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Dissolved Trace Elements dynamics during a rich-CO_2-water leakage in a near-surface carbonate freshwater aquifer

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Abstract:

An experimental leak “simulation” was carried out at the Saint-Emilion experimental site (France). A volume of 200 L of CO_2-rich water was injected into the shallow carbonated aquifer during low water table periods. One injection well and seven monitoring wells were equipped with either CO_2 probes or multi-parameters probes to follow the plume.

After the CO_2-rich water injection, dissolved CO_2 and electrical conductivity increased as the pH values decreased, highlighting the calcite dissolution. The calcite dissolution and desorption of iron oxides led to the migration of trace elements in the aqueous phase. As, V, Mo Cu, Ga, Co, Fe, and Cd showed a rapid increase in their concentrations. Mn, Sr, Li and Se showed the same evolution but with a temporal offset. The concentrations of some of these elements increased a second time several hours after the injection. Ba and Pb showed a major decrease immediately after injection, but Ba showed two peaks several hours after the injection. Zn and Si seemed to not be affected by the CO_2 injection.

Only As, Ba, and Se exceeded WHO/UE drinking water standards for a period of few hours. The global return to initial conditions was fast, showing the great resilience and the high buffering capacity of carbonate aquifers.

<u>Keywords</u>: CO_2 leakage, Shallow carbonate freshwater aquifer, CO_2-rock-water interactions, Field experiment, CO_2 geological storage, Trace Elements

1 Introduction

The international community awareness and the scientific data on global warming confirm the urgency of the deployment of technologies to reduce greenhouse gas emissions. At this time, CO_2 capture and storage (CCS) is a major scientific and technical issue and is a well-known and well-studied option for the past few years (IPCC, 2005). This technology involves the capture of the CO_2 from an industrial source and its transport of CO_2 to an injection site to store it for long-term in the deep underground geologic formations such as depleted oil and gas fields or saline aquifers (IPCC, 2005) that meet several criteria of injectability, storage capacity, and integrity (Bachu, 2008). The injected CO_2 is then progressively trapped by physical trapping mechanisms (i.e., when the CO_2 is immobilized as free gas or supercritical fluid) and chemical trapping mechanisms (i.e., when the CO_2 dissolves in subsurface fluids or adsorbs onto organic materials contains on coals and shales for example) (Bachu, 2008; Golding et al., 2011; Gunter et al., 2004; Zevenhoven et al., 2006). The main risk associated with geological storage are leakages which may occur during the process of injection (Damen et al., 2006) and/ or after, along with faults and fractures networks (Farret and Thoraval, 2013; Ringrose et al., 2009) or by the alteration induced by CO_2-water-rock interaction.

One of the major concerns is the possibility of CO_2 leakage to an underlying shallow freshwater aquifer, causing a change of chemical equilibrium between the gas, the water, and the rock of the aquifer, that could potentially lead to pollution of water resources due to the release of trace elements contained in the rock (Harvey et al., 2012; Jones et al., 2015; Lemieux, 2011; Lions et al., 2014; Qafoku et al., 2017). Over the last decade, many studies have been completed to understand the chemical processes involved in releasing trace elements of CO_2 leaks in groundwater. Different types of approaches covering a wide spectrum of spatial and temporal scales like laboratory experiments (Cahill et al., 2013; Humez et al., 2013; Lawter et al., 2018; Little and Jackson, 2010; Montes-Hernandez et al., 2013; Wunsch et al., 2014), field tests (Cahill and Jakobsen, 2013; Gal et al., 2013; Gal et al., 2014; Giese et al., 2009; Kharaka et al., 2010; Rillard et al., 2014; Trautz et al., 2013; Yang et al., 2013; Zhu et al., 2015), modeling studies (Apps et al., 2011; Bacci et al., 2011; Bacon et al., 2016; Tambach et al., 2011; Zheng et al., 2016) and natural analogs studies (Do et al., 2020; Keating et al., 2010) are discussed in the literature. Laboratory experiments are the main type of approach to study the gas-water-rock interactions as they permit the reproduction of these interactions under controlled conditions thus simplifying their understanding. Some of these have focused on rocks with varying carbonate contents. For example, Cahill et al., (2013) investigated risks due to water quality changes in shallow drinking aquifers from leakage of geological carbon sequestration in sediments of variable carbonate content *via* batch experiments. Lawter et al., (2018) studied the element mobilization and immobilization from carbonate rocks *via* batch experiment. They focused on the intermediate zone between CO_2 storage reservoirs and the overlying aquifers. Wang et al., (2016) worked on the geochemical impacts of CO_2 leakage to an unconfined oxidizing carbonate aquifer via batch and column experiments. Conversely, Wunsch et al., (2014) performed laboratory batch experiments to analyze the potential for trace element release due to carbonate mineral dissolution in limestone aquifers. However, these experiments have the disadvantage of not reproducing the geological physical (i.e., petrophysical rock properties and hydrodynamics properties of the aquifer) and chemical natural complexity of the aquifer and their heterogeneity.

Among the experiments carried out on a field scale, there are some which focus on CO_2 leak experiments in a shallow aquifer. To date, much of these field experiments have focused on siliciclastic aquifers with little carbonate content. For example, Yang et al., (2013) have carried out a single-well push-pull test for assessing potential impacts of CO_2 leakage on groundwater quality in a shallow Gulf Coast aquifer in Cranfield (Mississippi). In this study, 3825 L of gasified water was injected into a sand and clay aquifer. Cahill and Jakobsen, (2013) conducted a shallow CO_2 injection experiment in an unconfined, unconsolidated aquifer however, the aquifers were mainly siliciclastic. Rillard et al., (2014) performed a shallow push-pull field experiment to assess the geochemical impact of a CO_2 perturbation but in a fractured sandstone aquifer. To the best of our knowledge, no field experiment assessing the geochemical impact of a CO_2 leak in an exclusively carbonate near-surface freshwater aquifer has been conducted to date.

As trace elements are also present in the crystalline structure of carbonate minerals (Thorstenson and Plummer, 1977; Zachara et al., 1991) they can therefore be released into the aqueous phase during their dissolution and constitute a risk for the quality of drinking water. Moreover, carbonated aquifers are well represented around the world and 20 to 25% of the population uses the carbonate aquifer as a drinking water resource, and may therefore be subject to CO_2 intrusion in the case of a leak (Ford and Williams, 2007). Furthermore, the literature has shown that the effects of CO_2 leakage are site-specific (Zheng et al., 2015). The impact depends on the sedimentary formations, hydrogeology context, and geochemistry of the aqueous phase, implying that the extrapolation of the results for other sites is not possible. Studies are still needed to extend the comprehension of the effects of a CO_2 leak on water quality and finally to increase acceptance of this technology.

This work is part of the *Aquifer-CO_2-Leak Project* and follows the work of Gassara et al., (2021) on the pre-dimensioning of the experiment by numerical modeling of CO_2 leakage and the work of Petit et al., (2021) on the characterization of the physicochemical impact of the injection of CO_2-rich water in the carbonate aquifer of Saint-Emilion (France). The objective of this study is to understand, quantify and evaluate the impact of a CO_2-rich water leak on water quality and more specifically on the dynamics of dissolved trace elements in a shallow freshwater carbonate aquifer with a very high calcite content of 98 ± 2% $CaCO_3$ (Loisy et al., 2013). The objective is to acquire in situ data that would serve to identify and quantify trace elements concentrations which in turn could serve to model chemical mechanisms responsible for trace elements mobilization at a small experimental site scale.

This paper first presents the geological and hydrogeological context of the study, followed by the results of the rock characterization and the geochemical monitoring of the CO_2-rich water plume over time. Finally, these results are interpreted and discussed.

2 Materials and methods

2.1 Geographical, geological, and hydrological context of the study site

The experimental site is in an underground limestone quarry at Saint-Emilion, in the New Aquitaine region (France) (**Fig.1a**). The quarry is in a limestone formation dating from the Upper 1b Oligocene (Stampien; 28-30 Ma) and exploited on two levels (to 8 and 16 m deep on average) according to the “rooms and pillars” method (Loisy et al., 2013). The limestone formation of around 25 meter-thick is characterized by carbonate and biodetritic facies. This formation mainly consists of grainstone to wackestone facies (Dunham, 1962) and is associated with high values of porosity (28.5 to 41.5%) and permeability (4.3 and 11.8 D) according to a previous study taken place in the quarry (Cohen et al., 2013; Loisy et al., 2013; Rillard et al., 2015). Previous calcimetry measurements revealed a $CaCO_3$ content of the limestone of about 98% ± 2% (Rhino et al., 2016). Previous studies have highlighted that the porosity is only represented by the matrix pore network because all fractures present in the formation are filled by impermeable red clays (Cerepi et al., 1998) and that the heterogeneity of the pore structure and/or the alteration of the rock explained the high range of values (Rillard et al., 2014).

In the area of the experimental site, the hydrogeological system is composed of 0.30 m of soil (Combisol calcalric type; IUSS Working Group WRB, 2007) and 21 m of Oligocene limestone of which approximately 3 m rests in the saturated zone, depending on the aquifer recharge (**Fig.1a**). The water table is located at the lower part of Oligocene limestones and above levels of impermeable Sannoisian green marls (Vincent and Maton, 1999; Vouvé, 1990). Its drainage axis is NW-SE orientation. The range of the hydraulic gradient is between 2% at the lowest water table elevation to 5% at the highest water table elevation. At the time of this experiment, the hydraulic gradient was 2% with a water table elevation of 61.35 m NGF (General Levelling of France;) (**Fig.1a**). Groundwater resource is fed directly by meteoric water. The flows are vertical and controlled by gravity and the downward percolation takes place via the pillars of the quarry (Loisy et al., 2013).

2.2 Experimental methodology

2.2.1 Experimental site and injection of the CO_2-rich water

The pilot site is located approximately 16 m deep at level 2 of the quarry (**Fig.1a, b).** To carry out the CO_2-rich water injection experiment, eight boreholes of 8 cm in diameter, between 4.8 and 6.0 m deep were drilled along the hydraulic gradient (an injection well-named F1 and seven observation wells named from F2 to F8; **Fig.1b**) on 7.10 m of distance (i.e., between F1-F8). A PVC tube was placed on the upper part of the borehole to reinforce the backfill (**Fig.1c**). The drilling was carried out using a destructive technique using water from the boreholes to drill and cool the machine to minimize the disturbance to the system. Only one borehole (F2) has been used for taking core samples.

A 200 liters volume of Oligocene aquifer water drawn and stocked in a stainless tank was used for the water gasification and then the injection. A motor, pressure sensors, and an output flow meter were added to the tank to control the gasification and injection processes. The gas bottle of 50 L composed of a mixture of CO_2 (90 %), He (9%), Kr (1%) was bubbled in the tank with fluorescent molecules (fluorescent based Lanthanide, used as an inert tracer) about 24 hours until saturation. The rich-CO_2-water injection started on July 09th, 2019, at 10 a.m in the well F1, and lasted approximately 30 minutes. This corresponds to the time of the experiment which will be taken as a reference to describe the results. During this first step of the leak simulation, the dissolution of the CO_2 did not take place in the aquifer itself but the tank. We have chosen to not inject CO_2 directly into the aquifer to control all the physical and chemical parameters of the input signal. The end of the monitoring of all parameters combined is dated August 01st, 2019. The injection velocity was 2.20 L/min and was chosen as it was close to the speed of the water table. This made it possible to avoid hydraulic overload and a piston effect on water dynamics. The physicochemical parameters of the tank water are presented in **table 1**.

2.2.2 Physicochemical parameters monitoring

Four CO_2 probes of the CO_2-Pro ™ type (Pro Oceanus) (± 2% (P_{CO_2} 10-900 mbar)) and four multi-parameter probes of the Aqua TROLL 600 Multiparameter Probe type were respectively introduced into wells F1, F2, F3 and F6 and F1, F3, F6, and F8 (**Fig.1b**). These probes were immersed continuously in the aquifer and recorded physicochemical parameters every 30 min such as electrical conductivity (± 0.5% of reading plus 1.0 µS/cm), pH (± 0.1

pH units), oxidation-reduction potential (ORP, ± 0.5 mV), and temperature (± 0.1 °C). During the experiment, the multi-parameter probe in F1 was moved to well F8 after that the parameters had returned to the baseline in F1. The probes were isolated from the quarry atmosphere by packers (or inflatable stoppers) designed and produced especially for this experiment. They were kept inflated throughout the experiment using a compressor and a gas-tight tubing system hung from the quarry ceiling (**Fig.1b, c**).

2.2.3 Sampling strategy

All wells were equipped with water sampling tubing at two depths below the level of the water table (about 25 and 70 cm below, respectively 61.10 m NGF, and 60.65 m NGF for the well F1) to check if there were differences in concentrations on this scale. Previously, Petit et al., (2021) concluded that there were no significant differences between these two depths. Therefore, the results will be presented for one depth (25 cm below the level of the water table).

The water samples were taken using a type Ismatec® water pump connected to the tubing of each well. According to the pump flow rate and the volume contained in the pipe, one minute was necessary to purge the pipe. The water was collected in a beaker previously rinsed three times with the water withdrawn. Given the increased risk of degassing, pH, conductivity, and temperature were measured immediately after the sampling directly in the beaker using a Consort C561 multiparameter analyzer. A volume of 15 ml of water for the analysis of trace elements was taken from the beaker and filtered using a 0.2 µm nylon filter and placed in a 16 ml borosilicate glass vial previously decontaminated with aqua regia 5% (HNO_3 67-69%, Trace Metal ™ and HCl 37%, Trace Metal Analysis, d = 1.18, Primar Plus

™). Due to poor air renewal in the quarry and for safety reasons, the samples were acidified at the quarry exit (2% - HNO_3 67-69%, Trace Metal ™) approximately one hour after collection. Similarly, two water volumes of 16 ml were taken from borosilicate glass vials for the analysis of cations and anions concentrations and alkalinity analysis. They were directly stored and transported at 4 °C in the dark enclosure to the laboratory until analysis.

Samples were taken every 8 hours for the first two weeks, then every 12 hours, and finally every other day at the end of the experiment. Samples were not taken systematically from all wells each time. Sampling was concentrated on the wells according to the plume migration. This sampling strategy was determined following the results of preliminary salt tracing experiments (Petit et al., 2021). Due to the possible degassing, the samples for the cation-anion analysis were filtered with 0.2 µm nylon filters just before their analysis.

2.2.4 Rocks samples characterization

Six samples of limestone were analyzed to determine their trace elements concentration and their other petrophysical characteristics. Chemical and physical analyses were carried out on grainstone and boundstone facies samples to see their differences. They were sampled from the sediment core collected when drilling in the well F2 at 0.63, 1.15, 1.80, 2.22, 3.23, and 4.05 meters from the quarry floor (64.17 m NGF) (**Fig.1a**; **Fig.2a**). Porosity was measured by Hg-injection and permeability was measured by variable head air permeameter methods. The mineralogical composition of the samples was analyzed using the X-ray diffraction (XRD) type D8 Advance (Brucker). X-ray fluorescence (XRF) analyses of the limestone were carried out using a HORIBA XGT 5000. These analyses made it possible to obtain semi-quantitative concentrations of the elements constituting a circular target zone (diameter of 100 µm).

Total trace element analyses were carried out using the tri-acid digestion method. After having dried, crushed, and homogenized, a representative aliquot of rocks (i.e. 150 mg) were digested in acid-cleaned closed PP tubes (DigiTUBEs) in a Teflon-coated heating block (2 hours at 110 °C) with 1.5 mL HCl (10 M Suprapur), 750 µL HNO_3 (14 M Suprapur) and 2.5 mL HF (29 M Suprapur), as described in previous studies (Schafer et al., 2002; Gil-Díaz et al., 2018). After evaporation to dryness and re-dissolution of the residue with 250 µL HNO_3 (14 M) in the heating block, the samples were brought to 10 mL using Milli-Q® water. Concentrations of particulate Ag, As, Ba, Cd, Co, Cu, Cr, Mo, Ni, Pb, Sb, Sr, V and Zn were quantified using triple quadripole ICP-MS (iCAP-TQ) using an external calibration. To verify precision and accuracy, the analytical method was quality checked with international certified reference materials (NIST8704; SLRS-6). Concentrations of particulate trace elements such as Be, Fe, Ga, In, Li, Mn, Se and Si of the same samples were quantified using an ICP-AES (iCAP 6000 Series) using external calibration with a multi-element standard solution (Multi-element standards solution 5 for ICP, TraceCERT®).

2.2.5 *Water samples characterization*

Dissolved trace elements were analyzed using an ICP-AES (iCAP 6000 Series) with external calibration. Blank and standards were analyzed at the same time to control the drift of the ICP-AES. The calibration range varies from 10 to 100 µg/L using a multi-element standard solution (Multi-element standards solution 5 for ICP, TraceCERT®). Major ions were analyzed using an HPLC (High-Performance Liquid Chromatography) of the DIONEX type, equipped with a CS12A analysis column and an IONPAC® CG12A protection column (mg/L, ± 5%). The device is calibrated to be adapted to the sample matrix. The calibration range varies from 5 to 200 mg/L of $Ca^{2+,}$ Mg^{2+}, Na^{+}, NH_4^{+}, K^{+}, F^{-}, Cl^{-}, PO_4^{3-} and SO_4^{2-}. About 5 ml of standards or previously filtered samples were placed in closed vials. Between each series of 10 samples, blanks and standards were placed to check the stability of the analyses and the drift of the device. The alkalinity of each sample was measured in the laboratory directly after sampling using the Inflection Point Titration Method (USGS, 2012) with a pH-meter (Consort, ± 0.2%) and a titration solution of 0.1 M hydrochloric acid.

3 Results

3.1 Physical and chemical characterization of the Saint-Emilion limestones samples

The sediment core collected in well F2 presents three distinct lithologies (**Fig. 2a**) (Petit et al., 2021, modified). The floor of the site was composed of carbonate rock up to about 58.4 m NGF (i.e., General Leveling of France; official levelling network in metropolitan France), of which about 50 cm on the surface corresponds to backfill due to the accumulation of carbonate powders released during the digging of the quarry when it was in operation. It is in this porous zone of 58.4 to 61.4 m NGF that the water table is located. An impermeable clay zone (Sannoisian green marls) begins at plus or minus 58.4 m NGF.

The macroscopic study of the sediment core revealed grainstone, boundstone, mudstone, wackestone, and packstone facies, which follow one another or alternate them according to the depth. Several sedimentary structures were observed such as the straight structure, the oblique structure, and the cross-bedded structure.

Microscopic analysis of the six samples made it possible to visualize the differences in geometry, size, and distribution in the porosity between two facies (**Fig.2b**). These samples are mainly composed of remains of *foraminifers*, *bioclasts, Lamellibranchia*, *Oncoides*, *Rhodolithes*, *Bryozoans,* and debris of *Echinoderms*. Rare quartz crystals (< 1 %) were observed in all the thin sections whatever the facies. Iron oxides were also observed in lesser quantities (< 0.5%) in the micritic matrix in a diffuse manner, in certain figured elements, or at the edge of pores. The grainstones show sparitic to microsparitic edge cement and the boundstone have sparitic cements partially filling the pores (**Fig.2b**). No internal sediment was observed plating on the edge of the porosities according to the microscopic analysis.

The samples show high variability of porosity from 20 to 43% and permeability from 1 to 26 D (**Fig.2a)** The results are consistent with other analyses completed on the Saint-Emilion limestone in the past experiments (porosity values between 28.5% and 41.5%, and permeability values between 4.3 and 11.8 D) by Rhino et al., (2016).

According to the X-ray diffraction (XRD) analysis, the mineralogical composition of the samples is almost exclusively calcite ($CaCO_3$) with low traces of quartz (SiO_2). The calcite is shown by the presence of the peak located at 29.5° (main calcite peak) and several other peaks. For the quartz, the peak located at 26.8° is also clearly detectable. No peak corresponding to oxides or clays was found. The spectra of the XRD analysis of three powder samples can be shown in the **supplementary materials.1.** These results are consistent with other analyses on the Saint-Emilion limestone for past experiments. Rhino et al., (2016) presented results of calcimetry technics which revealed a $CaCO_3$ content of 98% ± 2%. Auffray et al., (2016) done XRD investigation and showed that the two main phases were $CaCO_3$ and SiO_2. Furthermore, Rock-Eval 6 analysis confirmed that no organic carbon (i.e., organic matter) was present in their samples and that mineral carbon was only contained by $CaCO_3$. The authors confirmed their results by SEM-EDXS analysis. To conclude, according to the analysis of the limestone of Saint-Emilion, $CaCO_3$ is the main mineralogical phase and

SiO_2, as well as the iron oxides observed with the microscope, are less abundant mineralogical phases present in very weak proportions.

Analyses (semi-quantitative) of the samples with X-ray fluorescence (XRF) show that Ca, Si, Fe, Mn, K and Al are the major elements while Cu, Ba, Sr, Zn, S, V, Ti and Pt appear to be minor components (**Tab.2**). The results show great variability within the same facies. For example, silica varies between 3.14 and 25.09% in grainstone samples. This variability is also true for the samples of the boundstone and those for all the elements identified by the XRF. Likewise, each element identified varies greatly along the sedimentary column. Thus, there seems to be a spatial geochemical heterogeneity that seems independent of the sedimentary facies.

Subsequently, analyses completed using the tri-acid digestion method were carried out to obtain quantitative results. The elements observed (Al, Ti and Pt) during the XRF analyses could not be analyzed using the ICP for lack of standards or methodological concerns. The details of the total trace elements concentrations of the six samples can be found in **supplementary material.2** and the means ± standard deviations for all the samples and for each facies (boundstone and grainstone) are presented in the **Table 3**.

The variation in concentrations (i.e., the standard deviation in percent) around the mean for each facies (three samples each) and the two facies together (six samples) was calculated to better compare the differences between the facies and between the elements (**Fig.3**). When we look at the degree of variation around the mean for all together facies, we notice that the elements Ba, Li, Mn, Pb, Sr and Zn vary between 0 and 25%. These results, therefore, show relatively similar concentrations along the sediment column. The degree of variation of the elements Ag, As, Cd, Co, Cr, Fe, Ga, Mo, Ni, Sb, Se, Si and V vary between 25 and 50% around their averages. The concentrations of these elements, therefore, seem to vary over a broad spectrum along the sedimentary column (**Fig. 3**). The degrees of variation around the mean of the Cu and In concentrations are very strong. The distribution of these elements, therefore, seems to be very uneven in the sedimentary column. When looking at the degree of variation around the mean for the grainstone and boundstone, it varies between 0 and 25% for elements such as Co, Sr and Zn and their respective means are between each facies are similar. Thus, the distribution of these elements is not specific to particular facies. The degree of variation of the elements such as Ag, Ba, Cd, Cr, Cu, Mn, Sb, Si, Ga and V between the grainstone and boundstone are very different. This indicates that these elements are homogeneous in one facies but not in the other. For example, Ag, Cd, Cr, Cu, Mn and Si have a low degree of variation in the grainstone and high in the boundstone. While Ba, Sb and Ga have a greater degree of variation in the grainstone than in the boundstone. Then there are the elements such as Zn, Se, In, Sr and Li, Mo and Pb which have a degree of variation around their similar means, and their respective mean concentrations for each facies are also similar. , In consequence, these elements do not make it possible to geochemically differentiate the boundstone and the grainstone.

3.2 Evolution of the physicochemical parameters in carbonate freshwater aquifer during the experiment

The evolution of the physicochemical parameters of the CO_2-rich water plume over time is presented for the wells F1, F2, F3, F6, and F8 in **Fig. 4**. Baseline measurements of physicochemical parameters recorded up to 25 hours before the injection showed little variation. The physicochemical parameters showed a small heterogeneity according to the baseline values recorded 25 hours before the injection. The pH varied in the range between 7.02 et 7.15 for the wells F1 and F3, the conductivity varied between 632 µS/cm and 738 µS/cm for the wells F3 and F1, the dissolved CO_2 varied in the range between 1.84% and

2.46% for the wells F2 and F1 and the ORP values varied between 233 mV and 376 mV. Finally, the temperature of the water table varied from 13.03 °C for the well F6 to 13.12 °C for the well F1. This baseline recording time was sufficient to avoid confusing the variations induced by the injection of CO_2-rich water with those resulting from the natural annual hydrogeological variability of the water table.

The injection of CO_2-rich water induced a rapid change of the physicochemical parameters of the water table over the first 120 hours as shown in **Fig. 4.** The variations were greater in the injection well F1 than in the others. The injection immediately produced a sharp drop in pH of 1.4 units (from 7.02 to 5.63 post-injection). It returned to its initial value after 40 hours. The other wells showed a lower pH drop, a wider peak, and a more time interval according to their distance with F1. The pH drop in F3 is 0.20 units (from 7.15 to 6.97 post-injection), was 0.07 units (from 7.03 to 6.96 post-injection) in F6, and 0.03 units (from 7.10 to 7.07 post-injection) in the well F8. The minimum pH values were recorded simultaneously with the maximum conductivity values. Conductivity rose from 679 to 1551 µS/cm in the well F1, which records the strongest rise 7 hours after the injection. The increase in conductivity was smaller in the other wells, with a rise from 617 to 729 µS/cm in the well F3, from 665 to 716 µS/cm in the well F6, and from 714 to 777 µS/cm in the well F8.

A rapid rise in dissolved CO_2 from 2.5 to 19.7% was noticeable immediately after the injection in the well F1 with a return to an initial value from 40 hours. The curve of dissolved CO_2 in well F1 showed a plateau due to the saturation of the probe which the range was limited to 20%. The dissolved CO_2 from well F1 was recalculated under PhreeqC software by inverse modeling from the analysis of cations and anions to obtain the maximum values of 30% (Petit et al., 2021). Wells F2 and F3 farther from the injection well showed a lower rise with a wider peak. Dissolved CO_2 increases to 3.54% between 20 and 60 hours in well F2. It rises to 3.67% between 40 and 120 hours in the well F3. The CO_2 probe initially installed in well F1 was moved to well F8 from 145 hours after the plume of CO_2 had dissipated in F1. Therefore, there are no data for the F8 well before 145 hours. The sudden decrease occurring at this time corresponds to the withdrawal and re-filling of the probe. The arrival of CO_2 occurred between 320 and 340 hours after the start of the injection.

The ORP recording showed minimal values in the F1 injection well while the other wells did not show significant variations after the injection. A temperature rise was only noticeable in the well F1 (14.60 °C after the injection.) Alkalinity (as HCO_3^-) showed the same trend as other parameters with a peak of 832.70 mg/L in F1 with lower peaks in other wells.

From a general point of view, the pH, alkalinity, conductivity, and dissolved CO_2 showed similar temporal offset between each well but there were slight shifts. The highest values for pH, ORP, and temperature were recorded less than 1 hour after injection in well F1 while the conductivity and alkalinity peaks were recorded after 7 hours and dissolved CO_2 between 1 hour and 40 min and 13 hours after injection. The dissolved CO_2 registers a peak 35 hours after injection in well F2. Then the plume moves to F3 and reaches the first peak at 68h after injection, followed by a second weaker peak between 120 and 140 hours after injection. Based on conductivity, the arrival of the plume in well F6 took place 138 hours after injection and 328 hours after injection into well F8.

For more details of the physicochemical parameters evolutions following the injection, see Petit et al., (2021).

3.3 Evolution of the trace elements concentrations variation during the experiment

The evolution of the concentrations of the trace elements over time for the wells F1 to F8 is shown in **Fig.5** and **Fig.6.** The black dashed axis at t_0 indicates the moment of the injection. The grey hatched area of some graphs represents the detection limit of the analytical device. Water samples were taken at two depths (i.e., 25 and 70 cm below the water table, respectively 61.10 m NGF, and 60.65 m NGF for the well F1). Petit et al., (2021) showed that there were no concentrations differences between these two depths for the major elements. The same has been concluded for the trace element concentrations. Results for the depth E2 are shown in the **supplementary material.3 and .4**. Furthermore, results for Ag, Sb, In, Ni, and Cr were below or very closer to the detection limits in the majority of the wells and will not be treated in the rest of this study.

When looking at the natural pre-injection concentrations for each of the trace elements, these are more or less variable between wells, showing some small-scale geochemical heterogeneity. The results showed that Se, Mn, Mo, Co and Cd concentrations were not detectable with our analysis method in the dissolved phase before the injection of the CO_2-rich water in all the wells. The concentrations of the other elements varied to a greater or lesser extent depending on the well and the element. For example,

As varied between 1.60 µg/L (well F4) and 3.37 µg/L (well F5)

Ba varied between 9.70 µg/L (well F2) and 1105.45 µg/L (well F7),

V varied between 0.89 µg/L (well F5) and 2.11 µg/L (well F8),

Sr varied between 118.20 µg/L (well F2) and 182.16 µg/L (well F8),

Ga were below the detection limit in the well F4 and F8 and showed a maximum of 7.17 µg/L in the well F6,

Fe was below the detection limit in the well F1, F2, F4, and F6 and showed a maximum of 129.47 µg/L in the well F8,

Pb varied from 2.27 µg/L (well F8) to 7.60 µg/L (well F1),

Si varied from 1397.00 µg/L (well F4) and 2233.00 µg/L (well F8),

Zn varied between 11.60 (well F2) and 365.30 (well F4), finally, Li varied between 1.40 (well F2) and 2.07 µg/L (well F8).

After the injection of the CO_2-rich water, the injection well F1 showed higher concentrations. They were close to or under the detection limit in the other wells. In the well F1, Ga, Cu, Fe, Co, and Cd concentrations increased immediately after injection. Ga and Cu had a higher dissolved concentration with a rise respectively to 116.04 µg/L and 22.18 µg/L. Before the beginning of the injection Fe, Co and Cd were not detected. They reached a concentration peak respectively of 57.88 µg/L, 4.65 µg/L and 0.35 µg/L during the injection. After reaching a peak, their concentrations decreased.

The concentrations of As, V and Mo increased immediately after injection in the injection well. They reached a concentration peak respectively of 17.08 µg/L, 11.92 µg/L and 5.01 µg/L. Then, their concentrations decreased but reached a second lower peak a few hours later in the same well. They reached a second peak respectively of 3.11 µg/L after 56 hours, 2.42 µg/L after 48 hours, and 1.51 µg/L after 56 hours after the injection.

The concentrations of Sr, Li, Se, and Mn increased 8 hours after the injection and reached a second peak a few hours later in the injection well. The concentration of Sr increased to 224.26 µg/L and reached the second peak of 129.57 µg/L 48 hours after the injection. The concentration of Li reached the first peak of 2.12 µg/L and the second peak of 1.53 µg/L 48 hours after the injection. Se concentration reached the first peak of 7.70 µg/L and a second of 15.96 µg/L after 56 hours. Then the concentration of Mn increased to 23.46 µg/L and decreased more slowly than the others.

On the overhand, Ba showed two peaks in the well F1 of 1305.50 µg/L after 40 hours and a second of 574.72 µg/L after 128 hours. Also, Ba was detected with high concentrations before injection.

Significant concentrations were measured for Pb in the injection well, and a major decrease was recorded immediately after injection. It was detected before the injection but not in all wells and decreased under the detection limit with the injection start.

Lastly, Zn and Si concentrations do not appear to be altered after injection in each well. They vary respectively between <0.00 µg/L (all wells) and 1582.90 µg/L (well F6) and 723.10 µg/L (well F1) and 3254.10 µg/L (well F4), and. After the injection in the well F1 the concentrations return to concentrations like those of the baseline or concentrations below these except for V, Ga, and Li where their concentrations rise after several days.

4 Discussion

4.1 General changes in groundwater chemistry due to the CO_2 leak in a shallow carbonated system

The injection of the CO_2-rich water caused a pH immediate decrease simultaneously with the $CO_{2\,(aq)}$ increase in the injection well F1. The dissolved CO_2 caused an increase in the concentration of carbonic acid (H_2CO_3), followed by deprotonation of thereof and further lowering the pH values of the solution, following the simplified equations (Appelo and Postma, 2005):

$CO_{2\,(g)} + H_2O_{\,(l)} \rightarrow H_2CO_3^{-}{}_{(aq)}$

$H_2CO_3^{-}{}_{(aq)} + H_2O_{\,(l)} \rightarrow HCO_3^{-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$

$HCO_3^{-}{}_{(aq)} + H_2O_{\,(l)} \rightarrow CO_3^{-}{}_{(aq)} + H_3O^{+}{}_{(aq)}$

Secondly, the released protons reacted with carbonates and are consumed during their dissolution (Lions et al., 2014; Smith and Mead, 1962). The attenuation of the pH is particularly marked in aquifers rich in carbonates because, in the presence of protons, the dissolution of carbonate minerals is more important. Indeed, the dissolution of carbonate minerals led to an increase in alkalinity, due to the increase in the concentrations of carbonate and bicarbonate ions, allowing the increase of the buffering capacity of the solution (Lions et al., 2014). Eventually, a physicochemical equilibrium between the CO_2, the rock and the water occurs:

$CaCO_{3\,(s)} + CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow 2\ HCO_3^-{}_{\,(aq)} + Ca^{2+}{}_{\,(aq)}$

Thus, the dissolution of calcite was the first phenomenon playing a buffer role on the pH in this aquifer (Qafoku et al., 2017). This effect was also reflected by the increase in pH values and the decrease in dissolved CO_2, alkalinity, and conductivity in well F1 once the peaks passed (**Fig.4**). It should also be remembered that the speed of the water table (0.8 m/day) also played a role in buffering the pH (**Tab. 1**). Our experiment took place in a carbonated aquifer with high values of $CaCO_3$ (98 ± 2%) with a low part of silica and explains the very fast buffering capacity of the aquifer.

Calcite dissolution can also lead to a release of major ions (Petit et al., 2021) and trace elements in the aqueous phase, which can be illustrated by the following relationship (Comans and Middelburg, 1987; Zheng et al., 2016):

$MCO_{3\,(s)} + H^+{}_{\,(aq)} \rightarrow HCO_3^-{}_{\,(aq)} + M^{2+}{}_{\,(aq)}$

The water-rock interface is the site of numerous reactions (e.g. sorption reactions, dissolution and precipitation reactions, ion exchange reactions) (Qafoku et al., 2017). These reactions are in turn influenced by physicochemical parameters (e.g. pH, temperature, redox potential) which will impact the mobility of traces elements (Tanji and Valoppi, 1989). When CO_2-rich water was added to the carbonated system, the physicochemical parameters of the environment changed and led to exchanges between the solid and liquid phases of the aquifer (Harvey et al., 2012). (**Fig.5; Fig.6**). Consequently, the increase of ions in the aqueous phase induced an increase in conductivity in the injection well F1 (**Fig.4**). The changes in oxidation-reduction potential (E_h) are explained by the rich dissolved CO_2 water intrusion (Harvey et al., 2012). The aquifer will be more anaerobic (low E_h) with the entrance of CO_2 and will induce a redistribution of oxidized and reduced species for those which are redox-sensitive in the aqueous phase (Marshall and Fairbridge, 1999). CO_2 intrusion can also induce changes in biological activity (Harvey et al., 2012), but this aspect is not treated in this article.

The rise of the temperature only observed in the well F1 is explained by the temperature difference between the water in the aquifer and the CO_2-rich water injected which is in equilibrium with the temperature of the underground quarry. The decrease is explained by the replacement of water coming upstream of the injection point.

The heterogeneous nature of the carbonate system was highlighted by the recording of two distinct increases of the conductivity, the pH, and the dissolved CO_2 in well F3. The assumption is that the water upstream arrived via two preferential paths (Petit et al., 2021) due to the heterogeneity of the porosity (also highlighted by Rhino et al., (2016) distinguished two types of porosity for the Saint-Emilion limestone) and permeability of the carbonated system at a small scale.

4.2 Trace elements release in the aqueous phase due to the CO_2 leak in a shallow carbonated system

When looking at the evolution of the trace elements concentrations along the longitudinal axis (F1-F2-F3-F6-F7-F8) and the perpendicular axis (F4-F3-F5) relative to hydraulic gradient, the increase in concentrations occurred significantly only in the injection well F1 (**Fig.4; Fig.5**). Only the concentrations of Se or Sr for example showed a slight increase in the wells F2 and F3. As dissolution only takes place in well F1, advection and dilution dominate the profile of the released elements and diffusion of the plume is not observed in the transverse axis. The low transverse dispersivity is controlled by the petrophysical characteristics and aquifer hydraulic gradient (Gassara et al., 2021). In addition, the high buffering capacity of the limestone in comparison to the small amount of CO_2-rich water injected during this experiment minimizes the dispersion of the plume. This is consistent with the study of the saturation indices by Petit et al., (2021) which showed that the calcite dissolution caused by the CO_2-$CaCO_3$-H_2O reaction only took place in the well F1 and that the variations of the other physicochemical parameters as well as the concentrations in major ions in the other wells were only due to the transport of $CO_{2\ (aq)}$ by advection and diffusion through groundwater flow. However, the behavior of the major ions did not show several peaks or temporal offset as for trace elements, suggesting a more complex chemistry.

The lack of concentration differences between the two sampling depths is due to the relative homogeneity of the physical (i.e. hydrodynamic variations) and chemical (i.e. petrography and lithology of the limestone) environment at this scale. However, this is not true on a larger scale as shown by Cahill et al., (2013). Homogenization of the volume of water contained in the well (i.e., 15 L) during injection may also be the cause. Nevertheless, there is some spatial heterogeneity in the chemical composition of the groundwater given the differences in concentrations observed between the wells for the same elements, according to the concentrations before the injection.

4.2.1 Origins of the trace elements of the Saint-Emilion limestone

According to the analysis of the limestone of Saint-Emilion, $CaCO_3$ is the main mineralogical phase. SiO_2, as well as the iron oxides observed with the microscope, are secondary mineralogical phases present in very weak proportions. The presence of iron oxides in amorphous form would explain that they were not detected with the XRD method and would also explain the number of trace elements detect using the XRF method.

Trace elements would be localized in the crystalline structure of carbonate minerals (Thorstenson and Plummer, 1977; Zachara et al., 1991). For example, many trace elements like Ba, Sr (Pingitore and Eastman, 1986), Co, Mn, Zn, and Cd (Comans and Middelburg, 1987), Pb (Rouff et al., 2004), Se (Aurelio et al., 2010; Reeder et al., 1994) and or As (Alexandratos et al., 2007; Bardelli et al., 2011) could been incorporated into the cristal lattice during the carbonate sedimentation. Then, the Oligocene limestone, emerged since 32 Ma, has undergone significant meteoric diagenesis and other elements may have been trapped in the cement during this period. Trace elements would be also adsorbed on the iron oxides (Ni et al., 2009; and references therein). During the CO_2-rich water injection experiment, the dissolution processes of carbonates as well as desorption of iron oxides will lead to the release of these trace elements into the aqueous phase.

4.2.2 Evolution of the trace element concentrations in the injection well

The dissolved trace elements of injection well F1 could be classified into six different groups according to their behavior after injection (**Fig.7**). Furthermore, the relationships between the alkalinity expressed as the HCO_3^- ion, considered as a marker for the dissolution of carbonates, and the different ions analyzed are shown in **Fig.8** to allow hypotheses to be made as to the mechanism of metal release which would be directly linking to the chemical reactions of calcocarbonic system. According to the evolution of the concentrations of the major ions, showed in Petit et al., (2021) and their correlations coefficients with the alkalinity showed in **Fig.8**, most of the changes of the water chemistry are the result of the dissolution of calcite caused by carbonic acid. Therefore the major constituent elements of the carbonate minerals and their potential cationic and anionic substitutions (Alexandratos et al., 2007;

Thorstenson and Plummer, 1977; Zachara et al., 1991) will initially be found in the aqueous phase.

First, the group of type 1 is composed of Ga, Cu, Fe, Co, and Cd. Their concentrations increased immediately following the CO_2-rich water injection and decreased in the same manner, implying that the mobilization mechanisms of these elements could be similar. Their relationship with the alkalinity is strong. The correlation coefficient (R^2) with the alkalinity is 0.92 for Ga, 0.95 for Cu and 0.88 for Co. This suggests that the release of these elements is directly related to the dissolution of calcite. The correlation coefficients for Fe and Cd could not be calculated due to a large number of data below the detection limits. Wunsch et al., (2014) also showed that Co was released into the solution through calcite dissolution. The Saint-Emilion limestone also contains SiO_2 and iron oxides which were observed in lesser quantities (< 0.5 %) in the micritic matrix in a diffuse manner, in certain figured elements, or at the edge of pores. The release of these elements may be due to a desorption reaction occurring at the same time as the dissolution of carbonates. This was also shown by Cahill et al., (2013) in batch experiments conducted on samples with variable content of $CaCO_3$. Iron concentrations were associated with the presence of ferrihydrite and gibbsite in the sediments. The authors concluded that the weak increase of the aqueous Fe concentration was due to the high buffering capacity of calcite and the pH-dependence of these minerals. This could explain the low concentration of iron in solution compared to its proportion in the Saint-Emilion limestone. Furthermore, the lower pH (e.g pH 5.45) of the injected solution may have also led to the initial dissolution of the iron oxides and explained the initial increase in Fe in the injection well F1.

Type 2 is composed of As, V, and Mo. Their concentrations increased directly after the injection as type 1. The correlation coefficient of As with the alkalinity is 0.98 and suggests a mechanism of release similar to type 1. However, Wunsch et al., (2014) also showed that As had the same tendency as calcium, markers of calcite dissolution, but they finally concluded that the aqueous As concentration was due to desorption mechanisms of arsenate and arsenite, known to can be also incorporated in calcite (Alexandratos et al., 2007; Bardelli et al., 2011). The correlation coefficient with the alkalinity of V and Mo are 0.23 and 0.76, suggesting that the calcite dissolution do not control these elements into solution.

Type 3 is composed of Sr, Li, Mn, and Se. The maximum concentration of these elements was not recorded directly after the injection as for types 1 and 2 but after a temporal offset of 8 hours. Li, Mn and Se showed a weak correlation coefficient with the alkalinity which are 0.44 for Li, 0.50 for Mn, and 0.44 for Se, suggesting that the calcite dissolution was not at the origin of this elements into the aqueous phase. Only Sr has a strong correlation coefficient of 0.96 with the alkalinity (**Fig.8**). An example of carbonate dissolution modeling including only Sr as $SrCO_3$ is shown in **Fig. 9**. The concentrations of Ca^{2+}, HCO_3^- and Sr obtained by modeling are consistent with the experimental results. These results and the strong correlation with the alkalinity suggest that Sr is controlled by carbonate dissolution and precipitation. This modelling work will further explore precipitation and sorption reactions in the future by including all trace elements. These results are also consistent with other studies (Cahill et al., 2013; Wunsch et al., 2014) where aqueous Sr concentrations increased directly with CO_2 exposure. The authors also concluded that the release of Sr was due to calcite dissolution.

Trace elements of types 2 and 3 showed a second peak between 48 and 56 hours after the injection. Limestones present a certain physical heterogeneity due to the double matrix porosity coupled with the creation of preferential paths due to the meteoric diagenesis of dissolution. This physical heterogeneity can have consequences on the dynamics of transport. However, this behavior is not observed in major ions (Petit et al., 2021).

The decrease in concentrations suggests the trapping of trace elements by reverse reactions like precipitation or adsorption as carbonate minerals, hydroxides or through sorption. It is also possible that the hydraulic gradient of the aquifer was at the origin of the water renewal in the well F1 and therefore of the dilution of the concentration.

The group of type 4 is composed of Pb which showed a major decrease in their concentration immediately after injection. The fact that they were detected before the injection suggests that these elements are scavenged immediately after their migrating onto the aqueous phase. For example, Gheno et al., (2012) have shown that Pb was potentially directly trapped by adsorption reactions with Fe and Mn oxyhydroxides released in the aqueous phase. This could explain the abrupt decrease of Pb at the time of injection until its depletion.

Type 5 is only composed of Ba. It can initially be considered as being of type 4 because it decreases directly after the injection of CO_2 as Pb but the concentration in the aqueous phase increased after several hours (**Fig.6; Fig.7**). Also, the relationship between alkalinity and Ba concentrations does not show a high correlation ($R^2 = 0.01$) (**Fig.8**) which means that calcite do not control the Ba concentration in the aqueous phase, although it is known that Ba is often present in the crystalline structure of carbonates (Dickens and Bowen, 1971; Saito et al., 2020). Some studies have shown that dissolved Ba concentrations increased with the intrusion of the CO_2-rich water plume (Cahill et al., 2013; Trautz et al., 2013; Wunsch et al., 2014), but this is not happening in our case. This suggests that Ba is trapped directly after the limestone dissolves by associating with other elements before being released.

Lastly, Zn and Si concentrations do not seem to be affected by the rich-CO_2 water injection and constitute type 6 behavior. These two ions did not seem to show peaks but show great variability in their concentration, which was completely anarchic over time. Either these two elements have their behaviors naturally and the injection does not play any role in the variations in their concentration, or the mechanisms are very complex, and we have sporadic release elements. Shao et al., (2020) showed in their experiment the same behavior for Zn while Wilkinson et al., (2020) show that Zn is strongly correlated with Ca and has the same behavior as type group 1. This highlights the difficulties to compare studies with each other's as the amount of trace elements released in the aqueous phase will depend essentially on the initial amount of trace elements present in the rock in the solid-state and the hydrogeological context of the site. Therefore, it is important to carry out investigations before setting up CO_2 storage systems.

4.3 Water quality impact

4.3.1 Comparison of total content to the maximum released elements

It is possible to look at which elements are present and which are more easily mobilized by the CO_2 exposure conditions by comparing the maximum concentration observed in the aqueous phase to the total concentration present in the sediment. **Table 3** shows a mean of total trace elements concentrations present in the six limestone samples and the maximums trace elements dissolved concentrations observed for the F1 injection well during the experiment. Results from Baptiste Auffray, (2014) thesis work on limestone come from Saint-Emilion quarry and Lavoux carbonate samples are also included to compare.

The elements that migrate the most in the aqueous phase are not those present in greater quantities in the rock. For example, the samples contain an average of 158.22 mg/kg of Si and only 1.52% has migrated into the aqueous phase while they contain on average 5.64 mg/kg of Ba and 23.15% has passed into the aqueous phase. This shows that the amount of trace elements does not control the water chemistry, which is mainly controlled by the reactivity of the minerals in the rock and the speciation of the elements in the aqueous phase after injection of CO_2-rich water. This also explains the fact that some species in large quantities in the rock are not released in large quantities in the aqueous phase, like Fe. Furthermore, the high buffer capacity of the carbonate aquifer could also limit the carbonate dissolution and the released of trace elements into the aqueous phase.

4.3.2 Comparison of the total content of trace elements in the Saint Emilion limestones

Total trace elements concentrations in the six limestone samples are in adequacy with the scientific literature of Graf (1962) and Thompson et al., (1970) which synthesize the chemical composition of several carbonate rocks of different ages, facies, and origins. Only Ba, Fe, Mn Si, and Sr total concentrations appear to be a little low than the majority of limestone samples studied (Thompson et al., 1970). In our study, analyzes carried out on the rock samples showed that certain elements distribution was heterogeneous over the entire sedimentary column. The difference in the homogeneity along with the sediment core between elements such as Ba, Li, Mn, Pb, Sr and Zn, more homogeneous and Ag, As, Cd, Co, Cr, Fe, Ga, Mo, Ni, Sb, Se, Si and V, less homogeneous can be explained by returning to the formation of the rock during the Upper 1b Oligocene. The former such as Sr and Ba are markers of marine sedimentation while the others are markers of erosion. However, it is important to remember that only six samples from a core over 4 m long were taken and analyzed. In the end, visibility is low when it comes to the variation in concentrations along the sedimentary column. Likewise, each facies is only represented by three samples. The hypotheses of variations in concentrations within the same facies, suggesting that this makes it possible to discriminate by their geochemical composition, nevertheless remain open to criticism. It would therefore be interesting in future work to perform additional analyzes on other samples from the same core to complete these results.

However, it is not possible to advance these conclusions for the entire carbonate system of Saint-Emilion. Auffray, (2014) (**Tab.3**) showed results that highlight higher concentrations in general. Except for the elements Sb, Cu, Co, Cd, As and Ag which seem to be in relatively similar orders of magnitude. This comparison between F2 samples and Auffray's samples is possible as the samples come from the same quarry and analysis methods were similar (Auffray, 2014). Thus, the highest concentrations observed for the rest of the elements highlight the heterogeneity contained within the same carbonate system. This can be explained during the formation of these carbonates. The results obtained on the F2 sediment core are therefore not representative of the entire Saint-Emilion carbonate system. This highlights the advantage of carrying out wider studies as the impact on water quality would not have been the same, even under these injection conditions, if the experiment had been conducted elsewhere. Conducting a large sampling and analysis campaign on the solid phase to be able to circumscribe the heterogeneity of the trace elements content of the rock seems essential. This is all truer when we look at the trace elements concentrations in Lavoux's samples (**Tab.4)** (Auffray, 2014). On another scale, a comparison of the mean total trace elements in the limestone samples from the wells F2 between the boundstone and the grainstone does not show a significant difference: facies do not seem a discriminant factor in the trace element concentrations in this study.

4.3.3 Comparison of the maximum dissolved concentration and the maximum concentrations limits

One of the consequences of CO_2 exposure from groundwater is exceeding the environmental quality standards imposed. **Table 4** compares the maximum dissolved concentrations of traces elements obtained in well F1 with environmental quality standards for drinking water destinations according to (1) annex I of the decree of January 11th, 2007, relating to the limits and quality references of raw water and water intended for human consumption modified by the decree of August 4, 2017, and (2) the decree of December 9th, 2015 (INERIS, 2018) and guide values assigned to natural chemicals whose presence in drinking water is important from a health point of view (WHO, 2017) and quality references for irrigation waters (Ayers and Westcot, 1976). Results showed (at the well F1 scale) that As, Ba, and Se exceeds UE standards, but they return to background concentrations in approximately 20 hours. The return to normal conditions was fast. The carbonated system has great resilience. The small quantity of carbonated water injected combined with the strong buffering capacity of the carbonate system has made it possible to limit the risk of exceeding environmental quality standards and to make the limits short-lived. No concentrations exceeded irrigation water quality standards. Despite these results, it is important to emphasize that the impact would not have been the same under other conditions. However, other studies like Kharaka et al., (2010) have shown that the rise of major ions like Ca, Mg, K, and Na and metal elements like Ba in the aqueous phase, even if they do not exceed the limits standards can also compromise the potable water quality due to their contributions to total dissolved solids (Kharaka et al., 2010). Admittedly, the impact on the quality of the water of our experiment is weak but it is about condition near the surface with a relatively low volume of carbonated water. We must put ourselves back in the context of storage of millions of tonnes of CO_2 and a leak that can last over time. Furthermore, the limits and quality reference are for a large-scale aquifer and here we just discuss it at a very local scale (i.e., a few meters around the injection well). Therefore, modeling from field data could be an interesting tool to provide an overview of the modifications at a more important scale and under more drastic conditions.

5 Conclusion

A first field CO_2-rich water leak experiment was carried out in a shallow freshwater carbonate aquifer at the Saint-Emilion (France) pilot site in a limestone quarry. The addition of $CO_{2\ (aq)}$ to the aquifer modified the initial calcocarbonic equilibrium of the carbonate system. The decrease in pH, induced by the increase of $CO_{2\ (aq)}$ in the water, led to the dissolution of carbonates and the contribution of ions in the aqueous phase, also evidenced by the simultaneous increase in conductivity. The study of the chemical composition of the rock showed that the trace elements were associated with calcite, quartz and iron oxides present in smaller quantities. After the CO_2-rich-water injection, trace elements concentrations changed according to six types of behavior. The release of these elements in the aqueous phase is often strongly correlated with increasing alkalinity, presumably due to carbonate dissolution. As for the major ions, the weaker increases of the trace element concentrations in the wells (except for the injection well) were the result of the transport of the plume and the dilution from the injection well. The small amount of carbonated water injected, combined with the buffering capacity of the carbonate system, made it possible to limit the migration of trace elements to the aqueous phase and highlight the rapid resilience of the carbonated system in these injection conditions.

The geochemical impact of this experiment on the water quality of the aquifer was minimal. Only As Ba, and Se exceeded the drinking water standards for a few hours. Nevertheless, it is important to remember that the impact of a CO_2 leak will depend on the volume of the aquifer, the composition of the rock, and the volume of CO_2 involved. Thus, the results of this experiment provide answers to the behavior of a carbonate aquifer involved in a potential CO_2 leak and supplement the data already present literature on this subject. These data will be used for calibrating and validating geochemical models aimed at determining the potential for mobilization of trace elements following a CO_2 leak in future work.

6 Declaration of interests

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

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Figures, tables, and their captions

Figure 1 (Color should be used in print)

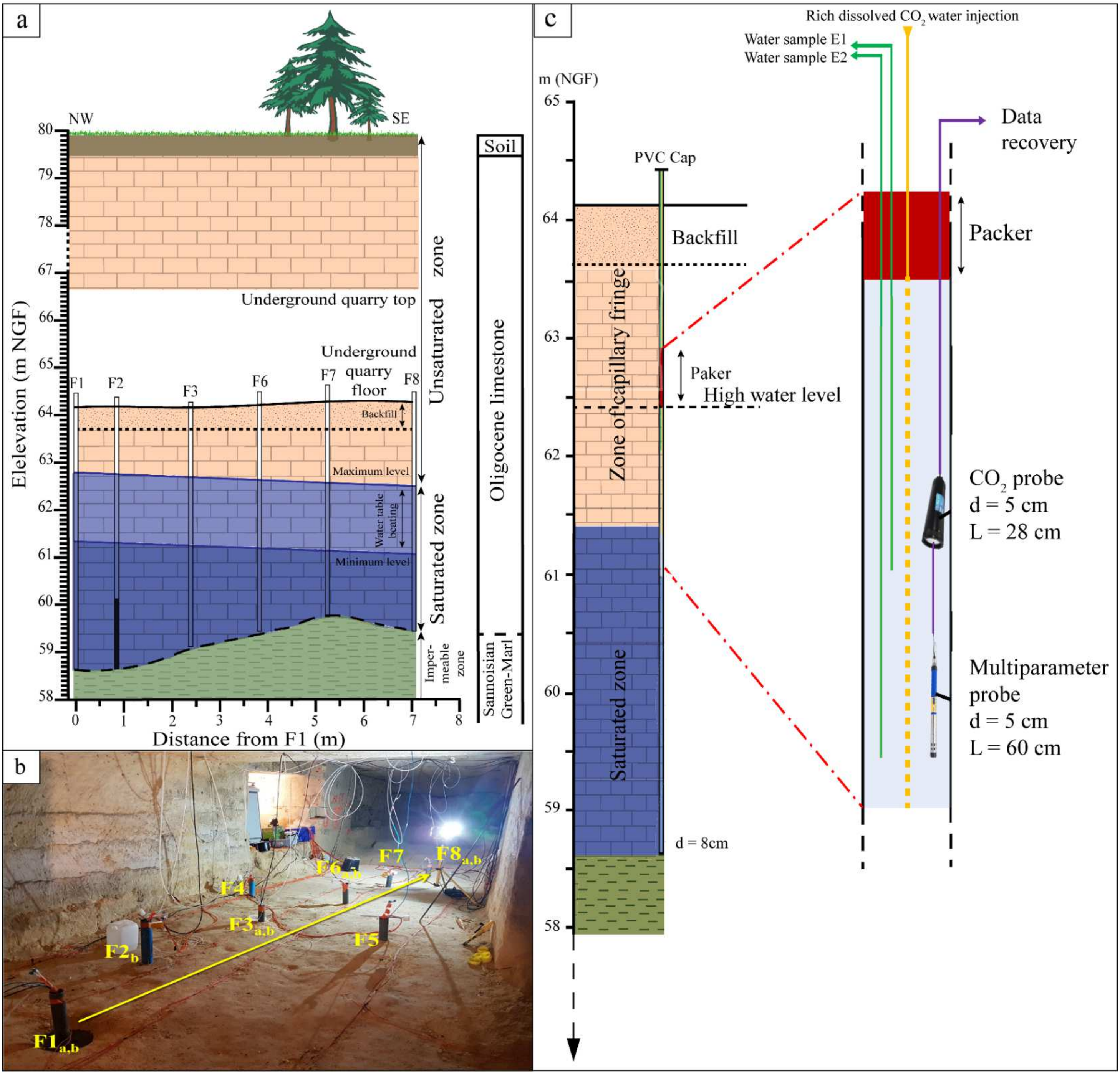


Fig.1: Configuration of the experimental site in the underground quarry **a:** Cross-section in the Upper 1b Oligocene limestone. The quarry floor is located approximately 16m from the surface. The water table is beaten over 1.40 m with a maximal hydraulic gradient of 5% and an NW-SE direction. The mean of the hydraulic gradient is 2% for this experiment and corresponds to the moment when the water table rise was 61.35 m NGF. Sannoisian green marls are visible around 59m NGF on average. The boreholes used for the experiment go through a part of the unsaturated zone and the saturated zone. **b:** Top view of the 8 boreholes (F1 to F8) on the quarry floor in the experimental zone. They are arranged along an axis parallel to the hydraulic gradient. The yellow arrow indicates the direction of the groundwater flow and the direction of propagation of the CO_2-rich water plume during the experiment. The index “a” near the borehole head indicates that the well is equipped with a multi-parameter probe. The index “b” indicates that the well is equipped with a CO_2 probe. F1 is the injection well. Samples of water were taken throughout the experiment in all boreholes and at two elevations. **c:** Example of configuration of well F1. The multiparameter probe, the CO_2 probe, and the sampling tubing are located below a packer. Samples were taken at depth E1 (25 cm) and E2 (70 cm) (respectively 61.10 m NGF, and 60.65 m NGF for the well F1).

Figure 2 (Color should be used in print)

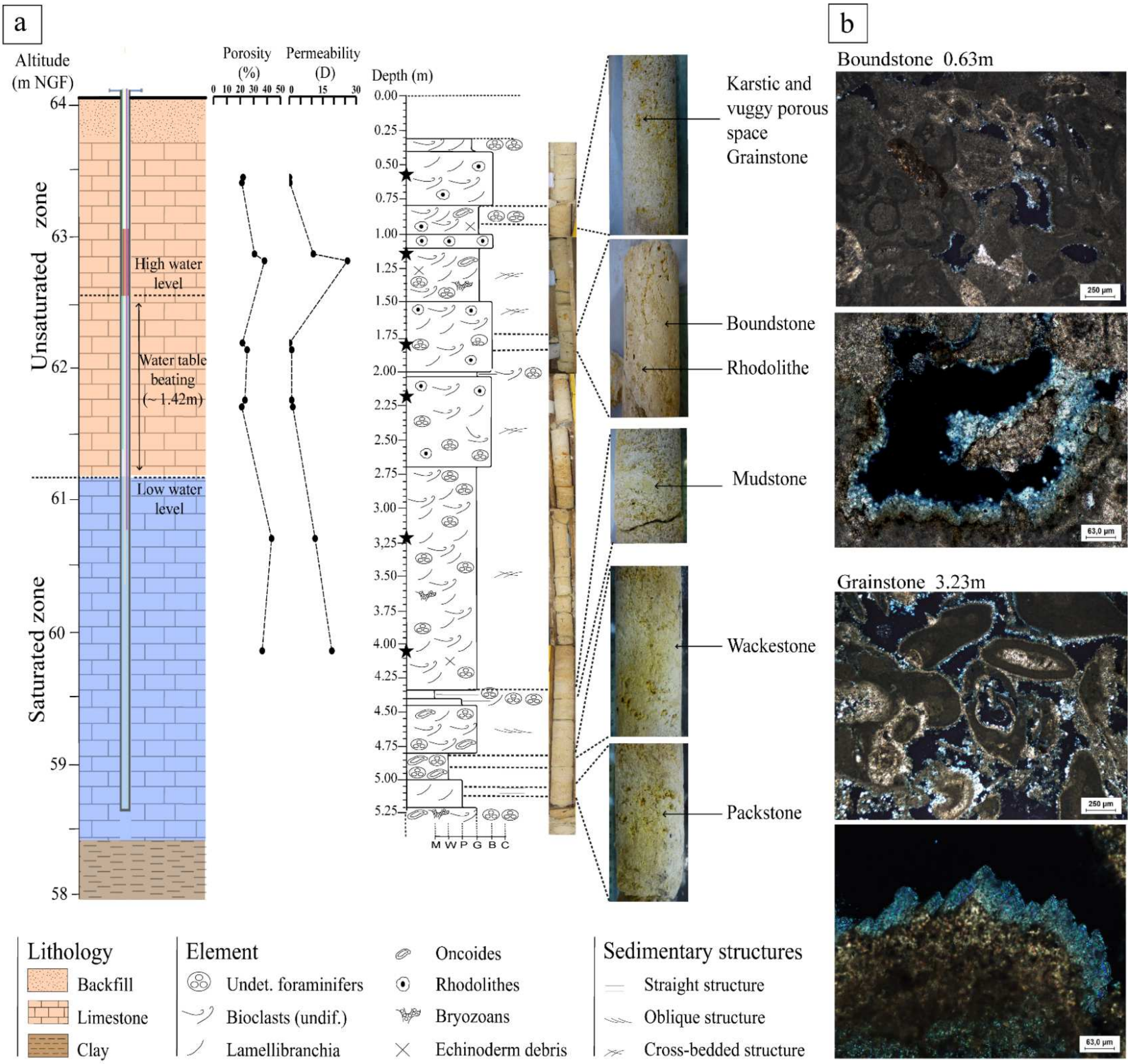


Fig.2: Physical characterization of the Oligocene limestone (Petit et al., 2021, modified). **a:** Cross-section of well F2: From right to left, the drawing shows (1) the hydrogeologic context with the maximum and minimum level of the water table beating, the thickness of the limestone layer, and the start of clay formation; (2) the evolution of porosity (%) measured by

Hg-injection; (3) the evolution of permeability (D) measured by variable head air permeameter methods respectively. The porosity and the permeability were measured at a different level from 63.5 m to 59.5 m NGF, throughout the capillary fringe and saturated zone; (4) the stratigraphic log and associated macroscopic facies. Black stars represent the places in the sediment core where samples were collected at 0.63, 1.15, 1.80, 2.22, 3.23 and 4.05 meters from the quarry floor (67.17m NGF). Total trace metal element concentrations were measured on these six limestone samples (**Tab.2**). The facies represented are for the most part grainstone and boundstone. **b:** Microscope photograph of the limestone: boundstone has been collected at 0.63 meters from the quarry floor and the grainstone at 3.23 m. These views highlight the porosity difference between the two facies. They also highlight the larger share of recrystallized space in the pores of the grainstone.

Figure 3 (Color should be used in print)

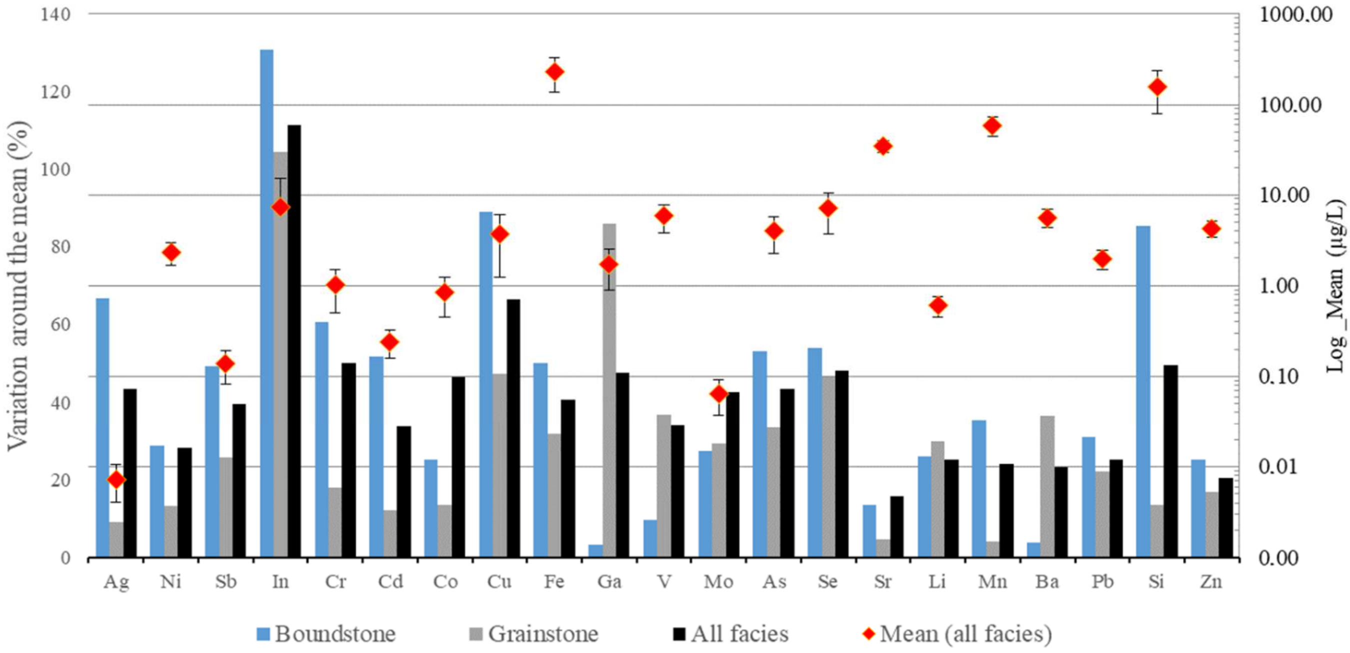
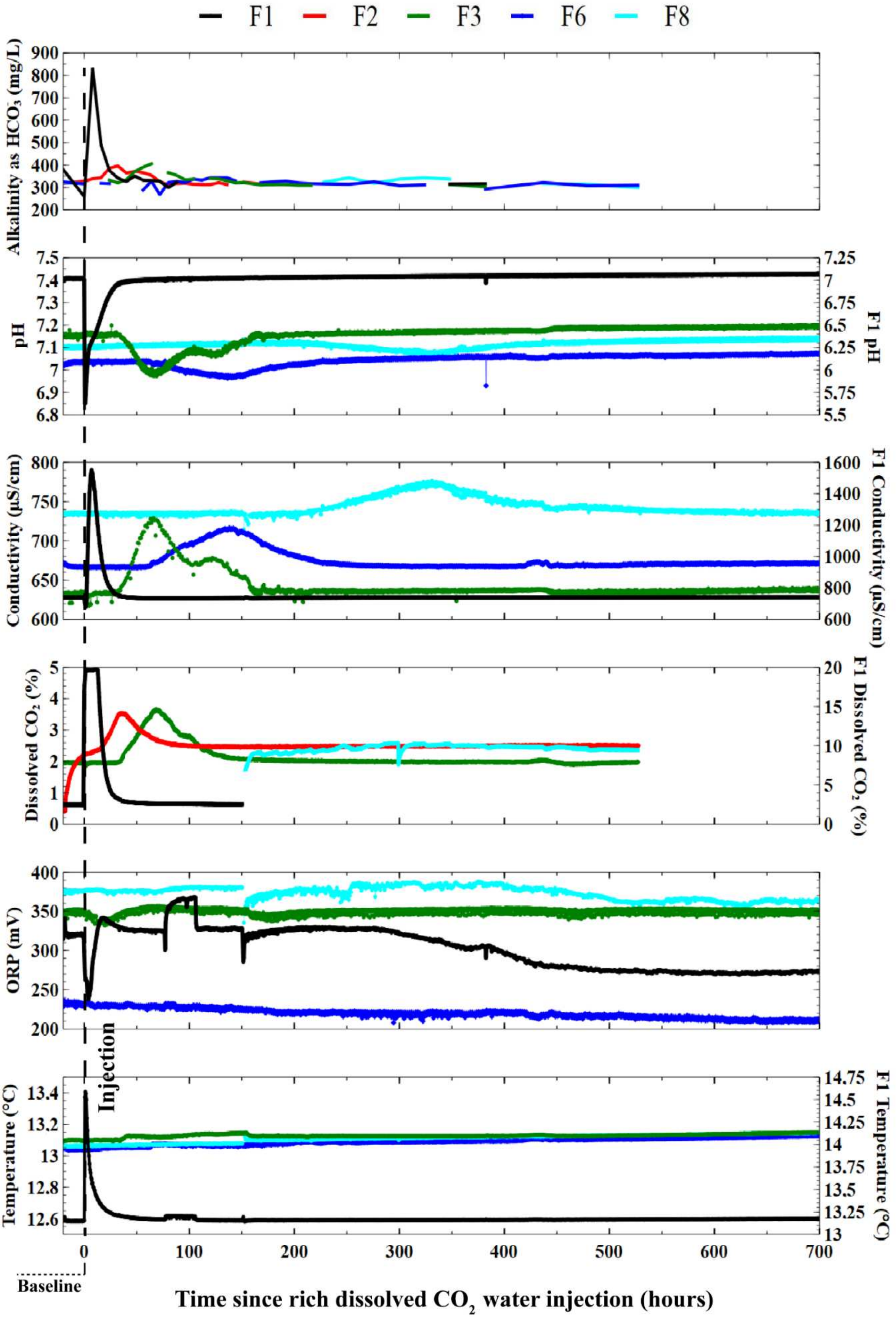


Fig.3: Variation of the concentrations around the mean in percent (i.e. standard deviation in percent) for each trace ion analyzed in the 6 carbonate rock samples taken from the F2 core. Blue bars represent the degree of percent variation around the mean in three boundstone samples. Grey bars represent the degree of percent variation around the mean in three grainstone samples. The black bars correspond to the degree of variation around the mean of the concentrations of each trace elements of the six samples. The mean concentrations of the six samples (± standard deviation) of each element are represented by the red diamonds (µg/L). The secondary vertical axis is expressed in log.



1142 **Figure 4 (Color should be used in print)**

Fig.4: Evolution and comparison of the different physic-geochemical parameters measured in wells F1, F2, F3, F6, and F8. The parameters were obtained using multiparameter probes (temperature (±0.1°C); ORP (±5.0 mV at 25°C); conductivity (± 0.5% of reading plus 1 µS/cm from 0 to 100.000 µS/cm) and pH (±0.1 pH units or better) and CO_2 probes (pCO_2 10-900 mbar ± 10%). Well F2 is only equipped with a CO_2 probe. Alkalinity (as HCO_3^- ; mg/L) were measured in the laboratory by the Inflection Point Titration Method. The injection started at t=0 and lasting 1.5 hours. For a better visibility, data for the conductivity, dissolved CO_2, and pH from well F1 have been added on a second y-axis on the right of the graph. The CO_2 probe initially installed in well F1 was moved to well F8 from 145 hours after the plume of CO_2 had dissipated in F1. Therefore, there are no data for the F8 well before 145h. The sudden decrease occurring at this time corresponds to the withdrawal and re-filling of the probe.

Figure 5 (Color should be used in print)

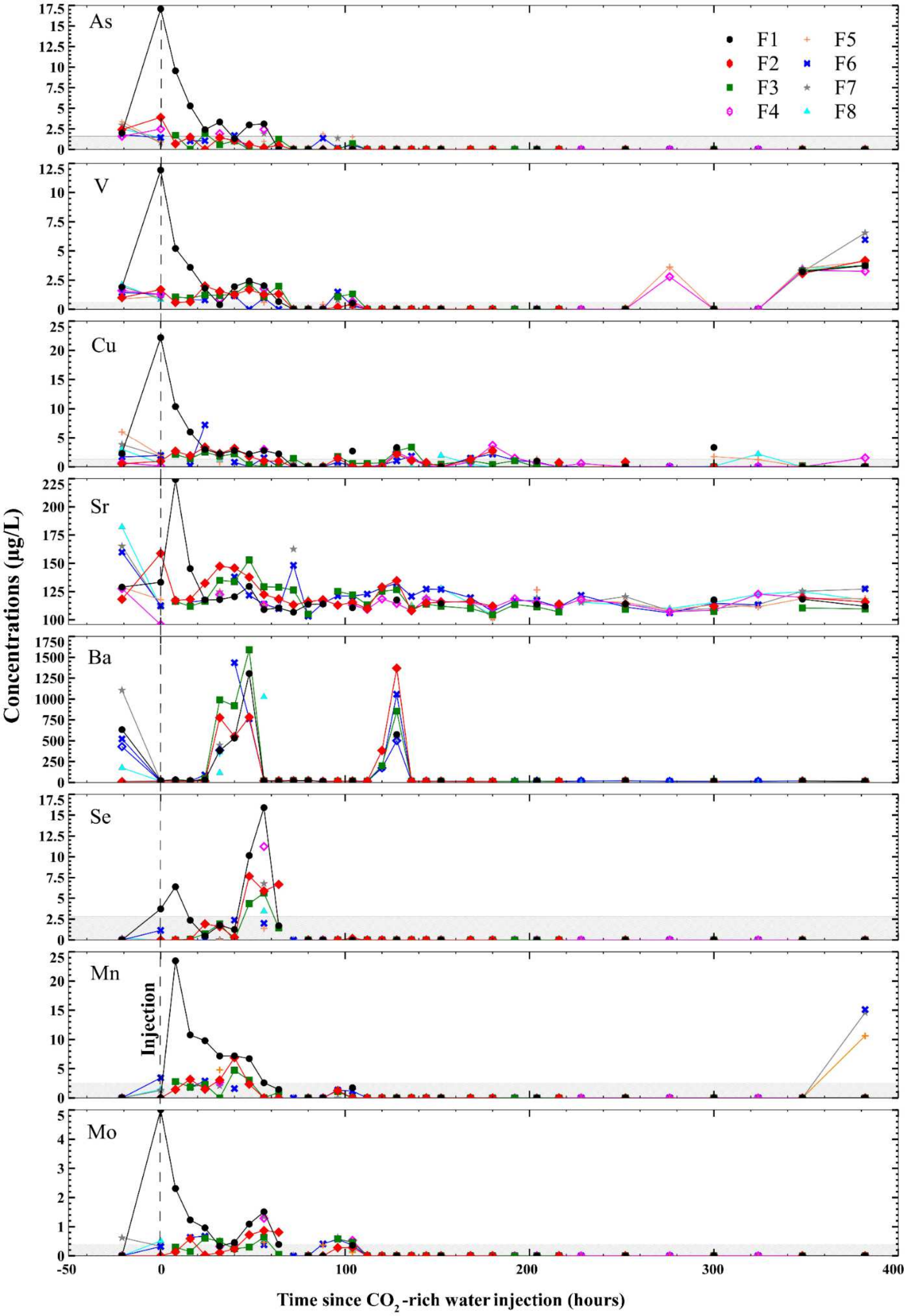


Fig.5: Evolution of As, V, Cu, Sr, Ba, Se, Mn, and Mo concentrations of the wells F1, F2, F3, F4, F5, F6, F7 and F8 in the function of time since CO_2–rich water injection. Concentrations units are in µg/L. The axis F1 to F8 is parallel to the flow direction of the aquifer (Fig.1). Waters samples were collected at 25 cm under the water table (i.e. 61.10 m NGF for the well F1). The hatched area highlights samples under the detection limit. The injection started at t=0.

1189

1190 **Figure 6 (Color should be used in print)**

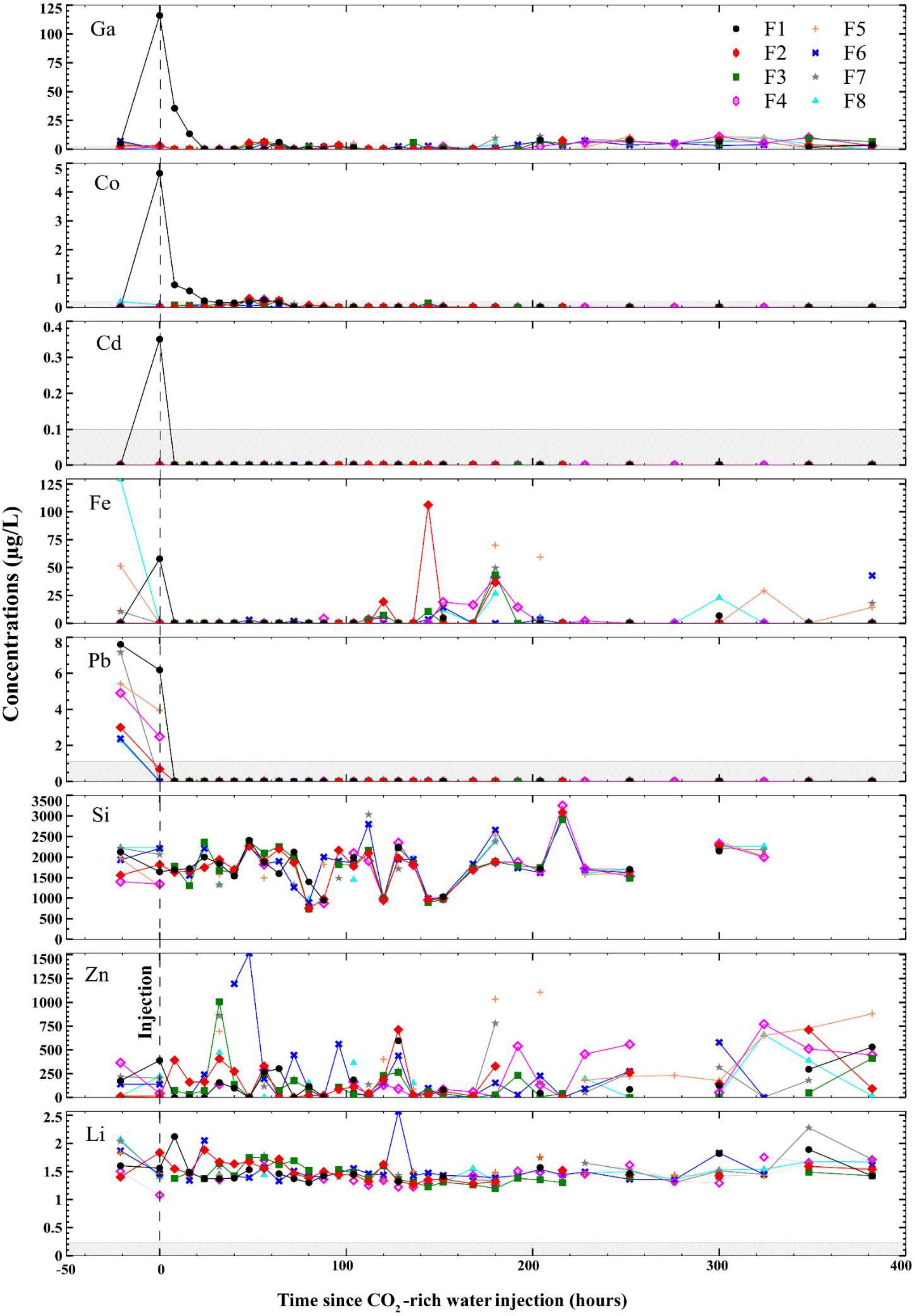


Fig.6: Evolution of Ga, Co, Cd, Fe, Pb, Si, Zn and Li concentrations of the wells F1, F2, F3, F4, F5, F6, F7 and F8 in the function of time since CO_2 -rich water injection. Concentrations units are in µg/L. The axis F1-F2-F3-F6-F7-F8 is parallel to the flow direction of the aquifer. The axis F3-F4-F5 is perpendicular to the flow direction of the aquifer. Waters samples were collected at 25 cm under the water table (i.e. 61.10 m NGF for the well F1). The hatched area highlights samples under the detection limit. The injection started at t=0.

Figure 7 (Color should be used in print)

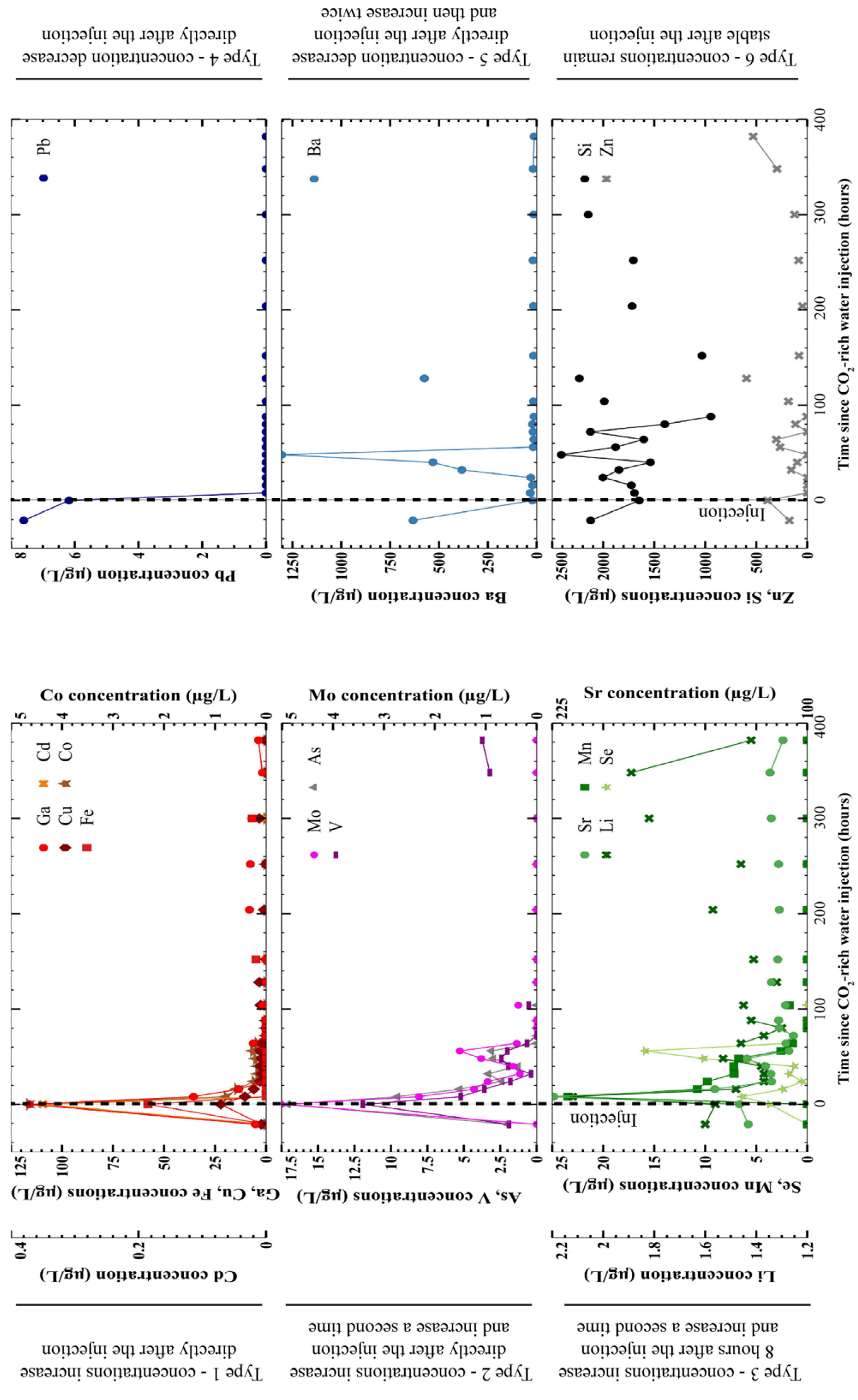


Fig.7: Evolution of the trace element concentrations of the well F1 function of time since injection (µg/L). The data presented correspond to the concentrations at depth E1 (25cm) under the water table (i.e. 61.15 m NGF). The injection started at t=0. Elements have been grouped into six types according to their behavior following the injection of CO_2-rich water.

Figure 8 (Color should be used in print)

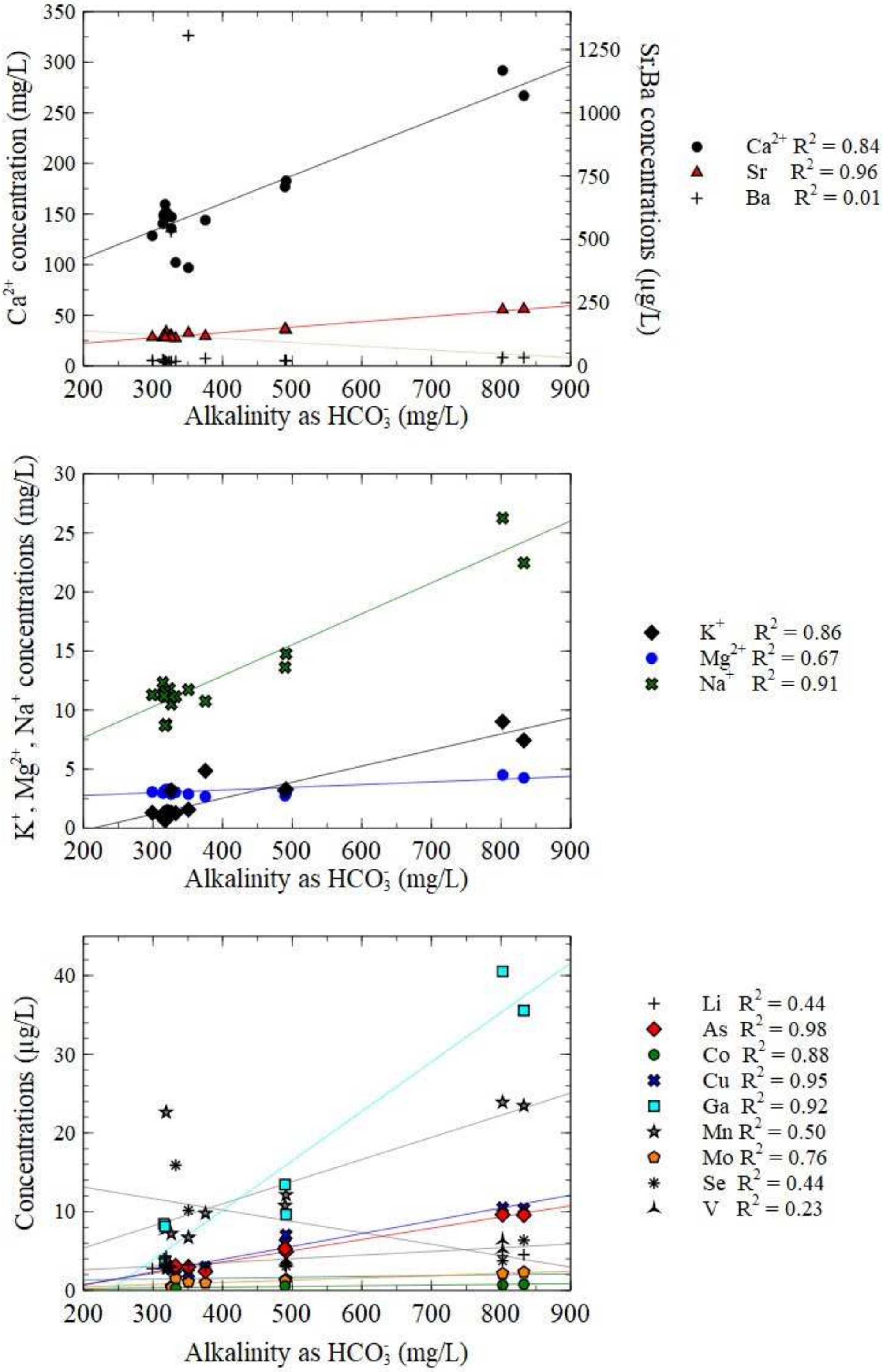


Fig.8: Relation between the alkalinity represented by the HCO_3^- concentrations and the different cations and trace elements analyzed. The concentrations of the cations K^+, Na^+, Ca^{2+} are given in mg/L and the concentrations of the trace elements are in µg/L. The coefficient of determination (R^2) has been added to the graph for each element.

Figure 9 (Color should be used in print)

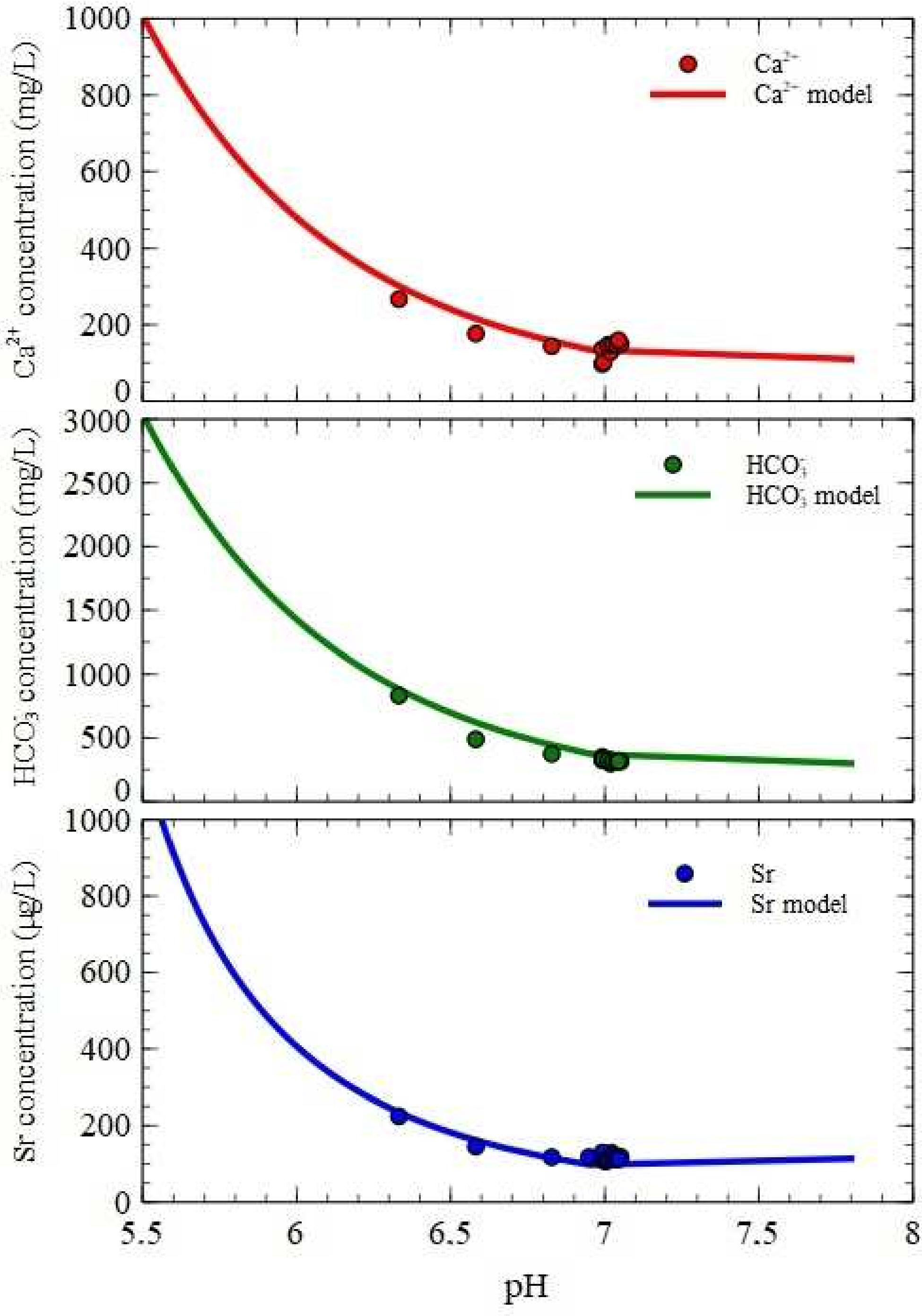


Fig.9: Concentrations of Ca^{2+}, HCO_3^- and Sr as function of pH. The points correspond to the experimental data. The curve corresponds to the results of the carbonate dissolution model performed using PhreeqC.

Table 1

Tab.1: Characteristics of the injection experiment: physicochemical parameters of the rich dissolved-CO_2-water injected and injection conditions.

Physicochemical parameters of the injected water	
Composition of the gas used for gasified	90% CO_2 + 9% He + 1% Kr
Gasified water volume (L)	200
pH	5.45
Conductivity (µS/cm)	645
Injection conditions	
Injection velocity (L/min)	2.2
Injection duration (hours)	1.5
Velocity of the groundwater (m/day)	0.8

Table 2

Tab.2: Elemental composition of the 6 samples of limestone analyzed using X-ray fluorescence (XRF). Values represent the mean of six punctual random analyses on a circle of 100 µm in diameter, on each powder samples. Results are semi-quantitative and in percent (%). The symbol ND means that the element was not detected by the machine. The grey columns underline the most represented elements.

	Mass (%)	Al	Si	S	K	Ca	V	Ti	Mn	Fe	Cu	Sr	Zn	Pt	Ba
Boundstone	**F2_0.63**	0.50	4.04	0.01	0.14	94.04	ND	0.09	0.09	1.10	ND	ND	ND	ND	ND
	F2_1.80	18.96	13.35	0.01	2.87	62.02	0.01	0.22	0.01	2.37	0.02	ND	0.01	0.05	0.10
	F2_2.22	ND	3.42	0.01	0.02	95.68	ND	ND	0.02	0.86	ND	ND	ND	ND	ND
Grainstone	**F2_3.23**	ND	3.14	0.50	ND	92.11	ND	ND	2.23	1.22	0.81	ND	ND	ND	ND
	F2_4.05	2.99	8.17	0.03	1.41	83.51	ND	0.06	0.24	3.59	ND	ND	ND	ND	ND
	F2_1.15	2.04	25.09	ND	2.74	69.56	0.04	0.05	0.06	0.34	0.00	0.03	ND	ND	ND

Table 3

Tab.3: Mean of the total trace elements concentrations contained in our six limestone samples collected during the F2 drilling (mg/Kg). Average concentrations were also calculated for each facies (3 samples per facies). After tri-acid digestion with HCl, HNO_3, and HF, concentrations of Ag, As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sr, V and Zn were obtained using an ICP-MS (EPOC Laboratory, France) while Be, Fe, Ga, Li, Mn, In, Se and Si were obtained using an ICP-AES (ENSEGID, France) on a representative aliquot of rocks samples (i.e. 150 mg of each samples). Sd means standard deviation. Values on the right are results come from Baptiste Auffray's (2014) thesis work on carbonates rocks come from Saint-Emilion quarry too and Lavoux carbonates samples. The <LD symbol is used to denote a value under the detection limit. The ND symbol indicates no data. Values on the left are the maximums concentrations of dissolved trace elements in the injection well F1.

(µg/L)	***Maximum concentration of $ETM_{dissolved}$ in the aqueous phase (Well F1)***	**Mean concentration on six limestone samples (this study) (mg/Kg)**		**Mean concentration on bounstone samples (this study) (mg/Kg)**		**Mean concentration on grainstone samples (this study) (mg/Kg)**		**Limestone samples *(Auffray. 2014)* (mg/Kg)**	
		(n=6)	***Sd***	***(n=3)***	***Sd***	***(n=3)***	***Sd***	**Saint Emilion limestone**	***Lavoux Limestone***
Ag	<LD	0.01	<0.00	0.01	<0.00	0.01	<0.00	0.04	0.02
As	17.08	3.97	1.72	3.15	1.68	4.79	1.61	9.42	1.26
Ba	1305.50	5.64	1.31	5.62	0.21	5.65	2.06	35.94	2.23
Be	<LD	<LD	<LD	<LD	<LD	<LD	<LD	ND	ND
Cd	0.35	0.24	0.08	0.24	0.13	0.24	0.03	0.89	0.41
Co	4.65	0.85	0.39	0.51	0.13	1.18	0.16	1.61	0.74
Cr	<LD	1.01	0.50	1.19	0.72	0.83	1.15	13.58	9.32
Cu	22.18	3.67	2.44	2.40	2.13	4.95	2.35	4.93	1.27
Fe	57.88	233.16	95.13	256.91	128.57	209.41	66.34	3981.65	1347.74
Ga	116.04	1.71	0.82	2.17	0.07	1.26	1.08	ND	ND
In	<LD	7.25	8.08	3.85	5.04	9.51	9.93	ND	ND
Li	2.12	0.61	0.15	0.60	0.16	0.61	0.18	ND	ND
Mn	23.46	58.53	14.08	51.28	18.20	65.78	2.62	282.80	33.41
Mo	5.01	0.06	0.03	0.04	0.01	0.08	0.02	ND	ND
Ni	<LD	2.32	0.65	1.86	0.53	2.78	0.37	6.68	5.80
Pb	6.18	1.98	0.50	1.83	0.57	2.13	0.47	5.09	0.43
Sb	2.53	0.14	0.05	0.11	0.05	0.17	0.04	0.24	0.05
Se	15.90	7.15	3.45	8.02	4.34	6.28	2.92	0.93	1.77
Si	2410.60	158.22	78.40	132.28	112.78	184.16	25.11	ND	ND
Sr	224.26	34.59	5.39	30.40	4.09	38.79	1.81	180.90	160.76
V	11.92	5.84	1.99	4.79	0.46	6.89	2.53	30.98	5.75
Zn	595.53	4.25	0.87	3.92	0.99	4.57	0.77	17.33	30.34

Table 4

Tab.4: Values on the left are the maximums concentrations of trace elements dissolved concentrations in the injection well F1. These values are compared with the quality standards for drinking water according to annex I of the decree of January 11th, 2007, relating to the limits and quality references of raw water and water intended for human consumption modified by the decree of August 4th, 2017, and the decree of December 9th, 2015 (INERIS, 2018) and guide values assigned to natural chemicals whose presence in drinking water is important from a health point of view (WHO, 2017). These values are also compared to the recommended maximum concentrations of trace elements in irrigation waters. These quality references are for water used continuously on all soils (Ayers and Westcot, 1976). The <LD symbol is used to denote values under detection limits. The symbol “-“ indicates that no data has been found for this element.

(µg/L)	F1 Maximum ETM dissolved	INERIS, 2018	WHO, 2017	Ayers and Westcot, 1976
Ag	<LD	-	-	-
As	23.9	10	10	100
Ba	1305.5	700	700	-
Be	<LD	-	-	100
Cd	0.7	5	3	10
Co	6.4	-	-	50
Cr	<LD	50	50	100
Cu	36.9	2000	2000	200
Fe	88.0	200	-	5000
Ga	116.0	-	-	-
In	<LD	-	-	-
Li	2.1	-	-	2500
Mn	23.9	50	-	200
Mo	5.5	-	-	10
Ni	<LD	20	70	200
Pb	7.6	10	10	5000
Sb	2.5	5	20	-
Se	15.9	10	40	20
Si	2410.6	-	-	-
Sr	224.3	-	-	-
V	11.9	-	-	100
Zn	1582.9	-	-	2000