

1 **Hydrological and geological controls for the joint**
2 **evolution of dissolved oxygen and iron in crystalline**
3 **rocks**

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7 **Key Points:**

- 8 • We derive and validate analytical expressions to predict the joint evolution of dis-
9 solved O_2 and Fe^{2+} in crystalline rocks.
10 • We show that the hydrological and geological controls can be discriminated by an-
11 alyzing both O_2 and Fe^{2+} as a function of depth.
12 • The modeling framework is used to analyze O_2 and Fe^{2+} data on two sites with
13 contrasted chemical properties.

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Abstract

Dissolved Oxygen (DO) plays a key role in reactive processes and microbial dynamics in the critical zone. While the general view is that oxygen is rapidly depleted in soils and that deeper compartments are anoxic, recent observations showed that fractures can provide rapid pathways for deep oxygen penetration, triggering unexpected biogeochemical processes. As it is transported in the subsurface, DO reacts with electron donors, such as Fe^{2+} coming from mineral dissolution, hence influencing rock-weathering. Yet, little is known about the factors controlling the spatial heterogeneity and distribution of oxygen with depth. Here we present analytical expressions describing the coupled evolution of DO and Fe^{2+} as a function of fluid travel time in crystalline rocks. Our model, validated with reactive transport simulations, predicts a linear decay of DO with time, followed by a rapid non-linear increase of Fe^{2+} concentrations up to an equilibrium state. Relative effects of the reducing capacity of the bedrock and of transport velocity are quantified through a Damköhler number, capturing key hydrological and geological controls of Fe^{2+} and DO distributions in the subsurface. This framework is used to investigate contrasted DO and Fe^{2+} concentrations observed in two crystalline catchments. These differences are explained by the Damköhler number: one system is reaction-limited while the second is transport-limited. We show that hydrological and geological drivers can be discriminated by analyzing both O_2 and Fe^{2+} . These findings provide a new conceptual framework to understand and predict the evolution of DO in the subsurface, a key element in the critical zone.

Plain Language Summary

In the critical zone, dissolved Oxygen (DO) is involved in pivotal biogeochemical reactions, such as the aerobic respiration of microbes, rock-weathering or contaminant degradation. The general view is that the deeper subsurface of continents is mostly anoxic. However, recent observations have shown that preferential flowpaths in rock fractures can favor oxygen penetration, thus extending deeper the influence of oxygen in reactions. Here, we present a modeling framework validated with field data to understand and predict the hydrological and geological controls on dissolved oxygen evolution in crystalline rocks, shedding new light on its influence on rock-weathering and microbial life in the critical zone.

1 Introduction

Oxygen is central in redox reactions because it the most abundant and readily available electron acceptor in the environment (Korom, 1992; Stumm & Morgan, 1996) and offers a strong redox potential. In aquatic environments, dissolved oxygen (DO) is mostly produced by photosynthesis and consumed by aerobic respiration of organic matter (Mader et al., 2017). In the subsurface, the transport of DO and CO_2 by fluid flow triggers the weathering of crystalline rocks (Fletcher et al., 2006; Kim et al., 2017; Li et al., 2017; Singha & Navarre-Sitchler, 2022), which represent a quarter of the outcropping Earth rocks (Hartmann & Moosdorf, 2012). The cycle of DO is thus closely related to the geochemical cycles of carbon (Petsch et al., 2004; Bar-on et al., 2018), iron (Melton et al., 2014; Napieralski et al., 2019; Kappler et al., 2021) and sulfur (Gu et al., 2020). Moreover, recent studies have pointed out that redox reactions, particularly involving DO, are often mediated by microbes (Erable et al., 2012; Napieralski et al., 2019; Kappler et al., 2021) because the redox potential of the reaction offers an energy source for microbes to thrive (Emerson et al., 2010). DO thus also exerts a key ecological role by impacting the biodiversity (Malard & Hervant, 1999; Hancock et al., 2005; Humphreys, 2009) and activity of aerobic microbial metabolisms (Druschel et al., 2008; Mader et al., 2017; Maisch et al., 2019).

63 When DO is not depleted in soils, either because of a limited soil-thickness or a low
 64 organic matter availability, oxic water can enter the bedrock and react with the electron
 65 donors available in the subsurface, such as $Fe(II)$, $Mn(II)$, CH_4 , H_2 or HS^- (Kartsen
 66 Pedersen, 1997; Tebo et al., 2005). Iron is the most abundant redox-sensitive element
 67 in the Earth crust (Frey & Reed, 2012), it is linked to biogeochemical cycles of carbon,
 68 sulphur and nitrogen (Casar et al., 2021). The reduction of DO by iron can occur either
 69 by Fe(II)-sites on mineral surfaces (White et al., 1985) or by Fe^{2+} dissolved in water sub-
 70 sequently to the release of structural Fe(II) by mineral dissolution (White & Yee, 1985).
 71 The most common Fe(II)-bearing primary minerals in hard-rocks are silicates such as
 72 biotite (Malmström et al., 1996; Aquilina et al., 2018; Holbrook et al., 2019; Hampl et
 73 al., 2021), pyroxene (Behrens et al., 2015) and hornblende (Fletcher et al., 2006) and in
 74 less proportion, sulfates such as Pyrite (Gu et al., 2020).

75 Several field works documenting weathering profiles in hard-rocks, either from out-
 76 crops (Antoniellini et al., 2017) or borehole cores (Dideriksen et al., 2010; Bazilevskaya
 77 et al., 2013; Holbrook et al., 2019; Hampl et al., 2021), have suggested that DO trans-
 78 port by subsurface flow could explain the presence of secondary minerals and weather-
 79 ing induced fracturing (WIF) in ferrous silicates (Bazilevskaya et al., 2013; Kim et al.,
 80 2017) from deep regolith. Likewise, evidence from field measurements in fractured-rock
 81 aquifers has shown that DO can effectively persist in deep aquifers (Winograd & Robert-
 82 son, 1982; Edmunds et al., 1984; Bucher et al., 2009; DeSimone et al., 2014; Sullivan et
 83 al., 2016; Ruff et al., 2022). Based on field observations, the presence or absence of DO
 84 in the subsurface has been attributed to lithological differences of the bedrock (Winograd
 85 & Robertson, 1982; Malard & Hervant, 1999). However, it is still challenging to predict
 86 the expected depth of dissolved oxygen in crystalline rocks as a function of lithology.

87 Fractures can provide fast transport pathways in the subsurface and therefore in-
 88 fluence reactive transport processes (Deng & Spycher, 2019). The transport and fate of
 89 DO in fractured rocks have been studied in the framework of risk assessments for DO
 90 penetration to nuclear waste repository sites. Numerical studies have simulated the ad-
 91 vance of the redox front in the matrix of granitic rocks (Macquarrie et al., 2010; Trincher-
 92 o, Molinero, et al., 2018; Trincherro et al., 2019) and in fracture networks (Trincherro, Sid-
 93 born, & Puigdomenech, 2018) providing insights into the mechanisms driving oxygen trans-
 94 port in fractured rocks. Approximate analytical solutions have been obtained (Sidborn
 95 & Neretnieks, 2007, 2008) by assuming that the dissolution of Fe(II) bearing minerals
 96 is rapid compared to transport, which is relevant for large time scales (thousands of years).
 97 For smaller time scales, oxygen transport and reaction is controlled by the interplay be-
 98 tween the characteristic dissolution rates and transport time scales (Trincherro, Sidborn,
 99 & Puigdomenech, 2018). However, this effect is not quantified analytically for the joint
 100 evolution of DO and Fe^{2+} concentrations, which limits current understanding of the hy-
 101 drological and geological controls on oxygen depth distribution in the subsurface.

102 The interplay between transport and reaction rates at catchment scale has been
 103 conceptualized using the Damköhler number, defined as the ratio of the characteristic
 104 transport and reaction time scales (Maher, 2010; Maher & Chamberlain, 2014). In this
 105 approach, structures such as fractures and rock matrix are not represented explicitly but
 106 instead integrated into an effective fluid travel time, representing the time during which
 107 fluid has been exposed to reactive minerals (Seeboonruang & Ginn, 2006).

108 In this study, we use a travel time formulation to develop approximate analytical
 109 solutions for coupled DO and Fe^{2+} transport and reaction in the subsurface. We for-
 110 mulate the geological and hydrological controls in a Damköhler number that quantifies
 111 the relative effect of Fe(II)-bearing minerals abundance and transport velocity. Analyt-
 112 ical solution are validated using reactive transport simulations with CrunchFlow. We use
 113 this framework to interpret field data in two critical zone observatories with contrasted
 114 chemical properties.

2 Reactive transport of dissolved oxygen and iron

2.1 Model conceptualisation

To unravel the respective roles of hydrological and geological controls on DO and Fe^{2+} , we consider a travel time formulation (Maher, 2010). For a given flowpath, we model a reaction in parcel of transported fluid as a kinetic system controlled by the travel time (Fig. 1). We quantify interactions between oxic recharge water and Fe(II)-bearing minerals and derive approximate analytical expression of both DO and Fe^{2+} as a function of fluid travel time. We assume that the flowpath cross a shallow regolith zone followed by an unweathered zone in which DO reacts with Fe^{2+} produced from minerals dissolution (Figure 1). We neglect here the transport time in the non-reactive regolith, which we assume to be short compared to the travel time in the non-weathered zone. Furthermore, we do not resolve explicitly the fracture-matrix exchanges and consider an effective travel time which represents effectively the time during which the fluid is in contact with reactive elements. In a second step, we relate time to depth using an average transport velocity and derive equations for the evolution with depth of DO and Fe^{2+} .

Table 1. Glossary of main variables in the text

Nomenclature	Units	Variable
a	$[mol.kg_w^{-1}]$	Activity
C	$[mol.kg_w^{-1}]$	Concentration
Da		Damköhler number
DO		Dissolved Oxygen
E_a	$[kcal.mol^{-1}]$	Activation energy
Fe^{2+}		Dissolved Fe(II)
$Fe - clay$		Fe-rich clay (secondary mineral)
Φ	[-]	Volume fraction
γ	$[mol_{Fe}.kg_w^{-1}.s]$	Reducing capacity of mineral species
Γ	[-]	Q for all ionic species in mineral excepting iron
Q	[-]	Ionic Activity Product
j		Index standing for b: biotite, c: Fe-clay, d: dissolving mineral, p: precipitating mineral
K_H	$[mol.atm^{-1}.kg_w^{-1}]$	Henry's constant
K_{sp}	[-]	Solubility product for mineral
K_w	$[mol^2.L^{-2}]$	Auto-dissociation constant of water
k	$[mol.m^{-2}.s^{-1}]$	Kinetic constant for mineral dissolution
k_{ox}	$[kg_w.mol^{-1}.s^{-1}]$	Kinetic constant for iron oxidation by DO
Λ	[-]	Lithological parameter
ν	[-]	number of Fe^{2+} atoms per mineral formula
R	$[mol.s^{-1}]$	Reaction rate
s	$[mol.L^{-1}]$	Mineral solubility
S_M	$[m^2.g^{-1}]$	Specific surface area
S_V	$[m^2.m^{-3}]$	Bulk surface area
t	[y]	Mean fluid travel time
τ_c	[y]	Characteristic time for DO consumption
τ_t	[y]	Characteristic time for DO transport
\bar{v}_a	$[m.y^{-1}]$	Apparent vertical velocity
ω	[-]	Porosity
z_c	[m]	Reference depth for DO transport

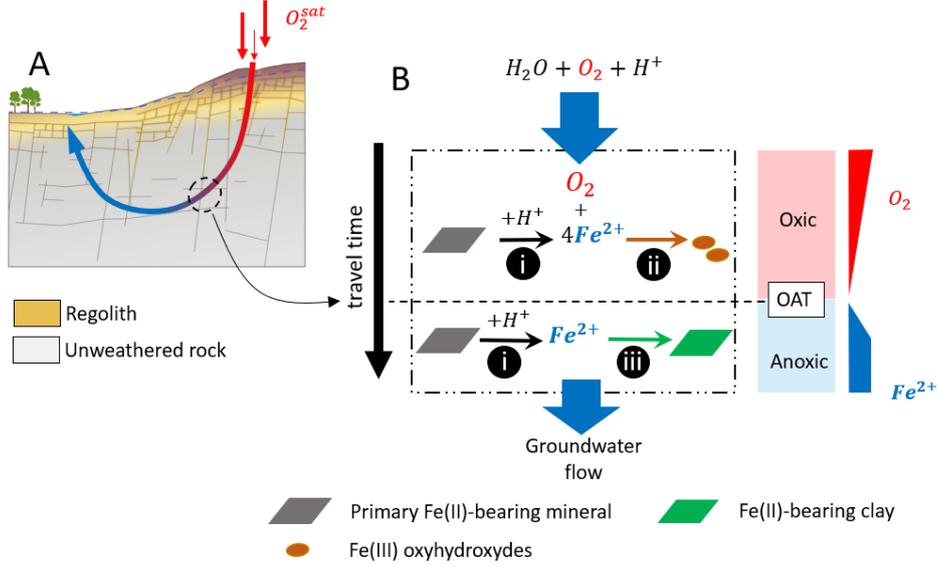


Figure 1. Conceptual model for the transport and reactivity of DO and Fe^{2+} along a flow-path (A). (B) In the unweathered rock, DO is consumed owing to the following reaction network i) Fe(II)-bearing minerals dissolution, promoted by groundwater acidity, releases Fe^{2+} ii) aqueous oxidation of dissolved iron by DO and precipitation of Fe(III) oxyhydroxydes iii) incongruent mineral dissolution releases Fe^{2+} and forms Fe(II)-bearing clay. OAT indicates the Oxidic-Anoxic Transition along the pathway.

130 2.2 Geochemical system

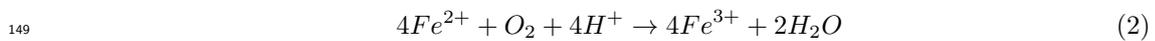
131 We study the coupling between two geochemical reactions: the dissolution of iron-
 132 bearing minerals to produce dissolved iron (Fe^{2+}) and its reaction with dissolved oxy-
 133 gen transported from recharge fluids (Fig. 1). Similarly to previous works (Sidborn &
 134 Neretnieks, 2008; Macquarrie et al., 2010), we assume that Fe(II)-bearing minerals dis-
 135 solve through a non-oxidative mechanism that liberates Fe^{2+} while consuming acidity,
 136 and that Fe(II)-bearing clays (Fe-clay) precipitate.

137 We model the dissolution and precipitation kinetics for mineral reactions using the
 138 Transition State Theory (TST), expressing the reaction rate for a mineral j (R_j) as (Lasaga,
 139 1984) :

$$140 R_j = S_{V,j} \Phi_j \omega^{-1} (k_{j,H} a_H^{n_H} + k_j + k_{j,OH} a_{OH}^{n_{OH}}) e^{-\frac{E_{a,j}}{RT}} \left(1 - \frac{Q_j}{K_{sp,j}}\right), \quad (1)$$

141 With $S_{V,j}$ [$m^2.m^{-3}$] the Specific Surface Area per volume, ($k_{j,H}, k_j, k_{j,OH}$) [$mol.m^{-2}.s^{-1}$]
 142 the intrinsic reaction constants at 25 °C at acid, neutral and basic pH, respectively; a
 143 the activity and n the affinity factor of the indicated ion accounting for reaction catal-
 144 ysis by pH, $E_{a,j}$ the activation energy, Q_i the activity product and $K_{sp,j}$ the solubility
 145 product for mineral species j , ω is the fracture porosity, R is the ideal gas constant and
 146 T the absolute temperature.

147 The aqueous reaction between dissolved oxygen and dissolved iron, and the cor-
 148 responding kinetic law, are respectively:



$$R_{ox} = k_{ox} C_{Fe^{2+}} P_{O_2} C_{OH^-}^2 \text{ for } pH > 4.5, \quad (3)$$

with R_{ox} the rate of Fe^{2+} oxidation, k_{ox} the intrinsic reaction constant of oxidation ($1.3 \times 10^{12} M^{-2} atm^{-1} s^{-1}$), C_i the concentration of species i in [$mol L^{-1}$] and P_{O_2} the partial pressure of oxygen in [atm] (Singer & Stumm, 1970).

Since groundwater in crystalline rocks is commonly slightly acid to near-neutral (DeSimone et al., 2014), pH is here buffered at 7, Equations 1 and 2 reduce to:

$$R_j = S_{V,j} \Phi_j k'_j \omega^{-1} \left(1 - \frac{Q_j}{K_{sp,j}} \right), \quad \text{with } k'_j = k_j |^{25^\circ C} e^{-\frac{E_{a,j}}{R^G T}} \quad (4)$$

and

$$R_{ox} = k_{ox}^* C_{Fe^{2+}} C_{O_2}, \quad \text{with } k_{ox}^* = \frac{k_{ox}}{K_H} C_{OH^-}^2 \quad (5)$$

2.3 Analytical model

At any time, the change on dissolved oxygen and dissolved iron concentration is the result of the iron release from Fe(II)-bearing minerals dissolution R_d , and iron retention processes, resulting from Fe^{2+} oxidation R_{ox} and precipitation of clay, R_p :

$$\begin{cases} \frac{dC_{Fe^{2+}}}{dt} = \nu_d R_d - \nu_p R_p - R_{ox} \\ \frac{dC_{DO}}{dt} = -\frac{1}{4} R_{ox} \end{cases} \quad (6)$$

where ν_d and ν_p correspond to stoichiometric coefficients accounting for the number of Fe^{2+} per mineral formula in the dissolving or precipitating minerals respectively. R_d and R_p are described by Equation 4 and R_{ox} by Equation 5. In order to solve the system of equations 6, we consider two regimes: i) initially oxic conditions, ii) anoxic conditions once oxygen has been depleted.

2.3.1 Oxic regime

At short travel times, DO is in excess with respect to Fe^{2+} and pH is close to neutrality. Under this condition, very little iron can persist in solution as it is rapidly oxidized according to Equation 2, which has a large kinetic constant. Considering that primary minerals are more abundant than secondary minerals in unweathered rocks, we assume that $R_p \ll R_d$. Therefore, equation 6 simplifies to:

$$\begin{cases} \frac{dC_{Fe^{2+}}}{dt} + R_{ox} = \nu_d R_d \\ \frac{dC_{DO}}{dt} = -\frac{1}{4} R_{ox} \end{cases} \quad (7)$$

As Fe(II)-bearing minerals are highly under-saturated, the saturation state of the mineral ($\frac{Q_j}{K_{sp,j}}$) tends to zero in Equation 4. Rearranging equation 7 with this assumption yields :

$$\frac{dC_{Fe^{2+}}}{dt} - 4 \frac{dC_{DO}}{dt} = \nu_d S_{V,d} \Phi_d k'_d \omega^{-1}. \quad (8)$$

Because DO is in excess, $C_{Fe^{2+}} \ll C_{DO}$ and thus $\frac{dC_{Fe^{2+}}}{dt} \ll \frac{dC_{DO}}{dt}$,

which leads to

$$\frac{dC_{DO}}{dt} = -\frac{1}{4} \nu_d S_{V,d} \Phi_d k'_d \omega^{-1}. \quad (9)$$

183 Hence, the decay of oxygen is controlled by the amount of dissolved iron produced from
 184 mineral dissolution. We define the reducing capacity of a mineral j (γ_j) as the flux of
 185 iron produced by mineral reaction per unit of volume of fluid:

$$186 \quad \gamma_j = \nu_j S_{V,j} \Phi_j k'_j \omega^{-1}, \quad (10)$$

187 By integration, considering the reducing capacity (γ_d) constant, the evolution of DO con-
 188 centration with the fluid travel time t is expressed by:

$$189 \quad C_{DO} = C_{DO}(0) \left(1 - \frac{t}{\tau_c}\right), \forall t < \tau_c, \quad (11)$$

190 where τ_c is the characteristic time required to consume DO and reach anoxic conditions,

$$191 \quad \tau_c = \frac{4C_{DO}(0)}{\gamma_d} \quad (12)$$

192 The concentration of dissolved iron $C_{Fe^{2+}}$ respects the kinetic law of Equation 5:

$$193 \quad \frac{dC_{DO}}{dt} = -\frac{1}{4} k_{ox}^* C_{Fe^{2+}} C_{DO}. \quad (13)$$

194 Hence,

$$195 \quad C_{Fe^{2+}} = -\frac{4}{k_{ox}^* C_{DO}} \frac{dC_{DO}}{dt}. \quad (14)$$

196 Inserting equations 11 and 9 into the above expression leads to the evolution of iron con-
 197 centration as a function of travel time in the oxic regime,

$$198 \quad C_{Fe^{2+}} = \frac{4}{k_{ox}^*} \left(\frac{1}{\tau_c - t}\right), \forall t < \tau_c \quad (15)$$

199 This analytical model thus yields the following solutions for the coupled evolution
 200 of DO and Fe^{2+} for the oxic regime.

$$201 \quad \begin{cases} C_{DO} = C_{DO}(0) \left(1 - \frac{t}{\tau_c}\right) \\ C_{Fe^{2+}} = \frac{4}{k_{ox}^*} \left(\frac{1}{\tau_c - t}\right), \forall t < \tau_c \end{cases} \quad (16)$$

202 We introduce the non-dimensional Damköhler number Da (Maher, 2010) as the ratio of
 203 the characteristic timescale for DO transport τ_t over the timescale for oxygen consump-
 204 tion τ_c (Equation 12):

$$205 \quad Da = \frac{\tau_t}{\tau_c}. \quad (17)$$

206 with τ_t the characteristic time for DO transport up to a reference depth z_c while flow-
 207 ing at an apparent vertical velocity \bar{v}_a :

$$208 \quad \tau_t = \frac{z_c}{\bar{v}_a}. \quad (18)$$

209 Da is thus proportional to the ratio of the reducing capacity (γ) to the apparent verti-
 210 cal velocity (\bar{v}_a):

$$211 \quad Da = \frac{\gamma}{\bar{v}_a} \times \frac{z_c}{4C_{DO}(0)}. \quad (19)$$

212 The system of equations for DO and Fe^{2+} can be expressed in terms of the Damköhler
 213 regime, such as :

$$214 \quad \begin{cases} C_{DO} = C_{DO}(0) \left(1 - Da \frac{t}{\tau_t}\right), \forall t < \tau_c \\ C_{Fe^{2+}} = \frac{4Da}{k_{ox}^*} \left(\frac{1}{\tau_t - Da t}\right), \forall t < \tau_c \end{cases} \quad (20)$$

215 For $Da > 1$, the timescale of DO transport τ_t is longer than the timescale of DO con-
 216 sumption τ_c . Thus, DO supply is transport-limited and the conditions transition from
 217 oxic to anoxic along flow paths. Conversely, for $Da < 1$ the timescale of DO consump-
 218 tion is longer than transport. In this case, DO is not depleted because transport over-
 219 comes DO consumption and the system remains oxic.

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2.3.2 Anoxic regime

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Once the available DO has been depleted, the concentration of Fe^{2+} is no longer limited by oxidation (R_{ox} becomes negligible) and then Equation 6 reduces to:

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$$\begin{cases} C_{DO} = 0 \\ \frac{dC_{Fe^{2+}}}{dt} = \nu_d R_d - \nu_p R_p \end{cases} \quad (21)$$

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Since the dissolution rate of primary silicates is lower than the precipitation rate of secondary phases (Helgeson et al., 1969), we assume that under reducing conditions, the dissolving Fe(II)-bearing mineral is still highly under-saturated ($\frac{Q_d}{K_{sp,d}} \ll 1$) while Fe(II)-bearing clay (Fe-clay) precipitates ($\frac{Q_p}{K_{sp,p}} \gg 1$). Thus, Fe^{2+} is released from the dissolution of primary mineral and part of it precipitates in secondary minerals. According to the definition of R_j (Equation 4) and considering the above approximations for $\frac{Q_j}{K_{sp,j}}$, Equation 21 simplifies to:

231

$$\frac{dC_{Fe^{2+}}}{dt} = \gamma_d - \gamma_p \frac{Q_p}{K_{sp,p}}, \quad (22)$$

232

233

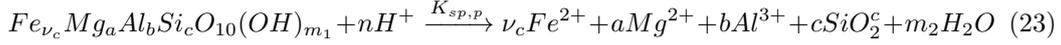
with γ_d and γ_p the reducing capacity, as defined by Equation 10, of respectively the dissolving Fe(II)-bearing primary mineral and the precipitating Fe-clay.

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For a general composition of the mineral Fe-clay, the corresponding solubility reaction may be written as:

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237

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Assuming that activity coefficients are close to 1, the ionic activity product (Q) for the above reaction can be defined as follows:

239

$$Q_p = \frac{C_{Mg}^a C_{Al}^b C_{SiO_2}^c}{C_H^n} C_{Fe^{2+}}^{\nu_p} = \Gamma_p C_{Fe^{2+}}^{\nu_p}, \quad (24)$$

240

241

242

where C_i is the concentration of species i and Γ_p the concentration product $\forall i \neq Fe^{2+}$ among the elements present in the Fe-clay mineral. The solubility product ($K_{sp,p}$) may be reformulated in an analogous way:

243

$$K_{sp,p} = \frac{(a s_p)^a (b s_p)^b (c s_p)^c}{10^{-n} p H} (\nu_c s_p)^{\nu_p} = \Gamma_p^s s_p^{\nu_p}, \quad (25)$$

244

245

where s_p is the solubility of Fe-clay and Γ_p^s is the solubility product $\forall i \neq Fe^{2+}$. Replacing the expressions for Q_p and $K_{sp,p}$ in Equation 22 and rearranging gives:

246

$$-\frac{\Lambda}{\gamma_d} \frac{dC_{Fe^{2+}}}{dt} = \left(\frac{C_{Fe^{2+}}}{s_p} \right)^{\nu_p} - \Lambda, \quad (26)$$

247

with the non-dimensional lithological parameter

248

$$\Lambda = \frac{\gamma_d \Gamma_p^s}{\gamma_p \Gamma_p} \quad (27)$$

249

250

which quantifies the relative reducing capacity between primary to secondary Fe(II)-bearing minerals (γ_d/γ_p) and the deviation from chemical equilibrium (Γ_p^s/Γ_p).

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The solution of the differential equation 26 depends on the stoichiometric coefficient for iron per mineral formula of Fe(II)-bearing clay (ν_p). Here, we assume $\nu_p = 2$, which characterizes a typical Fe(II)-rich clay composition according to Sugimori et al. (2008). Solving Equation (26) leads to following solutions under anoxic conditions:

255

$$\begin{cases} C_{DO} = 0 \\ C_{Fe^{2+}} = s_p \sqrt{\Lambda} \tanh\left(\frac{\gamma_d}{s_p \sqrt{\Lambda}} t\right). \end{cases} \quad (28)$$

256 For $t > \frac{s_p \sqrt{\Lambda}}{\gamma_d}$, the transient term in Equation 28 tends to 1 and a pseudo-equilibrium
 257 concentration of dissolved iron is reached and expressed by :

$$258 \quad C_{Fe^{2+}} \rightarrow s_p \sqrt{\Lambda} \quad (29)$$

259 Under anoxic conditions the pseudo-equilibrium concentration of dissolved iron is inde-
 260 pendent of time and is only driverled by geological factors, here synthesized through the
 261 lithological parameter Λ and the solubility of Fe-clay s_p .

262 **2.4 Reactive transport simulations**

263 **2.4.1 Base Case Simulation**

264 To test the validity of the approximate analytical expressions derived above, we per-
 265 form reactive transport simulations using the code CrunchFlow (Steeffel & Maher, 2009).
 266 We simulate the evolution of dissolved oxygen and Fe^{2+} , as a result of reactions between
 267 an oxic water typical of recharge water and a crystalline rock lithology containing quartz,
 268 feldspars, biotite and muscovite, with an initial porosity ϕ of 1 (Belghoul, 2010) (see com-
 269 positions in Suppl. Inf.). In unweathered crystalline rocks, biotite is an ubiquitous Fe(II)-
 270 bearing mineral present in high proportions (Bazilevskaya et al., 2013; Holbrook et al.,
 271 2019; Hampl et al., 2021; Kim et al., 2017).

272 Precipitation and dissolution of secondary minerals are allowed to simulate incon-
 273 gruent dissolution of silicate phases. The incongruent dissolution of feldspars is simu-
 274 lated with the formation of kaolinite (Figure 2). Biotite weathering is commonly described
 275 as an incongruent dissolution process in which the hydration and progressive replace-
 276 ment of inter-layer cations (i.e. K^+) forms a wide range of Fe-bearing clays (Fe-clay) and
 277 Fe(III) oxyhydroxides depending on the leaching and redox conditions (Acker & Bricker,
 278 1992; Scott & Amonette, 1985; Sequeira Braga et al., 2002; Murakami et al., 2003; Diderik-
 279 sen et al., 2010; Hampl et al., 2021). In the present simulations, we consider the precip-
 280 itation of goethite as a typical Fe-oxyhydroxyde found in oxic weathering fronts (Dideriksen
 281 et al., 2010) (Figure 2). For anoxic conditions, Sugimori et al. (2008) have documented
 282 that Fe-rich corrensite forms as the dominant secondary phase. However, because ther-
 283 modynamic and kinetic parameters for corrensite are poorly known, for our simulations
 284 we allow the formation of chlorite since this mineral has a similar stability field and par-
 285 agenetic relationships with corrensite (Beaufort et al., 1997) (Figure 2).

286 Figure 2 presents the evolution of DO, Fe^{2+} concentrations in the aqueous phase
 287 and mineral saturation indexes simulated with the numerical model as a function of the
 288 mean fluid travel time, over a period of 750 years. DO decreases linearly until it gets de-
 289 pleted and a non-linear transition from oxic to anoxic conditions is observed. The evo-
 290 lution of the saturation indexes (SI) of mineral species with the mean fluid travel time
 291 (Figures 2-B and 2-C) indicates that iron is being released from biotite during both oxic
 292 and anoxic conditions ($SI_{biotite} < 0$ indicates dissolution). Under oxic conditions, the
 293 Fe^{2+} concentration is driven by the presence of DO and its oxidation into Goethite ($SI_{goethite} >$
 294 0 indicates precipitation). On the other hand, when $t > \tau_c$, the Fe^{2+} concentration is
 295 driven by the precipitation of Fe(II)-bearing clay as indicated by the change on $SI_{chlorite}$
 296 from undersaturated (oxic conditions) to saturated (anoxic conditions) conditions.

297 **2.4.2 Validation of analytical expressions**

298 We compare numerical simulations with analytical solutions derived for the evo-
 299 lution of both DO and Fe^{2+} concentrations under oxic (Equation 16) and anoxic (Equa-
 300 tion 28) conditions. Thermodynamic parameters from Table 2 and mineral compositions
 301 are used to calculate the parameters of the analytical solutions. The analytical expres-
 302 sions for both DO and Fe^{2+} accurately capture the numerical simulations and the pre-
 303 dicted characteristic time τ_c (Equation 12) coincides with the non-linear oxic-anoxic tran-

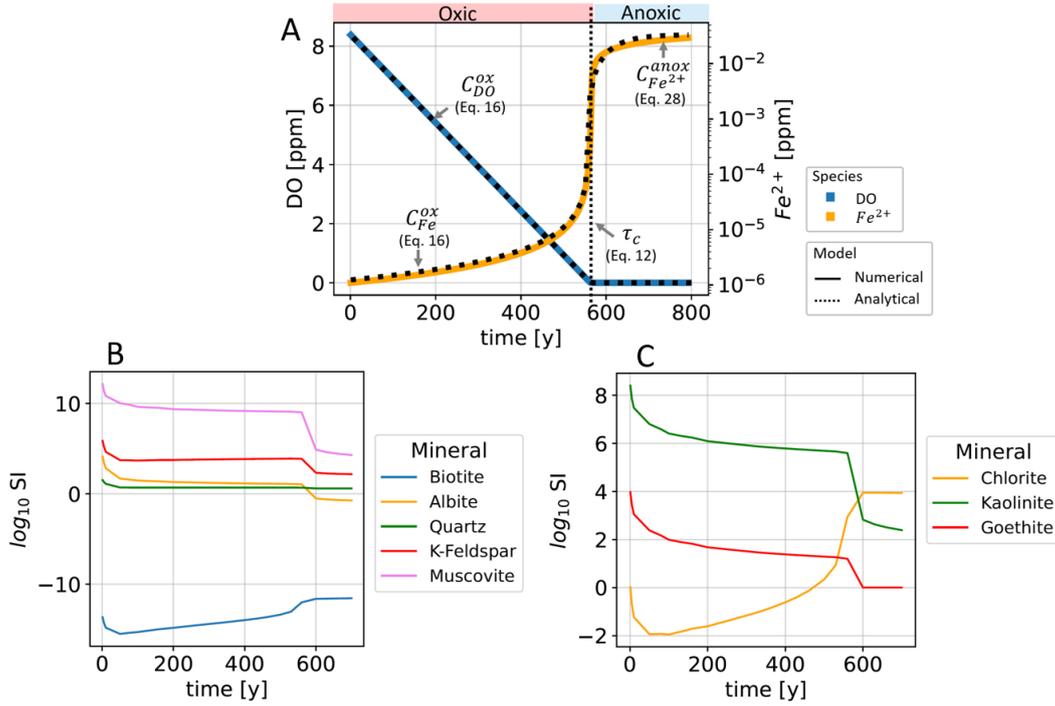


Figure 2. Simulation results for the Base Case scenario, obtained with Crunchflow for a lithological composition with $\gamma_d = 2 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3} \cdot \text{y}^{-1}$, $\Lambda = 20$. (A) Evolution of dissolved oxygen and iron concentration as a function of travel time. C_{DO}^{ox} and C_{Fe}^{ox} correspond to concentrations under oxic conditions, whereas C_{DO}^{anox} and C_{Fe}^{anox} represent concentrations at anoxic conditions. τ_c is the characteristic time for DO depletion. (B) and (C) represent the evolution of saturation Indexes (SI) as a function of fluid travel times for primary and secondary minerals, respectively.

304 sition from the numerical model, which validates the assumptions made to derive the analytical solutions.
 305

306 To further evaluate the validity of the analytical approximations, a sensitivity analysis
 307 is carried out by varying the main parameters identified from the analytical solutions.
 308 With the numerical model and the analytical solutions 16, we evaluate i) the influence
 309 of the reducing capacity (Eq. 10) and of the mean fluid travel time on DO and
 310 Fe^{2+} concentrations (Figure 3-A and B) in the oxic regime ; ii) the influence of the
 311 reducing capacity of biotite on the characteristic time for oxygen consumption τ_c (Figure
 312 3-C) ; iii) the influence of clay precipitation capacity on the equilibrium concentration
 313 of Fe^{2+} (Figure 3-D). The sensitivity on the reducing capacity of biotite is tested by vary-
 314 ing the specific surface area S_M over 4 orders of magnitude and the fraction of biotite
 315 in the rock Φ_d by a factor 20. The sensitivity on the clay precipitation capacity is tested
 316 by varying the specific surface area S_M over 3 orders of magnitude and the initial frac-
 317 tion of clay in the rock Φ_p over 4 orders of magnitude.

318 The approximated analytical solutions are in good agreement with the simulations
 319 for the full range of tested parameters and simulation times. The equilibrium Fe^{2+} con-
 320 centrations calculated with the analytical solutions are slightly lower than the numeri-
 321 cal simulations at low initial fraction of clay in the rock. This is due to the fact that the
 322 fraction of clay is recalculated at each time step in the numerical model while assumed
 323 constant in the analytical solution, and the change in clay fraction with time can be sig-
 324 nificant at very low initial clay fractions.

Table 2. Geochemical parameters used in the numerical modelling and to calculate non-dimensional numbers in the analytical solutions. References in column *Source* correspond to (1): (Robie A. & Philip M., 1962), (2): (Malmstrom et al., 1995), (3): (Palandri & Kharaka, 2004), (4): (Singer & Stumm, 1970)

Parameter		Value		Source
		biotite ^a	Fe-clay ^b	
Molar volume [$cm^3.mol^{-1}$]	V_m	149.65	215.88	(1)
Molecular weight [$g.mol^{-1}$]	MW	417.3	713.5	
Solubility product [-]	K_{sp}	$10^{41.1}$	$10^{47.6}$	(2)
Solubility [$mol.L^{-1}$]	s	$10^{-3.49}$	$10^{-6.85}$	
Activation energy [$kcal.mol^{-1}$]	E_a	5.26	21.03	(3)
kinetic dissolution constant [$mol.m^{-2}.s^{-1}$]	k_d	$10^{-12.55}$	$10^{-12.52}$	(3)
<i>Aqueous parameters</i>				
kinetic oxidation constant [$L^2.mol^{-2}.atm^{-1}.s^{-1}$]	k_{ox}	$10^{12.12}$		(4)
Initial DO concentration [$mol.kg_w^{-1}$]	$C_{DO}(0)$	2.62×10^{-4}		
Henry's constant for O_2 [$mol.atm^{-1}.L^{-1}$]	K_H	$10^{-2.89}$		
Water auto-dissociation constant [$mol^2.L^{-2}$]	K_w	10^{-14}		
pH		7.0		

^a: values for phlogopite

^b: based on properties for chlorite

325 As expected, less oxic conditions occur in systems with higher biotite contents (Fig-
326 ures 3-A and B). Insets in figures 3-A and B show that longer mean fluid travel times
327 can counterbalance low reducing capacity (low biotite content and/or low S_M), leading
328 to more persistent oxic conditions. This interplay between the reducing capacity and travel
329 time is captured by the characteristic time for oxygen consumption τ_c (Equation 12) in
330 agreement with simulations (Figure 3-C). The characteristic time for oxygen consump-
331 tion decreases with the reducing capacity (both with the biotite content and S_M), lead-
332 ing to a longer persistence of oxic conditions in low reducing capacity rocks. The equi-
333 librium Fe^{2+} concentration decreases with increasing clay precipitation capacity (ini-
334 tial Fe(II)-clay content and S_M), showing that Fe^{2+} remains dissolved if it can not pre-
335 cipitate into clays.

336 2.5 Hydrological and geological drivers for DO and Fe^{2+} concentrations

337 While the numerical model allows for a complex and realistic reactive modeling frame-
338 work, the analytical solutions provide a framework to understand and quantify the hy-
339 drological and geological drivers for the evolution of DO and Fe^{2+} in crystalline rocks
340 (Figure 4).

341 The dissolved oxygen concentration predicted by Equation 20 is represented as a
342 function of the fluid travel time and the reducing capacity, the two main parameters ex-
343 pressing the hydrological and geological controls in the Damköhler number (Figure 4).
344 The counteracting effects of fluid travel time and reducing capacity imply that there is
345 a fundamental indeterminacy on the hydrological and geological drivers when consider-
346 ing oxygen alone. A given concentration of oxygen can be obtained by a range of differ-
347 ent combinations of hydrological and geological parameters. In rocks with low reducing
348 capacities, DO concentrations are poorly sensitive to travel time since DO consumption
349 is very slow ($Da < 1$). For high reducing capacity values, DO concentrations evolve rapidly
350 with travel time due to fast reaction kinetics ($Da > 1$).

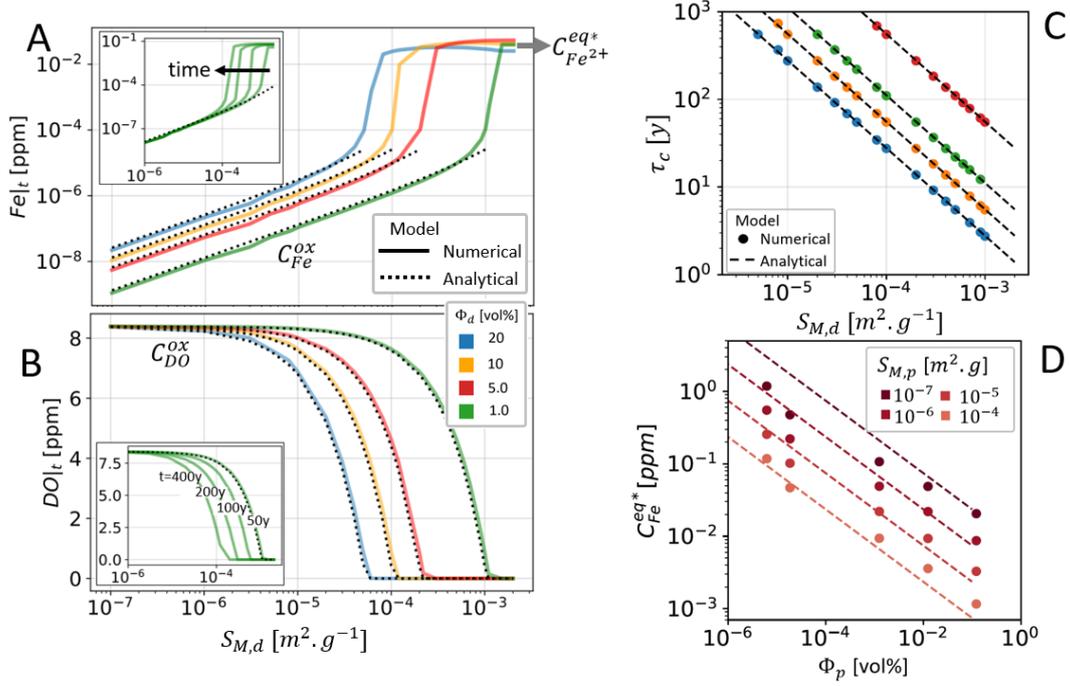


Figure 3. Sensitivity analysis for the numerical and analytical models. Subfigures (A) and (B) present concentration profiles vs S_M for DO and Fe^{2+} , respectively. Main plots are sensitivities to Φ_d at $t = 50y$ while inserts show the evolution with time for the $\Phi_d = 1\%$ case. Analytical solutions come from equations 16 and 28. Subfigure (C) presents the sensitivity of τ_c to the reducing capacity (Equation 12). Subfigure (D) presents the sensitivity of the equilibrium Fe^{2+} concentration to the clay precipitation capacity. Subscript d stands for dissolving mineral (e.g. biotite) and subscript p stands for precipitating mineral (e.g. Fe-clay).

351 When oxygen is depleted, Fe^{2+} concentrations tend toward the pseudo-equilibrium
 352 concentration (Equation 29), which is controlled by the relative abundance of primary
 353 and secondary Fe(II)-bearing minerals expressed through the non-dimensional number
 354 Λ (Equation 27). As a consequence, Fe^{2+} concentrations under anoxic conditions are mainly
 355 driven by the geological context of the subsurface. Therefore, the joint analysis of both
 356 DO and Fe^{2+} concentrations gives independent constrains on the potential roles of hydro-
 357 logical and geological processes on the distribution of oxygen in the subsurface, which
 358 we discuss using field data in the following section.

359 3 Field study at the Ploemeur CZO (France)

360 To evaluate the modelling framework presented above, we test it against extensive
 361 field observations of DO and Fe^{2+} concentrations in the subsurface available at the Crit-
 362 ical Zone Observatory of Ploemeur (France). The Ploemeur CZO includes two subcatch-
 363 ments located at a distance of about 4 km: the Kermadoye site and the Guidel site. Both
 364 catchments are characterized by a fractured bedrock with similar lithologies and an oceanic
 365 climate but differ significantly in their DO and Fe^{2+} concentrations. It is thus well suited
 366 to test the concepts presented above.

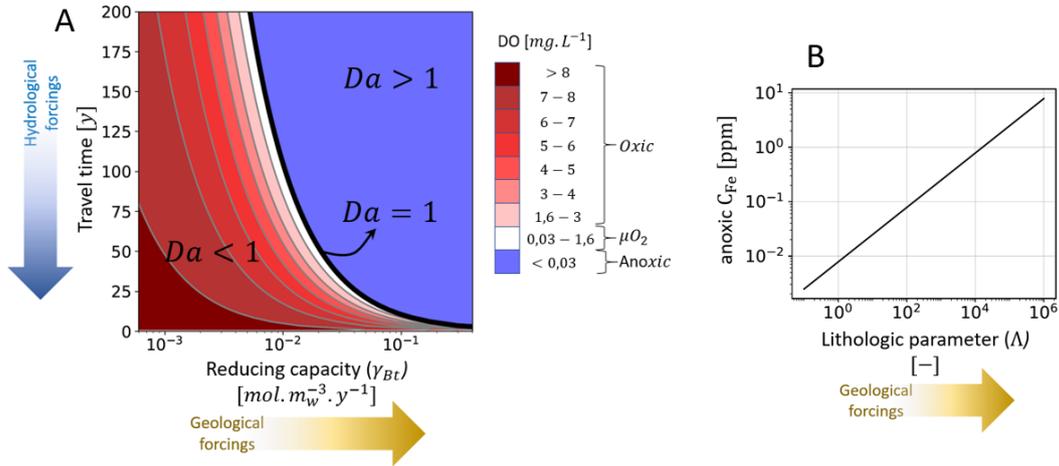


Figure 4. (A) Dependence of DO concentrations to geological (x-axis) and hydrological (y-axis) forcings. Multiple combinations of reducing capacity and travel time can result in a same prediction of DO concentration (e.g. iso-concentration lines for C_{DO}). Stronger geological forcings (higher reducing capacity of a certain lithology as in Equation 10) limit the persistence of DO to very short travel times (favor anoxic conditions) and vice versa. Higher hydrological forcings in y-axis (faster groundwater velocities) favor deeper transport of DO for a same travel time (Equation 30). (B) Dependence of iron concentrations to the lithological parameter (Λ) at anoxic conditions. The lithological parameter is defined in Equation 26

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3.1 Site presentation

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The Ploemeur Critical Zone Observatory (CZO) belongs to the H+ hydrogeological network (<http://hplus.ore.fr/en/>), the French network of critical zone observatories OZCAR (<https://www.ozcar-ri.org/fr/> and the e-LTER european infrastructure (<https://deims.org/731f3ced-148d-4eb5-aa46-870fa22be713>). It is located in the southern part of the Armorican massif in Brittany, France. The region is characterized by the intersection of two main tectonic features : (1) a gently dipping (around 30° to the north) contact zone between a Late Hercynian granite and the surrounding micaschist rock, (Touchard, 1999); and (2) a dextral-slip normal fault zone which strike Nord 20° and dip East 70° (Ruelleu et al., 2010). Both are the main transmissive structures of the fractured-bedrock aquifer, characterized by a relatively large average transmissivity on the order of $10^{-3} m^2/s$ sustained by a well connected fracture network (Le Borgne et al., 2007; Jiménez-Martínez et al., 2013)

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The Kermadoye aquifer has been exploited for drinkable water supply since 1991 at an average pumping rate of $1 Mm^3.yr^{-1}$. This particularly high production rate is attributed to the presence of the regional contact zone which drains flows towards the vertical faults (Leray et al., 2013; Jiménez-Martínez et al., 2013; Roques et al., 2016). The Kermadoye catchment is monitored with 22 boreholes, with depths ranging from 50 to 150 meters. The majority of them cross the contact zone between micaschist and granite or are entirely in the granite. The Guidel catchment is not pumped, although it has similar hydraulic properties as the Kermadoye catchment. Natural groundwater flows converge to supply a stream and a wetland. The Guidel catchment is located North of the contact zone (see Figure 5) and is monitored by 25 boreholes of depths ranging from 50 to 150 meters since 2009. These boreholes intersect mostly micaschists. Recent studies have shown that the mixing of oxygen rich and iron rich fluids at fracture intersec-

392 tions or in the wetland, sustains microbial hotspots, dominated by iron-oxidizing bac-
 393 teria (FeOB) (Bethencourt et al., 2020; Bochet et al., 2020). Understanding and mod-
 394 elling DO and Fe^{2+} concentrations at this site is thus of particular interest.

395 The comparison of the two sites is particularly interesting as the hydrological forc-
 396 ing is stronger at the Kermadoye site due to pumping. Furthermore, while the two sites
 397 have comparable geology, the contact zone is deeper at Guidel site, which may be more
 398 influenced by the micaschist lithology. Since the two sites have contrasted DO and Fe^{2+}
 399 signatures, they are particularly relevant test grounds to resolve the hydrological and ge-
 400 ological controls on these chemical properties.

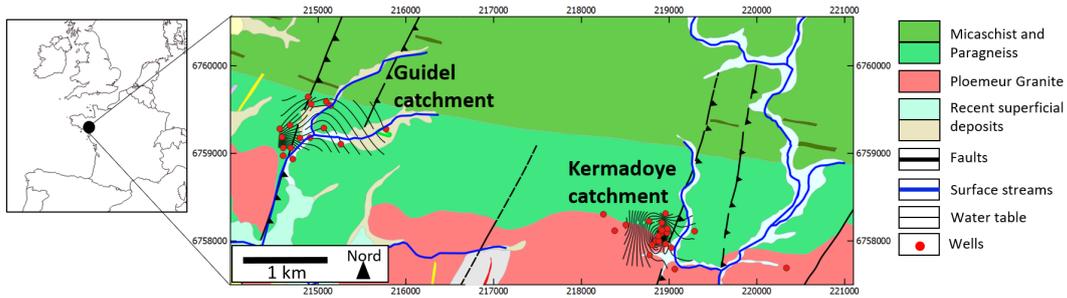


Figure 5. Geographical location, geological and hydrogeological maps of the Ploemeur Critical Zone Observatory and its two catchments, Guidel and Kermadoye. The geological map is reproduced from (Béchenneq et al., 2012a)

Table 3. General characteristics of the study site

	Guidel	Ploemeur
Generalities		
Lat. Long.	47°45'16" N 3°28'51" W	47°44'50" N 3°25'38" W
Mean Altitude (m.a.s.l.)	15.1	26.7
Groundwater flow-regime	Natural circulation	Pumped since 1991
Geology		
Dominant bedrock lithology	Mica-schist, Paragneiss	Granite
Age	Ordovician inf	Carboniferous
Mean [min, max] depth to fresh bedrock (m)	17 [4, 34]	30 [10, 44]
Climate		
Climate type	Oceanic	
Mean annual rainfall (mm)	924 ^a	
Mean annual temperature (°C)	12.1 ^a	
Mean Altitude (m.a.s.l.)	15.1	26.7

^a: data from Lann-Bihoué weather station, averaged from the period 2006 - 2014

3.2 DO and Fe^{2+} depth profiles

The DO and iron concentrations measured in the two catchments are represented as a function of depth in Figure 6. Each point represents the concentration measured in front of the main transmissive fracture in each borehole (see Supplementary information for DO and Fe^{2+} measurement methods). Since there are locally rapid vertical flows around boreholes, we converted the fracture depth to an effective depth representative of larger scale flow path using the temperature anomalies measured in boreholes (see Suppl. inf.). DO concentrations decrease with depth, from values close to saturation down to values close to the detection limit (0.1 mg.L^{-1}). Both catchments reach the oxic-anoxic transition, but at significantly different depths. The oxic-anoxic transition takes place between 100 and 150 m depth at the Guidel site. At the Kermadoye site it takes place between 200 to 400 m depth. The decrease in DO is associated with an opposite gradient of Fe^{2+} (see Figure 6-B). Fe^{2+} concentrations in Guidel increase up to an average value of 2.8 ± 1.7 ppm, while in Kermadoye, Fe^{2+} concentrations increase up to $6.3 \times 10^{-2} \pm 2.7 \times 10^{-2}$ ppm, i.e. about two orders of magnitude lower than in Guidel.

3.3 Model application to field data

In order to investigate the depth-distribution of DO and Fe^{2+} , we transform the mean fluid travel time into depth (z) by considering an apparent vertical velocity (\bar{v}_a), such as:

$$t = \frac{z}{\bar{v}_a} \quad (30)$$

Thus, the system of equations can be expressed as a function of depth:

$$\text{oxic} : \begin{cases} C_{DO}(z) = C_{DO}(0) \left(1 - Da \frac{z}{z_c}\right), \forall z < \frac{z_c}{Da} \\ C_{Fe^{2+}}(z) = \frac{4v_a}{k_{ox}^*} \left(\frac{1}{z_c - Da z}\right), \forall z < \frac{z_c}{Da} \end{cases} \quad (31)$$

$$\text{anoxic} : \begin{cases} C_{DO}(z) = 0 \\ C_{Fe}(z) = s_c \sqrt{\Lambda} \tanh\left(\frac{4C_{DO}(0)Da}{s_c \sqrt{\Lambda}} \frac{z}{z_c}\right), \forall z > \frac{z_c}{Da} \end{cases} \quad (32)$$

with z_c the reference depth in Equation 18. Here, we define $z_c = 100$ m, which corresponds to the average depth of our measurements (Figure 6). The dissolved iron concentration C_{Fe} only depends on both Da and Λ for $z < \frac{z_c s_c \sqrt{\Lambda}}{4C_{DO}(0)Da}$. At deeper depths, C_{Fe} only depends on the lithological parameter and Equation 32 reduces to the pseudo-equilibrium concentration (Equation 29).

3.4 Comparison of field data and model simulations of DO and Fe^{2+}

The analytical solutions for DO and Fe^{2+} for the oxic and anoxic regimes (equations 20 and 29) are fitted to the measured DO and Fe^{2+} depth-profiles at the two sites. Under oxic conditions, the solution for DO has one parameter, the Damköhler number Da , and the solution for Fe^{2+} depends on both Da and on the apparent vertical velocity (\bar{v}_a) (Equation 20). Theoretically, the combined resolution of the two equations for DO and Fe^{2+} should allow to fit Da and \bar{v}_a , and thus to estimate the reducing capacity of the bedrock (γ).

The analytical solution captures the approximate linear decrease in DO with depth in both catchments (Figure 6). The analytical solution is also compatible with the evolution of Fe^{2+} on both sites. For the Guidel site this evolution is well defined over about three orders of magnitude in concentration. For the Kermadoye site, the maximum concentration data is much smaller and therefore the range of observation is small above the detection limit. Some discrepancies are observed for few Fe^{2+} data points for shallow samples at the two catchments (blue box in Figure 6). This mismatch could be due to reactions of DO or Fe by other reaction pathways, particularly if organic matter is available (Wolthoorn et al., 2004; Serikov et al., 2009; Nordstrom, 2011).

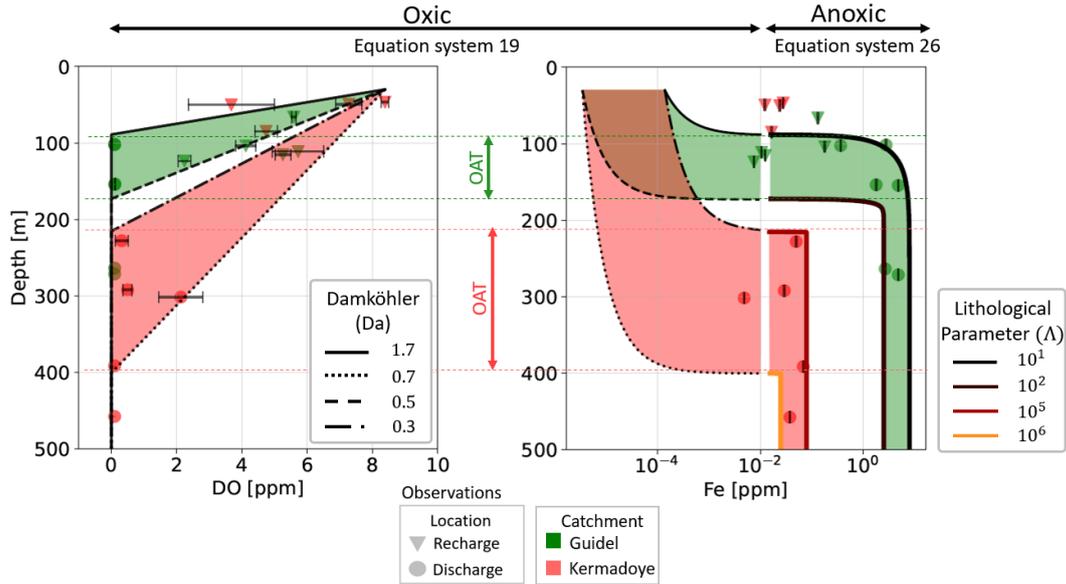


Figure 6. Distribution of DO and Fe^{2+} concentrations as a function of depth for two catchments. Measured field data are represented with dots and triangles, in green for the Guidel site and in red for the Kermadoye site. In the oxic part, analytical solutions are drawn as curves with different values of Da for DO and Fe^{2+} (Equations 20,19). In the anoxic part, analytical solutions for Fe^{2+} are drawn with different values of λ . Sample depth has been inferred using temperature as a proxy. OAT corresponds to the Oxic-Anoxic Transition ranges.

447 The range of Damköhler numbers can be relatively well constrained as consistent
 448 values of Da explain jointly the linear decrease of DO and the non-linear increase of Fe^{2+} .
 449 The Da values range between 0.7 and 1.7 at the Guidel site and between 0.3 and 0.5 at
 450 the Kermadoye site (Figure 6). On the other hand, the value of \bar{v}_a influences the very
 451 low concentrations of Fe^{2+} at shallow depths (see Suppl. info.), for which Fe^{2+}
 452 concentrations are below detection limits and therefore \bar{v}_a can not be constrained directly
 453 from these data. Under anoxic conditions, the pseudo-equilibrium concentration in Fe^{2+}
 454 only depends on the lithological properties (Equations 29). The parameter Λ is relatively
 455 well constrained since the maximum Fe^{2+} is very different between the two sites: Λ ranges
 456 between 10^1 and 10^2 for the Guidel site, and between 10^5 and 10^6 for the Kermadoye
 457 site (Figure 6). The large difference in the two values of Λ suggests that the contrast of
 458 the main lithological properties of the two sites is likely more important than possible
 459 differences in hydrological properties.

460 Therefore, the analysis of DO and Fe^{2+} concentration data under oxic conditions
 461 provides a good constrain on the Damköhler number, suggesting that the Guidel catchment
 462 is more reaction-limited than the Kermadoye catchment. However, this still leaves
 463 an uncertainty on whether this difference may be explained by a hydrological or geological
 464 contrast. An additional constrain is given when analyzing Fe^{2+} concentrations in
 465 the anoxic regime, suggesting an important lithological difference between the two catch-
 466 ments.

4 Discussion

4.1 Discriminating hydrological and geological controls from field data

Despite geographical, climatic and lithological similarities between the two sites, the DO and Fe^{2+} depth-profiles are significantly different. According to our model, this difference may be explained by a factor 3 in the Damköhler numbers Da , the ratio of the transport to reaction time scales, and a factor of 10^4 in the Λ number, which represents geochemical properties such as the reducing capacity of Fe(II)-bearing minerals and the deviation from chemical equilibrium for clay precipitation. The difference in Damköhler numbers can be either due to a contrast in transport velocity or dissolution rates. We discuss these two hypotheses in the following.

We first consider the hypothesis that would attribute DO and Fe^{2+} differences to a contrast in hydrological properties. This may be plausible since the Kermadoc site is pumped while the Guidel site is not. Under this hypothesis, the smaller Da for the Kermadoc site would indicate a factor three increase in average groundwater velocity compared to the Guidel site. However, a geochemical analysis at the Kermadoc site has shown that pumping tends to increase it due to the increase of the contribution of deep groundwater flow paths (Roques et al., 2018). This was confirmed by a hydrogeological model showing an increase in groundwater ages at the pumping well (Leray et al., 2014). Therefore, it is unlikely that flow acceleration due to pumping would explain the factor three contrast in Damköhler number.

We now consider the second hypothesis stating that the difference in Da would result from a 3-fold contrast in the reducing capacity γ_d of the rock. The Guidel site is composed mostly of micaschists, while the Kermadoc site is composed of both micaschists and granites (Figure 5). Mineralogical analyses carried on the two rocks indicate that micaschists contain about 7 times more biotite than granite. Therefore, assuming that about 50% of groundwater flowpaths were interacting with granites and 50 % with micaschists, the average reducing capacity of the Kermadoc aquifer would be around 3 times lower than the reducing capacity of the Guidel site. This hypothesis would therefore explain a difference of 3 in the Da of the two catchments. The difference in the lithology of both catchments is also supported by the large difference in the parameter Λ , that is entirely related to geochemical parameters (Equation 27). The difference of 4 orders of magnitude found on the two sites could be explained by higher inherited contents of clays in granite. Indeed, granites contain higher proportions of plagioclase that are readily weathered into clays (Goldich, 1938), and furthermore supported by the presence of kaolins at the edge of the granite in the site (Béchenec et al., 2012). However, the large difference in Λ could also be related to mineral surface areas which are hard to constrain and vary by orders of magnitude in rocks (Wild et al., 2019; Ackerer et al., 2020).

The analysis of DO and Fe^{2+} data with the presented modelling framework provides key constraints on the hydrological and geological drivers of reactive transport processes. Although the two considered sites are *a priori* very similar in terms of hydrological and geological contexts, our findings suggest that differences in the proportion of granite and micaschist lead to a strong contrast in DO penetration with depth and Fe^{2+} concentrations. Moreover, we provide new constraints on the hydrogeological functioning of the sites. While previous studies suggested that groundwater was recharged and transported through the micaschist and deeper collected at the contact zone between granite and micaschist (Leray et al., 2013) at the Kermadoc site, this analysis suggests here that there is also a significant proportion of groundwater flowing through the granite.

4.2 Controls of DO and iron concentrations in crystalline rocks

The depth of the oxic-anoxic transition in crystalline rocks is controlled by the relative importance of the reducing capacity of the rocks and the effective transport of oxy-

517 gen from the surface, quantified here by the Damköhler number (Figure 6-A). Linear trends
 518 of DO with depth have been observed in other hard-rock systems like the Clara mine in
 519 Germany (Bucher et al., 2009) or the Western Canadian Sedimentary Basin (Ruff et al.,
 520 2022), such as predicted by our model.

521 The reducing capacity can be considered as a value inherited from the geology, that
 522 varies slowly in time. For instance, Macquarrie et al. (2010) showed a decrease of 0.2 %
 523 of biotite content in 2 ky under oxic conditions. On the other hand, groundwater table
 524 fluctuations or perturbations of the flow regime (e.g. pumping) can be very rapid (timescales
 525 ranging from days to the season (Molenat et al., 1999; Jiménez-Martínez et al., 2013; Guil-
 526 laumot et al., 2022)). Thus, temporal changes in the oxic-anoxic depth in a particular
 527 system are likely mostly due to hydrological fluctuations.

528 4.3 Persistence of dissolved oxygen in the subsurface

529 Subsurface environments for which the timescales of DO transport are shorter than
 530 timescales of DO consumption (i.e. transport-limited regime, $Da < 1$) favor the deep
 531 transport of DO in crystalline rocks, which has a major impact on biogeochemical pro-
 532 cesses in the critical zone. The occurrence of DO in bedrock is responsible for deep weath-
 533 ering induced fracturing (WIF), Kim et al. (2017), which has been observed in 100 m-
 534 deep rock cores (Dideriksen et al., 2010; Bazilevskaya et al., 2013; Antoniellini et al., 2017;
 535 Holbrook et al., 2019; Krone et al., 2021; Hampl et al., 2021). By quantifying the dy-
 536 namics of DO and the parameter controlling the distribution of DO, we provide controls
 537 on the conditions favorable for the active oxidative weathering of the deep subsurface.
 538 For instance, Bazilevskaya et al. (2013) attributed the thicker regolith in felsic rocks (e.g.
 539 granites) compared to mafic rocks (e.g. micaschists) to higher degree of fracturing and
 540 higher advective transport of DO with groundwater. We argue that, besides differences
 541 in advective transport, the lower reducing capacity of felsic rocks could also explain deeper
 542 penetration of DO in the subsurface.

543 Furthermore, dissolved oxygen exerts a first control on subsurface microbial pro-
 544 cesses, such as aerobic respiration or denitrification (Dalsgaard et al., 2014; Kolbe et al.,
 545 2019) and therefore structures the habitability of subsurface ecosystems. The respira-
 546 tion of Fe-oxidizing bacteria (FeOB) is of particular interest because of the ubiquity of
 547 both iron and FeOB (Melton et al., 2014; Kappler et al., 2021) as well as the coupling
 548 of the iron cycle with biogeochemical cycles of carbon, sulphur and nitrogen (Casar et
 549 al., 2021). The activity of FeOB at near-neutral pH environments requires the simulta-
 550 neous presence of Fe^{2+} and microaerobic DO concentrations (Druschel et al., 2008; Maisch
 551 et al., 2019) while Fe^{2+} and DO often do not coexist because of the rapid oxidation of
 552 Fe^{2+} . From observations at the Guidel site, Bochet et al. (2020) suggested that the for-
 553 mation of subsurface FeOB hot-spots is favored by the mixing of oxic recharge water with
 554 deep anoxic iron-rich water at fracture intersections. As discussed above, the equilibrium
 555 Fe^{2+} concentration (Equation 29) is much lower for granite than for micaschist (Fig-
 556 ure 6-B). Therefore, even if oxic and anoxic groundwater mix in granite system, the low
 557 dissolved iron concentrations does not favor the formation of FeOB hot-spots because
 558 Fe^{2+} is limiting. The depth of formation of subsurface FeOB hot-spots therefore not only
 559 depends on the transport of DO but also on the availability of Fe^{2+} , which is function
 560 of the geological context.

561 5 Conclusions

562 In this study, we developed a modeling framework to describe the depth-distributions
 563 of dissolved O_2 and Fe^{2+} concentrations in crystalline rocks, which play a central role
 564 in a large range of biogeochemical processes. We derived a set of approximate analyt-
 565 ical solutions, validated with reactive transport simulations, that quantify the param-
 566 eters controlling jointly DO and Fe^{2+} evolution in the subsurface. Under oxic conditions,

567 DO concentrations decrease linearly with fluid travel time following a slope that is func-
 568 tion of the reducing capacity of the bedrock. In this regime, dissolved Fe^{2+} remains low
 569 because its aqueous oxidation by DO is faster than its release by minerals dissolution.
 570 At the Oxidic-Anoxic Transition, DO is depleted and Fe^{2+} concentrations show a rapid
 571 non-linear increase up to a pseudo-equilibrium concentration that is controlled by the
 572 relative abundance of primary to secondary Fe(II)-bearing minerals. These reactive trans-
 573 port dynamics can be understood with two non-dimensional parameters: the Damköhler
 574 number Da and the lithological parameter Λ .

575 We use this framework to interpret DO and Fe^{2+} concentrations measured exten-
 576 sively over two neighboring crystalline catchments with similar hydrogeological proper-
 577 ties but contrasted chemical properties. The differences in the depth of the oxidic-anoxic
 578 transition and in the Fe^{2+} pseudo-equilibrium concentration are successfully modeled
 579 and explained by differences in Da and λ . The interpretation of DO alone leads to a fun-
 580 damental indeterminacy in the respective role of geological and hydrological properties
 581 that may explain the difference in Damköhler numbers. However, the joint investigation
 582 of DO and Fe^{2+} provides additional constraints, point to the role of a geological contrast,
 583 here likely due to a difference in the relative proportion of granite and micaschist in the
 584 two sites.

585 The methodology presented here may be implemented on other sites and contexts,
 586 to understand and model the depth of the oxidic-anoxic transition. The two non-dimensional
 587 numbers can be estimated from field data as a guide for DO transport in the subsurface.
 588 Here, we investigated the oxidation of Fe^{2+} by dissolved oxygen and assumed that no
 589 other oxidants could oxidize Fe^{2+} after DO depletion. However, the presence of alter-
 590 native oxidizing agents such as Nitrates or Mn(IV) could promote further iron oxidation
 591 under anoxic conditions. In this case, the predicted rise of Fe^{2+} concentrations up to
 592 the pseudo-equilibrium concentration ($C_{Fe^{2+}}^{eq*}$) would be shifted deeper until the deple-
 593 tion of all oxidizing species. The derivation of the analytical solutions can also be adapted
 594 to other reactions involving dissolved reactants and minerals. While here we considered
 595 a simplified approach based on an effective travel time, it would be interesting to inves-
 596 tigate the form of the analytical solutions and the corresponding dimensionless param-
 597 eters when representing explicitly structural heterogeneities and fracture-matrix exchanges.

598 Acknowledgments

599 This research was funded, in whole, by ANR EQUIPEX CRITEX project (ANR-11-EQPX-
 600 0011) and the ERC project ReactiveFronts (648377). A CC-BY public copyright license
 601 has been applied by the authors to the present document and will be applied to all sub-
 602 sequent versions up to the Author Accepted Manuscript arising from this submission,
 603 in accordance with the grant's open access conditions. We are very grateful to the french
 604 networks of hydrogeological sites H+ (<https://hplus.ore.fr/en/>) and of critical zone ob-
 605 servatories OZCAR (<https://www.ozcar-ri.org/>) for providing access to the Ploemeur
 606 CZO. We also thank the technical services of Geosciences Rennes CONDATEAU and
 607 GeOHeLiS for their support with dissolved gases and groundwater chemistry analysis.
 608 Data for this paper is available in the Hplus database by following the permanent link:
 609 [https://doi.org/10.26169/hplus.ploemeur_field_data_dissolved_oxygen_and_iron](https://doi.org/10.26169/hplus.ploemeur_field_data_dissolved_oxygen_and_iron_landscapes)
 610 [_landscapes](https://doi.org/10.26169/hplus.ploemeur_field_data_dissolved_oxygen_and_iron_landscapes).

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