

1 On the Mobilization of Metals by CO₂ Leakage into Shallow Aquifers: Exploring Release 2 Mechanisms by Modeling Field and Laboratory Experiments

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10 11 12 **Abstract**

13
14 The dissolution of CO₂ in water leads to a pH decrease and carbonate content increase in
15 affected groundwater, which in turn can drive the mobilization of metals from sediments. The
16 mechanisms of metal release postulated in various field and laboratory studies often differ.
17 Drawing primarily on previously published results, we examine contrasting metal mobilization
18 behaviors at two field tests and in one laboratory study, to investigate whether the same
19 mechanisms could explain metal releases in these different experiments. Numerical modeling of
20 the two field tests reveals that fast Ca-driven cation exchange (from calcite dissolution) can
21 explain the release of most major and trace metal cations at both sites, and their parallel
22 concentration trends. The dissolution of other minerals reacting more slowly (superimposed on
23 cation exchange) also contributes to metal release over longer time frames, but can be masked by
24 fast ambient groundwater velocities. Therefore, the magnitude and extent of mobilization depends
25 not only on metal-mineral associations and sediment pH buffering characteristics, but also on
26 groundwater flow rates, thus on the residence time of CO₂-impacted groundwater relative to the
27 rates of metal-release reactions. Sequential leaching laboratory tests modeled using the same
28 metal-release concept as postulated from field experiments show that both field and laboratory
29 data can be explained by the same processes. The reversibility of metal release upon CO₂
30 degassing by de-pressurization is also explored using simple geochemical models, and shows that

31 the sequestration of metals by resorption and re-precipitation upon CO₂ exsolution is quite
32 plausible and may warrant further attention.

33
34 *Keywords:* groundwater, carbonic acid, leak, CO₂ sequestration, CCS, CCUS

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37 **1. Introduction**

38 CO₂ emissions from the burning of fossil fuels have become a serious concern because of their
39 impact on climate. As a result, CO₂ capture followed by geologic storage (CCS) into deep saline
40 aquifers is considered an important potential mitigation measure for climate change. Over the last
41 decade, many studies have been undertaken to assess the feasibility and safety of CO₂ geologic
42 storage, with an emphasis primarily on hydrological, geochemical, and mechanical processes
43 affecting deep injection and containment in storage reservoirs. A smaller number of studies have
44 been undertaken to assess the impacts of potential CO₂ leakage from deep storage reservoirs on the
45 quality of overlying freshwater aquifers (see review papers Lemieux¹ and Harvey et al.², and
46 references therein). Observations from these studies are summarized below, and provide
47 background to evaluations presented later about the chemical processes potentially responsible for
48 observed mobilization of metals at two field sites previously investigated by the authors.

49

50 **1.1 Observations from laboratory experiments**

51 Due to their low cost and relative ease of operation, several laboratory batch and column
52 experiments have been conducted to investigate the mobilization of trace elements in response to
53 CO₂ intrusion into potable groundwater. Typically, these experiments³⁻¹¹ have involved the release
54 of CO₂ into a pre-equilibrated water-rock environment, followed by monitoring of the
55 geochemical changes in the aqueous phase.

56 Smyth et al.³ and Lu et al.⁴ presented laboratory batch experiments exposing aquifer materials
57 from the Texas Gulf Coast region to elevated levels of CO₂. Two different types of responses were

58 observed in these studies: “Type I cations” (Ca, Mg, Si, K, Sr, Mn, Ba, Co, B, Zn) displayed a
59 rapidly increasing concentration at the start of CO₂ injection that became steady before the end of
60 the experiment, whereas “Type II cations” (Fe, Al, Mo, U, V, As, Cr, Cs, Rb, Ni and Cu) showed
61 an initial concentration increase at the start of CO₂ injection, followed by a decrease to values
62 lower than levels prior to injection. Little and Jackson⁵ performed laboratory experiments of CO₂
63 infiltration for more than 300 days on samples from different freshwater aquifers. While increases
64 in the concentration of alkali and alkaline earth metals were quite consistent in most of their
65 experiments, increases in trace element concentrations were observed only in some samples. Wei
66 et al.⁶ reacted gaseous CO₂ with soil sampled in the vadose zone, at a depth around 0.1 m below
67 the surface for three days, and observed increases in Mg, K, Al, Cr, Mn, Fe and Pb concentrations
68 ranging from 50% to 500%, depending on the metal and moisture content of the soil. Their study
69 demonstrates that CO₂ leakage could mobilize trace metals not only from an aquifer, but also from
70 the vadose zone. Viswanathan et al.⁷ conducted a batch experiment to specifically test the leaching
71 out of As from samples collected at the Chimayo, New Mexico, natural analogue site, aiming to
72 shed light on the high concentrations of As observed in a few wells with elevated levels of natural
73 CO₂¹². They observed a sharp increase of As concentrations as soon as pH dropped, but then a
74 slow decrease in concentrations (although pH remained low, suggesting that H-driven desorption
75 leads to the release of As). Humez et al.⁸ conducted a water-mineral-CO₂ batch experiment with
76 samples taken from the Albian aquifer in the Paris Basin (France). They observed an increase in
77 concentrations of Ca, Si, Na, Al, B, Co, K, Li, Mg, Mn, Ni, Pb, Sr, Zn, a decline in Fe and Be
78 concentrations, and no changes for Cl and SO₄ after initial CO₂ influx. Varadharajan et al.⁹
79 conducted a series of sequential leaching tests with sediments from a shallow groundwater
80 formation in Mississippi, USA. Constituents that were mobilized were As, Ba, Ca, Fe, Ge, Mg,
81 Mn, Na, Ni, Si, Sr, Zn, which are largely consistent with the Type I cations reported by Lu et al.
82 (2010). Wunsch et al.¹⁰ reacted rock samples from three limestone aquifers with 0.01–1 bar CO₂

83 for up to 40 days, and found increasing concentrations of Ca, Mg, Sr, Ba, Tl, U, Co, As and Ni
84 from the dissolution of mostly calcite and to a lesser extent pyrite. Researchers from the same
85 group (Kirsch et al.¹¹) reacted sandstone samples with CO₂ under similar conditions for 27 days,
86 showing a rapid increase in major (Ca, Mg) and trace (As, Ba, Cd, Fe, Mn, Pb, Sr, U) elements,
87 which was attributed to the dissolution of calcite.

88 Together, these experiments analyzed various types of sediments (e.g., essentially carbonate-
89 free in Varadharajan et al.⁹ vs. carbonate-dominated in Wunsch et al.¹⁰) in a variety of conditions
90 in terms of redox state (e.g., reducing in Varadharajan et al.⁹ vs. oxidizing in Little and Jackson⁵),
91 pressure conditions (e.g., 4 bars in Varadharajan et al.⁹ vs. atmospheric pressure in most batch
92 experiments, e.g., Humez et al.⁸), and reaction times ranging from a couple days⁶, tens of days⁸⁻¹¹
93 to hundreds of days.⁵ Although this wide range of experimental conditions with various sediment
94 types resulted in different dissolved metal concentration responses, one common observation
95 found in these experiments was the rapid increase in alkali and alkaline earth metals, including Na,
96 K, Ca, Mg, Sr and Ba. As will be discussed later in this paper, these increases, often displaying
97 parallel concentration trends, could be explained by ion exchange.

98

99 **1.2 Observations from field tests**

100 Although laboratory experiments facilitate the understanding of the potential impact of CO₂ on
101 groundwater, they cannot accurately represent *in situ* conditions. For example, pre-equilibration of
102 synthetic solutions³ or DI water⁴ with sediments, unwanted oxidation during the experiment⁵, or
103 neglecting the transport of groundwater and CO₂ can lead to laboratory conditions that do not
104 adequately represent field conditions. Field tests are therefore desirable, even though experimental
105 conditions in the field cannot be controlled as tightly as in the laboratory. Several fields test have
106 been conducted recently. Peter et al.¹³ reported on a field site where CO₂ was injected through
107 three wells for a period of 10 days into an aquifer at a depth of 18 m in Northeast Germany. Water

108 samples from downgradient monitoring wells showed a moderate increase in Ca, K, Mg and Fe
109 (~15% to 40%), and a significant increase in Al, Si, Mn (~120% to 180%) in comparison with
110 baseline groundwater. An increase in the dissolved concentrations of heavy metals was also noted.
111 Gahill and Jakobsen¹⁴ also reported a field scale pilot test in which CO₂ gas was injected at 5-10 m
112 depth into an unconfined aquifer in Denmark for two days, with monitoring of water geochemistry
113 for more than 100 days. In addition to a one-unit drop in pH and a two-fold increase in electrical
114 conductivity (EC), increases in major and trace element concentrations were ~260% and 320% for
115 Ca and Mg, respectively, ~50% for Na and Si, as well as ~730%, 370%, 330% and 160% for Al,
116 Ba, Sr, and Zn respectively.

117 Groundwater quality was also monitored at the CO₂-Field Lab test site in Southern Norway¹⁵.
118 This test consisted of a 6-day injection of CO₂ into a shallow glacio-fluvial aquifer at a depth of
119 20 m, followed by about a week of post-injection monitoring at various depths using multiple
120 observation wells. A significant increase in dissolved Ca and Si concentration was observed at
121 some locations, in addition to a strong pH drop and alkalinity increase. However, the sediment
122 heterogeneity and mixing of seawater with fresh water at this site complicated the interpretation of
123 the test results. Most recently, a single-well push-pull test was conducted in a shallow aquifer at
124 Cranfield, Mississippi¹⁶. In this case, the mobilization and/or retardation of major and trace
125 elements were quantified using a mixing model to evaluate the concentration trends observed
126 during the test. Although mobilization of major cations and most trace metals was confirmed by
127 this field test, the observed changes in the dissolved concentrations of major and trace elements
128 could not be used to pinpoint CO₂ leakage because of the wide spatiotemporal variability in
129 background groundwater compositions at the test site. The ZERT (Zero Emissions Research and
130 Technology) field test in Montana, USA,^{17,18} and a field test conducted in Mississippi¹⁹ are two
131 other field experiments that revealed the mobilization of dissolved metals upon introduction of

132 CO₂ into groundwater. These two tests are the focus of this paper and will be discussed later in
133 more details.

134 In general, observations from both field and laboratory experiments show an increase in the
135 dissolved concentrations of major and trace elements upon CO₂ release. However, there appears to
136 be two noticeable differences between the results of field and laboratory tests. First, the rise in
137 concentrations of dissolved constituents observed during field tests is typically much less
138 pronounced than in laboratory experiments— field tests show increases of about an order of
139 magnitude or less, compared to levels prior to CO₂ injection (20% to 700% in the studies cited
140 above), whereas orders-of-magnitude increases have been observed in laboratory tests. Second,
141 increases in trace element concentrations, especially those of environmental relevance such as As,
142 Pb, Ba, and Cd, are more frequently reported in laboratory tests than in field tests. Potential
143 reasons for these differences are investigated in the present study.

144

145 **1.3 Objectives of present study**

146 In this paper, we use numerical models to investigate two issues regarding the impact of CO₂
147 leakage into groundwater: 1) the chemical processes leading to the mobilization of metals and 2)
148 the potential reversibility of these processes upon CO₂ exsolution, which would occur if deep CO₂-
149 saturated groundwater migrated (or was pumped) to shallow depths. Our objectives are first to
150 compare previous and new modeling results for two different field tests and one laboratory study,
151 to determine whether the same mechanisms could explain the mobilization of metals in these
152 experiments. Another objective is to bring up the subject of metal release reversibility, which has
153 not been given much attention in the literature. Our investigations on reversibility are limited to the
154 use of simple models to illustrate the concept, with the goal to stimulate interest in this topic for
155 further studies.

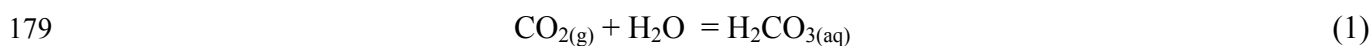
156 Numerical models have been used to perform generic evaluations of the potential impact of
157 CO₂ leakage on the water quality of shallow aquifers,²⁰⁻²⁴ to identify potential issues such as the
158 leaching out of organic compounds at depth by supercritical CO₂ and their release in shallow
159 aquifers,²⁵ and to interpret laboratory experiments,^{7,10,11} as well as field tests,^{19,26} to understand the
160 underlying transport and chemical processes that control the mobilization of major and trace
161 elements upon CO₂ dissolution in groundwater. By integrating modeling efforts with real data sets
162 from field and laboratory experiments, conceptual models of metal release can be tested, and their
163 application to different field settings and/or experimental conditions can be evaluated.

164 Here, we examine the contrasting metal-mobilization behavior at the Montana State University-
165 Zero Emissions Research and Technology (MSU-ZERT) field test in Montana,¹⁷ and a field test
166 conducted in Plant Daniel, Mississippi¹⁹, with the goal to advance our understanding of water-
167 quality changes that may occur due to CO₂ intrusion/influx under different hydrologic and
168 geochemical settings. We compare results of previous and new modeling investigations by our
169 group at the field scale. We then also model sequential leaching laboratory tests performed on
170 sediments collected at the site in Mississippi⁹ to evaluate whether the metal-release concepts
171 developed based on the field data is consistent with the laboratory study.

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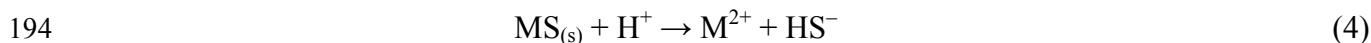
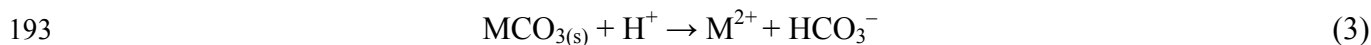
173 **2. Reactive Processes**

174 As postulated on the basis of laboratory tests,⁴ and revealed through simulations of laboratory
175 experiments^{7,8,10,11} and field tests,^{19,26} the chemical processes leading to the release of metals in
176 aquifers impacted by CO₂ can be summarized as follows. The dissolution of CO₂ in water
177 produces carbonic acid, which decreases pH and increases the dissolved carbonate content in
178 impacted groundwater:

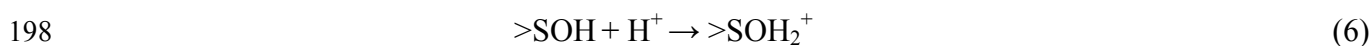
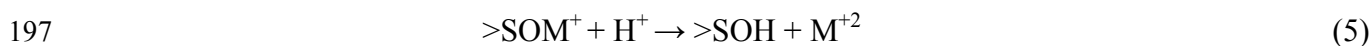


181 In pure water, the dissolution of CO₂ at pressure > 5 bars yields a pH near 3.5; however, in
 182 natural systems the pH drop is not as pronounced (values typically near or above 5) because of
 183 buffering by various reactions. For example, at the Frio deep CO₂ injection test site,²⁷ injection of
 184 supercritical CO₂ at pressures ~150 bar into a deep sandstone aquifer resulted in pH dropping from
 185 about 6.5 to 5.7. Under totally different conditions in shallow sandy gravels, a few meters below
 186 the ground surface at the MSU-ZERT site,¹⁷ the pH decreased from around 7 to 6 after injection
 187 of gaseous CO₂ through a horizontal pipe at 2-2.3 m deep. A more significant pH decrease, from
 188 about 8 to 5.1, was observed at the Mississippi site¹⁹ upon injection of groundwater carbonated at
 189 pressure near 4 bar into a confined, poorly buffered formation predominantly containing sandy
 190 sediments.

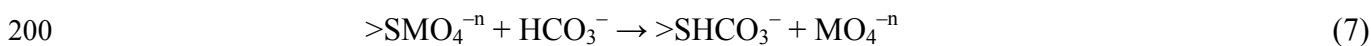
191 The decrease in groundwater pH upon carbonation can release metals (M) by the dissolution of
 192 minerals, most particularly carbonates and sulfides:



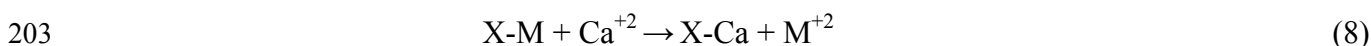
195 Adsorption-desorption reactions are also expected to play an important role in metal mobilization,
 196 and also in buffering pH in the absence of significant amounts of fast-reacting carbonate minerals:



199 Competitive sorption with bicarbonate ions (e.g., As, Se) could also release metal oxyanions:



201 In addition, metals released by the above reactions (e.g., Ca) may trigger exchange reactions that
 202 then cause the further release of other metals into solution:



204 These reactive processes were investigated by numerical modeling at both the MSU-ZERT²⁶
 205 and Mississippi test sites,¹⁹ as discussed below.

206 **3. Modeling Interpretations of Field Tests**

207 In the MSU-ZERT field experiment,¹⁷ gaseous CO₂ was injected for about one month into a
208 horizontal pipe located about a meter below the water table of a very shallow freshwater aquifer,
209 under natural (steep) hydraulic gradient conditions. Sediments beneath this site consisted primarily
210 of Cenozoic alluvial sandy gravel deposits. The groundwater composition was monitored prior to,
211 during, and (for about a week) following injection. Rain fell on several occasions over this shallow
212 test site, leaving a relatively small time window (about 10 days) during which the groundwater
213 composition was unaffected by rainfall during injection.¹⁷

214 The second study was conducted in Mississippi¹⁹ (hereafter referred to as the Mississippi site).
215 This field test was driven in part by the need for an experiment over longer time frames, under
216 better geochemically constrained conditions, and into a deeper (~50 m) geologic formation than at
217 the MSU-ZERT site. The sediments at this test site consist primarily of Cenozoic deltaic/near-
218 shore marine, poorly consolidated sands interbedded with clays. In this experiment, groundwater
219 from a confined hydrostratigraphic interval was pumped and carbonated above ground, then re-
220 injected into the same interval (in a dipole, closed loop system) to simulate leakage of CO₂ from a
221 deep storage reservoir into an overlying aquifer. Injection of carbonated groundwater at this site
222 lasted for about 5 months, preceded by an extensive monitoring period of background conditions
223 (13 months, including 2 months of pumping without carbonation) and followed by a post-injection
224 monitoring period of about 10 months.

225 In both studies, the groundwater quality was monitored using dedicated monitoring wells
226 installed up- and downgradient from the injection location (groundwater samples for analyses of
227 trace metals were filtered, prior to acidification, at 0.1 μm in the MSU-ZERT test and 0.2 μm in
228 the Mississippi experiment, to minimize possible colloidal materials). Sediments at both sites were
229 also characterized to determine metal-sediment associations and to help understand key reactive
230 processes resulting from carbonation of the groundwater. Results from both these studies indicated

231 a significant pH decrease upon carbonation (by ~0.8 pH units at the MSU-ZERT site, and ~3 pH
232 units at the Mississippi site), accompanied by the release of primarily alkali and alkaline earth
233 metals, Fe, and a few other trace elements (the concentrations of these dissolved species did not
234 exceed national regulatory drinking water standards).

235 Zheng et al.²⁶ ran modeling analyses to interpret the groundwater quality response to CO₂
236 injection at the MSU-ZERT site. It was determined that a dynamic reactive-transport model could
237 not be well constrained because only a short period of the test was unaffected by rainfall, and fast,
238 gaseous CO₂ migration in the vadose zone appeared to have contributed to the groundwater
239 response to CO₂ injection. For these reasons, geochemical modeling analyses were conducted
240 instead, examining groundwater chemistry as a function of pH and P_{CO_2} , independently of time.
241 The geochemical modeling analyses were supplemented with principal component (statistical)
242 analyses of the groundwater chemistry data, which suggested a correlated response to carbonation
243 for alkali and alkaline earth metals, and another different correlated response for trace metals
244 forming oxyanions (e.g., As, Se). Based on these investigations, Zheng et al.²⁶ suggested that at
245 this site, groundwater carbonation drove calcite dissolution, which resulted in the release of Ca,
246 which in turn drove exchange reactions with most major and trace metal cations. The release of Fe
247 was attributed to the dissolution of reactive Fe minerals (presumably ferrihydrite and/or fougérite
248 “green rust”), and the release of anions (As, Se) to competitive adsorption of carbonate. Both field
249 data¹⁷ and modeling results²⁶ showed a progressive increase in metal concentrations with a pH
250 decrease (and alkalinity increase), and a quick return to background concentrations after the
251 injection stopped.

252 The longer test period and extensive data set collected during the Mississippi field
253 experiment¹⁹ allowed for the development of 1D, 2D, and 3D reactive transport models of this
254 field experiment, drawing on extensive hydrogeologic and geochemical characterization efforts,
255 including detailed investigations of mineral-sediment associations by wet chemistry methods,

256 spectroscopic analyses, and laboratory CO₂ leaching experiments.^{9,19} A horizontal 2D reactive
257 transport model was presented in Trautz et al.¹⁹

258 At the Mississippi site, the pH drop (by ~3 units) upon carbonation was initially accompanied
259 by a pulse-like increase in the concentration of major cations (Ca, Na, Mg, K) and some trace
260 metals (e.g., Ba, Fe, Sr, Mn) (Figure 1). Initial reactive transport simulations¹⁹ showed that this
261 behavior could be reproduced by processes similar to those postulated for the MSU-ZERT site,
262 namely Ca from calcite dissolution driving exchange reactions with alkali and alkaline earth
263 metals, and dissolution of Fe sulfides releasing Fe. However, one important difference between
264 these test sites is the abundance of calcite at the MSU-ZERT site, compared to the rare occurrence
265 of this mineral at the Mississippi site, where it was found only in minute quantities, well below
266 conventional XRD and TIC-TOC detection limits. Our previous modeling analyses¹⁹ showed that
267 fast and complete dissolution of a limited amount of calcite could explain the observed pulse-like
268 behavior of dissolved Ca concentrations, and of other cations by exchange with Ca (Figure 1).
269 Modeling also showed that fast desorption could be an alternative process, yielding pulse-like
270 concentration trends for Ca, Fe, and other cations.

271 After publication of our initial results¹⁹, post-injection monitoring at the Mississippi site
272 revealed that the pulse-like response of dissolved metals observed during injection was followed
273 by slow-rising concentrations of alkali and alkaline earth metals starting almost immediately after
274 the end of the injection period (Figure 2). Also, the pH remained depressed at all monitoring wells
275 after the pump was turned off. This finding is different from observations at the MSU-ZERT site,
276 where the groundwater composition and pH quickly returned to ambient background conditions
277 after the injection of CO₂ was stopped.¹⁷ The contrasting behavior at these two sites may be
278 explained by the differences in regional hydraulic gradient and pH buffering capacity at these
279 sites. The abundance of carbonate minerals (buffering pH) and steep hydraulic gradient at the
280 MSU-ZERT site are favorable conditions for a quick pH rebound and fast return to background

281 concentrations of dissolved species after CO₂ injection. In contrast, the hydraulic gradient at the
282 Mississippi site is small, and sediments have a low buffering capacity. Thus, it is suggested that
283 once injection ended, the return to slow groundwater velocities (thus increasing residence time)
284 and persisting low pH provided conditions favoring continued (and increased) reactions between
285 sediments and groundwater.

286 To test this hypothesis, further modeling analyses were performed as part of the present study.
287 Simple reactive transport models were constructed using the same setup and mineralogical,
288 thermodynamic and kinetic data as implemented in our initial investigations¹⁹ (Appendix A). In
289 these new simulations, sediment-bound metals were included in the form of both (a) a fast-reacting
290 but limited pool, yielding a pulse-like response to a pH drop (as in initial simulations¹⁹) but also
291 (b) a slow-reacting but essentially unlimited pool, yielding rising dissolved metal concentrations
292 only upon decreased groundwater velocities, after the injection was ended. Such conceptualization
293 combines the initial fast pulsing behavior reported earlier¹⁹, together with transport-limited kinetic
294 dissolution trends (e.g., Johnson et al.²⁸) that are strongly dependent on groundwater residence
295 times, and only noticeable when the groundwater velocity is slow relative to reaction rates or
296 inversely, when reaction rates are fast relative to the groundwater velocity.

297 In the present study we applied this concept to the Mississippi test experiment, by modeling
298 the fast dissolution of a limited amount of calcite, superimposed with the slow dissolution of
299 plagioclase (ubiquitous in the sediments). Four simulations were run: a base-case that considers
300 the fast-reacting Ca pool (calcite) but no slow-reacting pool (no plagioclase, as in our previous
301 model¹⁹) and three other cases with the addition of plagioclase dissolution, at a different rate for
302 each case. Results show (Figure 2) that when the slow dissolution of plagioclase is added in the
303 simulations, both the observed short- and long-term concentration trends of Ca can be reproduced
304 fairly well (Figure 2), with the slow rise in Ca concentration becoming noticeable only during the
305 post-injection period when groundwater velocities returned to small values (essentially stagnant

306 hydraulic gradient < 0.0001 in this case). By Ca-driven cation exchange, the observed parallel
307 trend of Ba concentrations (and other cations as well) is also well reproduced (Figure 2).

308 These simulations convey the importance of considering groundwater residence time when
309 interpreting the results of field experiments and/or assessing the potential impact of CO₂ release at
310 a particular site. The slow dissolution of minerals (by carbonic acid from CO₂ dissolution) is likely
311 to present more of a potential concern (and be more noticeable) at sites where the regional
312 groundwater flow rate is low. Also, the fact that most laboratory experiments to investigate CO₂
313 impacts on groundwater are conducted under “batch” (stagnant) conditions may explain why the
314 release of metals observed in these experiments is generally much more noticeable than in the
315 field, where groundwater is seldom stagnant.

316

317 **4. Modeling Interpretation of Laboratory Experiments**

318 We report here on the modeling of sequential leaching tests⁹ conducted on two sandy sediment
319 samples collected from the injection interval at the Mississippi field site¹⁹ (these sequential
320 leaching tests were conducted to supplement the field test and evaluate possible screening
321 procedures⁹). The goal of this modeling effort was to determine whether the same geochemical
322 processes simulated to reproduce the field test results could also explain the results of these
323 laboratory experiments. To set the stage for this modeling investigation, before discussing its
324 results, we first summarize below the experimental procedure followed by Varadharajan et al.⁹
325 (readers are referred to their paper for more details).

326

327 **4.1 Summary of experimental approach**

328 In the experiments carried out by Varadharajan et al.⁹, synthetic groundwater solutions were
329 initially brought into contact with sandy sediments that were air-dried in a glove box. The
330 solutions were allowed to equilibrate with the sediments, then subsequently sampled and replaced
331 with fresh groundwater at time intervals of 1, 4, 11, and 25 days after the start of each experiment.

332 Two different types of experiments were used to distinguish between pH-driven and carbonate-
333 driven metal-release reactions. The first setup involved pressurized reactor cells (at pressure ~ 4
334 bar) that were filled with synthetic groundwater solutions saturated with CO₂, hereafter referred to
335 as the “CO₂-saturated” system. The second setup used vials that were filled with pH-amended,
336 synthetic groundwater solutions equilibrated with a CO₂-free atmosphere at atmospheric pressure,
337 and acidified with HCl to evaluate metal release driven by pH effects alone. These experiments are
338 hereafter referred to as the “pH-amended” system. The solid:solution ratio was maintained at 1:4.5
339 in the “CO₂-saturated” case, and 1:4 in the “pH-amended” case. Synthetic groundwater was
340 prepared with a composition similar to groundwater at the Mississippi field site, 6.4 mM NaHCO₃,
341 0.7 mM NaCl, 0.1 mM KCl, 0.1 mM CaCl₂, and 0.3 mM Na-acetate; no trace elements were
342 added to the solution.

343

344 **4.2 Modeling Approach and Results**

345 The numerical model was designed to mimic experimental procedure as closely as possible.
346 The water-sediment system was modeled as a “batch” system with a total volume of 1 L. The
347 solution (synthetic groundwater) was numerically reacted with the sediments and subsequently
348 withdrawn and replenished with fresh solution at the prescribed periods of time (1, 4, 11, and 25
349 days) to match the experimental procedure. The same synthetic groundwater composition and
350 solid-to-solution ratios were assumed as in the actual experiments. The chemical reactions and
351 reactive processes considered in the model were the same as those used for modeling the
352 Mississippi field test (Appendix A).

353 The same geochemical conceptual model, as adopted to simulate the MSU-ZERT and
354 Mississippi field tests (as presented earlier) was used to model the laboratory experiments; it is
355 thus postulated that the drop in pH induces the dissolution of calcite, and that the resulting increase
356 in Ca concentration subsequently triggers a series of cation exchange reactions, leading to an

357 increase in the concentrations of alkaline earth cations. The values of two key model input
358 parameters, the volume fraction of calcite and its specific surface area, were modified from the
359 values adopted to model the field test in order to match the experimental data. The volume fraction
360 of calcite was changed from 0.0086% (calibrated after the field test data) to 0.0073% in the “CO₂-
361 saturated’ case, and 0.0096% for the “pH-amended” case (calibrated after the laboratory test data),
362 which are essentially insignificant changes that could easily be attributed to heterogeneity or
363 measurement uncertainty. However, the dissolution of calcite had to be accelerated by increasing
364 the calcite specific surface area by two orders of magnitude (Equation A–1). Such an increase is
365 within the range typical of the discrepancy observed between field- and laboratory-scale rates
366 (e.g., Zhu,²⁹). For example, Yang et al.¹⁶ also mentioned that reaction rates estimated from batch
367 experiments using sediments from their test site were generally higher than those observed in the
368 field push-pull test. The use of a larger calcite surface area when modeling the laboratory
369 experiments can also be justified by the fact that the unconsolidated sediments in the reactor cells
370 were well-stirred to ensure good mixing and maximize the surface area available for reactions.
371 Figures 3 and 4 show the sensitivity of calculated Ca and Sr concentrations to the volume fraction
372 and specific surface area of calcite, indicating the need to change both the volume fraction of
373 calcite and its specific surface area to match the measured Ca and Sr concentrations.

374

375 An alternative conceptual model proposed by other studies^{4,10,11} is based on impurities that
376 may be present in carbonate minerals being the source of metals released when sediments are
377 reacted with carbonated water. To test this concept, we removed Sr from the list of exchangeable
378 cations, and instead included 1.5 mol% Sr impurity to calcite, an amount that was calibrated to
379 match the experimental results (in doing so, we also recomputed the equilibrium constant for Sr-
380 calcite by assuming an ideal solid solution between calcite and strontianite.) Figure 5 shows that
381 calcite with 1.5% Sr impurity leads to a reasonably good fit of the measured data, although the

382 concept of calcite dissolution plus cation exchange²⁶ adopted in the aforementioned models seems
383 to perform slightly better in terms of capturing the temporal changes. Nevertheless, considering
384 the large uncertainties exhibited by the data, this modeling exercise is unable to distinguish which
385 concept is more plausible.

386 **5. The Question of Reversibility**

387 It is well known that the exsolution of CO₂ from groundwater increases the water pH (reverse
388 of reactions 1 and 2) and thus is likely to result in immobilization metals by reversing Reactions 3
389 to 8. Examples of mineral precipitation upon CO₂ exsolution include the treatment of ferruginous
390 groundwater by pressure-driven CO₂ degassing³⁰, and the observation of dolomite precipitation
391 upon CO₂ exsolution (in this case thermally driven exsolution) during a CO₂-dolomite reaction
392 experiment.³¹ In fact, some metallic ore deposits are known to have formed due to the pH rise
393 driven by exsolution of CO₂ (and other acid gases) upon depressurization and boiling when metal-
394 loaded thermal waters ascend to the surface³². Furthermore, many naturally carbonated mineral
395 spring waters are of excellent (drinking) quality with respect to priority pollutant metal
396 concentrations.³³ Therefore, a logical question to raise is whether the mobilization of metals at
397 depth, by CO₂-saturated water could be mitigated when groundwater ascends toward the surface
398 and progressively depressurizes, leading to CO₂ exsolution.

399 To help illustrate this process in the context of shallow groundwater aquifers, we conducted
400 numerical experiments using simple geochemical simulations (Appendix B). In the first stage, the
401 CO₂-driven ($P_{\text{CO}_2} \sim 5$ bar) dissolution of FeS and trace-metal-bearing (Ba, Pb, Ni) calcite was
402 simulated, accompanied by desorption of cations (Fe⁺², Ni⁺², Ba⁺², and Pb⁺²) from a sorbent
403 arbitrarily modeled as iron hydroxide (ferrihydrite). In a second stage, the depressurization of this
404 system was simulated down to atmospheric P_{CO_2} levels, leading to re-sorption and re-precipitation
405 of trace metal-bearing calcite and also siderite. The degassing stage was conducted with water in
406 contact with the minerals and sorbent considered (i.e., solution with sediments), and then repeated

407 without contact with minerals or sorbent (i.e., with sediments removed from the solution). The
408 same initial general geochemical conditions as observed at the Mississippi field test site were
409 assumed, including the input water composition reported by Trautz et al.¹⁹, yielding a pH drop
410 from ~8 to ~5.6 upon CO₂ pressurization (Figure 6). However, it should be emphasized that these
411 simulations were not intended as predictions of the Mississippi field test, and are only meant to
412 illustrate the effect of CO₂ degassing in a generic, mostly qualitative manner.

413 Results are examined independently of time by plotting pH and aqueous metal
414 concentrations as a function of CO₂ pressure for the cases considered (Figure 7). Upon degassing
415 of CO₂, the concentrations of metals and pH return close to their original values, except for Ni in
416 the case without sediments. This is because in this example, the behavior of Ni is dominated by
417 sorption/desorption, whereas the concentrations of the other metals are mostly controlled by
418 dissolution/precipitation. Removing the sediment in this case obviously prevents Ni from re-
419 sorbing upon CO₂ degassing. In contrast, the concentration of Fe upon pressurization with CO₂ is
420 controlled by the dissolution of FeS followed by siderite precipitation, which is not initially
421 present but allowed to form. The concentrations of other metals (including Pb on Figure 7) are
422 dominated by the dissolution and re-precipitation of metal-bearing calcite, assuming reversibility
423 in the partitioning of trace elements, for simplicity. Upon degassing, without sediments present,
424 there is no precursor surface area for precipitation, which allows for a certain amount of
425 supersaturation to be reached until precipitation occurs (through a scheme approximating
426 nucleation implemented into the TOUGHREACT code³⁵). This causes a discontinuous pH curve
427 and unsymmetrical behavior between the CO₂ dissolution and exsolution stages (Figure 7), but as
428 would be expected, all paths for metals controlled by precipitation/dissolution eventually return
429 close to their starting points. These somewhat simplistic simulations illustrate how the system
430 behavior upon depressurization depends on the differences between dissolution and precipitation
431 rates (which in turn depend partially on differences in surface areas available for dissolution and

432 precipitation), relative rates of carbonate mineral precipitation (e.g., calcite vs. siderite), and on
433 whether sorption is considered reversible or not. Concentration trends also depend on the
434 partitioning (solid-solution) behavior of trace elements into re-precipitated carbonates, as a
435 function of water chemistry. All these characteristics are expected to be strongly influenced by the
436 physical path taken by groundwater as it ascends toward the surface. Therefore, the overall risk of
437 potential CO₂ leakage into groundwater should not only consider the chemical impact of carbonic
438 acid on the mobilization of metals, but should also take into account the path of contaminated
439 groundwater to potential receptors at shallow depths where the ambient pressure is too low to
440 maintain elevated CO₂ (carbonic acid) concentrations into solution.

441

442 **6. Summary and Conclusion**

443 The controlled release of CO₂ into shallow aquifers at the MSU-ZERT and Mississippi test sites
444 provided a unique opportunity to combine numerical modeling analyses with extensive datasets
445 collected in the field and the laboratory, to assess the effects of potential CO₂ leaks from deep
446 storage formations on the quality of freshwater aquifers. At both sites, the groundwater pH
447 responded quickly to carbonation, dropping by about 0.8 pH units in the MSU-ZERT experiment
448 (a well-buffered system) and about 3 pH units in the Mississippi experiment (a poorly buffered
449 system). At both sites, the pH decrease was accompanied primarily by increased dissolved
450 concentrations of alkali and alkaline earth metals as well as Fe. The concentrations of a few other
451 trace metals also increased, but to a lesser extent, and never exceeding regulatory limits. The main
452 differences in response to carbonation at these sites were the types of concentration profiles
453 observed with time for mobilized constituents. Fairly continuous increases with time (and pH
454 drop) were observed at the MSU-ZERT site, followed by a quick return to background conditions
455 once carbonation ended¹⁷. At the Mississippi site, however, the carbonation of groundwater first
456 yielded a pulse of mobilized constituents¹⁹, followed by slow concentration increases after the

457 injection ended (when the groundwater flow velocity decreased). The slow rise in concentrations
458 eventually reached new plateaus although the pH remained depressed for months after the
459 injection ended. This contrasting behavior at these two test sites is attributed to the slow ambient
460 groundwater velocity and lower pH buffering capacity (very small amounts of carbonate minerals)
461 at the Mississippi site compared to the MSU-ZERT site.

462 Characterization and modeling studies of the field data suggest that at both sites, calcite
463 dissolution, ion exchange and/or desorption were the primary mechanisms of initial (fast) release
464 of alkali and alkaline earth metals. Effects from slow dissolution of other minerals were only
465 noticeable in the Mississippi field experiment after the injection ended, due to the slow ambient
466 groundwater velocity at this site once the pump was turned off. This shows that the ambient
467 groundwater flow rate is an important parameter to consider, in addition to the pH buffering
468 capacity of an aquifer, when evaluating the potential impact of CO₂ leakage on groundwater
469 quality.

470 A series of previously published laboratory sequential leaching tests⁹ using sediments from the
471 Mississippi site were simulated. By applying our conceptual model of Ca-driven cation exchange
472 previously developed for the MSU-ZERT field test²⁶, then cross-tested with simulations of the
473 Mississippi field experiment¹⁹, we were able to simulate these laboratory experiments reasonably
474 well, and explain differences observed between laboratory and field test results. Our simulations
475 suggest that calcite dissolution and Ca-driven cation exchange may control the initial release of
476 alkali and alkaline earth metals in both the field and laboratory experiments, although the
477 dissolution of calcite containing metal impurities cannot be ruled out as another potential
478 mechanism of metal release.

479 A higher dissolution rate of calcite, compared to the rate used to model the field experiments,
480 was required to model the laboratory data. This suggests that laboratory tests might be too
481 aggressive in leaching out trace elements, relative to what would be expected in the field, as

482 solution and sediment are well mixed under a no-flow condition in the laboratory tests. This
483 should be taken into account when laboratory tests are used to evaluate the potential impact of
484 CO₂ leakage on groundwater quality.

485 Simple, generic numerical experiments illustrated how the mobilization of metals under
486 elevated P_{CO_2} could be reversed under depressurization, which would occur when groundwater
487 ascends (or is pumped) to the ground surface and CO₂ volatilizes under decreasing hydrostatic
488 pressure. The extent of reversibility is likely to depend on the path followed by groundwater when
489 it is brought to the surface, both in terms of physical path (affecting the surface area available for
490 metal re-precipitation and/or re-sorption) and temperature-pressure path (affecting the
491 thermodynamic drive for these reactive processes). The largest reversal would be expected to
492 occur between P_{CO_2} of a few bar and atmospheric values, when the gradient of pH change with
493 P_{CO_2} is the steepest. In contrast, the potential impacts from the mobilization of organic
494 compounds²⁵ and brine displacement³⁴ by supercritical CO₂ in deep saline aquifers, followed by
495 leakage to shallow groundwater bodies, could be much less reversible, and therefore may warrant
496 more attention than the impact from the CO₂ alone. However, the sequestration of metals by
497 resorption and re-precipitation upon CO₂ exsolution, in the context of impacts from CO₂ leakage,
498 has been given little attention and may warrant more study investigating the effects of CO₂
499 pressurization and depressurization along different flow paths.

500 Reactive transport models are important tools being used to assess the potential risk of CO₂
501 geological sequestration to groundwater over long periods of time. Geochemical reaction networks
502 implemented in these simulations form the core of such models. This paper demonstrates that the
503 close integration of field and laboratory tests with numerical modeling is crucial to assess various
504 key geochemical reactions and parameters, and thus to increase the confidence in, and
505 predictability of, numerical models.

506

508 ACKNOWLEDGMENT

509 This work was supported by the Electric Power Research Institute; the EPA, Office of Water,
510 under an Interagency Agreement with the U.S. Department of Energy (DOE) at LBNL, under
511 contract number DE-AC02-05CH11231; and the Assistant Secretary for Fossil Energy, National
512 Energy Technology Laboratory (NETL), National Risk Assessment Program (NRAP), of the US
513 Department of Energy under Contract No. DEAC02-05CH11231.

514

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Appendix A – Mississippi Field Site Reactive-Transport-Model Mineralogical, Thermodynamic, and Kinetic Data

659 Modeled geochemical processes include aqueous complexation, surface complexation (using a
660 double diffuse layer model), cation exchange (using the Gaines-Thomas convention), and mineral
661 precipitation/dissolution under kinetic constraints (using published rate laws). The implemented
662 cation exchange reactions and selectivity coefficients are listed in Table A-1. In this model, it is
663 assumed that ferrihydrite (as $\text{Fe}(\text{OH})_3(\text{s})$), is the adsorbent, and the surface complexation reactions
664 and constants are listed in Table A-2. Based on the sediment mineralogical characterization,⁹ the
665 model considered illite, smectite, $\text{Fe}(\text{OH})_3(\text{s})$ and amorphous iron sulfide (mackinawite, $\text{FeS}(\text{m})$),
666 in addition to major aquifer minerals such as quartz, K-feldspar, and plagioclase (Ab80An20). The
667 amount of iron sulfide ($\text{FeS}(\text{m})$) was estimated from selective extraction data (~0.02 vol%), and
668 the amount of $\text{Fe}(\text{OH})_3(\text{s})$ from the sediment acid titration data (~0.015 vol%), assuming this phase
669 dominates H^+ sorption, as a first approximation. Carbonates were not detected using XRD and
670 solid TIC-TOC analysis, but very rare gains in calcite were found by micro-X ray spectroscopy.
671 Therefore, trace amounts of calcite were included in the simulations (0.0058%), an amount that
672 was calibrated to yield best match of observed and modeled Ca response to CO_2 release. The
673 amount of illite, smectite, quartz, and K-feldspar were roughly estimated from examinations of
674 sediment cores and thin sections.

675

676 The simulations are conducted with TOUGHREACT³⁵ which uses a general form of rate
677 expression:³⁶

678

$$r = kA \left| 1 - \left(\frac{K}{Q} \right)^\theta \right|^\eta \quad (\text{A-1})$$

679 where r is the kinetic rate, k is the rate constant ($\text{mol}/\text{m}^2/\text{s}$), which is temperature dependent, A is
680 the specific reactive surface area per kg H_2O , K is the equilibrium constant for the mineral–water

681 reaction written for the destruction of one mole of mineral, and Q is the reaction quotient. Here,
682 we set the parameters θ and η to unity. The rate constant for calcite dissolution is given as a
683 combination of neutral, acid, and carbonate mechanisms:^{37,38}

$$684 \quad k = 1.5 \times 10^{-6} e^{-E_a^{nu}/RT} + 0.5 e^{-E_a^H/RT} \alpha_H + 9.6 \times 10^{-5} e^{-E_a^{CO2}/RT} \alpha_{CO2} \quad (A-2)$$

685 where E_a^{nu} , E_a^H and E_a^{CO2} are activation energies with values of 23.5, 14.4, and 35.4 (kJ/mol)
686 respectively, according to Palandri and Kharaka.³⁸ 1.5×10^{-6} , 0.5 and 9.6×10^{-5} are rate constant in
687 mol/m²/s for neutral, acid, and carbonate mechanisms, respectively. α_H is the activity of proton
688 and α_{CO2} is the activity of dissolved CO₂. R is the gas constant. The surface area, A , is a function
689 of specific surface area and the abundance of minerals. The specific surface area of calcite was set
690 to 9.8 cm²/g, a value which was calibrated, together with the initial calcite volume fraction, to
691 match the breakthrough curves of alkaline earth metals observed during the field experiment at the
692 Mississippi site. It should be noted that reaction rates depend on the reactive surface area A in
693 Equation A-1, which is a function of the product of the specific surface area and the volume
694 fraction of each mineral. Therefore, the calibrated values of specific surface area and volume
695 fraction of calcite should be viewed as arbitrary and non-unique (co-linearly varying) values, the
696 product of which being of relevance but not each value separately.

697 Thermodynamic data (Table A-3) were taken primarily from the EQ3/6 database
698 *data0.ymp.R4*,³⁹ which relies on Gibbs free energy data primarily from SUPCRT92^{40,41} for
699 aqueous species, and from Helgeson et al.⁴² for minerals.

700

701 **Appendix B – Setup of CO₂ reaction and degassing numerical experiments**

702 The problem was run with TOUGHREACT V2³⁵ and the same thermodynamic database as used
703 for the other simulations (Appendix A). CO₂ pressurization was simulated with one model
704 gridblock, fully liquid-saturated, in contact with a 5-bar CO₂ gas buffer allowed to dissolve at a
705 rate prescribed to yield stable pH values near ~5.5 within a couple months (down from ~8

706 initially) (Figure 6). The system at low pH and ~5 bar CO₂ was then allowed to degas through a
707 second large (essentially open) model gridblock at atmospheric CO₂ pressure, into which gas from
708 the first gridblock was allowed to slowly flow until atmospheric CO₂ levels was reached. The
709 leakage rate was adjusted such that the system returned to initial atmospheric CO₂ levels within
710 about 180 days (an arbitrary but realistic value).

711 Ba, Pb, and Ni were included in trace quantities into calcite (in arbitrary amounts of 2×10^{-5}
712 moles Ba, 0.5×10^{-5} moles Pb, and 0.5×10^{-5} moles Ni for each mole of Ca). These elements and Fe,
713 Ca, Mg, were also considered initially sorbed onto the sediment, assuming sorption data for iron
714 hydroxides from Dzomback and Morel,⁴⁴ except Fe⁺² from Liger et al.⁴⁶ (from the *phreeqc.dat*
715 database, corrected for consistency with the other data). The solid phase (sediments) prior to
716 addition of CO₂ was assumed to contain (by solid volume) 10% plagioclase (An₂₀), 0.1% FeS,
717 0.1% calcite, and 0.01% iron hydroxides (as ferrihydrite). Siderite was allowed to precipitate but
718 not assumed initially present. The initial water composition was taken from Trautz et al.¹⁹, with
719 adjusted initial Fe, Ca, and Al concentrations to yield chemical equilibrium with FeS, calcite, and
720 plagioclase, respectively, at 25°C.

721

722 Table A-1. Cation exchange reactions and selectivity coefficients.⁴³

Cation exchange reaction	$K_{Na/M}$
$Na^+ + X-H = X-Na + H^+$	1
$Na^+ + X-K = X-Na + K^+$	0.2
$Na^+ + 0.5X-Ca = X-Na + 0.5Ca^{+2}$	0.4
$Na^+ + 0.5X-Mg = X-Na + 0.5Mg^{+2}$	0.45
$Na^+ + 0.5X-Ba = X-Na + 0.5Ba^{+2}$	0.35
$Na^+ + 0.5X-Mn = X-Na + 0.5Mn^{+2}$	0.55
$Na^+ + 0.5X-Sr = X-Na + 0.5Sr^{+2}$	0.35
$Na^+ + 0.5X-Zn = X-Na + 0.5Zn^{+2}$	0.4
$Na^+ + X-Li = X-Li + Li^+$	1.1

723

724 Table A-2. Surface complexation reactions and surface complexation constants (logK) on
 725 ferrihydrite. The reaction constants for surface protonation are from Dzombak and Morel⁴⁴ and
 726 surface complexation reactions of carbonate are from Appelo et al.⁴⁵

Surface complexation	logK
$HFO_sOH_2^+ = HFO_sOH + H^+$	-7.29
$HFO_wOH_2^+ = HFO_wOH + H^+$	-7.29
$HFO_sO^- + H^+ = HFO_sOH$	8.93
$HFO_wO^- + H^+ = HFO_wOH$	8.93
$HFO_wCO_2^- + H_2O = HFO_sOH + HCO_3^-$	-2.45
$HFO_wCO_2H + H_2O = HFO_sOH + HCO_3^- + H^+$	-10.4

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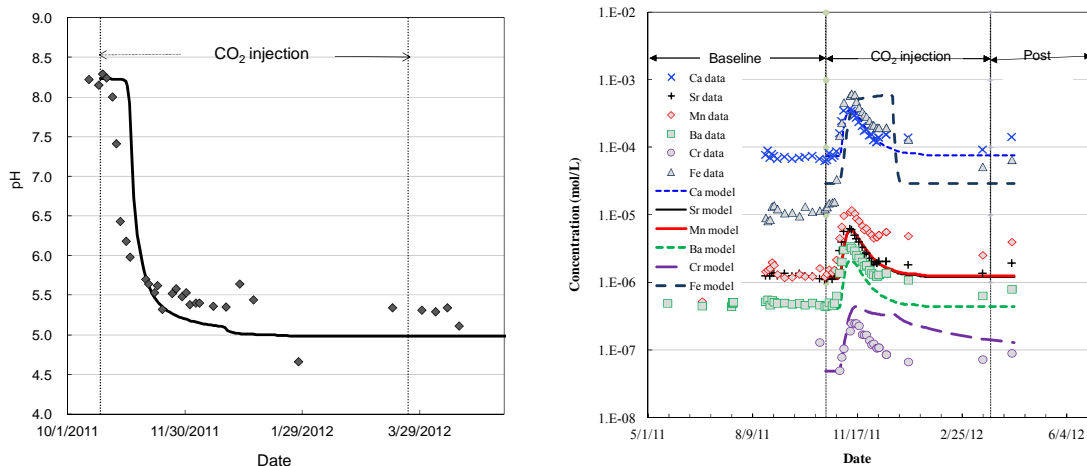
729 Table A-3. Equilibrium constants and volume fraction for minerals

Primary Mineral	Volume fraction (%)	logK(25°C)	Secondary Mineral	logK(25°C)
Quartz	92	-3.75	Gypsum	-4.48
Calcite	0.0058*	1.85	Dolomite	2.52
FeS(m)	0.02	-3.5	Siderite	-0.25
K-feldspar	2	-22.39	Witherite	1.77
Smectite-Na	0.5	-38.32	Rhodochrosite	0.252
Illite	1	-42.69	Strontianite	-0.31
Fe(OH) ₃ (s)	0.15	-5.66	Dawsonite	-17.9
Ab80An20	4	-14.8		

730 *varies depending models

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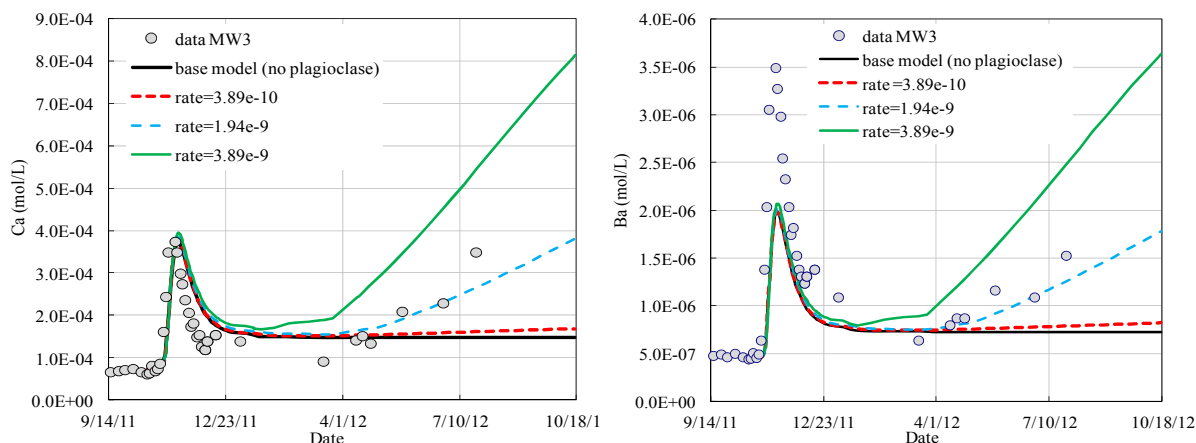
734

735 Figure 1. pH (left) and breakthrough of Ca, Sr, Mn, Ba, Cr, and Fe at about 5 m from a carbonated groundwater
 736 injection well; model predictions (lines) compared to observations (symbols) (data reported in Trautz et al. ¹⁹).

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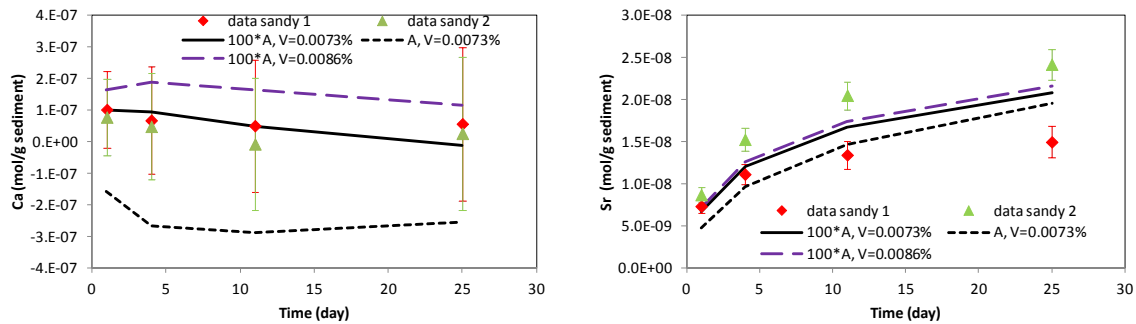
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741 Figure 2. Observed (symbols) and modeled concentration time profiles (lines) for Ca on the left and Ba on the
 742 right. Model results are shown for a base-case considering only the presence of fast-dissolving calcite in a
 743 limited amount, and three other cases with added slow dissolution of plagioclase at different rates as shown
 744 ($\text{mol s}^{-1} \text{kg}_w^{-1}$). See text.



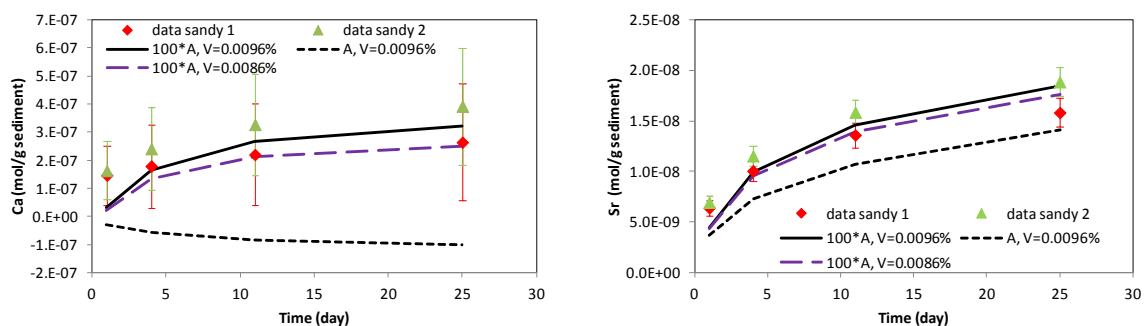
745

746 **Figure 3.** Measured Ca and Sr concentration (symbols) for the “pH-amended” experiment, and
 747 model results (lines) using different combination of parameters (calcite volume fraction, V;
 748 specific surface area, A; and the latter increased a hundred-fold, 100*A). Solute concentrations
 749 represent net changes after the subtraction of respective background concentrations measured in
 750 sediment-free controls, and normalized for solid weights (negative values represent uptake by the
 751 sediments). All concentration values are averages of duplicate samples; error bars for the
 752 laboratory data represent propagated standard errors based on analytical standard deviations and
 753 duplicate samples.

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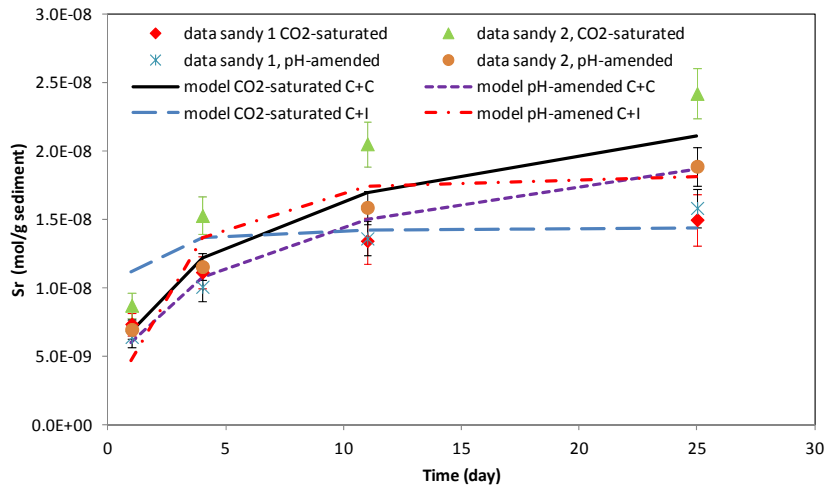
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758 **Figure 4.** Measured Ca and Sr concentrations (symbols) for the “CO₂-saturated” experiment and
 759 models results (lines) using different combinations of parameters. See caption of Figure 3 for
 760 additional information.



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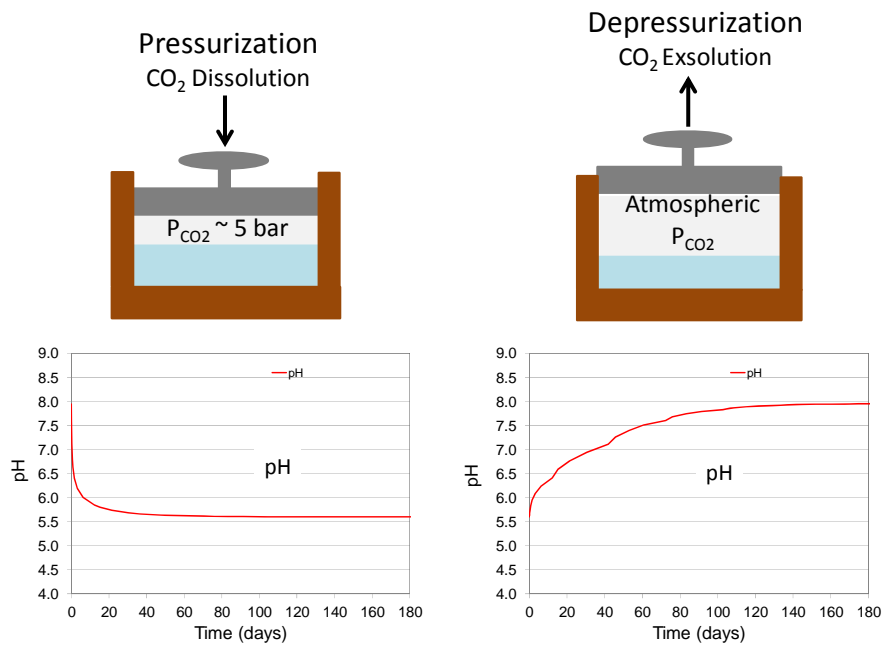
762 **Figure 5.** Measured Sr concentration (symbols) for “CO₂-saturated” and “pH-amended”
 763 experiment and the corresponding simulated concentration (lines) using different conceptual
 764 models: pure calcite dissolution plus cation exchange²⁶ (C+C) and dissolution of Sr-bearing calcite
 765 (C+I).

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771 **Figure 6.** Illustration of numerical experiments of CO₂ pressurization and depressurization, with

772 resulting pH shown (see Appendix B for details on initial conditions).

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