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► To cite this version:

Jean Rillard, Olivier Pourret, Paolo Censi, Claudio Inguaggiato, Pierpaolo Zuddas, et al.. Behavior of rare earth elements in an aquifer perturbed by CO₂ injection: Environmental implications. *Science of the Total Environment*, 2019, 687, pp.978 - 990. 10.1016/j.scitotenv.2019.05.490 . hal-03826819

HAL Id: hal-03826819

<https://hal.science/hal-03826819>

Submitted on 26 Oct 2022

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1 **Title: Behavior of Rare Earth Elements in an Aquifer Perturbed by CO₂ Injection : Environmental**
2 **Implications**

3 **Highlights**

- 4 • The behavior of dissolved REE in groundwater within the critical zone is difficult to evaluate
- 5 • Behavior of REE and trace metals was studied upon an aquifer perturbed by CO₂ injection
- 6 • A geochemical model was used to evaluate dissolved REE behavior
- 7 • REE complexation is/are the main factors controlling REE release and fractionation
- 8 • REE fractionation can be used to predict bulk water-rock interaction

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23 **Keywords :**

24 Rare Earth Elements, CO₂ perturbation, REE model complexation, lanthanide tetrad effect, field
25 experiment, Critical zone

26

27 **Abstract**

28 Three cubic-meters of CO₂-saturated water was injected into a subsurface fractured aquifer in a post-
29 mined area, using a push-pull test protocol. Groundwater samples were collected before and after
30 CO₂-injection to quantify geochemical changes. CO₂-injection initially reduced the pH from 7.3 to 5.7,
31 led to the enrichment of major ions (Ca²⁺, Mg²⁺, and alkalinity), and dissolved trace metals (including
32 Fe, Mn, As, and Zn) in the groundwater. Rare earth elements (REE) and yttrium concentrations were
33 also measured in these samples before and after CO₂ perturbation, to evaluate their behavior. An
34 enrichment of total Y plus REE (REY) occurred. REY fractionation was observed with higher heavy REE
35 (HREE) enrichment compared to light REE (LREE), and significant variations in La/Yb and Y/Ho ratios
36 were observed following CO₂ perturbation. Enrichment by a factor of three was observed for Y, Lu, and
37 Tm, and by nearly one order of magnitude for Dy and Yb. A geochemical model was used to evaluate
38 the amount of REE aqueous ions complexed over the experiment. Modeling of the results showed that
39 speciation of dissolved REE with carbonate, and desorption from an iron oxyhydroxide surface were
40 the main factors controlling REE behavior. This study increases an understanding of dissolved REE
41 behavior in the environment, and the potential use and limitations for applying iron oxides for REE
42 recovery from mine drainages. Furthermore, the description of REE fractionation patterns may assist
43 in surveying CO₂ geological storage sites, surveying underground waste disposal sites, and for
44 understanding the formation of ore deposits and fluid inclusions.

45 **Introduction**

46 The behavior of rare earth elements (REEs) in natural environments has been extensively studied
47 (Michard 1989; Johannesson et al. 1995, 1997; Choi et al. 2009; Noack et al. 2014). REEs are valuable
48 as components in electronic and renewable energy technologies. The European Community classifies
49 REEs as critical raw materials (European Community, 2010, 2017).

50 An understanding of REE mobility, their accumulation, and their global cycling mechanisms in the
51 natural environment, is important for evaluating their reserves for future use (Pourret and Tuduri
52 2017), and to anticipate environmental issues involved in the intensive exploitation of these materials
53 (Filho 2016; Edahbi et al. 2018a).

54 Extraction of REEs and associated critical elements have been optimized using in-situ leaching
55 techniques to enhance their extraction rates (Haschke et al. 2016; Vahidi et al. 2016). Dissolved REE
56 fractionation patterns have been used as a proxy for understanding many geodynamic processes, such
57 as magmatic melting and water-rock interactions (Bau 1996, 1999; Irber 1999). Dissolved REE studies
58 also suggest methods for tracing the environmental impacts of human activity, including shale gas
59 hydraulic fracturing fluid analysis (Yang et al. 2018). The physico-chemical properties of REEs allow

60 them to be used as robust proxies for studying low and high-temperature geochemical reactions
61 (Pérez-López et al. 2010; [Hannigan and Sholkovitz](#) 2001).

62 The geological storage of CO₂, which is part of carbon capture and storage (CCS) technology, has been
63 considered a potential method for reducing the accumulation of atmospheric greenhouse gases (IPCC
64 2005). Geological storage involves injecting CO₂ previously captured from industrial processes into
65 deep underground rock formations. The aim of doing so is to permanently remove CO₂ from the
66 atmosphere. The effectiveness of storage depends on the reservoir storage site's capacity and
67 integrity. CO₂ storage capacity is driven by porosity, reservoir permeability, and the existence of a
68 sufficient impermeable barrier or cap rock for containing the CO₂ permanently. Several types of
69 geological formations have been identified as having a suitable capacity for CCS. To date, these
70 reservoirs include deep saline aquifers, coal bed formations, oil and gas reservoirs exploited through
71 enhanced oil recovery technics using CO₂, and finally, depleted oil and gas reservoirs. Among these
72 storage sites, deep saline aquifers have been identified for having larger storage capacity and
73 worldwide distribution (Bachu et al. 2007).

74 Once injected, part of the CO₂ will be physically trapped beneath the impermeable cap rock, which
75 acts as a seal, and the remaining CO₂ will dissolve into the aqueous phase. Part of this dissolved CO₂
76 may react with reservoir rocks to form a new mineral (CO₂ mineral trapping), or alternatively, may
77 remain dissolved into the aqueous phase (solution trapping) (Bachu et al. 1994). As such, an
78 understanding of CO₂-water-rock interaction processes are of primary importance for validating the
79 feasibility and effectiveness of CCS. To study this phenomenon, numerous experiments have been
80 performed under laboratory conditions alongside geochemical models (Little and Jackson 2010; Liu et
81 al. 2012; Humez et al. 2013; Pearce et al. 2015). Modeling of experimental data offers accuracy for
82 chemical reaction descriptions, but is fairly limited in terms of time and scale. The study of natural CO₂
83 hydrothermal-rich water offers good analogues for studying long-time CO₂-water-rock interaction, but
84 appears limited in its ability to describe chemical phenomena with a good degree of precision (Gilfillan
85 et al. 2009; Keating et al. 2010; Gal et al. 2012). Several field experiments have been performed as pilot
86 tests for identifying the scale of CCS sites, and to identify technical and scientific gaps (see Jenkins et
87 al. 2015, and references therein).

88 The above-noted experimental works have shown that several issues must be resolved, including the
89 environmental risks involved in CCS processes. Several preliminary experiments, in the field and in the
90 laboratory, suggest the potential risks of releasing dissolved trace metals into subsurface freshwater
91 aquifers. The release of dissolved metals may be caused by CO₂-enriched brine leaking from an initial
92 deep storage reservoir, and moving toward the surface. Among other phenomena, the remobilization

93 of trace metals is related to in-situ pH and redox perturbations involved in CO₂-injection or leakage. In
94 particular, CO₂ perturbation may involve pH acidification, thereby enhancing dissolution of the
95 reservoir rock, and generating the release of trace metals that may initially be present in the reservoir
96 rock minerals, or that have been sorbed onto mineral surfaces (Kharaka et al. 2006; Little and Jackson
97 2010; Wilkin and Digiulio 2010; Siirila et al. 2012; Wunsch et al. 2013; Rillard et al. 2014; Jenkins et al.
98 2015). Understanding the fate and transport of trace metal elements in subsurface geological
99 environments is therefore important. These issues are also valuable for other geoenvironmental
100 applications such as toxic waste disposal, long-term underground storage of radioactive waste, and
101 monitoring of waste landfills.

102 CO₂-water-rock interactions are driven by the crystallization of newly-formed minerals at the fluid-rock
103 interface. Thus, the feasibility of CO₂ storage is based on a surface-driven process and elements of the
104 lanthanide series which, along with yttrium, represent a promising geochemical tool for describing
105 processes occurring at the interface between injected fluids and host rock. The behavior of REY in
106 groundwater may help to understand the reactions occurring at the water-rock interfaces following
107 interaction with injected CO₂.

108 Shand et al. (2005) highlight that the concentration of dissolved REE in groundwater is controlled by
109 several factors. These include the release of chemical elements resulting from weathering processes,
110 groundwater pH and redox reactions, adsorption processes, complexing ligands in groundwater, and
111 physical hydrogeological factors (hydrodynamic processes and residence time). Studies of dissolved
112 REE behavior within geothermal fluids and natural CO₂-rich water sources have produced useful
113 results. A fractionation pattern for REEs occurs during CO₂, water, and rock interaction processes, and
114 a strong relationship has been identified between dissolved REEs and water pH (Lewis et al. 1998;
115 Michard 1989; Shand et al. 2005; Inguaggiato et al. 2015). The use of REEs as tracers of high salinity
116 brine leakage detection in CCS applications has been studied under laboratory conditions (McLing et
117 al. 2014). However, several issues were presented, such as the high salinity content of samples, which
118 caused analytical problems for trace metal analyses.

119 REE signatures in fluid inclusions is also a key parameter for enhancing an understanding of the
120 behavior of deep geological fluids. In particular, REE fractionation patterns are good proxies for
121 evaluating the physico-chemical conditions, fluid-mixing, and precipitation processes operating during
122 the genesis of valuable geological resources, such as oil, gas, and ore deposits (Zwahlen et al. 2019;
123 Shu and Liu 2019; Perry and Gysi 2018)).

124 During mineral crystallization, REEs behave as a function of their ionic charge and radius (charge and
125 radius controlled (CHARAC) processes; see Bau 1996). During aqueous processes, however, these

126 metal cations react based on their external electronic configuration. As such, the main change in the
127 features of normalized REE concentrations, and in the Y/Ho ratio, can be recognized through
128 interactions at the rock-fluid interface (Bau et al. 1998, 2003; Irber 1999; Negrel et al. 2000; Takahashi
129 et al. 2002). Of special importance is the scavenging of REEs by metallic oxide and hydroxide phases
130 (i.e. oxyhydroxides such as iron and manganese oxyhydroxides), which affects the form of REEs in
131 aqueous media (De Carlo et al. 1998; Quinn et al. 2006; Schijf and Marshaal 2011; Liu et al. 2017).
132 Complexation of REEs onto iron and manganese oxides is strongly pH-dependent (Bau 1999; Verplanck
133 et al. 2004; Quinn et al. 2006, 2007). The binding of these cations to an amorphous phase such as
134 ferrihydrite (e.g. $\text{Fe}(\text{OH})_3$) is important, due to the large reactive surface area. Using zerovalent iron
135 nanoparticles for REE recovery from acid mine drainage under laboratory conditions showed the ability
136 of these oxyhydroxide minerals to remove REEs from a solution (Crane and Sapsford 2018).
137 Fractionation between light REEs (LREEs) and heavy REEs (HREEs) occurs during scavenging onto metal
138 oxides. This is primarily driven by dissolved species complexation, particularly in the presence of
139 carbonate species (De Carlo et al. 1998; Bau 1999; Ohta and Kawabe 2001; Quinn et al. 2007; Schijf
140 and Marshall 2011; Munemoto et al. 2015). Many studies have evaluated REE complexation with
141 organic and inorganic ligands. The complexation process of REEs occurring on mineral or organic
142 surfaces is key to understanding the behavior of dissolved REE patterns in the environment (Wood
143 1990; Tang and Johannesson 2003; Pourret et al. 2007; Pourret and Martinez 2009; Pourret et al.
144 2010).

145 Understanding dissolved REEs' behavior is challenging, due to the involvement and interdependence
146 of the phenomena described above. The aim of this experimental work is to study the potential
147 enrichment of dissolved trace metals and REY in groundwater perturbed by CO_2 , and its potential
148 application to CO_2 geological storage safety site assessment. An existing study employing this
149 experiment focused on major chemical elements and trace metal remobilization for studying the
150 potential environmental issues involved in CCS (Rillard et al. 2014). A second set of samples, collected
151 during the same fieldwork, was used to study the behavior of dissolved REE. The aim of the present
152 study is to quantify the effect of CO_2 and pH-perturbation of the aquifer on release of dissolved REY.
153 This work may enhance an understanding of the fate and transport of dissolved REEs and associated
154 trace metals into the environment, for evaluating the safety of geological CO_2 storage. The results may
155 also be useful for other geoengineering applications, including the geological storage of radioactive
156 waste and mine site remediation.

157

158

159 **1. Geological and hydrogeological site setting**

160 The detailed geological and hydrogeological settings of the experimental site is described in Rillard et
161 al. (2014). The experimental site is located in the Lodève area, Southern France, roughly 80 km north
162 of Montpellier. The local geology involves large Permian sandstones and shales lying on top of
163 Cambrian dolomites. Sandstones are dark-red in color, due to high concentrations of iron hydroxides,
164 while shales are characterized by grey coloring, due to their high organic matter content. The
165 experiment site is situated within a 400 m-thick sandstone and shale formation. From the 1950s to the
166 early 1990s, this area had been extensively mined for uranium and arsenic using underground galleries
167 and open pit mines, due to the high concentration of trace metals in the bedrock.

168 Denser mineralized deposits representing higher concentrations of metals can be found in vein
169 deposits throughout the fractured network. The mineralization processes have been attributed to
170 hydrothermal fluid circulation and associated secondary mineral precipitation (Brockamp and Clauer
171 2013; Laurent et al. 2017). The primary mineralogical association between arsenic and uranium refers
172 to arsenuranoapatite deposits (Dal Bo et al. 2015). This area is also characterized by hydrothermal
173 activity, with hot springs that are sometimes naturally enriched with CO₂, and locally exploited for
174 geothermal energy (Bonnaveira et al. 1999).

175 The sandstone and shale formations are characterized by low permeability (estimated by a pumping
176 test at 10⁻⁷ m.s⁻¹) and low total porosity (estimated at less than 5%). Groundwater circulation mainly
177 occurs via a network of rock fractures.

178 The following average modal composition of major minerals in the host-rock was determined:
179 dolomite (20%), albite (20%), K-feldspar (30%), quartz (15%), illite (10%), other (5% calcite and iron
180 oxihydroxide, siderite, and pyrite) (Brockamp and Clauer 2013; Chopin 2016). However, mineral
181 compositions may vary among different strata. Indeed, significant amounts of neoformed mineral
182 phases were observed along the surface fractures by camera logging, performed immediately after
183 experimental well implementation. In particular, the presence of amorphous iron oxihydroxides was
184 identified as a product of pyrite oxidation (Rillard et al. 2014).

185 **2. Materials and methods**

186 A field experiment using a CO₂-rich water injection was performed following a push-pull test protocol
187 (Haggerty et al. 1998; Istok et al. 1997; Matter et al. 2007). This experiment configuration offered an
188 intermediate scale between laboratory experiments, where chemical reactions can be constrained and
189 accurately described, and larger scale studies in natural CO₂ hydrothermal fields. In the latter, the CO₂
190 quantity involved and the hydrodynamic processes (mixing, residence time, etc.) is difficult to quantify.

191 A 115 m-deep well was drilled through the sandstone and shale formations. The well was cemented
192 and equipped with PVC tubing on the uppermost 20 m, in order to avoid contamination from surface
193 and subsurface water. No equipment (or tubing) was installed from 20 m to 115 m deep in order to
194 avoid contamination by well-tubing alteration, as shown in previous works (Kharaka et al. 2006). The
195 entire geological well-log is presented in Rillard et al. (2014). Several hydrogeological prospections
196 (pumping tests, packer test, microflow logging, tracing test, well-logging, physicochemical
197 groundwater logging) were performed to determine the most suitable depth interval for injecting CO₂-
198 saturated water. The injection was performed along a 3 m interval located at a 56 m depth within a
199 fractured zone, through the sandstone layer. This injection zone was isolated using a double-packer
200 system.

201 A 3 m³ volume of baseline groundwater was initially pumped from the isolated well interval,
202 temporarily stored in a water tank, and then saturated with pure CO₂ using a bubbling system. Once
203 CO₂-saturation was reached (determined by a stable pH of 5.7, from an initial value of 7.3), the 3 m³
204 volume was injected through the packer system, following a single-well push-pull test protocol
205 (Haggerty et al. 1998; Istok et al. 1997; Matter et al. 2007). Samples were collected into the water tank
206 before and after CO₂-saturation in order to determine baseline groundwater composition. An elapsed
207 time of 80 h was employed following the injection phase, to provide a sufficient interaction time
208 between the injected solution and the host rock. This 'interaction' time was followed by a 80 h
209 pumping period to re-pump the 3 m³ injected volume, plus the mixed-formation water. This protocol
210 was adapted from studies by Haggerty et al. (1998), Istok et al. (1997), and Matter et al. (2007).

211 Samples were systematically collected over the entire pumping period to evaluate the impact of CO₂
212 perturbation on groundwater chemical composition. A sampling protocol using a glovebox and inert
213 plastic bottles, previously filled with nitrogen gas, was used to minimize sample oxidation and
214 contamination. Samples used for metal analysis were filtered in the field using a 0.2 µm filter, and
215 acidified using HNO₃ Normapur (70%), until reaching a pH<2. A second set of samples was filtered in
216 the field using a 0.45 µm filter for major cations and anions analysis. Physicochemical parameters, pH,
217 conductivity, temperature, and redox potential were continuously monitored using a flow-through
218 cell, installed at the top of the well during the injection and pumping phase. Fe (II) was measured in
219 the field for individual samples collected, using a portable spectrophotometer-specific IRON(II) LR®
220 reagent. Alkalinity was measured in the field by HNO₃ acid titration of regularly-collected individual
221 samples.

222 A list of the samples used for specific REE analyses is presented in Table 1. The corresponding pH, redox
223 potential, and conductivity measured in the field, and the pumped volume on injected volume ratio

224 illustrates the pumping stage evolution corresponding to each individual sample. Samples one to 19
225 were collected at different intervals during the pumping phase. Sample one was collected a few
226 minutes after the start of pumping. Sample 19 was collected roughly 24 h after the start of pumping.

227

228

229 The analysis for REEs and several additional trace elements was performed at the Istituto Nazionale di
230 Geofisica e Vulcanologia (INGV) geochemical laboratory in Palermo, Italy. REEs were analyzed by Q-
231 ICP-MS (Agilent 7500ce). A mass spectrometer was calibrated in the range of 5-5000 ng/L, with 11
232 calibration points obtained by stepwise dilution of a REE multi-element standard solution. The
233 sensitivity variations were monitored using internal standards ^{103}Rh , ^{115}In , and ^{185}Re , which were added
234 directly online by an appropriate device, by mixing an internal standard solution to the sample
235 immediately before the nebulizer. A 60 s rinse using a 2% HNO_3 solution and 0.5% HCl solution, plus a
236 60 s rinse using a 2% HNO_3 solution reduced memory interferences between samples. Standards and
237 samples were replicated five times to evaluate the data precision by relative standard deviation (RSD),
238 which was always <15%. The standard reference materials SLRS4 (Lawrence et al. 2006), and
239 SpectraPure Standards SW1 and SW2 were analyzed to evaluate data accuracy, which never exceeded
240 10%.

241

242 **3. Speciation model with PHREEQC**

243 To understand the parameters controlling REE behavior as a result of CO_2 -injection, a geochemical
244 model was used, with particular attention paid to sorption/desorption processes and speciation
245 phenomena.

246 The speciation modeling for Fe-oxide equilibrium calculations was achieved using hydrogeochemical
247 code PHREEQC ver. 3.3.9 (Parkhurst and Appelo 2013), as well as the wateq4f database. This database
248 was updated using the well-accepted stability constants for the 14 naturally occurring REEs at zero
249 ionic strength, and at 25°C. These constants account for inorganic aqueous complexes with carbonate,
250 hydroxyl, sulfate, chloride, and fluoride anions. The stability constants for LnCl_2^{2+} and LnCl_2^+ were taken
251 from Luo and Byrne (2001), and LnF_2^{2+} and LnF_2^+ were taken from Luo and Millero (2004). Those for
252 LnSO_4^+ were obtained from Schijf and Byrne (2004), and those for LnNO_3^{2+} from Millero (1992).
253 Constants for $\text{Ln}(\text{OH})_2^{2+}$ and $\text{Ln}(\text{OH})_2^+$ were taken from Lee and Byrne (1992), and those for $\text{Ln}(\text{OH})_3(\text{a})$
254 from Klungness and Byrne (2000), respectively. Equilibrium constants for the formation of LnCO_3^+ and
255 $\text{Ln}(\text{CO}_3)_2^-$ were taken from Luo and Byrne (2001). Scavenging model parameters for HFO were taken

256 from Liu et al. (2017). Precipitation of HFO was quantified from dissolved Fe measured in groundwater
257 samples, and the corresponding equilibrium constants were taken from Nordstrom et al. (1990). The
258 number of REE binding sites in the reactive solid surfaces was determined by the moles of HFO,
259 precipitated and defined explicitly by the keyword data block 'EQUILIBRIUM PHASES'. The specific
260 surface area (SSA) was defined relative to the moles of HFO, in which the amount of specified binding
261 sites changed as the SSA varied during the batch-reaction simulation. Upon HFO formation, the two
262 types of oxide surface binding sites ($= S^{\circ}OH$ and $= S^{w}OH$) were assumed to be available for REE
263 complexation. For surface complexation modeling, both the surface-bound and diffuse layer species
264 were taken as components of the system in the presence of iron oxyhydroxides. In this modeling
265 configuration, iron hydroxides were only considered as solid phase (i.e., colloid or mineral phase).

266 All of the REEs considered in the model were trivalent, and followed the hypothesis of Bau (1999) that
267 oxidation-scavenging of Ce by metal oxides included three independent steps: (1) sorption of Ce(III)
268 from solution; (2) partial oxidation of Ce(III) to Ce(IV) on the iron or manganese oxide surface; (3)
269 partial desorption of Ce(IV) to solution.

270 **4. Results**

271 **4.1 REY enrichment and fractionation following CO₂ perturbation**

272 The physicochemical parameters (pH, redox, and conductivity) measured in the field during the
273 experiment are listed in Table 1 and represented in Fig. 1 as functions of the ratio of pumped volume
274 to injected volume (i.e. $V_p./V_{inj.}$). The evolution of iron and manganese, as major reactive metals
275 following the CO₂-injection, is represented in Fig.2a. Other parameters that may influence REY
276 behavior such as aluminum content did not show clear evolution following CO₂ perturbation. Dissolved
277 organic carbon (DOC), as well as total organic carbon (TOC), were below the detection limit for all
278 samples. A clear increase for As and Zn was correlated with CO₂ perturbation. The specific behavior of
279 these elements, as well as other major parameters (Ca^{2+} , Mg^{2+} ; alkalinity, etc.) are presented in detail
280 in Rillard et al. (2014). Only parameters that have been identified as having an impact on REY behavior
281 were studied in the present paper.

282

283 In this study, the entire REEs series plus Y was analyzed; however, only REEs used in the geochemical
284 model (see part 3) were employed. A small number of representative elements per group of REEs is
285 presented in molar concentration as a function of $V_p./V_{inj.}$ ratio (see Fig.3): Ce for the LREE group, Gd
286 and Dy for MREE, and Yb and Y for HREE. A $V_p./V_{inj.}$ ratio close to zero represents the beginning of the
287 pumping stage, and the most CO₂-perturbed sample. A global enrichment in REY concentration was

288 observed following CO₂-injection (Fig.3). The Σ REY increased from $1.2 \cdot 10^{-9}$ mol/L to $4.3 \cdot 10^{-9}$ mol/L,
289 following a pH decrease (Fig.4). Higher enrichment was observed for Y (from $8.1 \cdot 10^{-10}$ mol·L⁻¹ to $3.2 \cdot 10^{-9}$
290 mol·L⁻¹) (Fig.3, Y image). Global REE enrichment following CO₂ perturbation was induced by
291 acidification related to carbonic acid production. Acidification enhanced host rock mineral weathering,
292 releasing trace metals into the aqueous phase. Global REY enrichment mimics the global increase in
293 dissolved metals, such as iron and manganese (see Fig.2, and Rillard et al. 2014). This was evident when
294 comparing the baseline groundwater composition (baseline groundwater sample) to the most
295 perturbed CO₂ sample (sample one). However, the enrichment was not homogeneous along the entire
296 REEs spectrum. Enrichment in dissolved REEs and global correlation with CO₂ perturbation appeared
297 greater for Y and HREE (Fig.3). Good correspondence between dissolved concentration and CO₂
298 perturbation was observed for Y, Dy, Er, Tm, Yb, Lu, Gd, and Tb (i.e. MREE and HREE). A regular increase
299 in the concentration of Σ HREE (plus Y) occurred alongside a pH decrease, as a result of CO₂
300 perturbation, until the end of the pumping phase, as shown in Fig. 4. The increase in MREE appeared
301 less-marked as a function of pH and Vp./Vinj (Fig. 4). In contrast, no systematic evolution was observed
302 for LREE as a function of pH and Vp./Vinj.

303 Typical REE parameter (La/Yb, Ce/Ce*) evolution as a function of Vp./Vinj. is shown in Fig. 5. The La/Yb
304 ratio shows an abrupt decrease following CO₂-injection, and a smooth increase toward the baseline
305 water ratio after Vp./Vinj. reached 0.5. No clear evolution was apparent for Ce/Ce* as a function of
306 Vp./Vinj. A decrease in Ce anomaly appeared to have occurred immediately after CO₂-injection, but no
307 clear trend was observed as a function of Vp./Vinj. The fractionation of HREE compared to LREE
308 appeared quite clear and was also confirmed by the evolution of La/Yb ratio as a function of Vp./Vinj.
309 (Fig.5). The Eu/Eu* anomaly was not considered, since interference with BaO during analysis was
310 suspected (Shabani et al. 1992; Dulski 1994; Zwahlen et al. 2019). Despite the absence of a clear
311 correlation between Ba and Eu (see supplementary materials), the ratio Eu/Ba was >4000, and this
312 may have led to a false positive Eu signal.

313 The entire REE pattern of the experimental samples, normalized to PAAS (Post Archean Australian
314 Shale), is shown in Fig.6a. In order to simplify the visual result, only the most representative
315 experimental samples are presented: baseline groundwater; Vp./Vinj. = 0, representing the most
316 perturbed sample; Vp./Vinj. = 0.033 was the second most perturbed sample; Vp./Vinj. = 1.489 was
317 representative of a sample collected at the end of the pumping phase. Data for Eu are not shown, since
318 interference with Ba was suspected, as discussed above. The REE pattern showed a net enrichment of
319 HREE in both the baseline groundwater composition (baseline groundwater sample), following CO₂-
320 injection. This trend did not change significantly due to CO₂ perturbation. However, the fractionation
321 of HREE was significant following CO₂ perturbation. For comparison, the entire REE pattern normalized

322 to PAAS for bulk rock samples analysis is also presented in Fig 6b. These samples were collected on the
323 same shale and sandstone formation as the experimental site in this study (data issued by Chopin
324 2016). The normalized to PAAS concentration of the bulk rock shows a clear enrichment of HREE
325 compared to LREE, in correlation with the general trend of REE observed for water samples. However,
326 a weak MREE enrichment (particularly for Gd, Tb, and Dy), compared to LREE was observed. This point
327 was not clearly indicated in the water samples. However, the amplitude of this enrichment in MREE
328 concentration remained limited (lower than 0.2).

329 **4.2. REE speciation**

330 REE speciation calculation results are shown in Fig. 7. The baseline water plot represents the baseline
331 groundwater sample, while sample one, with the lowest pH, represents the earliest sample collected
332 following CO₂ perturbation. The total proportion of REE complexes (%Ln³⁺; %LnCO₃⁺ (CO₃)₂; %LnSO₄;
333 %LnHFO) are represented as a function of pH and V_p/V_{inj} ratio (see Fig.8).

334 The dissolved REE-carbonate complex is indicated as the dominant species prior to CO₂ perturbation
335 (Fig. 7, baseline groundwater sample). The proportion of REE complexation with carbonate was nearly
336 homogenous along the entire REE pattern, with no particular fractionation effects. REEs sorbed to iron
337 oxyhydroxide (Fig.7, Ln-HFO) indicates the second highest proportion in baseline groundwater
338 composition. The proportion of Ln-HFO complex increased with atomic weight along the REE series,
339 with a higher proportion of HREE sorbed, compared to LREE, for all samples. The proportion of REE-
340 sulfate complex (Ln-SO₄⁺) appeared low compared to the proportion of carbonate complex. A similar
341 observation was made for free REE ions (Ln³⁺).

342 Following CO₂ perturbation (see Fig.7, sample one, and Fig. 8), the REE-sulfate complex became the
343 dominant species, except for Tm, Yb and Lu, for which the REE-carbonate was the dominant species.
344 The proportion of Ln-SO₄ complex decreased regularly alongside REE atomic weight, and the opposite
345 trend was observed for REE-carbonate (see Fig. 7, sample one to sample 19). The REE-iron
346 oxyhydroxide complex (HFO) decreased following CO₂ perturbation; this is particularly significant when
347 comparing the baseline groundwater to sample one (Fig. 7). From sample one to sample 19, the Ln-
348 carbonate and Ln-HFO complex proportions increased, and REE-sulfate complex decreased as CO₂
349 perturbation diminished (Fig. 7). However, the total concentration of sulfate in groundwater did not
350 change significantly following CO₂ perturbation. The baseline concentration in sulfate was relatively
351 high. The sulfate concentration stayed at the same order of magnitude over the entire experiment
352 (within 7 mol/L to 9·10⁻³ mol/L; see Rillard et al. 2014). A weak variation in SO₄ concentration was,
353 however, observed during the experiment, but was attributed to the mixing process, in accordance
354 with hydrogeological information observed in the field (Rillard et al. 2014). The initial high amount of

355 sulfate in baseline groundwater was attributed to mixing with local groundwater contaminated by
356 former mine activities in the area (influence of acid rock drainage, sulfide mineral oxidation, etc.).
357 Therefore, the higher proportion of Ln-SO₄ following CO₂ perturbation is related to the higher affinity
358 of dissolved REEs for complexing with sulfate in acidic conditions (Decree et al. 2015), but not to an
359 increase in sulfate concentration induced by CO₂ perturbation.

360 Enrichment of dissolved REEs was greater for Y and HREE. This was clear when comparing the La/Sm
361 ratio normalized to PAAS (La/Sm)_{N-PAAS}, and the La/Yb)_{N-PAAS} ratio (Fig.5). La/Sm and La/Yb ratios
362 decreased after CO₂-injection, due to the higher amounts of HREE and MREE released in the water,
363 compared to the LREE. Similarly, a large increase in the Yb/Gd ratio (from 0.54 to 2.23) was observed
364 following CO₂ perturbation.

365 **5. Discussion**

366 **5.1. Effects of CO₂ perturbation on REY enrichment**

367 CO₂ perturbation increased the concentration of major elements (e.g. Ca²⁺ and Mg²⁺) by nearly 30%,
368 and alkalinity doubled (Rillard et al. 2014). The pH initially decreased from 7.3 to 5.7, dissolved Fe rose
369 from 2.15·10⁻⁵ mol/L to 1.17·10⁻⁴ mol/L, and Mn from 1.35·10⁻⁶ mol/L to 5.01·10⁻⁶ mol/L. Significant
370 increases in dissolved trace metals, mainly As and Zn, were also observed (Rillard et al. 2014). Redox
371 perturbation throughout the experiment was evaluated by comparing redox potentials measured by
372 electrodes in the field, with those calculated from the Fe (II)/Fe (III) equilibrium. Redox potential was
373 controlled by iron oxyhydroxide equilibrium, but was weakly perturbed and nearly constant
374 throughout the entire experiment (Fig.1).

375 The main geochemical reactions are identified by the geochemical model. The release of major
376 elements was attributed to weak dissolution and equilibrium of major minerals composing the host
377 rock, particularly dolomite and calcite. The increase in dissolved Fe was attributed to dissolution of
378 amorphous iron oxyhydroxides such as ferrihydrite (Fig. 2b). A good correlation was identified between
379 the saturation index of ferrihydrite and the dissolved iron concentration (Fig.2b). This is also in
380 agreement with the high amount of neoformed iron oxyhydroxide phases observed during drilling
381 operations. The release of dissolved iron is therefore mainly attributed to ferrihydrite dissolution. The
382 enrichment in Mn arose from the dissolution of Mn-oxides, but the specific phase could not be
383 identified using the geochemical model. The enrichment of trace metals, particularly As, is associated
384 with the desorption or dissolution of iron oxyhydroxides. The major factor for the enrichment of trace
385 metals induced by CO₂ is considered to be the acidic pH, derived from carbonic acid production. The
386 perturbation of redox conditions was not considered to be significant (Rillard et al. 2014).

387 The Ce/Ce* did not show clear evolution as a function of Vp./Vinj. (Fig. 5). The global anomaly of Ce for
388 all samples appeared negative (Tostevin et al. 2016), and a weak decrease appeared to have occurred
389 immediately after CO₂-injection, but this is not clearly evidenced in other samples. A cerium anomaly
390 is known for being a good proxy of redox potential variation (Bau and Alexander 2009; Frei et al. 2013;
391 Tostevin et al. 2016). A decrease in cerium anomaly can corroborate an oxidative perturbation.
392 However, the redox potential did not change significantly throughout the entire experiment. The redox
393 potential increased from +130 mV in baseline groundwater to +187 mV following CO₂-injection (Fig.1).

394 Fig.10 illustrates the Y/Ho molar ratio as a function of Vp./Vinj. ratio. The Y/Ho ratio increased from 57
395 in baseline groundwater composition to >100 following CO₂ perturbation, before decreasing to <80
396 when the V p./Vinj. ratio reached 1. The Y/Ho signatures are known to present different behaviors
397 during interactions with Mn and Fe-oxyhydroxides (Bau, 1996, 1999). An increase in Y/Ho ratio was
398 observed following CO₂ perturbation. Such enrichment of Y with respect to Ho was also observed in
399 natural CO₂-rich fluid by Shand et al. (2005). This result, however, is not consistent with the
400 dissolution/desorption of Fe/Mn-oxyhydroxides as the main sources of dissolved REEs. These solids
401 generally preferentially adsorb Ho, relative to Y, during authigenic crystallization (Bau 1999; Bau and
402 Koschinsky 2009). Therefore, the observed Y/Ho variation suggests that another REE-enriched source
403 released REEs into groundwater. This other source may be the desorption of REEs from organic-rich
404 shale surfaces (Haley et al. 2004; Takahashi et al. 2010). Another hypothesis is the dissolution of
405 carbonates or minerals, which may act as a source of anomalous Y (Tostevin et al. 2016). This final
406 hypothesis is consistent with the dissolution of carbonate minerals (such as calcite and dolomite)
407 previously identified as a primary source of Ca²⁺, Mg²⁺, and alkalinity release, following CO₂-injection
408 (Rillard et al. 2014).

409 The enrichment in HREE relative to PAAS, within the entire REE series, in both baseline water
410 composition and following CO₂ perturbation, are described in natural CO₂ rich water (Shand et al.
411 2005), and in volcanic hydrothermal water sources (Inguaggiato et al. 2015, 2016, 2017). These data
412 support the preferential enrichment of HREE during weathering processes induced by CO₂
413 perturbation. However, as suggested above, some issues regarding analytical precision may have
414 affected some of the results. Due to the very limited volume of water in collected samples (less than
415 10 mL) and technical limitations, a preconcentration step could not be performed prior to REY analyses
416 with ICPMS. Overall REE concentrations ranged from 1241 pmol/L to 4300 pmol/L. These
417 concentrations are beyond the values in which REE preconcentration and a matrix-free method of
418 analysis are essential. However, the large variation observed in shale-normalized patterns for some
419 samples (the baseline groundwater sample in particular) may have been due to a lack of precision

420 resulting from chemical analyses. However, this point does not affect the general trend observed for
421 each individual REY element over the entire CO₂-injection experiment, as shown in Fig.3 and Fig.4.

422

423 **5.2 Effects of speciation and surface complexation on REY behavior**

424 Bau (1999) and Verplanck et al. (2004) showed that neoformed iron oxyhydroxides have a higher
425 affinity for HREE scavenging compared to LREE. Therefore, the higher enrichment of HREE may be
426 related to easier dissolution of neoformed hydroxide minerals such as ferrihydrite, following CO₂
427 perturbation (see Fig. 2, and Rillard et al. 2014). This hypothesis is supported by speciation calculations
428 showing a rapid decrease in the proportion of the Ln-HFO surface complex following CO₂ perturbation
429 (see Fig.7, baseline groundwater sample, sample one, and Fig.8). HREE enrichment is also illustrated in
430 Fig.11, which represents the La/Yb ratio as a function of dissolved Fe concentration. As the pH
431 decreased, enhanced protonation of ferric oxide surfaces occurred, reducing the proportion of
432 negatively charged groups able to complex REE (Bethke, 2007). The modeling configuration only
433 considered the surface complexation onto solid iron hydroxide phases, as calculated in equilibrium,
434 with dissolved iron measured in the samples (this included the colloid or mineral phase comprising the
435 host rock of the aquifer). This model did not take into account solution complexation with iron oxides.
436 Thus, the development of a specific model is needed to study solution complexes with dissolved iron.
437 However, iron is known to easily form large-size colloids in a solution that mainly control REE sorption
438 and speciation (Pourret al. 2007, 2010).

439

440 Crane and Sapsford (2018) studied the sorption and fractionation of REE ions with zerovalent iron
441 nanoparticles. The aim of their work was to test the potential of recovering the dissolved REEs
442 contained in an acidic rock drainage solution. Their results showed that HREE had a higher
443 concentration, and faster scavenging, on a neoformed iron oxyhydroxide surface, compared to LREE.
444 Differences in coordination numbers between LREEs and HREEs helped to explain this phenomenon.
445 The differences affected the hydration number, with the number of REE ions decreasing from nine for
446 LREEs to eight for HREEs, with a transition region between Sm to Gd (Wood, 1990). This higher
447 coordination number may therefore preferentially restrict the bulk diffusion of LREE compared to HREE
448 on sorption sites. However, the experimental conditions were significantly different in the work
449 presented by Cran and Sapsford (2018), compared to the present study (use of zerovalent iron with
450 larger pH variation and redox potential).

451

452 Furthermore, the global proportion of Ln-carbonate complexes decreased between baseline water
453 (baseline groundwater sample) and the most CO₂ perturbed sample (sample one in Fig.7 and Fig.8).
454 This decrease was less marked for HREE, and similar results were reported by Sholkovitz (1995), Byrne
455 and Sholkovitz (1996), De Carlo et al. (1998) and Bau (1996). The greater stability of HREE carbonate
456 complexes compared to LREE carbonates may explain the preferential release of HREE in water under
457 the experimental conditions of this study.

458 Speciation calculations show that in the more acidic samples (samples one, two, and three), REE
459 complexes occurred mainly with sulfate (LnSO₄⁺), along with a higher proportion of complexed LREE
460 (Fig.7 and Fig.8). However, this phenomenon did not involve the obvious enrichment of dissolved LREE.
461 The proportion of REE sulfate complexes may have been overestimated by the model calculation. A
462 higher proportion of REE sulfate complexes under acidic conditions was observed by Decree et al.
463 (2015) and Verplanck et al. (2004).

464

465 This speciation model was constructed using the database on speciation constants of REEs available to
466 date. While these constants are well-documented for REE speciation carbonate and iron oxide species,
467 a lack of data remains for other constants dealing with REE speciation in the presence of manganese
468 oxyhydroxides, which may play an important role in dissolved REE behavior (Pourret et al. 2007b;
469 Pourret and Tuduri, 2017; Liu et al. 2017). However, this model was able to provide important
470 information for studying REE complexation with iron oxyhydroxides in Fe-rich groundwater aquifer
471 systems (Verplanck et al. 2004; Quinn et al. 2007; Liu et al. 2017). The complexation with organic
472 molecules (such as humic substances) was not taken into account, since the organic carbon
473 concentration (TOC and DOC) of the samples was below the detection limit. However, organic matter
474 is known to effect important control on REE behavior (Pourret 2007a, 2007b, 2009). Further
475 developments in modeling techniques should incorporate Mn-oxides, organic humic substances, and
476 Fe-oxides simultaneously in a model, in order to better understand the roles of particle colloids in REE
477 mobility in natural systems (Liu et al. 2017).

478

479 **5.3 Tetrad effect**

480 Employing the tetrad effect (Masuda and Ikeuchi, 1979) can be useful for understanding the behavior
481 of REE on water-rock interaction processes. This is based on shale-normalized patterns divided into
482 four downward convex segments across the entire REE spectrum. A tetrad effect was observed in
483 patterns of the Ln-carbonate complex and REE iron oxyhydroxide complex, represented in samples
484 with pH values ranging between 5.70 and 6.51 (Fig.7). Four upward-curved segments (La-Nd (I), (Pm)-
485 Gd (II), Gd-Ho (III), and Er-Lu (IV) were observed. These patterns are commonly referred to as the M-

486 type lanthanide tetrad effect (TE) (Masuda et al. 1987; Bau 1996, 1999). The amplitude of the tetrad
487 effect can be used to study the partial dissolution of rock (Bau, 1996, 1999; Irber 1999; Monecke et al.
488 2002). However, observed M-tetrad effects in Fig.7 were based on modeled complex abundance. It
489 therefore cannot be ruled out that the tetrad effect observed in Fig.7 had been induced by an artifact
490 from speciation modeling. The analytical quality of the data did not allow for quantifying the tetrad
491 effect amplitude with sufficient accuracy. However, the use of the tetrad effect to understand REE
492 behavior through water-rock interactions represents a good perspective for future studies. In
493 particular, the addition of a preconcentration stage will allow for better data accuracy and therefore,
494 better confidence for quantifying the TE, Eu, and Ce anomalies.

495

496 **Conclusions**

497 A 3 m³ volume of water saturated with CO₂ was injected into a subsurface fractured aquifer in host
498 rock naturally enriched with trace metals, including REEs. The CO₂-injection into groundwater caused
499 a rapid initial pH decrease (from 7.3 to 5.7), followed by a gradual increase. Chemical changes in the
500 studied system caused by CO₂-injection created significant changes in the geochemical behavior of
501 major elements, trace metals, and dissolved REEs. Enrichment by a factor of nearly four was observed
502 for dissolved REY species. This enrichment was greater for HREE than LREE. The behavior of dissolved
503 REE was evaluated using a geochemical model. Results indicate the main process controlling the
504 release of dissolved REY following CO₂-injection to be the dissolution of iron oxyhydroxides, enhanced
505 by complexation with aqueous carbonate species (LnCO₃²⁻ and LnCO₃⁻). However, the Y/Ho ratio in
506 groundwater suggests that a second source of REEs may have been involved, such as the desorption
507 from carbonate minerals or organic-rich shales.

508

509 This study demonstrates the capability of REEs to provide an indication of geochemical interfacial
510 processes occurring at the nanoscale level, during increased interaction between groundwater and
511 host rock, induced by CO₂-injection. This model can help to provide a better understanding of the roles
512 of particle colloids on REEs' mobility in natural systems. These results also present a starting point for
513 evaluation of the environmental impacts of REE exploitation, and for enhancing REE recovery rates
514 using metal oxides under field conditions such as mine drainage. In addition, this study also presents
515 several valuable tools for the understanding of geological fluid-mixing processes, or fluid inclusions
516 formations, which can be useful for understanding deep geological processes.

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521 **Acknowledgments**

522 The field experiments were performed with the financial support of INERIS, as a part of the EVARISTE
523 internal research project on the long term impacts of geological CO₂ storage. We thank the Istituto
524 Nazionale di Geofisica e Vulcanologia (INGV) from Palermo (Italy) and Dr. Sergio Bellomo for analytical
525 support. We also thanks Dr Jose Cruz (associate editor) and two anonymous reviewers for their
526 constructives comments that improved the quality of the original manuscript. Dr. Raul E. Martinez is
527 acknowledged for post-editing the English style.

528

529 **Conflict of interest:**

530

531 The authors declare no conflict of interest.

532

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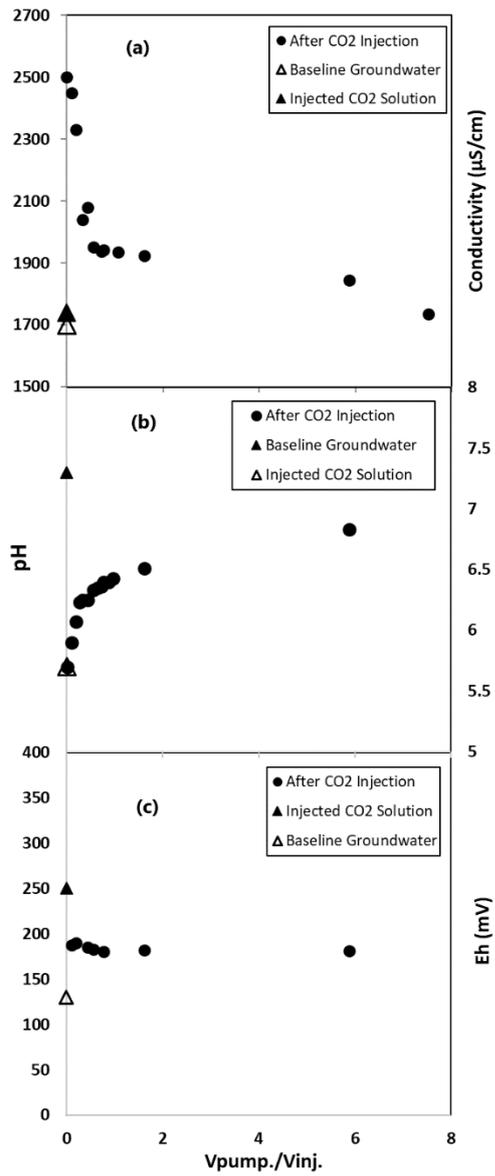


Fig. 1: (a) Conductivity ($\mu\text{S}/\text{cm}$) of groundwater as a function of a function of the ratio pumped (V_p .) volume to injection volume ($V_{inj.}$). Values are indicated for baseline groundwater, injected CO_2 solution and groundwater re-pumped after CO_2 injection; (b) pH values as a function of ratio $V_p./V_{inj.}$; (c) Redox potential (Eh in mV) measured as a function of ratio $V_p./V_{inj.}$.

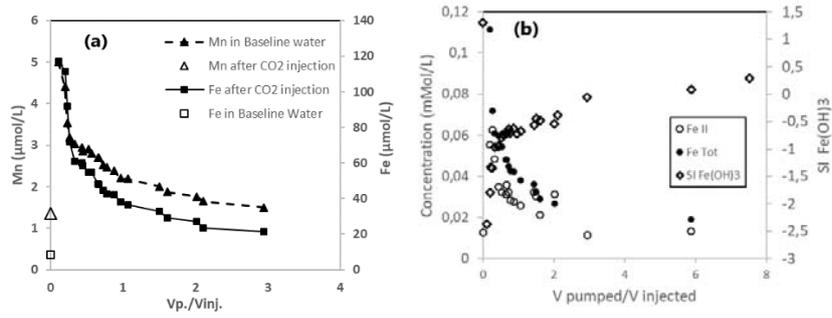


Fig. 2 : (a) Molar concentration ($\mu\text{mol/L}$) of dissolved iron (Fe, right axis) and manganese (Mn, left axis) as a function of the ratio pumped volume ($V_p.$) to injection volume ($V_{inj.}$);(b) Molar concentration (mMol/L) of total dissolved iron (Fe Tot, left axis), iron two Fe²⁺ (Fe II) and Saturation Index in Ferrihydrite Fe(OH)₃ (left axis) as a function of ratio $V_p./V_{inj.}$. Figure (b) is extracted from Rillard et al 2014.

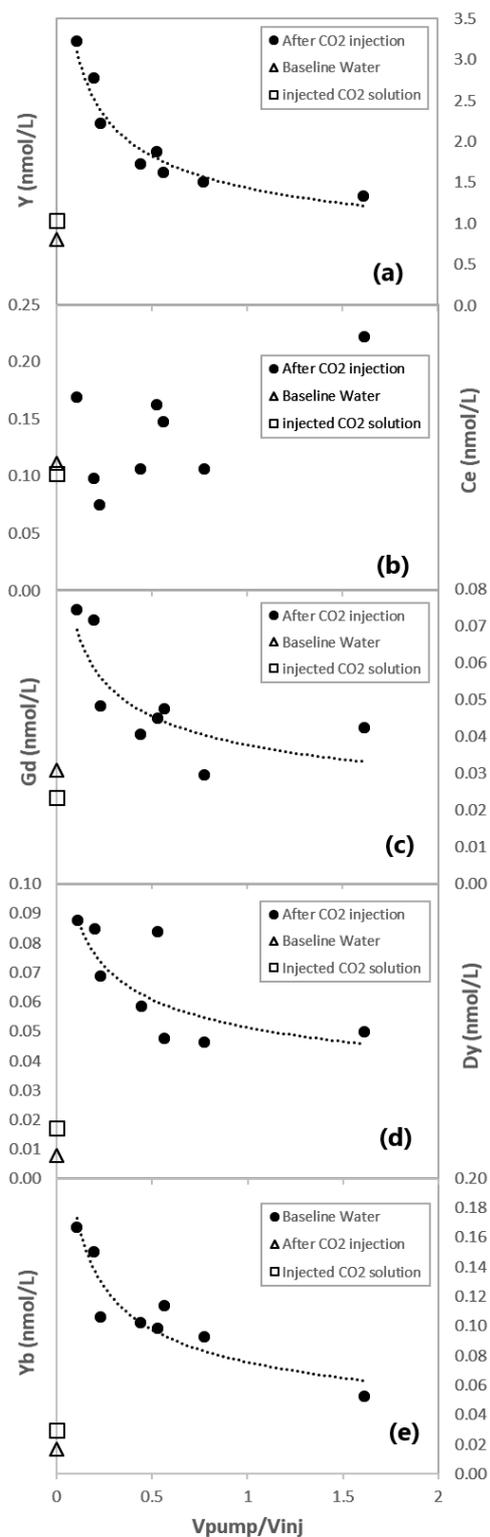


Fig. 3: (a) Molar concentration (nmol/L) in yttrium as function of the ratio pumped volume (V_p) to injection volume (V_{inj}), representative of HREE group; (b) Cerium concentration as a function of V_p/V_{inj} ratio, representative of LREE group; (c) Gadolinium concentration (nmol/L) as a function of ratio V_p/V_{inj} representative of MREE group; (d) Dysprosium concentration (nmol/L) as a function of

ratio V_p/V_{inj} . representative of MREE group; (e) Ytterbium concentration (nmol/L) as function of ratio V_p/V_{inj} . representative of HREE group.

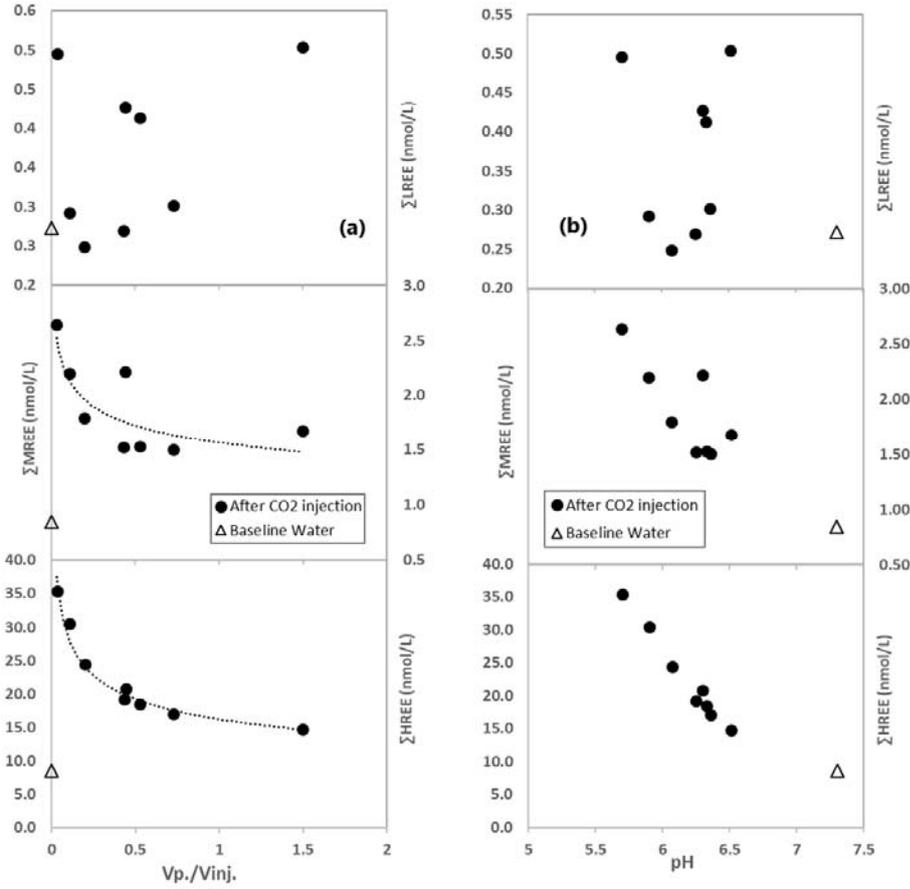


Fig. 4 : (a) Sum of LREE (La, Ce, Pr, Sm), MREE (Eu, Gd, Tb, Dy, Ho), HREE (Er, Tm, Yb, Lu, Y) as function of the ratio pumped volume ($V_p.$) to injection volume ($V_{inj.}$) ; (b) Sum of LREE (La, Ce, Pr, Sm), MREE (Eu, Gd, Tb, Dy, Ho), HREE (Er, Tm, Yb, Lu, Y) as function of pH

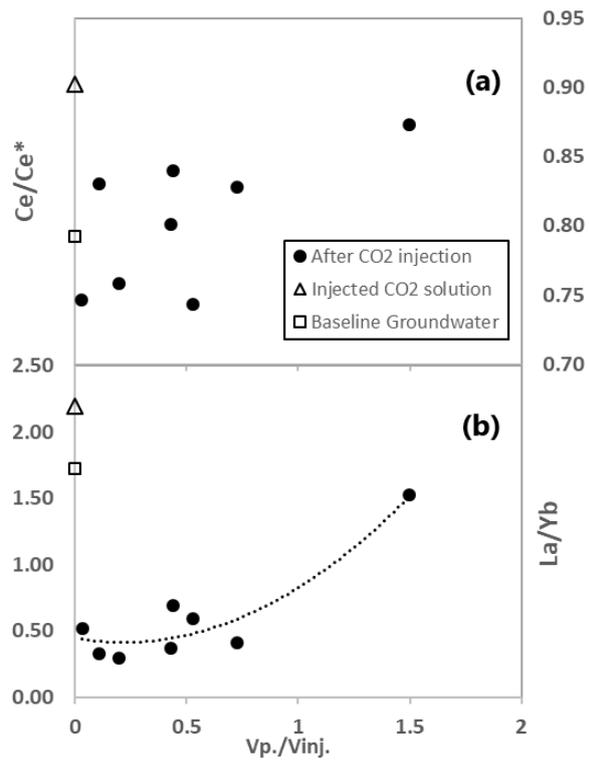


Fig. 5 : (a) Cerium anomaly Ce/Ce^* as a function of the ratio pumped volume ($V_p.$) to injection volume ($V_{inj.}$); (b) La/Yb ratio as a function of the ratio pumped volume ($V_p.$) to injection volume ($V_{inj.}$)

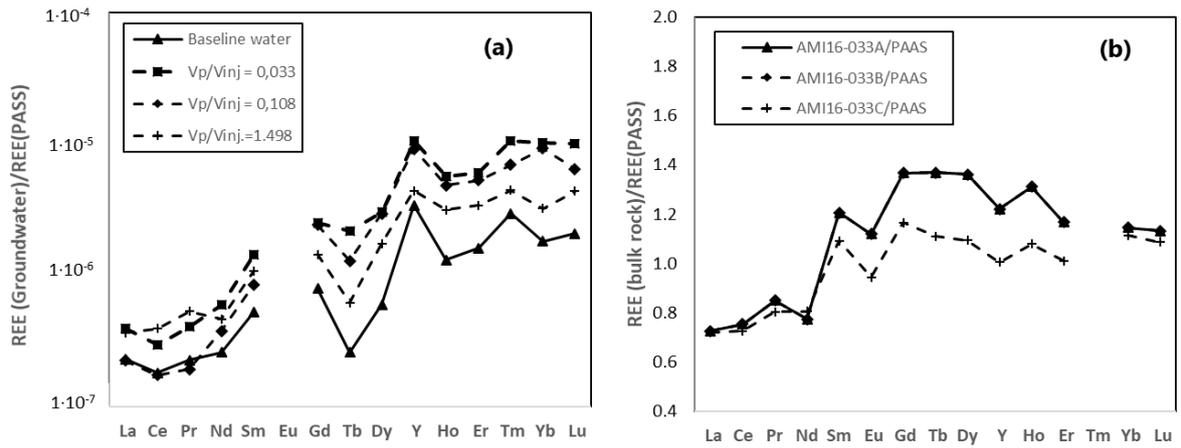


Fig. 6: (a) Dissolved REE concentrations in groundwater samples normalized to Post Archean Australian Shale (PAAS), four representative samples are illustrated (baseline groundwater, $V_p/V_{inj} = 0.033$, $V_p/V_{inj}=0.108$, $V_p/V_{inj}=1.498$); (b) REE concentrations in bulk rock samples normalized to Post Archean Australian Shale (PAAS), data issued from Chopin (2016).

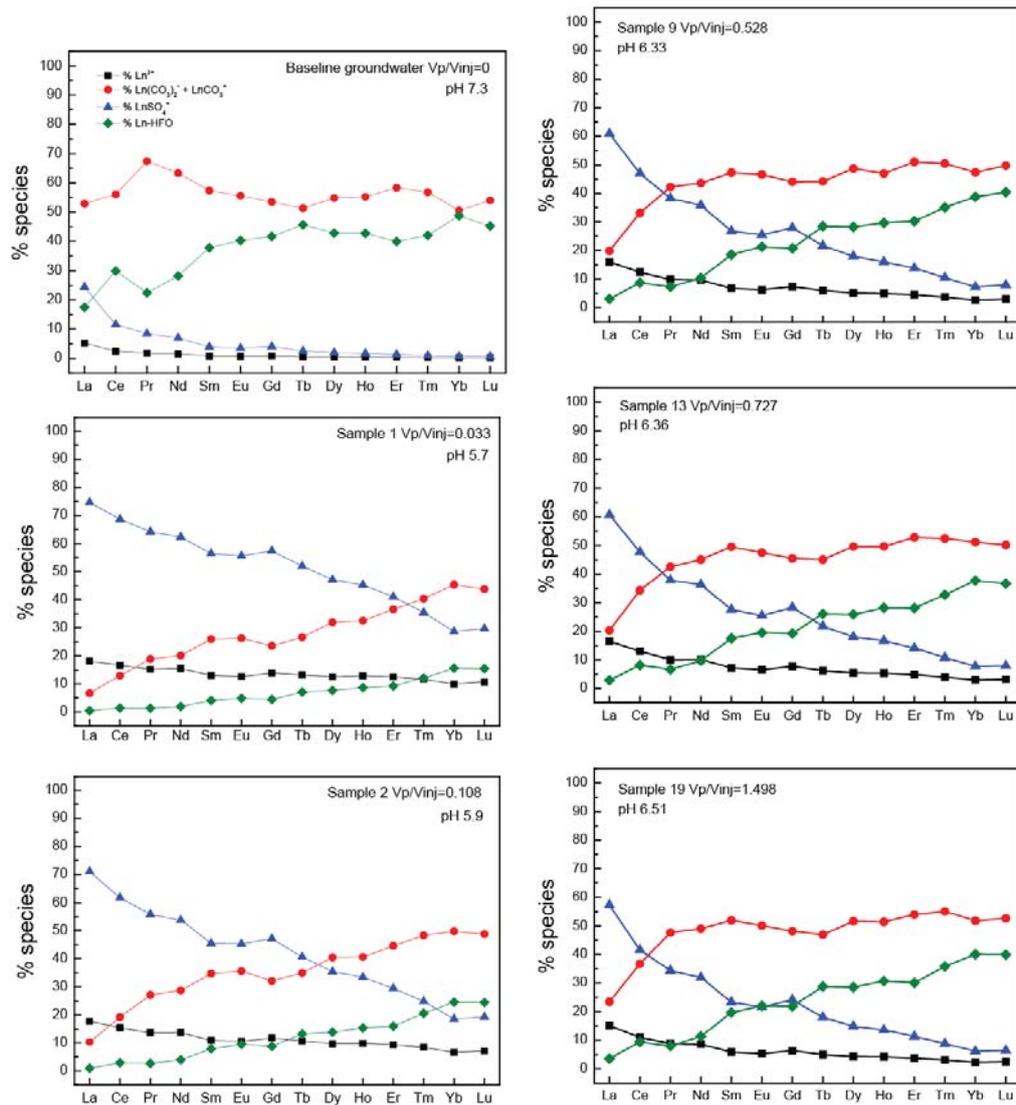


Fig. 7 : Proportion (%) of Ln-Carbonate, Ln-Sulphate, Ln-iron oxihydroxide complex and free Ln³⁺ calculated by the geochemical model in sample Baseline Water, and selected samples following CO₂ injection (Sample 1, Sample 2, Sample 9 , Sample 13, Sample 19). The pH values and Vp/Vinj ratio of each individual sample are indicated in the diagrams.

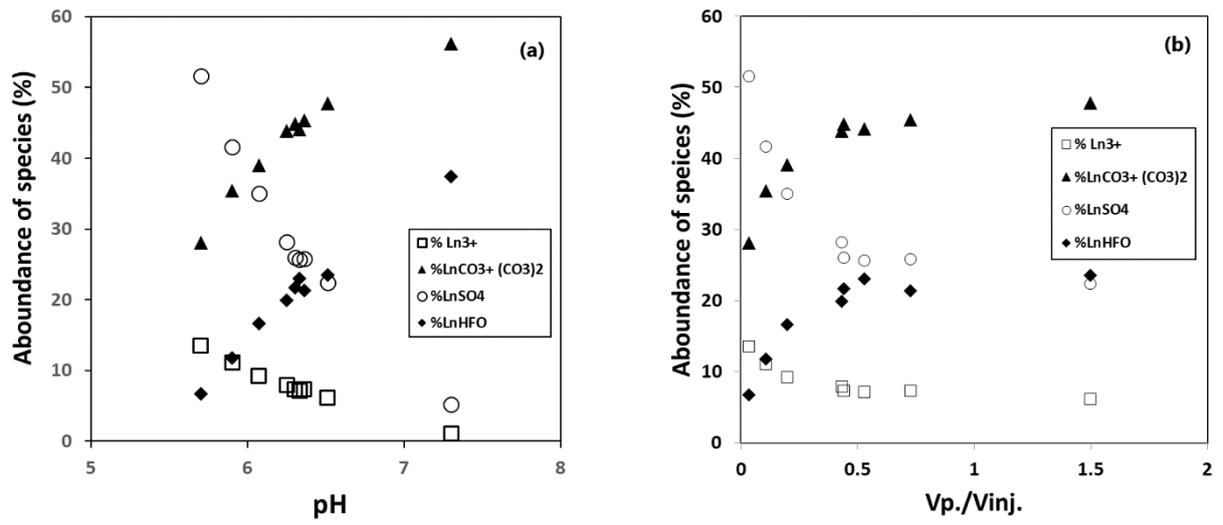


Fig.8: Total proportion (%) of Ln-Carbonate, Ln-Sulphate, Ln-iron oxihydroxide complex and free Ln³⁺ calculated by the geochemical model as a function of (a) pH and (b) the ratio pumped volume (Vp.) to injection volume (Vinj.)

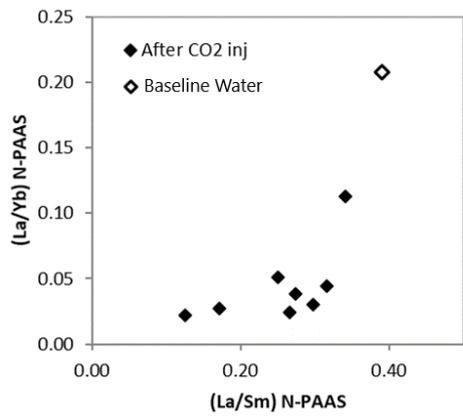


Fig. 9: La/Yd ratio as a function of La/Sm ratio (normalized to PAAS)

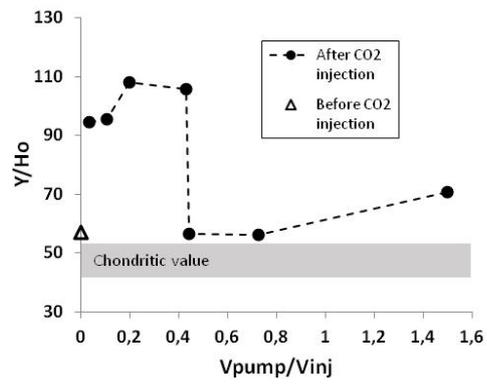


Fig.10: Y/Ho molar ratio as a function of Vpump./Vinj. ratio. Groundwater composition before CO₂ injection is represented by white triangle.

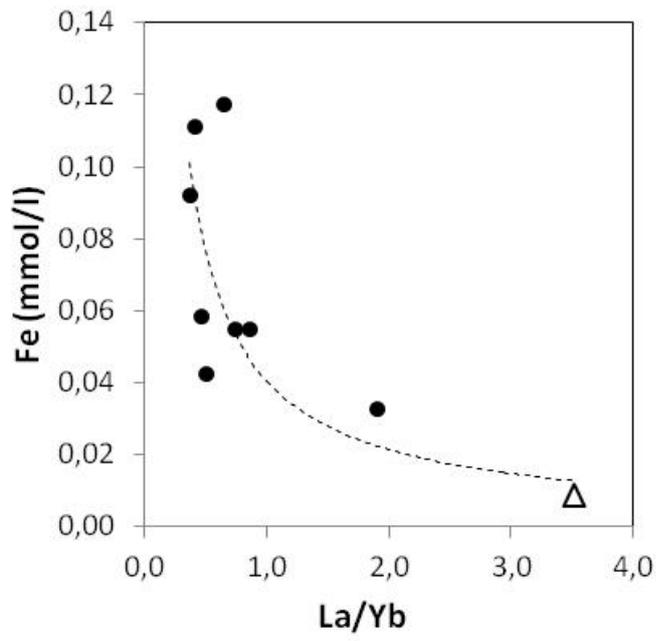


Fig.11: Molar concentration in dissolved iron (mmol/l) as a function of La/Yb ratio. Groundwater composition before CO₂ injection is represented by white triangle.