deep CZ different from  
107 the shallow subsurface system? What is the role of the deep water circulation in CZ evolution?  
108 How deep do models need to go to capture the hydrological and geochemical dynamics of a  
109 watershed?

110 A promising direction to explore these questions is the reactive transport modeling of the  
111 geochemical composition of deep water. Reactive transport models are a unique tool to  
112 evaluate in an integrative way the coupling between hydrologic and geochemical processes  
113 in the CZ (e.g. Moore et al., 2012; Salehikhoo and Li, 2015; Steefel et al., 2015; Heidari et al.,  
114 2017; Li et al., 2017; Ackerer et al., 2020a; 2020b). Reactive transport models were frequently  
115 applied in the context of fractured systems (MacQuarrie and Mayer, 2005; Yasuhara and  
116 Elsworth, 2006; Deng and Spycher, 2019), with a specific focus on the modeling of fracture  
117 aperture change, the formation of an altered layer in the fracture region, or the physics of  
118 fluid flow in fractured media (Steefel and Lichtner, 1998; Meakin and Tartakovsky, 2009;  
119 Battiato et al., 2011; Deng et al., 2016). Reactive transport models provide a new opportunity  
120 to link the large variety of data collected from borehole campaigns, including deep water  
121 geochemistry, fracture mineralogy and fracture geometry.

122 However, only few studies have attempted to capture the geochemical composition of deep  
123 water with a reactive transport model (e.g. Lucas et al., 2017). Even rare are studies that  
124 estimate the mean transit time of deep water through reactive transport simulations and seek  
125 to quantify the spatial variability of deep water geochemistry at the watershed scale. These  
126 investigations are challenging, especially because they require an extensive  
127 hydrogeochemical database for several deep boreholes distributed across a single watershed.  
128 These data are available for the Strengbach watershed (figure 1), one of the reference  
129 headwater sites of the French critical zone network (OZCAR), where multidisciplinary studies  
130 have been conducted since 1986 (“Observatoire Hydrog ochimique de l’Environnement”,  
131 OHGE; El Gh’Mari, 1995; Fichter et al., 1998; Viville et al., 2012; Ackerer et al., 2016; 2020;  
132 Schmitt et al., 2017; Chabaux et al., 2017; 2019; Daval et al., 2018; Pierret et al., 2018). In this  
133 study, we aim to strengthen our understanding of weathering processes in the deep CZ with

134 the help of 1D reactive transport simulations capturing deep water geochemical composition  
135 along major fractures in boreholes. More specifically, our study focused on the following  
136 research questions: (1) What is the spatial variability of deep water geochemical composition  
137 collected from several boreholes probing the deep CZ in an elementary watershed? (2) What  
138 is the difference of hydrogeochemical functioning between the deep CZ and the shallow  
139 subsurface? And (3) what is the significance of deep weathering processes in CZ evolution  
140 compared to shallow subsurface weathering processes?

## 141 **2. Study site**

142 The Strengbach watershed is a small watershed (0.8 km<sup>2</sup>) located in the Vosges Mountains of  
143 northeastern France at elevations between 883 and 1147 m (figures 1a and 1b). The climate  
144 is mountainous oceanic, with an annual mean temperature of 7 °C and an annual mean rainfall  
145 of approximately 1400 mm. 10 to 20% of the total precipitation is falling as snow during two  
146 to four winter months. The annual mean evapotranspiration and runoff are of approximately  
147 600 mm and 800 mm, respectively (Viville et al., 2012; Pierret et al., 2018). The vegetation is  
148 currently dominated by beech and spruce forest. High-flow events in the Strengbach stream  
149 occur at the end of winter season or in the early spring and drier conditions commonly happen  
150 at the end of summer or during autumn. An updated overview of the Strengbach hydrologic  
151 and climatic characteristics can be found in Pierret et al. (2018).

152 The bedrock is a base-poor Hercynian granite (-330 to -323 Ma; Schulmann et al., 2002),  
153 fractured and hydrothermally overprinted, with a degree of hydrothermal alteration  
154 decreasing from north to south (El Gh'Mari, 1995; Fichter et al., 1998). Fractures are primarily  
155 present as a set of ~N30 fractures sub-parallel to the main fault zones around the Strengbach  
156 watershed. The granite is mainly composed of quartz (35%), albite (31%), K-feldspar (22%)



157 and biotite (6%); it also contains small amounts of muscovite (3%), anorthite (2%), apatite  
158 (0.5%) and clay minerals (0.5%; El Gh'Mari, 1995). During the Tertiary (-45 to -10 Ma), rifting  
159 leading to the Rhine graben formation was associated to fluid circulations and formation of  
160 secondary minerals as carbonates and clays in fractures (Dezayes and Lerouge, 2019). The  
161 bedrock was also affected by meteoric weathering and glacial/periglacial processes during  
162 the Quaternary (Ackerer et al., 2016), and the watershed's surface is currently covered by a  
163 50 to 100 cm-thick acidic and coarse-in-texture soil (Hyperdystrict Cambisol). The saprolite  
164 developed into the bedrock constitutes an aquifer from 1 to approximately 8 meters of  
165 thickness with an average thickness of four meters. Saprolite is thinnest (1m) at the  
166 watershed's crest and thickest (8-15m) near the stream (Weill et al., 2019; Ackerer et al.,  
167 2020a).

168 An extensive database exists for the study of the CZ structure and its dynamic in the  
169 watershed, including regolith profiles (Ackerer et al., 2016), soil solutions (Gangloff et al.,  
170 2014; Prunier et al., 2015), shallow subsurface and spring waters (0-15 m of depth; Ackerer  
171 et al., 2018), stream waters (Viville et al., 2012), and rock and water samples from deep  
172 boreholes (20-60 m of depth; Chabaux et al., 2017).

### 173 **3. Database**

#### 174 **3.1 Boreholes**

175 This study is based on data obtained from the hydrologic and geochemical monitoring carried  
176 out in the Strengbach watershed since 1982. More specifically, the core of the study relies on  
177 data from drilling campaigns undertaken since 2012 to investigate the deep CZ in the  
178 watershed (Chabaux et al., 2017; Ranchoux, 2020; Ranchoux et al., 2021). Six boreholes were  
179 drilled to study the bedrock properties, the mineralogy along fractures, and to collect the

180 deep water in the watershed bedrock. Borehole locations were selected strategically to  
181 sample two elevation profiles along the two main slopes of the watershed (figures 1b, 1c, 1d).  
182 F1a, F1b and F5 boreholes are located on the southern part and F6, F7 and F8 boreholes are  
183 located on the northern part of the watershed (figures 1c and 1d). All these boreholes cut  
184 across the soil (0-2 m), the saprolite (2-15 m) and the deep bedrock (15-120 m). Soil and  
185 saprolite thicknesses vary between boreholes and are in general thinner for boreholes nearby  
186 the watershed crests and thicker nearby the Strengbach stream. Drill cores were extracted  
187 from boreholes and stored at ITES (Institut Terre et Environnement de Strasbourg), formerly  
188 LHyGeS (Laboratoire d'Hydrologie et de Géochimie de Strasbourg), for further petrological,  
189 mineralogical, and geochemical analysis.

190

### 191 **3.2 Fractures**

192 The fracture network in the bedrock was constrained by geophysical mapping of boreholes,  
193 including optic scanner, acoustic scanner, and natural gamma ray measurements (Ranchoux,  
194 2020; Ranchoux et al., 2021; illustration in figure 2a). For each fracture, depth, dip, azimuth,  
195 and aperture were measured. Fracture mineralogy was studied by macroscopic description,  
196 X-ray analysis, and thin section observation. X-ray analysis was performed at ITES and  
197 following the method presented in Ackerer et al., 2016. The mineralogical compositions of all  
198 powdered 250- $\mu\text{m}$  bulk samples were determined with a Siemens D5000 diffractometer with  
199 scanning from 4 to 84°, a space step of 0.04° and a time step of 18 s. The <2- $\mu\text{m}$  clay fractions  
200 were separated by centrifugation and analyzed after air drying and treatment with glycol  
201 ethylene and hydrazine to distinguish illites, smectites, kaolinites and inter-stratified clays.  
202 The quantitative estimation of the proportion of the different minerals was performed by the

203 Rietveld method with the Siroquant software (Ackerer et al., 2016). The analytical uncertainty  
204 was approximately 3 % for the mass fraction of primary minerals and 5 % for the mass fraction  
205 of clays.

206 Thin section observation was performed at BRGM (“Bureau des Recherches Géologiques et  
207 Minières”, Orléans, France), including natural light, polarized light and cathodoluminescence  
208 images. Sampling was emphasized for major fractures in the deep CZ with a large aperture  
209 and showing evidence of deep water circulation, as the observation of weathered granite,  
210 granitic gruss, clay filling and/or trace of hydroxide minerals (an example of deep weathering  
211 evidence is shown in figure 2b). Mineralogical samples were collected on fracture planes to  
212 analyze weathered granite in contact with water. Few samples were also taken perpendicular  
213 to the fracture direction to analyze less weathered material and protolith. Major fractured  
214 zones were located at approximately 45 m of depth for F5, 63 m for F6, 42 m for F7 and 27 m  
215 for F8. These major fractured zones are named F5 45 m, F6 63 m, F7 42 m and F8 27 m,  
216 respectively. The geometry of fractures in these major fractured zones is reported in table 1  
217 and mineral mass fractions and reactive surfaces are given in table 2.

218 All fractures contain the main silicate minerals found in the granite, as quartz, albite,  
219 anorthite, K-feldspar, muscovite, and biotite (figure 3). Thin section observation spotted few  
220 traces of weathering for quartz (figure 3a and 3c) and an increase of the weathering degree  
221 from K-feldspar to anorthite (figure 3a and 3d). Traces of hydroxide minerals and clay minerals  
222 were detected in the fractures, and clays were dominated by montmorillonites-smectites and  
223 illites (figure 3c). A modest variability of the abundance of the primary silicate minerals was  
224 observed for the major fractures (table 2). Thin section observation also showed carbonate  
225 minerals, mainly in the form of secondary dolomite precipitated during past hydrothermal

226 circulations in fracture fillings (figure 3b). Contrary to the silicate minerals, a high variability  
227 of the dolomite abundance was observed from one fracture to another, with the highest  
228 amount of dolomite in F6 at 63 m depth, intermediate amounts in F7 at 42 m and F5 at 45 m,  
229 and the lowest amount in F8 at 27 m (table 2). These data are supplemented by mineralogical  
230 analysis in soils and regolith from Ackerer et al., 2016.

### 231 **3.3 Deep and shallow subsurface waters**

232 Several sampling campaigns for deep water from boreholes were realized under different  
233 hydrologic conditions in the watershed (sampling dates in table 3). The deep water was  
234 sampled for each date in front of the major fractured zones F5 45 m, F6 63 m, F7 42 m and F8  
235 27 m. For example, one sample was collected at 45 m depth in F5 borehole on May 5, 2015,  
236 merging the water delivered by the three fractures in this fractured zone (table 1). Pumping  
237 tests and in situ conductivity measurements were performed to confirm the inflow of deep  
238 water at these depths (Ranchoux, 2020). The geochemical composition of the deep water  
239 samples was determined at ITES for main cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ), main anions ( $\text{Cl}^-$ ,  
240  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ),  $\text{H}_4\text{SiO}_4$ , pH and alkalinity following the analytical procedure classically used in the  
241 laboratory and detailed in Gangloff et al., 2014 and Lucas et al., 2017 (results in table 3).  
242 Hydrological and geochemical data were also available for the shallow subsurface water from  
243 previous studies conducted in the watershed (0-15 m of depth; stream, springs, and water  
244 collected in piezometers; Viville et al., 2012; Ackerer et al., 2018; 2020a).

## 245 **4. Reactive transport modeling**

### 246 **4.1 Governing equations of reactive mass transport**

247 Most coupled reactive transport models rely on the resolution of the partial differential  
 248 equation in a saturated porous medium and that resulting from geochemical phenomena,  
 249 added to the transport equation as a sink / source term (e.g. M'nassri et al., 2019). The  
 250 classical hypotheses of instantaneous homogeneous reactions, of equal diffusion coefficients  
 251 of all present aqueous species and only considered kinetics of heterogeneous reactions allows  
 252 us to express the mass balance equation in terms of generalized concentrations  $\Psi_j$  (in mol per  
 253 water mass or volume) of primary species. Under these conditions, the mass balance equation  
 254 of reactive transport in a one-dimensional porous medium is written as (e.g., Lichtner, 1988;  
 255 Gérard et al., 1998; M'nassri et al., 2019):

$$256 \quad \frac{\partial}{\partial t}(\phi\Psi_j) = \phi D \left( \frac{\partial^2 \Psi_j}{\partial x^2} \right) - v \frac{\partial \Psi_j}{\partial x} - \sum_{r=1}^M \alpha_{jr} \frac{\partial}{\partial t}(\phi_r \widetilde{V}_r^{-1}) \quad (j = 1, \dots, N), \quad (1)$$

257 and

$$258 \quad \frac{\partial}{\partial t}(\phi_r \widetilde{V}_r^{-1}) = v_r \quad (r = 1, \dots, M), \quad (2)$$

259 where equation (1) refers to N aqueous primary species, and equation (2) to M primary  
 260 species of reacting minerals. In these equations  $\phi$  denotes the porosity of the porous  
 261 medium,  $\phi_r$  and  $\alpha_{jr}$  denote the volume fraction and the stoichiometric reaction coefficients,  
 262 respectively, of the r mineral with molar volume  $\widetilde{V}_r$ .  $v_r$  represents the reaction rates of the  
 263 irreversible reaction of minerals and fluids equivalent to the rate of precipitation or  
 264 dissolution of reacting minerals r per unit of the rock and fluid system (by convention,  $v_r$  is  
 265 taken as positive for precipitation and as negative for dissolution reactions). D denotes the  
 266 longitudinal hydrodynamic dispersion coefficient, and  $v$  denotes the Darcy velocity. Note that  
 267 the mean velocity U is generally defined by  $U = v/\phi$ . The generalized concentration  $\Psi_j$  is  
 268 defined according to the expression (M'nassri et al., 2019):

269 
$$\Psi_j = C_j + \sum_i \alpha_{ji} C_i \quad , \text{ with } C_i = K_i \gamma_i^{-1} \prod_{j=1}^N (\gamma_j C_j)^{\alpha_{ji}} \quad (3)$$

270 where  $C_j$  refers to the concentration of the  $j$  primary species, and the sum runs over all  
271 aqueous secondary species with concentration  $C_i$  related to the concentrations of the  
272 primary species through the mass action equation. The quantity  $\alpha_{ji}$  denotes the molar  
273 stoichiometric coefficient of species  $j$  in secondary species  $i$ ,  $\gamma$  are the activity coefficient of  
274 the aqueous species, and  $K_i$  denotes the equilibrium constant. From (1) and (2) one obtains  
275 a system of  $N + M$  coupled nonlinear partial differential equations.

## 276 **4.2 The reactive transport model KIRMAT**

277 The simulations of the water chemical composition along the fractures were performed with  
278 the reactive transport KIRMAT code (Kinetic of Reaction and MAss Transport; Gérard et al.,  
279 1998; Lucas et al., 2017; 2020; Ngo et al., 2014). KIRMAT is a thermokinetic model derived  
280 from the Transition State Theory (TST) that simultaneously solves the equations describing  
281 transport mass balance and geochemical reactions along a 1D direction. The mass transport  
282 comprises the effects of one-dimensional advection, diffusion, and kinematic dispersion.  
283 Chemical reactions consider the dissolution of primary minerals and oxido-reduction  
284 reactions, in addition to the precipitation of secondary minerals and clay minerals. In KIRMAT,  
285 the water-rock interactions involve dissolution and precipitation processes (see eq. 2), which  
286 are controlled by many factors including the mineral reactive surface, the aqueous solution  
287 composition (ion activities), the temperature, and the degree of saturation of the aqueous  
288 solution with respect to the studied mineral.

289 The workflow in KIRMAT is organized in three steps (M'nassri et al., 2019). In the first step,  
290 the ionic speciation (initial equilibrium) and the saturation index are calculated. During the

291 second step the perturbation of this initial partial equilibrium state by irreversible water-rock  
 292 interactions due to dissolution or precipitation of minerals (reaction term  $v_r$ , see eq. 2),  
 293 resulting in either supplying or removing elements from the aqueous solution, is modeled.  
 294 Then, finally, the (N+M) partial differential equations (1) and (2) are solved simultaneously  
 295 with a one-step algorithm. The mass transport equations are solved using the finite difference  
 296 approximation in an explicit scheme.

### 297 **4.3 Water-rock interactions in KIRMAT**

298 In KIRMAT, the kinetic of primary mineral dissolution  $v_r$  (in mol per water mass) is quantified  
 299 by (Ngo et al., 2014):

$$300 \quad v_r = k_{d,r} S_r^{\text{eff}} \alpha_{\text{H}^+}^n \left[ 1 - \left( \frac{Q_r}{K_r} \right)^{n1} \right]^{n2} \quad (4)$$

301 where  $k_{d,r}$  is the kinetic rate constant of dissolution ( $\text{mol m}^{-2} \text{yr}^{-1}$ ) of the reactive mineral  $r$ ,  
 302  $S_r^{\text{eff}}$  the reactive surface area of the reactive mineral  $r$  ( $\text{m}^2 \text{Kg}^{-1} \text{H}_2\text{O}$ ),  $\alpha_{\text{H}^+}^n$  the activity of proton,  
 303  $Q_r$  the ion activity product of the reactive mineral  $r$ ,  $K_r$  the thermodynamic equilibrium  
 304 constant of the hydrolysis reaction of the reactive mineral  $r$ , and  $n1$  and  $n2$  the exponents  
 305 depending on the pH of the water (M'nassri et al., 2019; Lucas et al., 2020). Oxido-reduction  
 306 reactions are described through Nerst equations, and the precipitation rate  $v_r$  of a secondary  
 307 mineral other than clay minerals (ex: calcite, goethite) is described by the expression:

308

$$309 \quad v_r = k_{p,r} S_r^{\text{eff}} \left[ \left( \frac{Q_r}{K_r} \right)^p - 1 \right]^q \quad (5)$$

310 with  $k_{p,r}$  the kinetic rate constant of precipitation ( $\text{mol m}^{-2} \text{yr}^{-1}$ ) of the reactive mineral  $r$ , and  
311  $p$  and  $q$  the exponents describing the dependence of the reaction from the saturation state  
312 (Ngo et al., 2014). The saturation index (SI) of the reactions occurring between the aqueous  
313 species and minerals is defined by:

$$314 \quad SI_i = \log \frac{Q_i}{K_i} \quad (6)$$

315 where  $Q_i$  denotes the ion activity product and  $K_i$  denotes the thermodynamic equilibrium  
316 constant. If the water sample is completely saturated with the dissolved mineral, SI equals to  
317 zero. Positive values of SI indicate super-saturation and the mineral would tend to precipitate;  
318 negative ones indicate under-saturation and the mineral would tend to dissolve. For each  
319 species and minerals in the studied system, the equilibrium constants are obtained by  
320 applying the corresponding activity coefficients. The formation of clay minerals is handled  
321 with a clay solid solution in KIRMAT. The clay fraction is defined as a solid solution made up  
322 of a combination of pure clay end-members. The ion activity product  $Q_i$  of the pure clay end  
323 member  $i$  is expressed by:

$$324 \quad Q_i = K_i X_i \gamma_i \quad (7)$$

325 with  $K_i$  the thermodynamic equilibrium constant of the hydrolysis reaction of the clay end  
326 member  $i$ ,  $X_i$  the molar fraction of the clay end member  $i$  in the solid solution, and  $\gamma_i$  the  
327 activity coefficient of the clay end member  $i$ . The clay solid solution is precipitated at  
328 thermodynamic equilibrium and its chemical composition varies over time, depending on the  
329 evolution of the water chemistry and the rock mineralogy. This multicomponent solid solution  
330 aims to imitate the impurity of clay minerals precipitated during low-temperature water-rock  
331 interactions typical of chemical weathering reactions (Tardy and Fritz, 1981).



#### 332 **4.4 Modeling strategy**

333 The strategy to capture the geochemical composition of deep water was adapted from  
334 previous modeling studies conducted in granitic headwater watersheds (Strengbach and  
335 Ringelbach watersheds; Lucas et al., 2017; Ackerer et al., 2018; 2020a). In contrast to shallow  
336 subsurface flow (0-15 m), which is localized in the soil or in the saprolite, deep water flow  
337 observed in boreholes is controlled by the major fractures existing in the granitic bedrock  
338 (Lucas et al., 2017). The reactive transport modeling was therefore adapted to consider  
339 water-rock interactions occurring along fractures (figure 4).

340 Starting point was the choice of the input soil solution used for the modeling (figure 4a). The  
341 soil solutions from the beech site (HP-70, Prunier et al., 2015), collected at 70 cm of depth on  
342 the southern slope (figure 1b), were assumed to be representative of the input  
343 concentrations of aqueous species percolating into the granitic bedrock for F5 45 m (F5  
344 borehole located on the southern slope, figure 1b). The soil solutions from the spruce site  
345 (VP-60, Prunier et al., 2015), collected at 60 cm of depth on the northern slope (figure 1b),  
346 were assumed to be representative of the initial input solution for F6 63 m, F7 42 m and F8  
347 27 m (F6, F7 and F8 boreholes located on the northern slope, figure 1b). This choice assumes  
348 that the deep water circulation is most likely supplied by infiltrations of water from the upper  
349 regolith. The chosen modeling approach is based on the main assumption that soil solutions  
350 recharge fractures only at the top of the watershed and then react along fractures. Soil  
351 solutions do not enter along fractures at greater depth, which is supported by the absence of  
352 weathering signs in the protolith surrounding fractures.

353

354 For each borehole, the deep water flow was assumed to occur along the main fractures  
355 identified by the borehole imaging (table 1). The fracture was modeled as a 1D stream tube  
356 following the direction of the local slope, with a length equal to the distance between the  
357 fractured zone in the borehole and the top of the corresponding hillside (figure 4a). The  
358 stream tube was discretized with a spacing of 1m long meshes. This modeling scheme did not  
359 consider the tortuosity of the fracture network, which was largely unknown, and assumed  
360 that all the fractures were extending along a simple line following the local slope. The  
361 aperture known from the borehole imaging (table 1) was supposed constant along the  
362 fracture and extended to the whole length along the hillslope (figure 4a).

363 In the case of a fractured zone with a single fracture intersecting a borehole (which is the case  
364 of F8, fractured zone at 27 m depth), only one simulation for each sampling date was  
365 performed to capture the water-rock interactions and the geochemical composition of deep  
366 water along the fracture. When several fractures are present in a fractured zone (for example  
367 F5 45 m, see figure 4b, F6 63 m, F7 42 m), independent simulations were performed for each  
368 sampling date and for each fracture, and the arithmetic mean of solute concentrations  
369 simulated for all fractures was calculated to quantify the mean chemical composition of the  
370 water in the fractured zone. Mean pore velocities along the fractures were adjusted to obtain  
371 the best agreement between modeled and measured concentrations in the fractured zones  
372 (F5 45 m, F6 63 m, F7 42 m, and F8 27 m), as the mean pore velocities in the deep fracture  
373 network are unknown. By combining the mean pore velocities and the fracture lengths, the  
374 optimized mean transit time of water was calculated along each fracture. Optimized mean  
375 transit times are therefore dependent on fracture geometry, flow velocity, mineralogical  
376 composition and mineral reactive surfaces in fractures.

377 A simple planar geometry was assumed for all the fracture surfaces to calculate the contact  
378 surface area between the water and the fracture rock (illustration in figure 4b, values of  
379 specific surface of water-rock contact in table 1). The reactive surfaces of minerals were  
380 determined by assuming that the surface area proportions of minerals along a fracture are  
381 identical to the mass fractions of minerals in the bulk samples of the fracture rock. For each  
382 fracture, the initial mineralogy used in the reactive transport modeling was adapted and  
383 constrained by the mineralogical composition of weathered granite along fracture planes  
384 (table 2). During simulations, the mineralogy evolves through time and varies spatially along  
385 fractures depending on water-rock interactions as primary mineral dissolution and clays  
386 precipitation. Thermodynamic and kinetic data for all the primary and secondary minerals are  
387 available in Ackerer et al., 2020a and in the supplementary material (tables EA1 and EA2). All  
388 the simulations were performed at the temperature of 7 °C, a temperature corresponding to  
389 the mean annual temperature measured in the borehole waters.

390 For the clay solid solution, clay end-members were defined on the basis of X-ray diffraction  
391 analyses and thin section observation of clay minerals present in fractures (figure 3). Clay end-  
392 members consist of K-Illites, Mg-Illites, Ca-Illites, Montmorillonites, Na-Montmorillonites, K-  
393 Montmorillonites, Ca-Montmorillonites and Mg-Montmorillonites, similarly to the clay end-  
394 members used in the simulation of the shallow subsurface water chemistry (Ackerer et al.,  
395 2020a). Chemical compositions and thermodynamic data for clay end members are available  
396 in Ackerer et al., 2020a and in the supplementary material (table EA3).

## 397 **5. Results: geochemical water composition**

398 On the basis of pH and alkalinity measurements, two groups of water are identified in the  
399 watershed: shallow subsurface water collected from 2 to 10 m depth (CS1 spring, PZ3, PZ5,

400 PZ7 piezometers) and deep water sampled in boreholes from 27 to 63 m (F5 45 m, F6 63 m,  
401 F7 42 m, and F8 27 m; figure 5a). Spring water and water from piezometers collected within  
402 the shallow subsurface show acidic pH ( $\text{pH} < 7$ ) and low alkalinity (alkalinity  $< 0.1$  meq/L). In  
403 contrast, deep borehole water shows slightly basic pH ( $7.5 < \text{pH} < 8.2$ ) and much higher  
404 alkalinity ( $1 \text{ meq/L} < \text{alkalinity}$ ). Alkalinity and pH gradually increase from F7 42 m, F8 27 m,  
405 F5 45 m to F6 63 m (figure 5a).

406 Overall, solute concentrations of basic cations ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$ ) and dissolved silica  
407 ( $\text{H}_4\text{SiO}_4$ ) are lower in the shallow subsurface water compared to the deep water (figures 5b,  
408 5c and 5d). Solute concentrations are relatively homogeneous in the shallow subsurface  
409 system for spring and piezometer waters, especially for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  concentrations  
410 (figures 5b and 5c). For  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , the shallow subsurface water exhibits much lower  
411 concentrations compared to the deep water, while for  $\text{H}_4\text{SiO}_4$ , the trend in solute  
412 concentrations is more continuous between shallow and deep waters (figure 5d).

413 The geochemical water composition also indicates that for the deep water, there is not a  
414 single geochemical signature at the watershed scale, and each borehole has a deep water  
415 with a distinctive chemical composition. The variability of water chemical composition  
416 between boreholes is higher for  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , but relatively lower for  $\text{K}^+$  and  $\text{H}_4\text{SiO}_4$   
417 (figures 5b, 5c and 5d, not shown for  $\text{K}^+$ ). The water sampled from F6 63 m has the particularity  
418 to show highest  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations, but the lowest  $\text{Na}^+$  and  $\text{H}_4\text{SiO}_4$  concentrations.  
419 In contrast, the water sampled from F8 27 m has the highest  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{H}_4\text{SiO}_4$   
420 concentrations, but lower  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. Water samples collected from F7  
421 42m and F5 45m show most of the time intermediate concentrations in basic cations and  
422 dissolved silica and their concentrations are framed by F6 63 m and F8 27 m.

423 To identify the stable minerals under thermodynamic conditions encountered in the deep  
424 water, stability diagrams (also called activity diagram, e.g. Maher et al., 2011) were drawn to  
425 visualize the stability domains of several common minerals (figure 6). The chemical  
426 composition of all the deep water samples falls in the stability zone of montmorillonites, as  
427 exemplified in stability diagrams (figures 6a and 6b). The precipitation of other clay minerals  
428 (kaolinite, pyrophyllite) and of secondary minerals as hydroxides (gibbsite) is not favored  
429 under the given thermodynamic conditions. The instability of anorthite indicates that primary  
430 silicate minerals may experience dissolution even in the deep part of the CZ (figure 6a).  
431 Overly, the obtained stability diagrams indicate that at the first order, the weathering  
432 processes taking place in the deep water tend to dissolve primary minerals (ex: anorthite) and  
433 to precipitate clay minerals of the type of montmorillonites.

## 434 **6. Results: reactive transport modeling**

435 The chemical composition of the deep water is controlled by both the mineralogy and the  
436 hydrodynamic conditions along the fractures. Reactive transport modeling allows to  
437 understand the variability of geochemical water composition across boreholes and to link  
438 hydrodynamic conditions, water transit time, mineralogy, and solute concentrations.

### 439 **6.1 Hydrodynamic conditions and mean transit time**

440 The fracture lengths determined by taking the distance between the four fractured zones and  
441 the appropriate hillcrests are 700 m, 100 m, 350 m, and 400 m for F5 45 m, F6 63 m, F7 42 m  
442 and F8 27 m, respectively (table 4). The best agreement between measured and simulated  
443 solute concentrations are obtained with the mean pore velocities of  $3.33 \text{ m yr}^{-1}$ ,  $1 \text{ m yr}^{-1}$ ,  $2.33$   
444  $\text{m yr}^{-1}$ , and  $0.67 \text{ m yr}^{-1}$  for F5 45 m, F6 63 m, F7 42 m and F8 27 m, respectively (mean Kling-  
445 Gupta efficiency of 0.85, optimized parameters in table 4). By combining the mean pore

446 velocities and the fracture lengths it is possible to calculate the mean transit time of the deep  
447 water in the deep CZ. Results point to a general increase of the deep water transit time from  
448 F6, F7, F5 and F8 boreholes, which is compatible with deep water flowing from the top to the  
449 bottom of the hillslope (table 4). The shortest mean transit time is determined for F6 63 m  
450 (100 yrs) located near the top of the crest line in the northern part of the watershed (figure  
451 1). Longer transit times are calculated for F7 42m and F5 45m (150 – 210 yrs) located at  
452 intermediate elevations, and the longest transit time is determined for F8 27 m (597 yrs)  
453 located near the Strengbach stream at the bottom of the northern slope (figure 1).

## 454 **6.2 Water-rock interactions and mineralogy**

455 Patterns of primary mineral saturation states in current weathering conditions are similar for  
456 all the boreholes and results are shown in the following for the fractured zone F5 45 m (figure  
457 7a). The calculated saturation states of primary minerals indicate that anorthite, apatite,  
458 albite and dolomite are systematically undersaturated along the fractures ( $\log(Q/K) < 0$ ; figure  
459 7a). K-feldspar is slightly undersaturated at the beginning of the flow path but reaches a state  
460 of chemical equilibrium after approximately 100 years at the middle of the flow path ( $\log(Q/K)$   
461  $= 0$ ; figure 7a). Biotite and quartz are oversaturated along the whole flow path ( $\log(Q/K) > 0$ ;  
462 figure 7a).

463 Patterns of primary mineral dissolution rates are more variable between boreholes due to  
464 the difference of mineral reactive surfaces in the fractured zones. This difference is controlled  
465 by the mineralogical variability (mineral mass fractions in the fractured zones, table 2) and  
466 the variability of fracture geometry (specific surface of water-rock contact, table 1). In  
467 general, the highest dissolution rate is simulated for the dolomite ( $1.5 \times 10^{-6} \text{ mol.yr}^{-1} \cdot \text{kg H}_2\text{O}^{-1}$ ),  
468 followed by the dissolution rates of albite and anorthite ( $1 \times 10^{-6}$  and  $7 \times 10^{-7} \text{ mol.yr}^{-1} \cdot \text{kg H}_2\text{O}^{-1}$ ,

469 illustration for F5 45 m in figure 7b). The dissolution rate of dolomite tends to decrease along  
470 the flow path while dissolution rates of albite and anorthite remain stable (figure 7b). Apatite  
471 and K-feldspar show lower dissolution rates ( $5 \times 10^{-8}$  and  $1 \times 10^{-7}$  mol.yr<sup>-1</sup>.kg H<sub>2</sub>O<sup>-1</sup>), with the  
472 dissolution rate of K-feldspar decreasing before reaching a zero value approximately after 100  
473 years at the middle of the flow path. The dissolution of biotite and quartz does not take place  
474 because of the oversaturated state of these minerals. This general pattern illustrated with the  
475 fractured zone F5 45 m is modulated by the difference of primary mineral reactive surfaces  
476 for the other boreholes. Higher reactive surfaces enhance higher dissolution rates, with for  
477 example higher dissolution rate of dolomite in F6 63 m due to the higher amount of dolomite  
478 in this fractured zone.

479 Precipitation rate and chemical composition of clay minerals precipitated during the  
480 simulations are similar for all the boreholes. A low precipitation rate of a clay solid solution is  
481 simulated all along the flow path in the fractured zones and its composition is made up of  
482 montmorillonites, in accordance with their thermodynamic stability in the deep water (figure  
483 6). The chemical composition of the clay solid solution becomes stable after approximately  
484 50 yrs (illustration for F5 45 m in figure 7d). The clay solid solution primarily constitutes of Ca-  
485 montmorillonite and Mg-montmorillonite (mass fractions of 42 % and 43 %, respectively), and  
486 secondarily of Na-montmorillonite and K-montmorillonite (mass fractions of 8 % and 7 %, respectively;  
487 illustration for F5 45 m in figure 7d).

### 488 **6.3 C-MTT slopes and solute concentrations**

489 The dynamic behavior of primary mineral dissolution and of clay mineral precipitation has a  
490 strong impact on the relationship between solute concentrations and mean transit time of  
491 deep water. The sensitivity of a solute concentration to an increase of the mean transit time

492 along the fractures can be quantified with the Concentration-Mean Transit Time slopes (C-  
493 MTT slopes, Ackerer et al., 2020a). C-MTT slopes are controlled by the competition between  
494 primary mineral dissolution and element incorporation into clay minerals along the flow path.  
495 When elemental fluxes from primary mineral dissolution to solution are much higher than  
496 fluxes from solution to clay minerals, the element can accumulate in solution, resulting in a  
497 strong C-MTT slope. By contrast, when elemental fluxes from primary mineral dissolution to  
498 solution are only slightly higher than fluxes from solution to clay minerals, the element  
499 accumulates only slowly in solution, resulting in a weak C-MTT slope (Ackerer et al., 2020a).

500  $\text{Ca}^{2+}$  is the basic cation with the highest C-MTT slope in the deep water system because  $\text{Ca}^{2+}$   
501 concentrations rapidly increase along the fractures due to the fast dissolution rates of several  
502 Ca-bearing minerals as dolomite, anorthite, and apatite (illustration for F5 45 m in figure 7c).  
503  $\text{Mg}^{2+}$  also shows a relatively strong C-MTT slope due to the fast dissolution of dolomite in the  
504 fracture network (figure 7c). Because  $\text{Na}^+$  in solution is only provided by the dissolution of a  
505 single primary mineral with a lower dissolution rate (i.e. albite), the C-MTT slope of  $\text{Na}^+$  is  
506 intermediate.  $\text{H}_4\text{SiO}_4$  in solution is provided by the dissolution of many primary minerals  
507 (albite, anorthite, K-feldspar, ...), however, the precipitation of clay minerals also transfers Si  
508 from water to the clay mineral structures, resulting in an intermediate C-MTT slope for  $\text{H}_4\text{SiO}_4$ .

509  $\text{K}^+$  is the basic cation with the lowest C-MTT slope because  $\text{K}^+$  in solution is only provided by  
510 the slow dissolution of K-feldspar (figure 7c). The K-feldspar also reaches a state of chemical  
511 equilibrium along the flow path (figure 7a), which limits the increase of  $\text{K}^+$  concentrations in  
512 the deep water. Elements with stronger C-MTT slopes (e.g.  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ) are therefore more  
513 suitable as indicators of mean transit time than others with lower C-MTT slope because their  
514 solute concentrations do not reach a plateau (figure 7c).



515

516 As for the mineral dissolution rates, C-MTT slopes are therefore impacted by the  
517 mineralogical variability and the difference of mineral reactive surfaces between fractured  
518 zones. By consequence, the evolution of the simulated chemical composition of the deep  
519 water is specific along each fractured zone, as exemplified by the different chemical trends in  
520  $\text{H}_4\text{SiO}_4 - \text{Na}^+$ ,  $\text{Ca}^{2+} - \text{Na}^+$  and  $\text{Mg}^{2+} - \text{Na}^+$  elementary diagrams (figure 8). Higher amounts and  
521 higher reactive surfaces of dolomite in F6 63 m (table 2, figure 3b) promote a rapid increase  
522 of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations compared to  $\text{Na}^+$  concentrations (figures 8b and 8c). Lower  
523 amounts and lower reactive surfaces of dolomite in F8 27 m imply a slow increase of  $\text{Ca}^{2+}$  and  
524  $\text{Mg}^{2+}$  concentrations compared to  $\text{Na}^+$  concentrations (figures 8b and 8c). F5 45 m and F7 42  
525 m show intermediate trends in  $\text{Ca}^{2+} - \text{Na}^+$  and  $\text{Mg}^{2+} - \text{Na}^+$  diagrams. In the  $\text{H}_4\text{SiO}_4 - \text{Na}^+$  diagram,  
526 F6 63 m and F7 42 m show a similar trend, while F5 45 m and F8 27 m show a parallel trend  
527 shifted by the difference of chemical composition of the initial input soil solution (figure 8a).  
528 These trends are explained by the competition between albite dissolution, the dissolution of  
529 the other silicate minerals, and the precipitation of clay minerals.

530 The final solute concentrations generated by the reactive transport model in the deep water  
531 of the fractured zones depend on both the C-MTT slopes and the mean transit time along  
532 fractures. Simulations capture the mean chemical composition in basic cations and in  
533 dissolved silica in the deep water of the fractured zones of all boreholes (figures 9). The low  
534  $\text{Na}^+$  and  $\text{H}_4\text{SiO}_4$  concentrations in F6 63 m are primarily explained by the short mean transit  
535 time at F6 (figure 9a and 9b). The higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations are controlled by the  
536 strong C-MTT slopes for these elements in the fracture network of F6, implying a fast increase  
537 of these elements in solution (figure 9c and 9e). F8 27 m follows the opposite trend with a

538 longer mean transit time enhancing higher  $\text{Na}^+$  and  $\text{H}_4\text{SiO}_4$  concentrations (figure 9a and 9b).  
539 Lower C-MTT slopes for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  elements are explaining lower concentrations at F8  
540 (figure 9c and 9e). F5 45 m and F7 42 m have intermediate C-MTT slopes and mean transit  
541 time, resulting in intermediate concentrations (figure 9).  $\text{K}^+$  concentrations are less variable  
542 between the four boreholes due to the state of chemical equilibrium of K-feldspar along the  
543 fractures, which reduces the difference of  $\text{K}^+$  concentrations between boreholes (figure 9d).  
544 The pH of water is slightly higher in the fractured zones with higher reactive surfaces of  
545 dolomite (figure 9f).

## 546 **7. Discussion**

### 547 **7.1 Modeling scheme and uncertainties**

548 Results from reactive transport simulations are strongly dependent on the modeling scheme  
549 assuming that deep water circulates along 1D independent fractures where minerals are only  
550 exposed along a planar fracture surface. In our simulations, the flow velocity was adjusted  
551 until the simulated water chemical composition matched the chemistry of sampled water  
552 from boreholes (section 4.4). With the choice to model mineral surfaces as only in contact  
553 with water along the fracture aperture and planar, the model generates slow weathering  
554 reactions, which in turn relates to long residence times of deep water. Several additional  
555 simulations were performed to evaluate the relevance of the modeling scheme and to provide  
556 an estimation of uncertainties on reactive surfaces and mean transit times.

557 A way to evaluate if a planar geometry is realistic is to consider simulations in which reactive  
558 surfaces along fractures are set equal to reactive surfaces from the shallow subsurface, as if  
559 fractures were completely filled with a porous regolith. Reactive surfaces in the shallow  
560 subsurface were calculated using a spherical geometry and assuming a porous and  
561 homogeneous regolith (Ackerer et al., 2018; 2020a). Their values were able to capture the

562 geochemical composition of spring and piezometer waters and to reconcile hydrological and  
563 geochemical modeling without modifying kinetic constants or rising a field-laboratory  
564 discrepancy of kinetic rates. Simulations with shallow subsurface reactive surfaces thus  
565 consider the fastest reaction rates given the background of hydrogeochemical modeling in  
566 the watershed. Following the same modeling method detailed in section 4.4, flow velocity  
567 along fractures was then adjusted to try to match deep water chemical composition.  
568 However, whatever the flow velocity used in our simulations, it was not possible to capture  
569 deep water chemistry with shallow subsurface reactive surfaces. One important particularity  
570 of the deep water chemistry that could not be captured with shallow subsurface reactive  
571 surfaces was the very high  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations contrasting with moderate  $\text{Na}^+$  and  
572  $\text{H}_4\text{SiO}_4$  concentrations. This pattern is explained by dolomite dissolution. In a granitic setting,  
573 dolomite cannot be present in the porous matrix of the bedrock, it is only present as  
574 secondary mineral on fracture surfaces. This is why a planar geometry with minerals assign  
575 on fracture planes is more realistic than a geometry with fractures filled with a porous  
576 medium and high reactive surfaces.

577 The chemical contrast between deep water samples collected from different boreholes also  
578 supports our modeling scheme based on independent fractures. Both major element  
579 concentrations (this study) and isotopic compositions (U, Sr; Ranchoux et al., 2021) are  
580 contrasted between boreholes, even while considering boreholes located on the same  
581 hillslope. A highly fractured zone behaving like a porous medium or well connected fractures  
582 would homogenize solute concentrations between boreholes located on the same hillslope  
583 (F6, F7, F8). This is not the case, and the unique geochemical signature of each borehole  
584 supports the view of discrete independent fractures. All of these points explain why a

585 modeling scheme based on discrete independent fractures with water-rock interactions  
586 occurring along a planar geometry is a reasonable modeling approach.

587 Another way to constrain the discussion about reactive surfaces and mean transit time is to  
588 compare the mean transit time of deep water inferred from the reactive-transport modeling  
589 with independent age estimates obtained from other geochemical tracers. In parallel with  
590 this study, CFCs (chlorofluorocarbons) concentrations were measured and modeled for deep  
591 water from the main boreholes in the Strengbach watershed (Ranchoux et al., 2021). Deep  
592 water ages inferred from CFCs data range between 50 and 200 years. The mean transit time  
593 of deep water inferred from the reactive-transport modeling, between 100 and 600 years,  
594 falls in the same order of magnitude of CFCs estimates (50-200 years). This underlines that  
595 mineral reactive surfaces used in the modeling with a planar geometry are within a realistic  
596 order of magnitude, otherwise a strong discrepancy would rise between numerically  
597 calculated mean transit times and CFCs water ages. To estimate a plausible range of reactive  
598 surfaces, we performed several additional simulations with higher reactive surfaces (initial  
599 reactive surfaces multiplied by a factor of 2, of 5 and of 10). In accordance with the modeling  
600 strategy detailed in section 4.4, the mean pore velocity was adjusted to match the chemical  
601 composition of deep water and the optimized mean transit time was calculated for each  
602 borehole. Simulations with reactive surfaces multiplied by a factor 2 and 5 cannot be  
603 discarded as they render the water chemistry with mean transit times also compatible with  
604 CFCs estimates. The mean transit times calculated in simulations with reactive surfaces  
605 multiplied by a factor of 5 are near the lowest estimates of water ages determined from CFCs  
606 (for example, in the case of F5 borehole, the optimized mean transit time is 42 years for the  
607 5 times increased reactive surface, while the range of ages inferred from CFCs is between 61  
608 and 124 years). Simulations with reactive surfaces multiplied by a factor of 10 and any

609 simulations with higher reactive surfaces produce too young waters for being compatible with  
610 CFCs estimates. Therefore, a reasonable maximum uncertainty on reactive surfaces, flow  
611 velocity and mean transit time is around a factor of 5.

612

## 613 **7.2 Hydrogeochemical functioning of the deep CZ compared to the shallow subsurface**

614 Our results clearly show that the deep water chemistry is very distinctive from the shallow  
615 subsurface water chemistry monitored by previous studies conducted in the Strengbach  
616 watershed (Viville et al., 2012; Prunier et al., 2015; Chabaux et al., 2017; 2019; Ackerer et al.,  
617 2018; 2020a). The difference of hydrogeochemical functioning between the shallow  
618 subsurface and the deep CZ can be explained in detail with the reactive transport model  
619 developed in our study.

620 From the hydrologic point of view, the shallow subsurface flow (0-15 m) is a relatively  
621 homogeneous flow in the porous regolith (Ackerer et al., 2020a), while the deep water flow  
622 (20-60 m) is much more localized along the major fractured zones in the bedrock (Lucas et al.,  
623 2017; Ranchoux, 2020). This difference in hydrologic functioning promotes a modest spatial  
624 variability of the shallow subsurface water chemistry (Ackerer et al., 2018) and, in contrast, a  
625 high spatial variability of the deep water chemistry in the watershed (Chabaux et al., 2017;  
626 this study; figure 5). Because each borehole has a specific water chemical composition (figure  
627 5), the fracture network in the bedrock is likely not connected between boreholes and each  
628 fractured zone behaves as an independent system. Shallow subsurface and deep water  
629 circulations also contrast by the difference of water velocities. Mean pore velocities are low  
630 in the deep water system ( $0.5 - 3.5 \text{ m. yr}^{-1}$ ) and much higher in the shallow subsurface of the  
631 watershed ( $1000 - 3000 \text{ m. yr}^{-1}$ ; Ackerer et al., 2020a). Such difference of water velocities

632 implies that the mean transit time of water is much longer in the deep CZ. Mean water transit  
633 time in the shallow subsurface is typically ranging between 1 and 4 months (Ackerer et al.,  
634 2020a), while the reactive transport modeling of the deep water chemistry indicates transit  
635 times of several hundreds of years in the deep CZ (100 – 600 yrs; this study). The spatial  
636 variability of mean transit time is therefore also higher for the deep water circulation,  
637 depending on the borehole and the fractured zone.

638 From the mineralogical point of view, the shallow subsurface water is in contact with a porous  
639 regolith showing a relatively homogeneous mineralogy while the deep water circulation  
640 occurs along independent fractures with a unique mineralogy. Carbonate minerals were  
641 never observed in the soil or in the regolith of the watershed (Fichter et al., 1998; Ackerer et  
642 al., 2016), and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the shallow subsurface water are primarily  
643 controlled by the dissolution of apatite, anorthite and biotite (Godd ris et al., 2006; Ackerer  
644 et al., 2018). These primary minerals are rather homogeneously dispersed in the regolith,  
645 promoting the modest spatial variability of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the shallow  
646 subsurface water at the watershed scale (figure 5). The presence of secondary carbonate  
647 minerals in the fracture network favors higher  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in the deep  
648 water. Furthermore, the highly variable amounts of these carbonates from one fractured  
649 zone to another explain the stronger variability of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations between  
650 boreholes (figure 5). The trend in  $\text{H}_4\text{SiO}_4$  and  $\text{Na}^+$  is more continuous between shallow  
651 subsurface and deep waters because the proportions of primary silicate minerals are less  
652 variable from the regolith to the fracture rocks. The mean dissolution rate of primary silicate  
653 minerals is on average 50-100 times lower in the fractures compared to the shallow  
654 subsurface due to the lower mean pore velocity and the longer mean transit time.

655 The difference of chemical water composition between shallow subsurface and deep waters  
656 is also reinforced by a state of chemical equilibrium reached for several minerals in the deep  
657 CZ. Previous reactive transport modeling studies indicated that the primary minerals as biotite  
658 and K-feldspar never reach a state of chemical equilibrium in the shallow subsurface due to  
659 the fast flow and the short transit time in the regolith (Ackerer et al., 2020a). This study  
660 focusing on the deep water shows that a state of chemical equilibrium can be reached in the  
661 deep CZ for biotite and K-feldspar (figure 7a). Chemical equilibrium of these minerals limits  
662 the increase of  $\text{H}_4\text{SiO}_4$  and  $\text{K}^+$  in the deep water, explaining why  $\text{H}_4\text{SiO}_4$  and  $\text{K}^+$  concentrations  
663 are only 2-3 times higher in the deep water while mean transit time is much longer in the  
664 fractures. In contrast, albite never reaches a state of chemical equilibrium in the deep CZ and  
665  $\text{Na}^+$  concentrations gradually increase with the mean transit time.  $\text{Na}^+$  concentrations reach a  
666 maximum value for the deep water with the longest transit time in F8 27 m.

667 The dynamic of clay minerals also plays a role in contrast to chemical composition between  
668 shallow subsurface and deep waters. The precipitation rate of the clay solid solution is 50-100  
669 times lower in the fractures than in the shallow subsurface due to the higher pH and the  
670 limiting concentrations of aluminum in the deep water. The nature of clay minerals  
671 precipitated along the fractures is also different from the clay minerals formed in the shallow  
672 subsurface. The solid solution of clay minerals precipitated in the fractures is only composed  
673 of Montmorillonites (figure 7d), while the solid solution in the shallow subsurface is made up  
674 with a combination of Illites and Montmorillonites (Ackerer et al., 2020a). Montmorillonites  
675 incorporate higher amount of K and Si than Illites, limiting the increase of  $\text{H}_4\text{SiO}_4$  and  $\text{K}^+$   
676 concentrations in the deep water. In contrast to this, only few Na is incorporated in the clay  
677 solid solution which promotes the gradual increase of  $\text{Na}^+$  concentrations along fractures and  
678 the higher  $\text{Na}^+$  concentrations in the deep water with longer mean transit time (F5 45 m and

679 F8 27 m). The amounts of Mg and Ca incorporated in the clay solid solution remain limited  
680 compared to the high fluxes of Mg and Ca from dissolution of dolomite, apatite and anorthite.  
681 Illites, iron hydroxides, goethite and micro quartz are not precipitated in the simulations  
682 capturing the chemical composition of the deep water, indicating that these minerals were  
683 probably formed during different conditions in the past (higher temperature water-rock  
684 interactions; hydrothermal alteration; El Gh'Mari, 1995; Fichter et al., 1998).

### 685 **7.3 Hydrologic and weathering fluxes in the deep CZ compared to the shallow subsurface**

686 By using the fracture cross sections and the mean pore velocities determined with the  
687 reactive transport model, it is possible to calculate the annual water fluxes carried by the four  
688 fractured zones F5 45 m, F6 63 m, F7 42 m and F8 27 m. These deep water fluxes represent a  
689 negligible part of the annual water fluxes carried by the stream at the outlet, with 10 m<sup>3</sup>/yr  
690 carried by the four fractured zones versus 640 000 m<sup>3</sup>/yr carried by the stream. Despite the  
691 fact that we investigated the largest fractured zones in the boreholes, the deep water has a  
692 limited role with respect to water fluxes at the watershed scale.

693 The finding that the deep water accounts for a negligible part of the total water fluxes is in  
694 accordance with several investigations conducted so far in the Strengbach watershed. The  
695 hydrologic budget of the watershed is correctly closed within uncertainties when only  
696 considering mean annual precipitations (1400 mm/yr), mean evapotranspiration (600  
697 mm/yr), and mean runoff at the outlet (800 mm/yr; Viville et al., 2012; Pierret et al., 2018).  
698 Water discharge in the Strengbach stream is correctly modeled solely with a shallow  
699 subsurface water storage in the regolith (aquifer thickness of 1-10 m; Weill et al., 2017; 2019;  
700 Ackerer et al., 2020a). This is also in accordance with results inferred from hydrograph



701 separation concluding that streamflow is dominated by water mobilized from regolith layers  
702 (Ladouche et al., 2001).

703 By combining the chemical composition of the deep water and the mean pore velocity along  
704 the fractures, it is also possible to estimate the geochemical fluxes carried by the deep water  
705 along fractures. In addition, the solute concentrations, water velocity and geochemical fluxes  
706 in the shallow subsurface system are constrained from previous monitoring and reactive  
707 transport modeling studies (Viville et al., 2012; Ackerer et al., 2018; 2020a). Despite the higher  
708 concentrations in the deep water (figure 5), the lower mean pore velocity along the fractures  
709 limits the geochemical fluxes carried by the deep water. Basic cation and dissolved silica  
710 concentrations in the deep water are in general 2 to 20 times higher than the concentrations  
711 in the shallow subsurface water, but the mean pore velocity is approximately 1000 to 2000  
712 times faster in the shallow subsurface, implying that the contribution of the deep water to  
713 the total geochemical fluxes exported from the watershed is minor (0.8-4 %, table 5). For Na<sup>+</sup>,  
714 K<sup>+</sup> and H<sub>4</sub>SiO<sub>4</sub>, the contributions of the deep water are 0.6-2.7 %, 0.3-1.4 % and 0.5-2.4 %,   
715 respectively (table 5). The contribution is slightly higher for Ca<sup>2+</sup> and Mg<sup>2+</sup> due to the  
716 dissolution of carbonate minerals along the fractures, with contributions of 3.3-19.5 % and  
717 4.6-14.5 %, respectively (table 5). Overall, the deep water circulation contributes for less than  
718 0.8-4 % of the total geochemical fluxes exported from the watershed (table 5). The mobility  
719 of elements along a regolith profile located on the top of the watershed also indicated that  
720 shallow weathering processes (0-15 m) are sufficient to explain the geochemical fluxes carried  
721 by the stream (Ackerer et al., 2016).

722 The limited role of deep weathering processes is also supported by other observations. When  
723 looking at the chemical composition of the Strengbach stream water in a H<sub>4</sub>SiO<sub>4</sub>/Cl<sup>-</sup> vs Ca<sup>2+</sup>/Cl<sup>-</sup>

724 mixing diagram, the stream water clearly falls in the area defined by spring and piezometer  
725 waters (figure 10). A mixing analysis including two end members defined by the average  
726 chemical composition of stream and deep waters was performed to test which contribution  
727 of deep water is potentially present in the stream. Because the deep water has a much higher  
728  $\text{Ca}^{2+}/\text{Cl}^-$  ratio than the stream water, the maximum contribution of deep water in the stream  
729 flow is around 2 % (figure 10). A higher contribution of deep water would deviate the stream  
730 chemistry toward values of  $\text{Ca}^{2+}/\text{Cl}^-$  ratio that were never observed in the stream. In a  
731 watershed like the Strengbach watershed, the deep water circulation (20-60 m) is probably  
732 not an important process in shaping the concentration-discharge relations at the stream  
733 outlet. All these considerations show that the deep water circulation contributes only to a  
734 negligible part of the total chemical weathering in the watershed. The exact extent of deep  
735 water connectivity with the stream probably needs to be tested in future studies with more  
736 accurate isotopic tools, as deep water could leave the system undetected by the stream when  
737 only looking at major elements or leave the system as deep flow only relevant for inter-basin  
738 circulations.

#### 739 **7.4 The role of deep water in CZ evolution**

740 The competition and interplay between hydrogeochemical processes involved in the shallow  
741 subsurface and deep CZ in shaping the CZ structure have recently received a growing interest  
742 from the scientific community (e.g. Brantley et al., 2013; Buss et al., 2013; Chabaux et al.,  
743 2017; Riebe et al., 2017; Holbrook et al., 2019; White et al., 2019). The extensive database  
744 and the modeling work undertaken in the Strengbach watershed allow to revisit the  
745 discussion on the respective role of shallow subsurface and deep water processes at the scale  
746 of a headwater watershed.

747 Our results show that in the setting of a mountainous and granitic catchment, the deep water  
748 is an atypical component of the hydrologic cycle with a negligible role in hydrogeochemical  
749 budgets. This finding advocates for an up-bottom control of the CZ evolution because the  
750 dynamic of this type of watershed is primarily driven by surface erosion, high water fluxes,  
751 and fast weathering rates in the shallow subsurface (figure 11). These surface and shallow  
752 subsurface processes are controlling the downward migration of weathering fronts and the  
753 overall chemical weathering (Viville et al., 2012; Ackerer et al., 2016; 2020a), while the slower  
754 processes occurring in the fracture network of the bedrock are unable to adjust with the  
755 geochemical fluxes and the evolution rate of the near surface environment (this study, section  
756 7.3). Our study therefore does not support the hypothesis that drainage of chemically  
757 equilibrated water into the bedrock is an important process (Rempe and Dietrich, 2014;  
758 hypothesis 2 in Riebe et al., 2017), but underlines the fact that the control through erosion,  
759 shallow subsurface water circulation, and fluid transit time is primarily responsible for the CZ  
760 evolution (Lebedeva and Brantley, 2013; hypothesis 4 in Riebe et al., 2017).

761 Our results can also be used to revisit the concept of rock moisture at the scale of a headwater  
762 watershed. Rock moisture is defined as the exchangeable water stored in the weathered  
763 bedrock (Salve et al., 2012; Rempe and Dietrich, 2018). The impact of rock moisture storage  
764 on the Strengbach stream is primarily controlled by the saprolite moisture storage, the  
765 saprolite being hydrologically active and sustaining the majority of the stream flow at the  
766 outlet (Weill et al., 2017; 2019; Ackerer et al., 2020a). Mixing calculations performed in this  
767 study also support that rock moisture storage from the deep CZ cannot explain a significant  
768 fraction of the stream flow (figure 10). Therefore, our study and previous modeling studies  
769 undertaken in the catchment clearly emphasize that the active rock moisture storage is  
770 located in the saprolite, while the fractured bedrock contains mostly inactive rock moisture

771 storage at the watershed scale. The rock moisture storage within the saprolite should not be  
772 confounded with the rock moisture storage in the fractured bedrock.

773 This conclusion contrasts with the results from several recent studies where the deep water  
774 from fractured aquifer systems significantly contributes to streamflow (e.g. Frisbee et al.,  
775 2017; White et al, 2019). These differences are possibility explained by the geological setting.  
776 Our findings can probably be extended to small watersheds with a crystallin bedrock, but  
777 different conclusions are possible for karstic or volcanic systems. In these hydrogeologic  
778 systems, large and connected fractures can carry high water fluxes into the bedrock and  
779 sustain stream flow (White et al., 2019). This is not the case in a headwater granitic watershed  
780 like the Strengbach watershed where the stream chemistry is fully explained by the shallow  
781 subsurface water (figure 10).

782 Possibly, the deep water circulation plays a role at a larger spatial scale in the Rhine graben,  
783 where a regional flow of deep water from the Vosges massif may recharge deep aquifers in  
784 the Rhine alluvial plain (mountain block recharge; Ajami et al., 2011; Markovich et al., 2019).  
785 The role of bedrock geology (distribution and thickness of Mesozoic sedimentary cover, e.g.  
786 sandstone) or the large Hercynian deformation zones in the Vosges massif might have  
787 different properties with respect to water circulation and storage. Based on our results,  
788 however, the ability of headwater watersheds to generate an important regional circulation  
789 of deep water appears limited in crystallin landscapes, as the hydrologic budget of the  
790 Strengbach watershed is correctly closed without invoking a deep water storage. The mean  
791 annual precipitations of 1400 mm/yr are well partitioned between mean evapotranspiration  
792 of 600 mm/yr and mean runoff at the outlet of 800 mm/yr (Viville et al., 2012; Pierret et al.,  
793 2018).

794 The conclusions brought by our study are applicable from annual to millennial timescales  
795 because the timeframe spanned by the mean transit time of shallow subsurface and deep  
796 waters ranges from few months to 600 years. The comparison between shallow subsurface  
797 and deep weathering fluxes is therefore relevant at this timescale, but it is questionable to  
798 extrapolate these estimates at the million year timescale. A coupling between tectonic  
799 forcing, topographic stress, and the deep water circulation initiating the bedrock weathering  
800 is possible and has been highlighted by previous studies (Slim et al., 2015; St Clair et al., 2015;  
801 Hypothesis 1 in Riebe et al., 2017). Our results indicate that this coupling is not dominant at  
802 the millennial timescale in a granitic headwater watershed, but it may become critical at the  
803 geologic timescale. If this is true, the control on the CZ evolution would be shifting from a  
804 bottom-up to an up-bottom control from geologic to millennial timescale. In any case, the  
805 majority of the fresh water available for water supply at a human timescale originates from  
806 stream, spring, and shallow subsurface waters in this type of granitic headwater watershed.  
807 The deep water circulation is too low for being critical at a timescale relevant for water supply  
808 and societal needs in this type of geological context.

## 809 **8. Conclusion**

810 Major fractures from four boreholes and deep water collected from these fractures were  
811 studied to improve our understanding of deep water circulation and of weathering processes  
812 in the deep CZ of a headwater watershed. Geochemical analysis indicates that chemical  
813 composition of deep water (20-60 m of depth) is clearly different from shallow subsurface  
814 waters (0-15 m), with higher mean concentrations and a larger spatial variability across the  
815 watershed. Our reactive transport modeling study highlights the role of dolomite dissolution  
816 and of longer mean transit time in the deep CZ for explaining these differences. The modeling

817 results also throw light on the difference of hydrogeochemical functioning between shallow  
818 subsurface and deep systems: if the shallow system is characterized by relatively  
819 homogeneous flow, high mean pore velocities, and water-rock interactions in a porous  
820 regolith, the deep water circulation behaves much more as an independent system along  
821 fractures, with low mean pore velocities, and variable mineralogy and hydrodynamic  
822 conditions. A state of chemical equilibrium can be reached in the deep CZ for some primary  
823 minerals (biotite and K-feldspar), a feature never observed in the simulations of shallow  
824 subsurface water chemical composition in the Strengbach watershed. Even if the deep water  
825 exhibits higher concentrations, significantly lower mean pore velocities inferred in the  
826 fractured zones imply that the deep water is only responsible for a negligible part of the total  
827 hydrologic and weathering fluxes in the watershed. The limited role of the deep weathering  
828 processes (20-60 m) compared to the shallow subsurface processes (0-15 m) suggests an up  
829 to bottom control of the CZ evolution, at least at a millennial timescale and in this type of  
830 granitic headwater watershed. Our study also indicates that the majority of fresh water  
831 available for water supply at a human timescale originates from shallow subsurface waters,  
832 as the deep water circulation is too slow for being critical at a timescale relevant for water  
833 supply and societal needs in this type of geological context.

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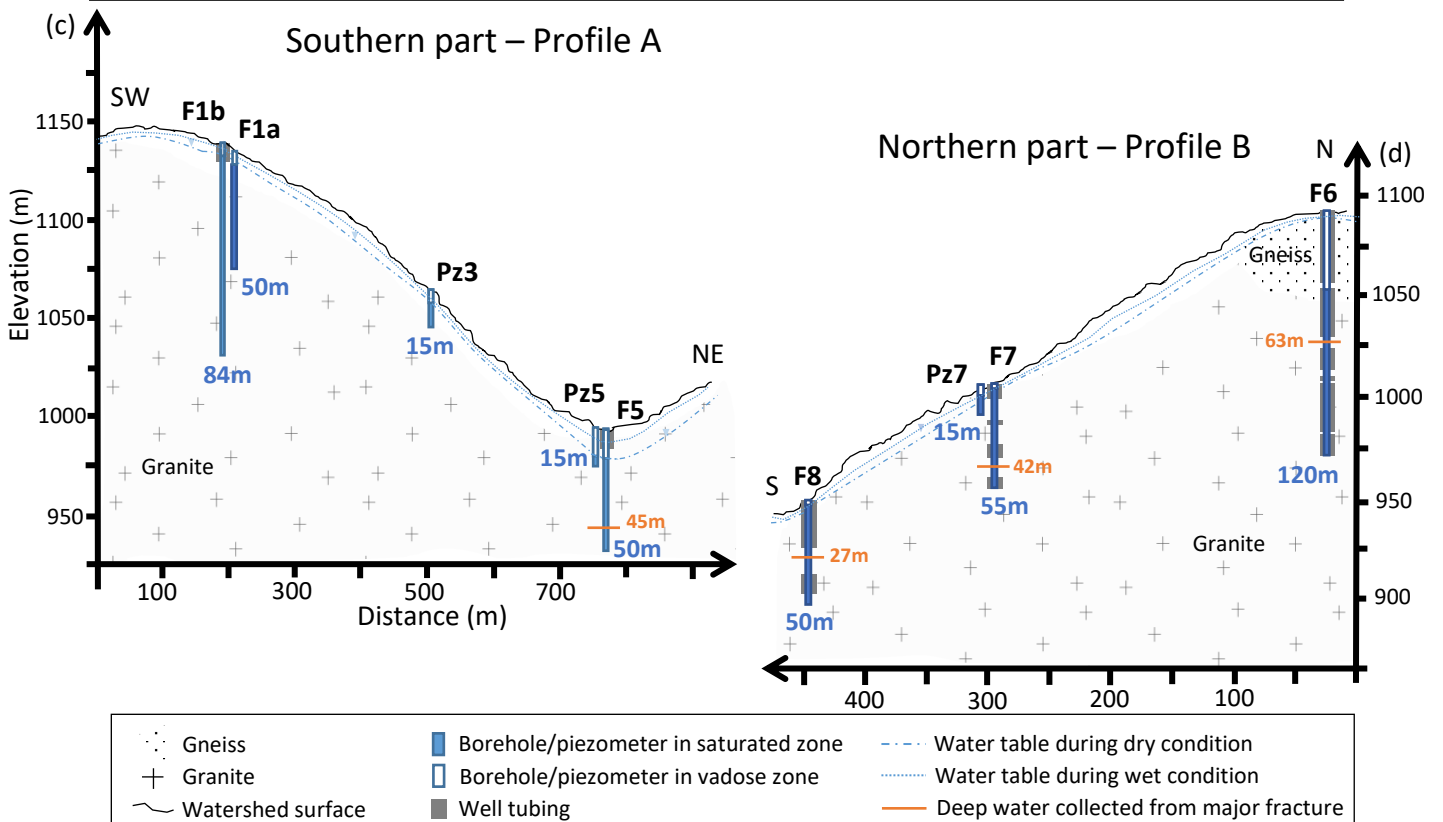
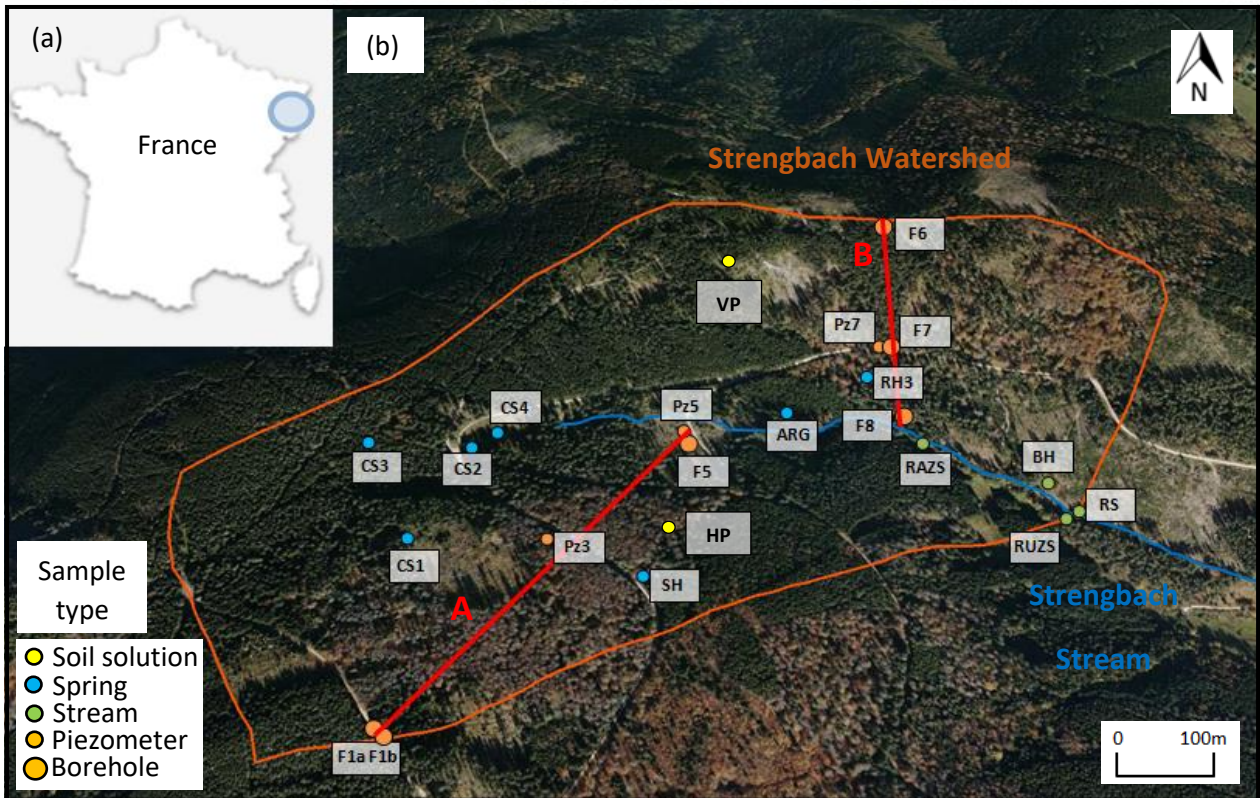
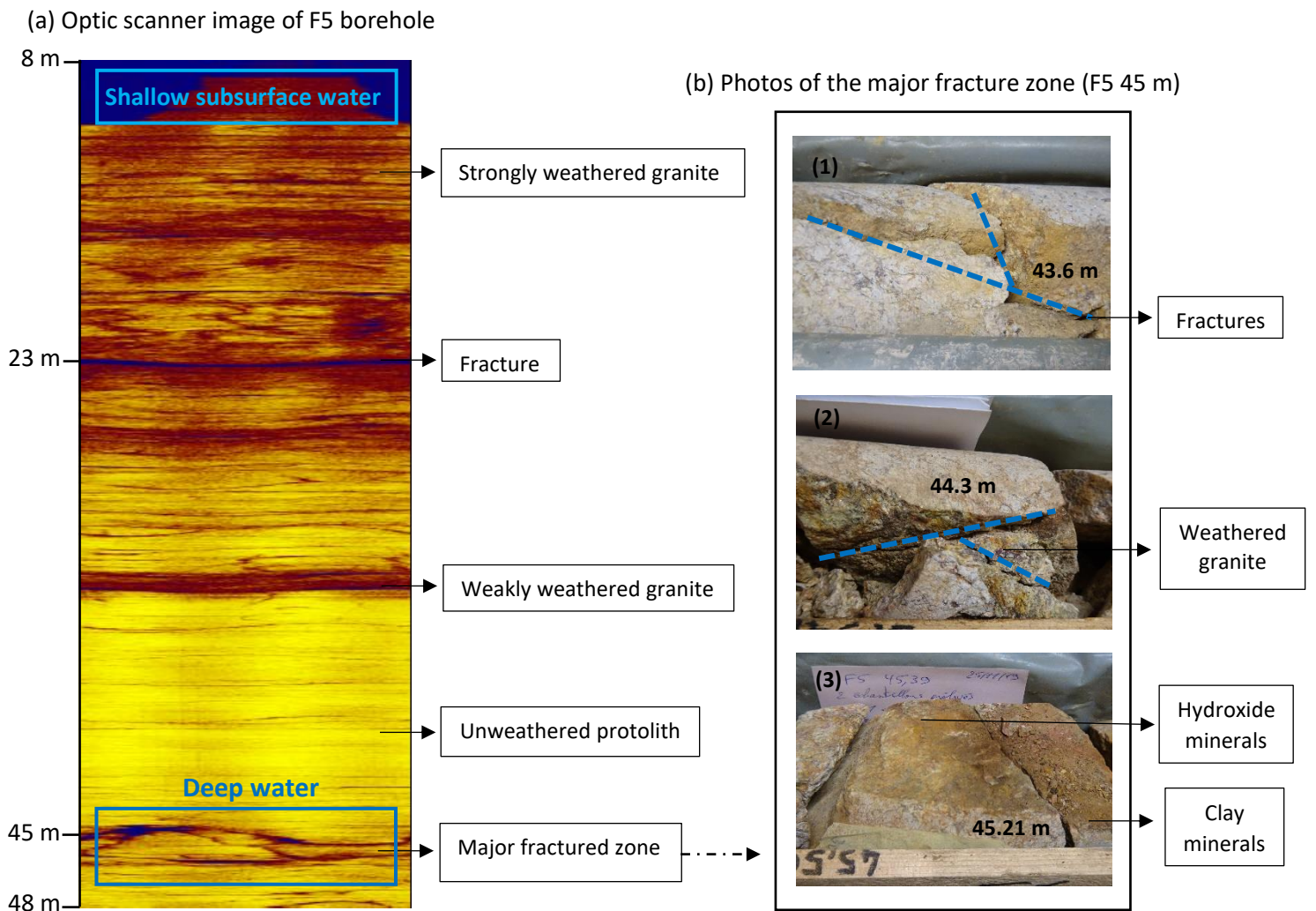


Figure 1: watershed and sampling location (a) Strengbach watershed location in northeastern France. (b) Sampling location of spring, stream, piezometer, and borehole waters within the watershed. (c) Profile A on the southern part of the watershed including F1b and F5 boreholes, and Pz3 and Pz5 piezometers. (d) Profile B on the northern part of the watershed including F6, F7 and F8 boreholes, and Pz7 piezometer.





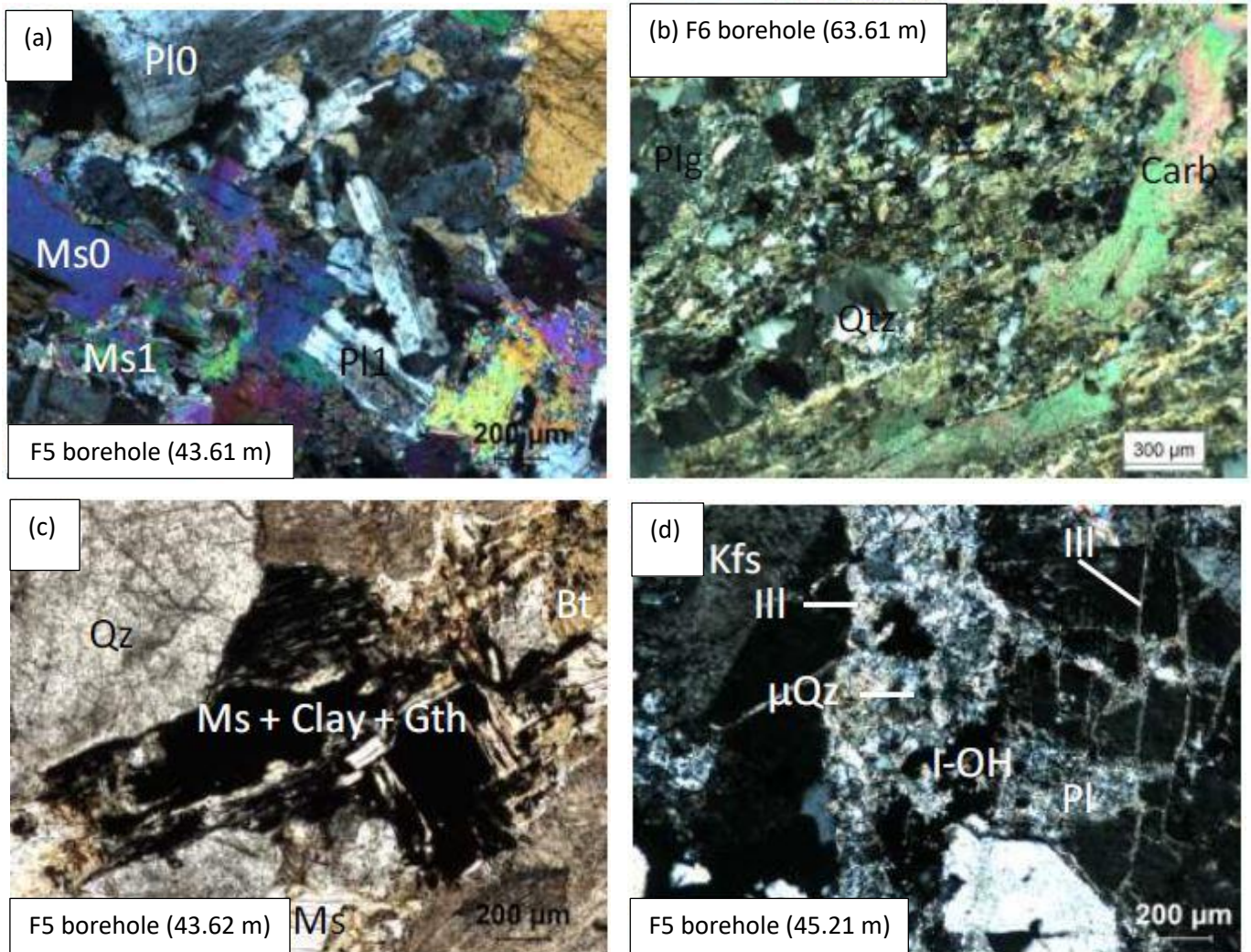


Figure 3: thin sections of rock samples collected on fracture planes intercepting deep boreholes. (a) thin section from F5 borehole showing typical mineral assemblage of the granite with plagioclase, muscovite, and quartz. (b) thin section from F6 borehole showing secondary carbonate minerals (dolomite) surrounded by quartz and plagioclase. (c) thin section from F5 showing quartz, muscovite, biotite, with typical weathering of biotite into secondary clay minerals (presence of montmorillonites, smectites, illites) and iron hydroxides. (d) thin section from F5 showing micro-quartz, plagioclase, K-feldspar, and secondary minerals (iron hydroxides and clay minerals). Abbreviations used in the figure are quartz (Qz/Qtz), micro-quartz ( $\mu$ Qz), plagioclase (Plg/Pl), carbonates (carb), muscovite (Ms), biotite (Bt), Goethite (Gth), K-feldspar (Kfs), iron hydroxides (I-OH), clay minerals (Clay) and illites (Ill).

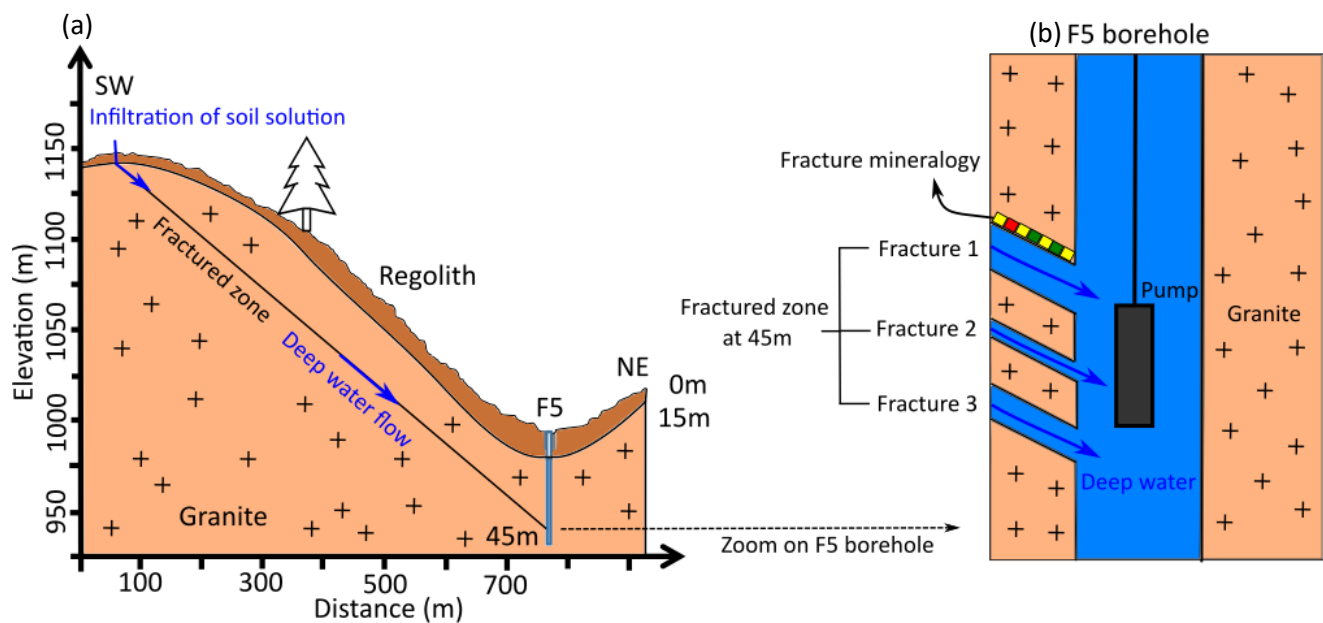


Figure 4: modeling scheme used for the reactive-transport modeling of deep water. (a) Modeling strategy at the hillslope scale shown for the F5 borehole on the southern part of the watershed. Water infiltrates on watershed crest and flows along a fractured zone intercepting the borehole (b) Zoom on the major fractured zone at F5 45 m and illustration of fractures, fracture mineralogy, and pump sampling. Minerals are illustrated by color boxes on a fracture plane. Water-rock interactions described by the reactive transport modeling as primary mineral dissolution and clay mineral precipitation occur along fracture planes.

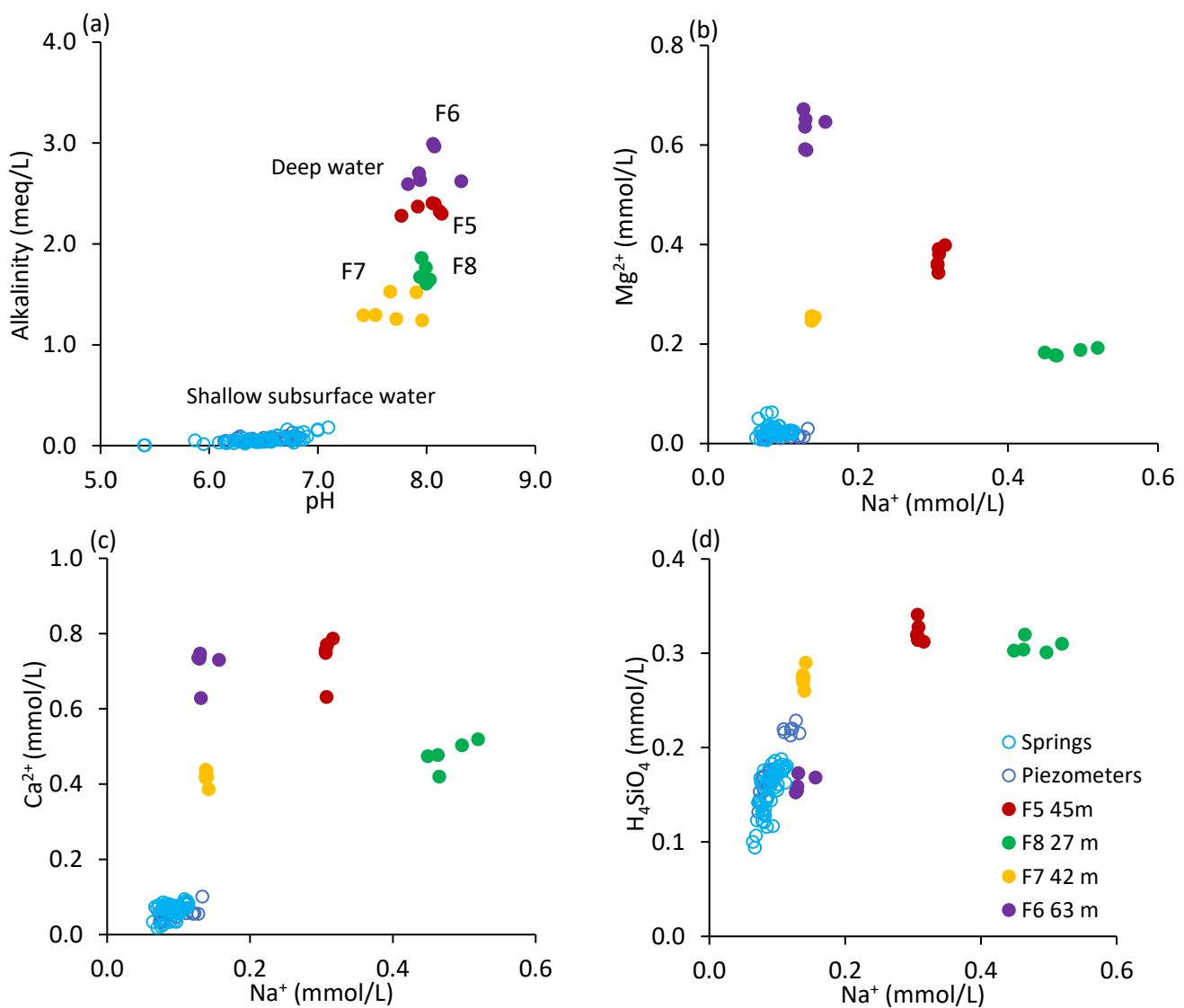


Figure 5: geochemical composition of deep and shallow subsurface waters in the Strengbach watershed (a) pH-alkalinity diagram for the Strengbach waters, including spring (3-5 m of depth), piezometer (PZ3 11 m, PZ5 15 m, PZ7 12 m) and borehole waters (F5 45 m, F6 63 m, F7 42 m, F8 27 m). (b)  $Mg^{2+}$  -  $Na^+$  diagram. (c)  $Ca^{2+}$  -  $Na^+$  diagram. (d)  $H_4SiO_4$  -  $Na^+$  diagram.

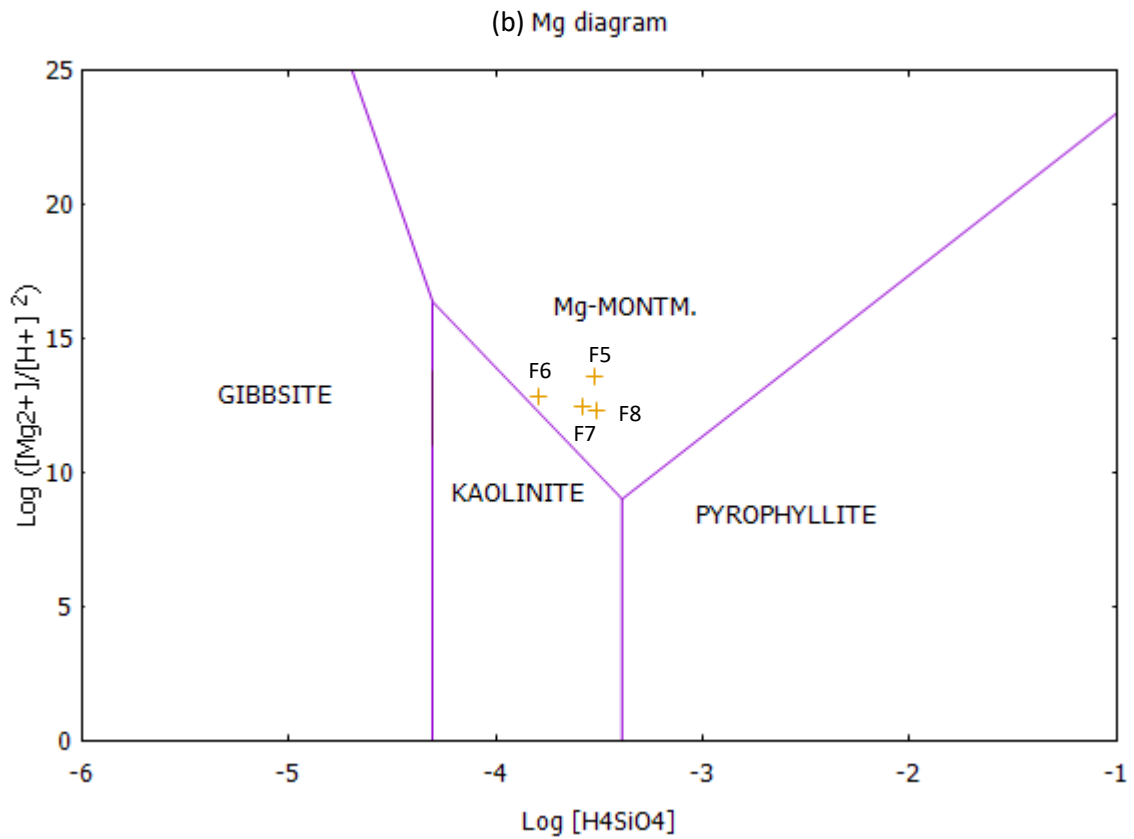
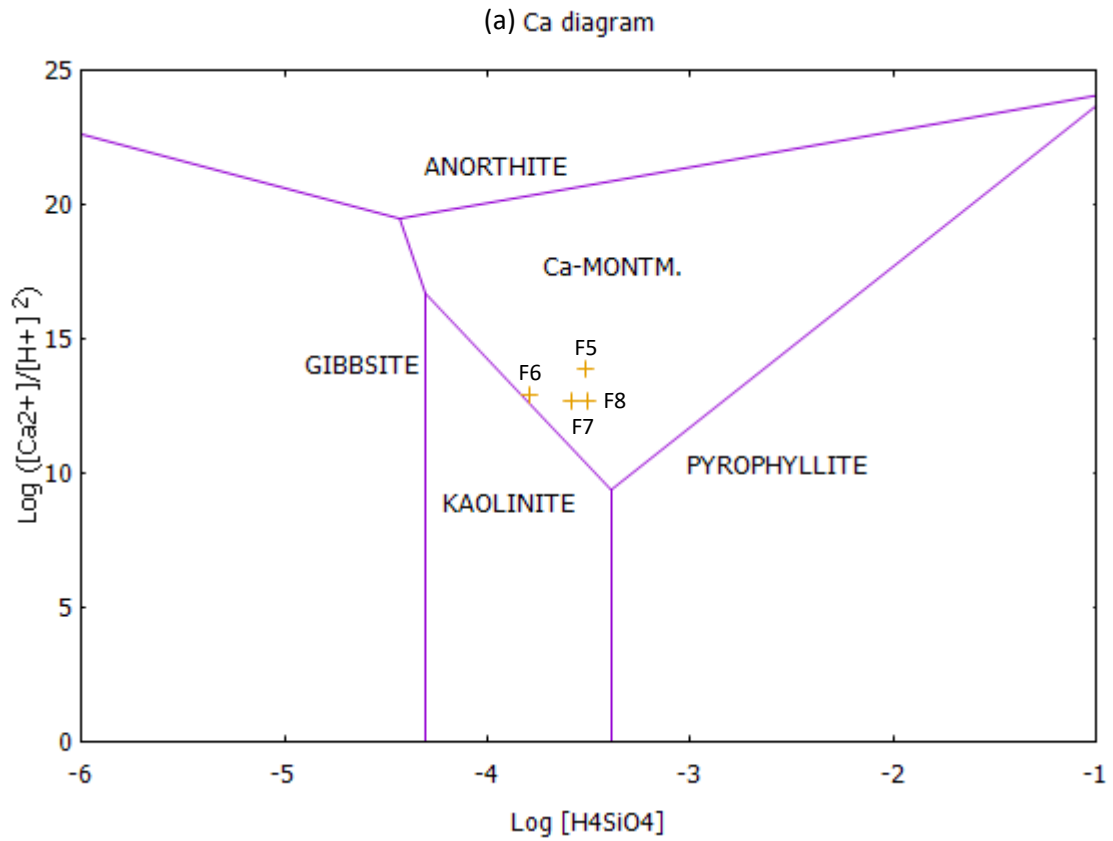


Figure 6: stability diagrams under thermodynamic conditions encountered in deep water samples collected from major borehole fractured zones. (a) diagram for Ca showing stability of Ca-montmorillonite. (b) diagram for Mg showing stability of Mg-montmorillonite. Crosses represent data points calculated from mean concentrations in borehole waters collected from F5 45 m, F6 63 m, F7 42 m and F8 27 m.

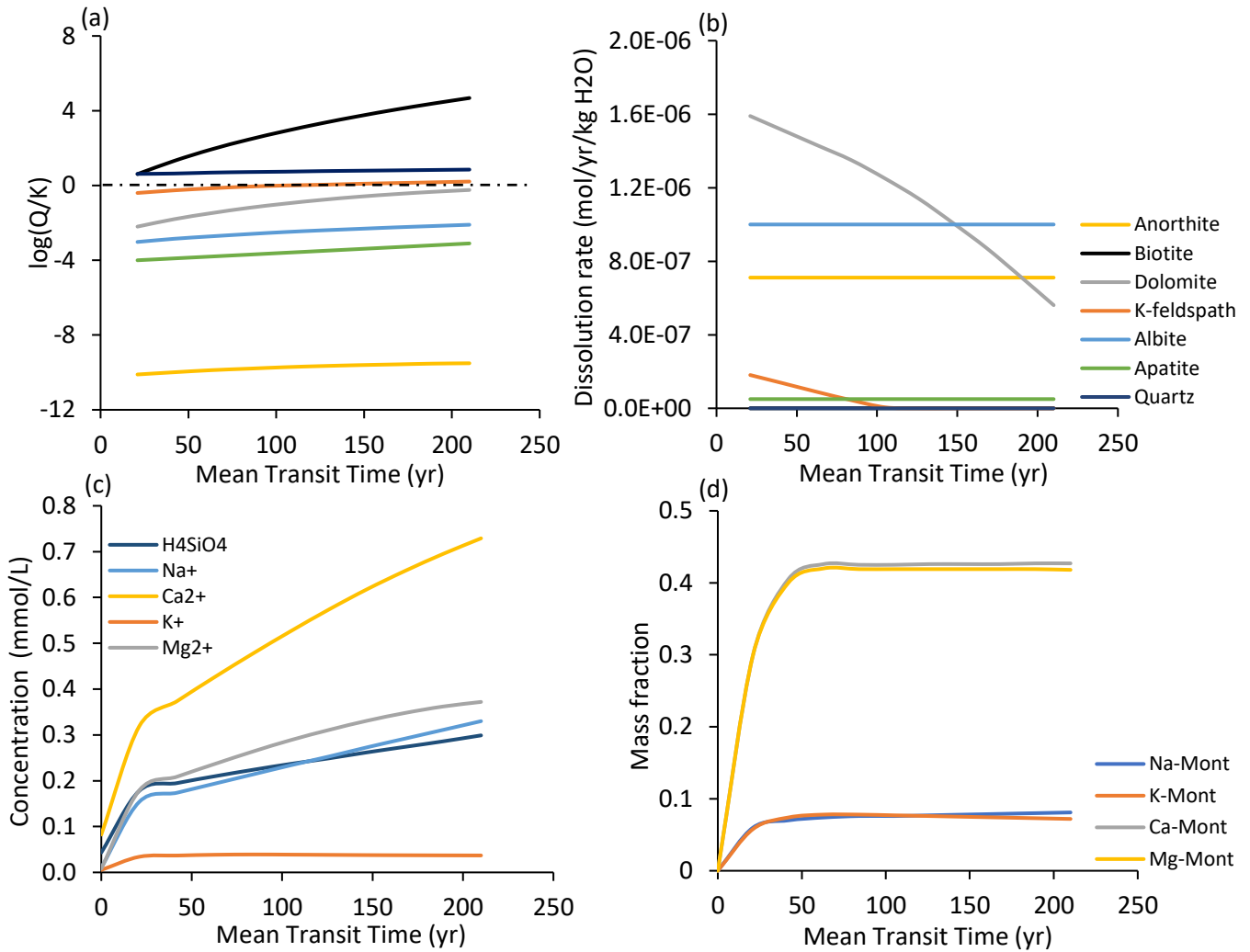


Figure 7: primary mineral saturation states, dissolution rates, solute concentrations, and clay minerals along the fracture network at F5 45m as function of mean transit time. (a)  $\log(Q/K)$  of primary minerals versus mean transit time of the deep water. (b) dissolution rates of primary minerals. (c) solute concentrations of silica and basic cations. (d) mass fraction of clay end members in the clay solid solution. The end of simulation corresponds to the optimized mean transit time of 210 yrs obtained by calibration.

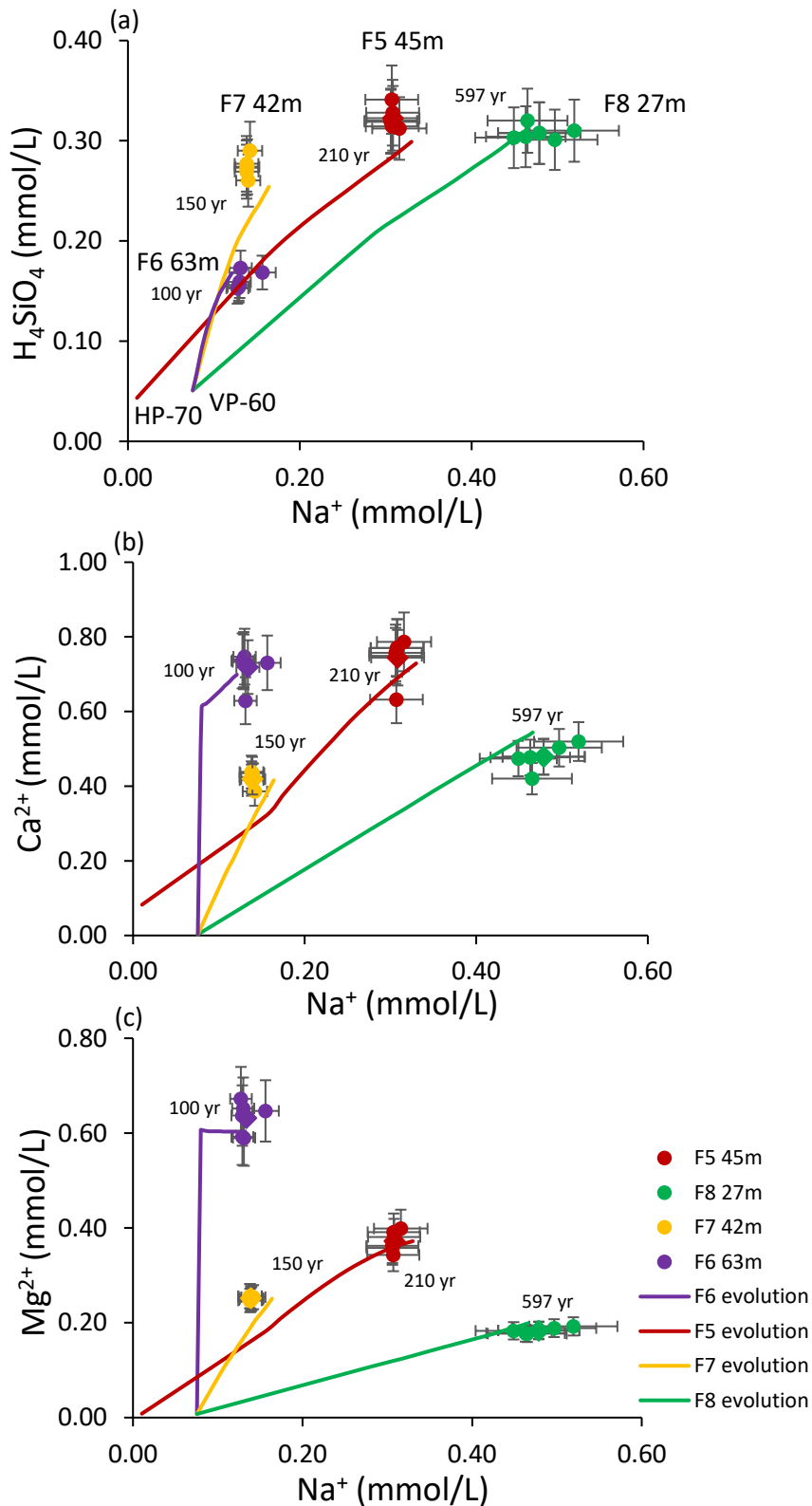


Figure 8: elementary diagrams showing the chemical composition of the deep water. Individual samples (points), mean values (diamonds), and evolution of the simulated chemical composition of the deep water along fractured zones (lines) are represented. Simulations shown on this figure targeted mean values. Initial values are soil solution values (HP-70, VP-60). (a) subplot for  $\text{H}_4\text{SiO}_4$  and  $\text{Na}^+$ . (b) subplot for  $\text{Ca}^{2+}$  and  $\text{Na}^+$ . (c) subplot for  $\text{Mg}^{2+}$  and  $\text{Na}^+$ .

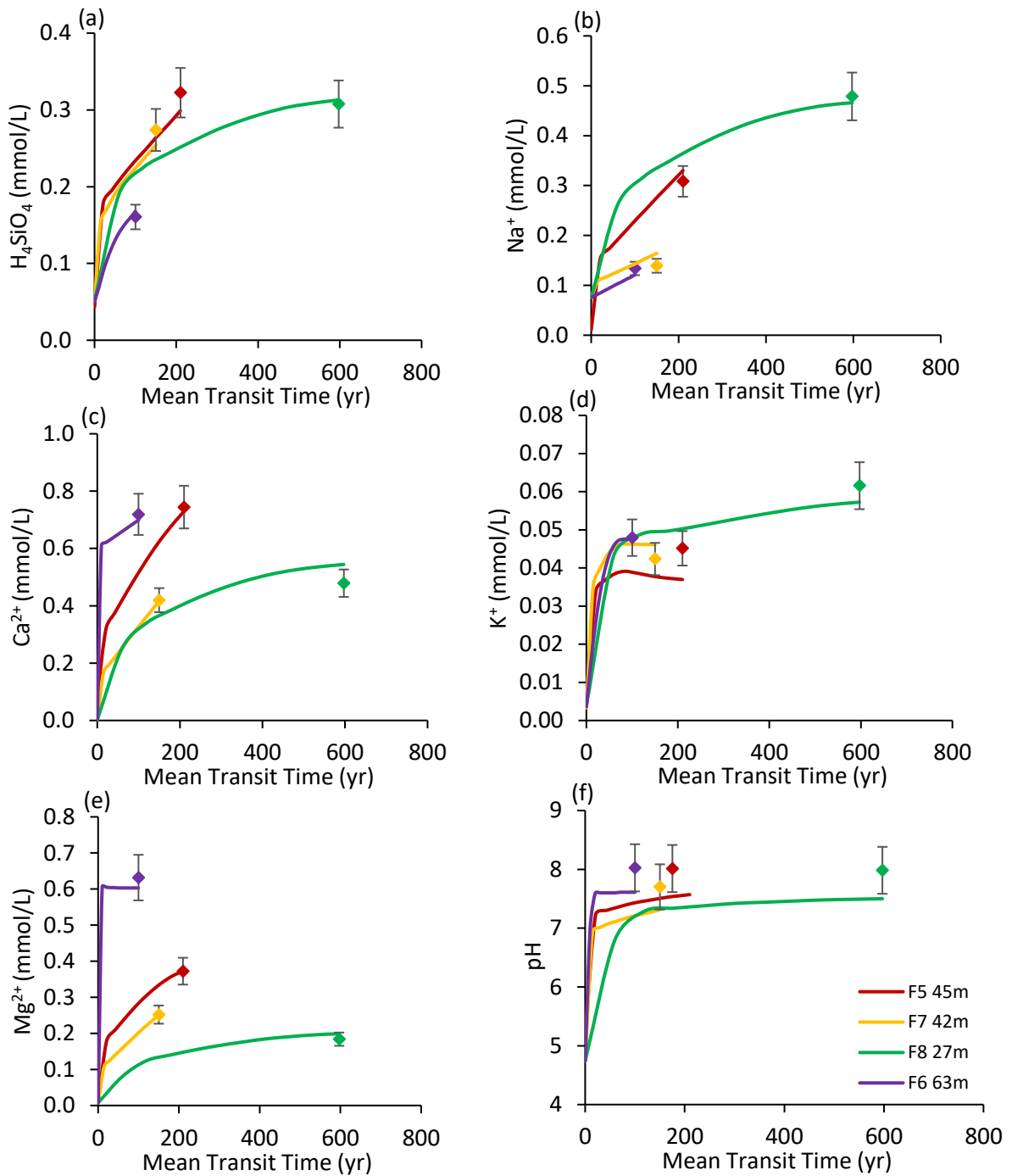


Figure 9: simulation of the deep water chemical composition and of the mean transit time along main fractured zones of F5, F6, F7 and F8 boreholes. Diamonds represent average values of measured parameters from deep water samples and lines represent simulated values. (a) subplot for  $H_4SiO_4$ . (b) subplot for  $Na^+$ . (c) subplot for  $Ca^{2+}$ . (d) subplot for  $K^+$ . (e) subplot for  $Mg^{2+}$ . (f) subplot for pH.

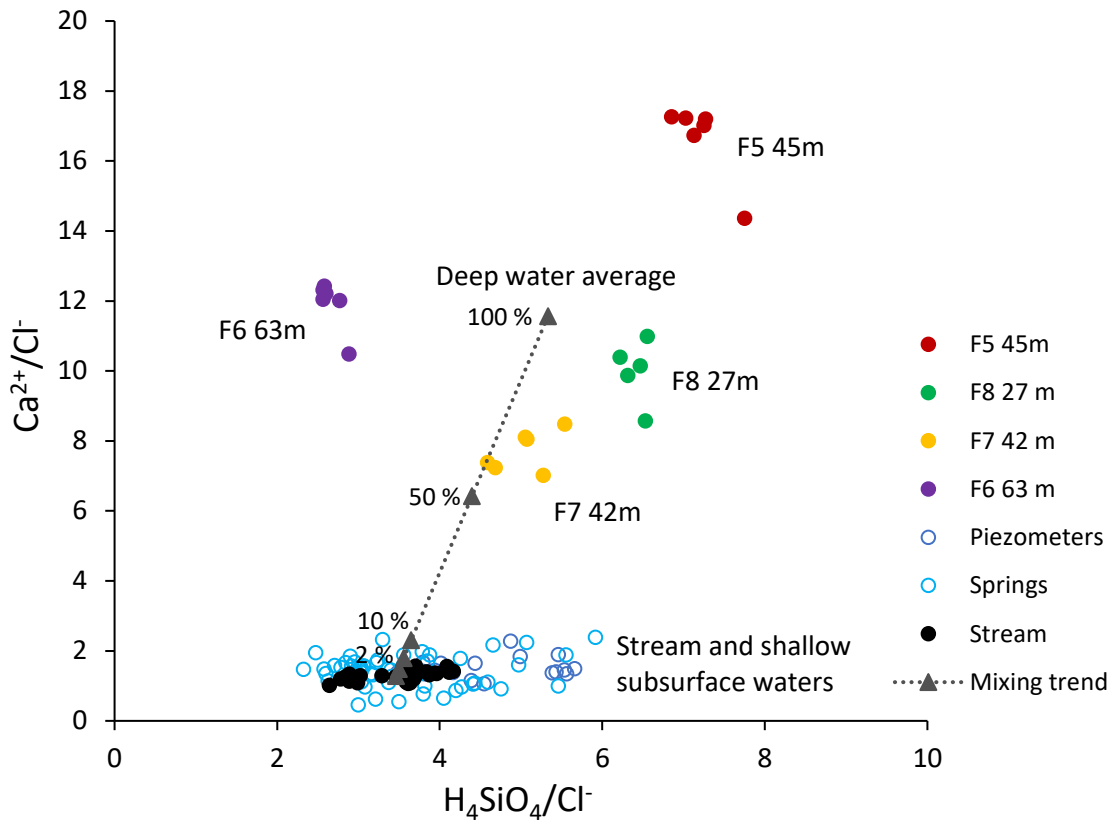


Figure 10: mixing  $\text{H}_4\text{SiO}_4/\text{Cl}^-$  vs  $\text{Ca}^{2+}/\text{Cl}^-$  diagram showing the chemical composition of the deep water (F5 45 m, F8 27 m, F7 42 m and F6 63 m), the shallow subsurface water (Strengbach springs and piezometers) and the Strengbach stream water. Mixing trend between deep water average and stream water average is shown in dotted line with deep water contribution expressed in %.



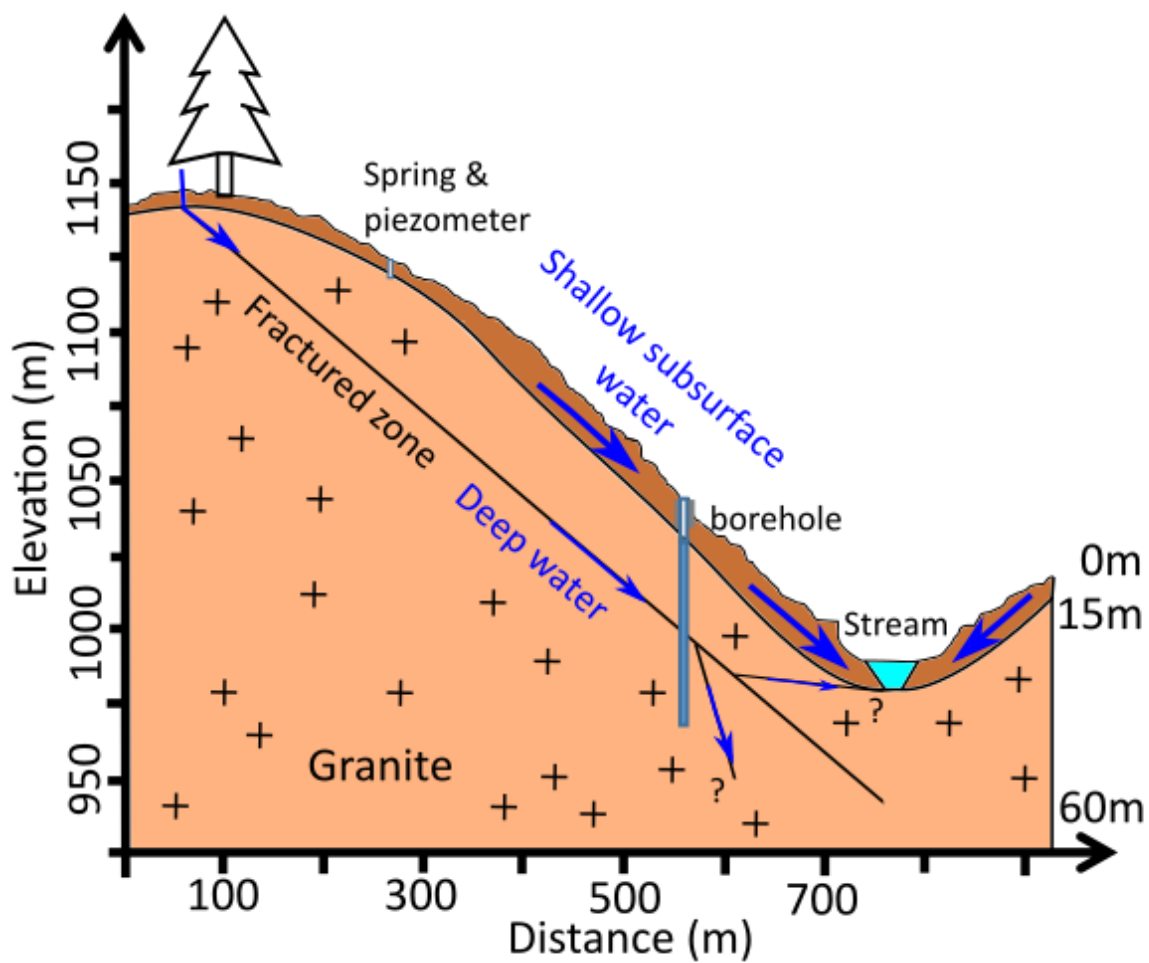


Figure 11: summary figure of the hydrogeochemical functioning of the Strenzbach watershed. The shallow subsurface water carries most of the hydrological and geochemical fluxes at the watershed scale and explains most of the stream flow at the outlet. The deep water flows along independent fractures and represents only a minor part of total hydrological and geochemical fluxes. This hydrogeochemical functioning implies a up-bottom control on CZ evolution where the watershed dynamic is primarily driven by surface erosion, high water fluxes, and fast weathering rates in the shallow subsurface.

Structural data of the major fractures from boreholes F5, F6, F7 and F8 where deep water samples were taken. Geochemical analysis and reactive transport modeling of the water chemical composition were performed on water samples from these fractured zones.

Southern slope borehole		Depth (m)	Azimuth (°)	Aperture (mm)	Dip (°)	specific surface of water-rock contact (m <sup>2</sup> .kg H <sub>2</sub> O <sup>-1</sup> )
F5	fracture 1	43.61	89	75	53	0.055
	fracture 2	44.30	96	19	40	0.016
	fracture 3	45.21	91	11	22	0.024
Northern slope boreholes		Depth (m)	Azimuth (°)	Aperture (mm)	Dip (°)	specific surface of water-rock contact (m <sup>2</sup> .kg H <sub>2</sub> O <sup>-1</sup> )
F6	fracture 1	62.70	105	5	66	0.028
	fracture 2	63.47	175	7	9	0.034
	fracture 3	63.61	173	59	44	0.059
F7	fracture 1	39.96	166	23	43	0.037
	fracture 2	41.42	159	20	52	0.042
	fracture 3	42.13	143	22	56	0.050
F8	fracture 1	27.53	143	16	53	0.170

Table 1

Mass fractions and reactive surfaces of minerals in the major fractured zones from boreholes. Mass fractions are averaged values from the analysis of fracture planes. Reactive surfaces are given for the major fractured zones intercepting the boreholes by taking the sum of the reactive surfaces from individual fracture planes and are expressed in  $\text{m}^2 \text{kg H}_2\text{O}^{-1}$ .

Southern slope borehole		Quartz	Albite	Anorthite	K-feldspar	Muscovite	Biotite	Apatite	Dolomite
F5 45 m	mass fraction	0.37	0.32	0.03	0.19	0.03	0.05	0.005	0.005
	reactive surface	0.035	0.030	0.002	0.018	0.002	0.004	0.0005	0.0005
Northern slope boreholes		Quartz	Albite	Anorthite	K-feldspar	Muscovite	Biotite	Apatite	Dolomite
F6 63 m	mass fraction	0.38	0.27	0.02	0.24	0.02	0.06	0.005	0.010
	reactive surface	0.045	0.032	0.002	0.028	0.002	0.007	0.0006	0.001
F7 42 m	mass fraction	0.38	0.28	0.02	0.24	0.03	0.04	0.005	0.005
	reactive surface	0.049	0.036	0.002	0.031	0.003	0.005	0.0006	0.0006
F8 27 m	mass fraction	0.36	0.34	0.03	0.20	0.02	0.04	0.0050	0.0010
	reactive surface	0.061	0.057	0.005	0.034	0.004	0.007	0.0008	0.0002

Table 2

Geochemical composition of deep water collected from the major fractured zones in boreholes.

Piezometric levels are expressed in m below surface, concentrations are in mmol/L and alkalinity in meq/L.

<b>Southern slope borehole</b>	<b>Sampling date</b>	<b>Piezometric level</b>	<b>Alkalinity</b>	<b>pH</b>	<b>Na<sup>+</sup></b>	<b>K<sup>+</sup></b>	<b>Mg<sup>2+</sup></b>	<b>Ca<sup>2+</sup></b>	<b>H<sub>4</sub>SiO<sub>4</sub></b>
<b>F5 45 m</b>	27/10/2016	11.59	2.396	8.08	0.316	0.044	0.399	0.787	0.312
	23/11/2016	10.30	2.403	8.06	0.308	0.045	0.391	0.771	0.314
	10/10/2017	11.22	2.321	8.12	0.306	0.068	0.362	0.757	0.320
	10/01/2018	6.37	2.278	7.77	0.307	0.036	0.343	0.632	0.341
	24/04/2018	10.62	2.300	8.14	0.308	0.039	0.381	0.77	0.328
	23/10/2018	11.64	2.369	7.92	0.306	0.039	0.358	0.749	0.319
<b>Northern slope boreholes</b>	<b>Sampling date</b>		<b>Alkalinity</b>	<b>pH</b>	<b>Na<sup>+</sup></b>	<b>K<sup>+</sup></b>	<b>Mg<sup>2+</sup></b>	<b>Ca<sup>2+</sup></b>	<b>H<sub>4</sub>SiO<sub>4</sub></b>
<b>F6 63 m</b>	27/10/2016	42.07	2.631	8.07	0.156	0.054	0.647	0.730	0.168
	22/11/2016	39.08	2.645	8.06	0.127	0.049	0.672	0.736	0.153
	09/10/2017	40.16	2.632	7.94	0.129	0.066	0.592	0.733	0.156
	09/01/2018	36.28	2.593	7.83	0.131	0.037	0.59	0.629	0.173
	25/04/2018	39.18	2.622	8.32	0.13	0.041	0.652	0.747	0.159
	23/10/2018	41.08	2.701	7.93	0.129	0.041	0.637	0.739	0.154
<b>F7 42 m</b>	26/10/2016	3.99	1.227	7.91	0.140	0.042	0.250	0.419	0.260
	22/11/2016	2.39	1.208	7.67	0.138	0.043	0.256	0.416	0.269
	10/10/2017	3.43	1.254	7.72	0.138	0.054	0.247	0.424	0.277
	09/01/2018	1.22	1.291	7.42	0.142	0.036	0.254	0.386	0.29
	26/04/2018	3.08	1.242	7.96	0.138	0.039	0.256	0.438	0.273
	23/10/2018	4.2	1.296	7.53	0.139	0.04	0.248	0.435	0.274
<b>F8 27 m</b>	26/10/2016	1.87	1.766	7.99	0.497	0.063	0.189	0.503	0.301
	22/11/2016	1.88	1.859	7.95	0.519	0.065	0.192	0.520	0.310
	09/10/2017	1.96	1.671	7.94	0.449	0.061	0.183	0.474	0.303
	09/01/2018	1.41	1.607	8	0.465	0.062	0.177	0.42	0.32
	23/10/2018	2.33	1.645	8.03	0.463	0.057	0.178	0.477	0.304

Table 3

Hydrodynamic parameters used for the reactive transport modeling of the deep water geochemical composition and mean transit time of deep water inferred in the fractured zones.

<b>Southern slope borehole</b>	<b>Fracture lengths (m)</b>	<b>Mean pore velocity (m. yr<sup>-1</sup>)</b>	<b>Optimized mean transit time (yr)</b>
<b>F5 45 m</b>	700	3.33	210
<b>Northern slope boreholes</b>			
<b>Northern slope boreholes</b>	<b>Fracture lengths (m)</b>	<b>Mean pore velocity (m. yr<sup>-1</sup>)</b>	<b>Optimized mean transit time (yr)</b>
<b>F6 63 m</b>	100	1	100
<b>F7 42 m</b>	350	2.33	150
<b>F8 27 m</b>	400	0.67	597

Table 4

Geochemical fluxes and relative contributions of the shallow subsurface and deep waters to the chemical weathering in the Strengbach watershed. Calculations for the deep water are based on F5 45 m and calculations for the shallow subsurface water are based on CS1 spring (data in Ackerer et al., 2020). Geochemical fluxes are given for a unitary cross section of 1 m<sup>2</sup> of shallow subsurface and fractured zone in the bedrock.

		Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	H <sub>4</sub> SiO <sub>4</sub>	Total
<b>Geochemical fluxes</b>	<b>Shallow subsurface water (kg yr<sup>-1</sup>)</b>	3.839	1.547	0.767	3.251	28.300	37.704
	<b>Deep water (kg yr<sup>-1</sup>)</b>	0.021-0.107	0.005-0.023	0.037-0.186	0.110-0.549	0.141-0.703	0.314-1.569
<b>Relative contribution</b>	<b>Shallow subsurface water (%)</b>	97.3-99.4	98.6-99.7	80.5-95.4	85.5-96.7	97.6-99.5	96-99.2
	<b>Deep water (%)</b>	0.6-2.7	0.3-1.4	4.6-19.5	3.3-14.5	0.5-2.4	0.8-4

Table 5

**Supplementary material: tables**

Mineral	Chemical composition	Log (K) (25°C)
Quartz	$\text{SiO}_2$	-3.999
Albite	$\text{NaAlSi}_3\text{O}_8$	-20.178
K-feldspar	$\text{KAlSi}_3\text{O}_8$	-23.192
Biotite	$\text{Si}_3\text{AlMgFe}_2\text{O}_{10}(\text{OH})_2\text{K}$	9.482
Muscovite	$\text{Si}_3\text{Al}_3\text{O}_{10}(\text{OH})_2\text{K}$	-53.169
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	-19.488
Apatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$	-59.590
Illite	$\text{Si}_{3.5}\text{Al}_{2.1}\text{Fe}_{0.34}\text{Mg}_{0.04}\text{O}_{10}(\text{OH})_2\text{K}_{0.6}$	-36.389

*Table EA1: Chemical compositions and laboratory measured thermodynamic constants at 25°C for the different primary minerals used in this study. Data are from the KIRMAT database which is consistent with the Thermoddem database.*



Mineral	Chemical composition	Kinetic constants (25°C) (mol.m <sup>-2</sup> .an <sup>-1</sup> )			$\alpha^n_{H^+}$		Boundary pH		Activation energy (kJ.mol <sup>-1</sup> )
		Acid	Neutral	Basic	Acid	Basic	Acid	Basic	
Quartz <sup>(1)</sup>	SiO <sub>2</sub>	-	3.15×10 <sup>-6</sup>	2.50×10 <sup>-9</sup>	-	-0.5	3	6	85.0 <sup>(1)</sup>
Albite <sup>(2)</sup>	NaAlSi <sub>3</sub> O <sub>8</sub>	5.61×10 <sup>-3</sup>	5×10 <sup>-5</sup>	2.94×10 <sup>-7</sup>	0.45	-0.3	4.5	8	58.6 <sup>(12)</sup>
K-feldspar <sup>(3,4)</sup>	KAlSi <sub>3</sub> O <sub>8</sub>	2.68×10 <sup>-3</sup>	1.02×10 <sup>-5</sup>	9.31×10 <sup>-13</sup>	0.44	-0.69	4.5	10	38.0 <sup>(13)</sup>
Biotite <sup>(5,6)</sup>	Si <sub>3</sub> AlMgFe <sub>2</sub> O <sub>10</sub> (OH) <sub>2</sub> K	4.56×10 <sup>-3</sup>	2.39×10 <sup>-5</sup>	1.09×10 <sup>-13</sup>	0.41	-1.05	5	8	35.0 <sup>(7)</sup>
Muscovite <sup>(7)</sup>	Si <sub>3</sub> Al <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> K	1.99×10 <sup>-5</sup>	-	6.15×10 <sup>-5</sup>	0.17	-0.16	4	7	22.0 <sup>(7)</sup>
Anorthite <sup>(8,9)</sup>	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	-	3.23×10 <sup>-4</sup>	-	-	-	4	8.5	40.0 <sup>(14)</sup>
Apatite <sup>(10)</sup>	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	5.50×10 <sup>2</sup>	2.96×10 <sup>-3</sup>	-	0.91	-	6	-	34.7 <sup>(10)</sup>
Illite <sup>(11)</sup>	Si <sub>3.5</sub> Al <sub>2.1</sub> Fe <sub>0.34</sub> Mg <sub>0.04</sub> O <sub>10</sub> (OH) <sub>2</sub> K <sub>0.6</sub>	7.92×10 <sup>-5</sup>	3.71×10 <sup>-8</sup>	3.88×10 <sup>-14</sup>	0.64	-0.62	5	9.5	14.0 <sup>(11)</sup>

Table EA2: Kinetic constants at 25°C and activation energies of the dissolution reactions for the primary minerals used in this study. Data are from laboratory measurements and from <sup>(1)</sup> Dove (1994), <sup>(2)</sup> Chou and Wollast (1984), <sup>(3)</sup> Schweda (1989), <sup>(4)</sup> Lundström and Øhman (1990), <sup>(5)</sup> Acker and Bricker (1992), <sup>(6)</sup> Malmström and Banwart (1997), <sup>(7)</sup> Nagy (1995), <sup>(8)</sup> Amrhein and Suarez (1992), <sup>(9)</sup> Berg and Banwart (2000), <sup>(10)</sup> Guidry and Mackenzie (2003), <sup>(11)</sup> Köhler et al. (2003), <sup>(12)</sup> Blum and Stillings (1995), <sup>(13)</sup> Helgeson et al. (1984), <sup>(14)</sup> Madé (1991). The acid, neutral, and basic domains correspond to the domains where hydrolysis reactions are promoted by H<sup>+</sup>, H<sub>2</sub>O and OH<sup>-</sup> respectively.

Mineral	Chemical composition	Log (K) (25°C)
K-Illite	$\text{Si}_{3.5}\text{Al}_{2.3}\text{Mg}_{0.25}\text{O}_{10}(\text{OH})_2\text{K}_{0.6}$	-43.192
Mg-Illite	$\text{Si}_{3.43}\text{Al}_{2.24}\text{Mg}_{0.38}\text{O}_{10}(\text{OH})_2\text{K}_{0.8}$	-38.760
Ca-Illite	$\text{Si}_{3.2}\text{Al}_{2.2}\text{Mg}_{0.1}\text{Fe}_{0.5}\text{O}_{10}(\text{OH})_2\text{K}_{0.6}\text{Ca}_{0.15}$	-40.943
Montmorillonite	$\text{Si}_{3.83}\text{Al}_{1.84}\text{Mg}_{0.38}\text{O}_{10}(\text{OH})_2\text{K}_{0.4}$	-35.723
Na-Montmorillonite	$\text{Si}_{3.667}\text{Al}_{2.333}\text{O}_{10}(\text{OH})_2\text{Na}_{0.333}$	-47.951
K-Montmorillonite	$\text{Si}_{3.667}\text{Al}_{2.333}\text{O}_{10}(\text{OH})_2\text{K}_{0.333}$	-48.191
Ca-Montmorillonite	$\text{Si}_{3.667}\text{Al}_{2.333}\text{O}_{10}(\text{OH})_2\text{Ca}_{0.167}$	-48.101
Mg-Montmorillonite	$\text{Si}_{3.667}\text{Al}_{2.333}\text{O}_{10}(\text{OH})_2\text{Mg}_{0.167}$	-48.201

Table EA3: Chemical compositions and laboratory measured thermodynamic constants at 25°C for the different clay solid solution end members used in this study. Data are from the KIRMAT database which is consistent with the Thermodem database.

Mineral	Chemical composition	Dissociation equations
Quartz	$\text{SiO}_2$	$\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_4\text{SiO}_4$
Albite	$\text{NaAlSi}_3\text{O}_8$	$\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_4^- + \text{Na}^+ + 3\text{H}_4\text{SiO}_4$
K-feldspar	$\text{KAlSi}_3\text{O}_8$	$\text{KAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_4^- + \text{K}^+ + 3\text{H}_4\text{SiO}_4$
Biotite	$\text{Si}_3\text{AlMgFe}_2\text{O}_{10}(\text{OH})_2\text{K}$	$\text{Si}_3\text{AlMgFe}_2\text{O}_{10}(\text{OH})_2\text{K} + 4\text{H}_2\text{O} + 6\text{H}^+ \rightarrow \text{Al}(\text{OH})_4^- + \text{K}^+ + \text{Mg}^{2+} + 2\text{Fe}^{2+} + 3\text{H}_4\text{SiO}_4$
Muscovite	$\text{Si}_3\text{Al}_3\text{O}_{10}(\text{OH})_2\text{K}$	$\text{Si}_3\text{Al}_3\text{O}_{10}(\text{OH})_2\text{K} + 12\text{H}_2\text{O} \rightarrow 3\text{Al}(\text{OH})_4^- + \text{K}^+ + 3\text{H}_4\text{SiO}_4 + 2\text{H}^+$
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}_2\text{O} \rightarrow 2\text{Al}(\text{OH})_4^- + \text{Ca}^{2+} + 2\text{H}_4\text{SiO}_4$
Apatite	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 \rightarrow 10\text{Ca}^{2+} + 2\text{F}^- + 3\text{PO}_4^{3-}$

Table EA4: Chemical compositions and dissociation equations for primary minerals used in reactive-transport simulations.

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