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German Montes-Hernandez, François Renard, Romain Lafay

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1 **Experimental assessment of CO₂-mineral-toxic ion interactions in a**
2 **simplified freshwater aquifer: Implications for CO₂ leakage from deep**
3 **geological storage**

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5 German Montes-Hernandez^{*a}, François Renard^{a, b}, Romain Lafay^a
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8 ^a CNRS and University Joseph Fourier-Grenoble 1, Institut des Sciences de la Terre (ISTerre),
9 OSUG/INSU, BP 53, 38041 Grenoble Cedex 9, France.

10 ^b Physics of Geological Processes, University of Oslo, Norway

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19 * Corresponding author: German Montes-Hernandez

20 E-mail address: german.montes-hernandez@ujf-grenoble.fr

1 **Abstract**

2 The possible intrusion of CO₂ into a given freshwater aquifer due to leakage from deep
3 geological storage involves a decrease in pH, which has been directly associated with the
4 remobilization of hazardous trace elements via mineral dissolution and/or via desorption
5 processes. In an effort to evaluate the potential risks to potable water quality, the present
6 study is devoted to experimental investigation of the effects of CO₂ intrusion on the mobility
7 of toxic ions in simplified equilibrated aquifers. We demonstrate that remobilization of trace
8 elements by CO₂ intrusion is not a universal physicochemical effect. In fact goethite and
9 calcite, two minerals frequently found in aquifers, could successfully prevent the
10 remobilization of adsorbed Cu(II), Cd(II), Se(IV) and As(V) if CO₂ is intruded into a drinking
11 water aquifer. Furthermore, a decrease in pH resulting from CO₂ intrusion could reactivate the
12 adsorption of Se(IV) and As(V) if goethite and calcite are sufficiently available in
13 underground layers. Our results also suggest that adsorption of cadmium and copper could be
14 promoted by calcite dissolution. These adsorbed ions on calcite are not remobilized when CO₂
15 is intruded into the system, but it intensifies calcite dissolution. On the other hand, arsenite
16 As(III) is significantly adsorbed on goethite, but is partially remobilized by CO₂ intrusion.

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1 **Keywords:** CO₂ leakage, Freshwater aquifer, Goethite; Calcite; Remobilization,

2 Metalloids; Heavy metals

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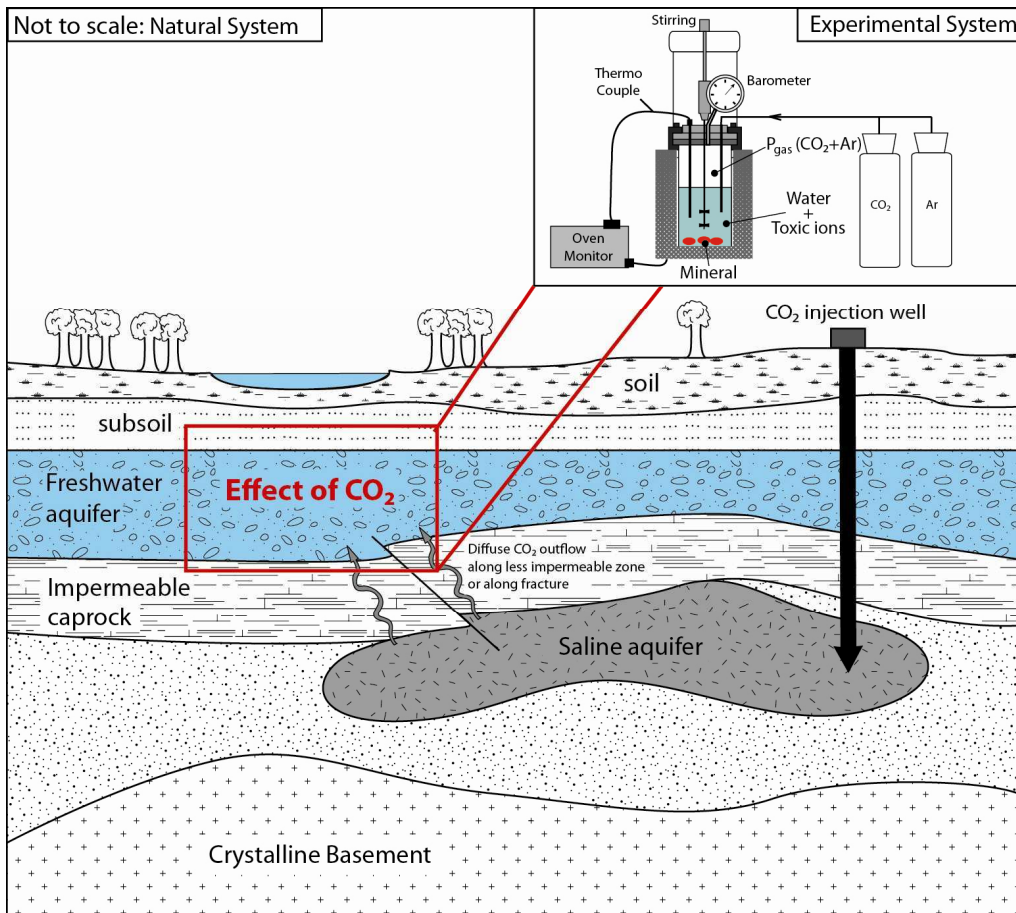
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1 **Introduction**

2 Unregulated CO₂ emissions into the Earth's atmosphere (about 22x10⁹ ton CO₂/year),
3 caused mainly by fossil fuel combustion, have led to concerns about global warming. To
4 maintain the atmospheric CO₂ level below 500 ppm, CO₂ emissions will have to be stabilized
5 at current levels, although they are forecast to double over the next 50 years (1). Capture from
6 individual industrial sources and long-term geological storage are realistic and available ways
7 of reducing CO₂ emissions because large volumes of this gas can be stored in various deep
8 geological formations (2-5). However, CO₂ injection into porous media (deep geological
9 formations) can significantly modify their storage properties. For example in brine aquifers,
10 nucleation-growth and/or dissolution of minerals are envisaged and these reactions can be
11 enhanced by high in-situ temperatures (80-110°C) and pressures (100-400 bar). Toxic
12 elements (e.g. metalloids or heavy metals) could be liberated or released by native mineral
13 dissolution reactions as measured and/or simulated in some studies (6-8); subsequently,
14 dissolved or released ions could be sequestered by nucleation-growth of secondary mineral
15 phases (9-10). In summary, several physicochemical reactions at fluid-rock interfaces have
16 been envisaged and they need to be studied in detail in the coming years as claimed by
17 various recent studies (5, 8-13).

18 The deep geological formations considered (e.g. brine aquifer) are always isolated by
19 impermeable layers, so-called caprock formations. Unfortunately, CO₂ leakage from storage
20 sites to higher formations (e.g. drinking water sources) by diffusion through less impermeable
21 zones or transport along (micro-) fractures could be a potential risk in the long term, possibly
22 aggravated by seismic activity and micro-seismicity (14). In this hypothetical case, CO₂
23 dissolution could influence the mobility and/or retention of hazardous trace elements (e.g.
24 heavy metals and/or metalloids) contained in native aquifer minerals, as recently investigated
25 by reactive transport simulations (7, 15-18), laboratory experiments (19-22) and field tests

1 (e.g. MSU-ZERT field site) (23-24). In this way, various trace elements such as Cd, Pb, Zn, U
2 and As, which can be toxic to humans or wildlife at $\mu\text{g/L}$ - mg/L concentrations, have been
3 predicted to be released by dissolution reactions of native aquifer minerals (15-18). All
4 simulations in these studies have assumed that the intrusion of CO_2 into drinking water
5 aquifers decreases their pH, enhancing the dissolution reactions of native aquifer minerals and
6 consequently remobilizing trace metal species if such metals are contained in the minerals.
7 Unfortunately, few experimental data are available in the literature in order to challenge or
8 support such predictions. Moreover, the sorption/desorption processes of trace elements (fast
9 or instantaneous processes at the mineral-fluid interfaces) are also rarely simulated because it
10 is difficult to combine them with dissolution-precipitation reactions in reactive transport
11 simulations (16). It should be noted that desorption/adsorption via surface complexation is
12 possibly the most important process controlling the fate of toxic trace elements mobilized by
13 CO_2 leakage (7, 15).

14 For the above reasons, the present study is devoted to experimental investigation of the
15 effects of CO_2 intrusion on the mobility/retention of toxic ions in simplified equilibrated
16 aquifers (drinking water sources). In our study, “simplified equilibrated aquifer” means a
17 synthetic solution enriched with one or two metal(loid) ions equilibrated for 24h with a single
18 or binary mineral system at 20°C and 10 bar of argon prior to CO_2 injection (8 bar). In this
19 context, six metal(loid) ions ((Cd(II), Cu(II), Se(IV), Se(VI), As(III) and As(V)) and two
20 widespread minerals (goethite, calcite and goethite-calcite composite) were investigated. A
21 schematic illustration of this experimental study with emphasis on CO_2 leakage from deep
22 geological storage is provided in Figure 1. Goethite and calcite were chosen because of their
23 abundance in nature as minerals (abiotic origin) and biominerals (biotic origin). Both minerals
24 can co-exist in several terrestrial environments such as deep geological formations, aquifers
25 (drinking water sources), soils and aerosols, playing an important role in the fate and transport

1 of several metalloid and heavy metal trace elements and organic molecules at the mineral-
2 fluid interfaces (25-29). Finally, it should be noted that various suspensions were withdrawn
3 from the reactor before and after injection of CO₂ in each experiment or run, in order to
4 monitor the pH and ion concentration ([Ca], [Fe], [Na], [As], [Se], [Cd] and [Cu]) ex-situ as a
5 function of time (up to 48 hours). This allows a simple macroscopic evaluation of element
6 transfer at the mineral-solution interfaces, involving mineral dissolution and/or
7 retention/mobility of adsorbed toxic ions related to the intrusion of CO₂ in the system.

8

9 **Materials and methods**

10 *Minerals*

11 Pure goethite, pure calcite and a goethite-calcite composite were synthesized as mineral
12 analogues for a given simplified potable aquifer. In this experimental study powdered and
13 high-purity minerals were used in order to increase their surface reactivity and also to
14 identify/quantify clearly their physicochemical affinity with investigated toxic ions interacting
15 in CO₂-poor and CO₂-rich solutions as schematically illustrated in Fig. 1. A brief description
16 of these mineral syntheses is provided in the following paragraphs.

17 Goethite: Low acicular goethite with a high specific surface area (130m²/g) was synthesized
18 by placing 1mol of NaOH and 0.2mol of FeCl₃.6H₂O in a 2L reaction cell and adding 1L of
19 high-purity water. Constant agitation (400rpm) of the solution and a moderate temperature
20 (30°C) for 24h of reaction were required. For more specific details on the synthesis procedure
21 and goethite characterization refer to Montes-Hernandez et al. (30).

22 Calcite: Nanosized calcite with a moderate specific surface area (7m²/g) was synthesized via
23 gas-solid carbonation of Ca(OH)₂ nanoparticles in a static bed reactor. The specific procedure
24 and fine calcite characterization have already been reported by Montes-Hernandez et al. (31).

25 In short, pure calcite was synthesized by placing 74g of Ca(OH)₂ in a 2L reaction cell slightly

1 heated to 30°C and by injecting high-purity CO₂ at 20 bar. Complete Ca(OH)₂-to-CaCO₃
2 (calcite) transformation was reached after about 24h of reaction.

3 Goethite-Calcite composite: Low acicular goethite intimately adhering to sub-micrometric
4 calcite - so-called goethite-calcite composite - with a high specific surface area (90m²/g) was
5 synthesized via three sequential precipitation reactions: (1) Fast precipitation of nanosized
6 acicular goethite (α-FeOOH) using a high OH/Fe molar ratio (=5); (2) Instantaneous
7 precipitation of portlandite (Ca(OH)₂) by adding CaCl₂ salt into a goethite alkaline
8 suspension, and; (3) Sub-micrometric calcite precipitation by injecting CO₂ into a goethite-
9 portlandite alkaline suspension. These sequential precipitation reactions and textural
10 characterization of goethite-calcite composite have been specifically described by Montes-
11 Hernandez et al. (32).

12

13 *Aqueous solutions*

14 One liter of high-purity water was used to prepare synthetic solutions enriched with
15 single or double metal(loid) ions by using commercial salts of As(III), As(V), Se(IV), Se(VI),
16 Cd(II) and Cu(II). The chemical compositions of all the salts used are summarized in Table 1.
17 For the double metal(loid) ion solutions, two ions were arbitrarily combined as follows:
18 As(III)-Se(IV), As(V)-Se(VI) or Cd(II)-Cu(II). In all cases, a high initial element
19 concentration of about 50mg/L was also arbitrarily considered. This high concentration is not
20 realistic in a given potable water aquifer, but it leads to a high saturation on the surface of the
21 minerals being investigated through a sorption process prior to CO₂ injection. Moreover, it is
22 easy to quantify the release and/or mobilization of adsorbed ion(s) due to CO₂ intrusion into
23 the system.

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1 *Experiments: CO₂-mineral-toxic ion interactions*

2 One liter of single or double metal(loid) ion solution and 3g of calcite, goethite or
3 goethite-calcite composite were placed in a 2L reaction cell. This suspension was
4 immediately stirred using constant mechanical agitation (400 rpm) and argon was also
5 immediately injected at 10 bar in order to simulate pressures of the kind relating to potable
6 water aquifers. After 24h of mineral-ion solution equilibration at room temperature ($\approx 20^{\circ}\text{C}$),
7 i.e. assuming that adsorption of a given ion takes place during the first 24h, high-purity CO₂
8 was injected at 8 bar into the dispersion in order to assess the release of adsorbed toxic ions
9 and also to quantify the mineral dissolution, both processes being possibly intensified by
10 intrusion of CO₂ into the system. In all experiments, about 15ml of dispersion were
11 withdrawn from the reactor as a function of time before (from 0 to 24h) and after (from 24 to
12 48h) injection of CO₂. The pH of each sample of suspension was measured at room
13 temperature. The suspensions were then filtered through a 0.2 μm Teflon filter. 10 ml of the
14 resulting filtered solutions were acidified for measurement of [Ca], [Fe], [Na], [As], [Se],
15 [Cd] and [Cu] by inductively coupled plasma optical emission spectrometry (ICP-OES).

16

17 **Results and discussion**

18 As predicted and/or measured, the intrusion of CO₂ within a freshwater aquifer decreases the
19 pH, enhancing dissolution reactions of native aquifer minerals and consequently remobilizing
20 trace metal species if such metals are contained in them. Here, various trace elements such as
21 Cd, Pb, Zn, U and As were predicted to be released by dissolution reactions of native aquifer
22 minerals and/or by fast desorption (7, 15-18). In this experimental study, we provide more
23 specific insights into the remobilization of Se(IV), Se(VI), As(III), As(V), Cd(II) and Cu(II)
24 related to CO₂ intrusion into a pre-equilibrated mineral-metal(loid) ion solution system. The
25 chemical speciation of these six ions in solution before and after injection of CO₂ was

1 determined by using the Phreeqc numerical code (33) in order to understand certain observed
2 behaviors more easily (see below). pH data (measured and calculated) and the dominant
3 species in solution are summarized in Table 1.

4 Goethite as an aquifer mineral analogue

5 Figure 2 displays a compilation of five different adsorption experiments using pure goethite
6 as adsorbent. Here, the adsorbed/remobilized amount of a given metal(loid) ion at the
7 mineral-solution interfaces was normalized with respect to the available surface area in the
8 system ($3\text{g} \cdot 130\text{m}^2/\text{g}$). In short, Cd(II), Cu(II) and As(III) are significantly adsorbed on the
9 goethite prior to CO₂ intrusion into the system. A lower adsorption capacity was measured for
10 Se(IV) and Se(VI) in the conditions investigated. After CO₂ intrusion, residual dissolved
11 Se(IV) is largely removed from the solution onto the goethite, i.e. the adsorption process is
12 reactivated by CO₂ intrusion. Conversely, adsorbed Cd(II) and Cu(II) are largely removed
13 from the goethite by CO₂ intrusion into the system. Adsorbed arsenite As(III), which is
14 reputed to be a very highly mobile element, was slightly affected by CO₂ intrusion. In general,
15 the so-called oxyanions were re-adsorbed or slightly remobilized (case: As(III)). However, the
16 heavy metals investigated (Cd(II) and Cu(II)) (single cations) were preferentially remobilized
17 from the goethite. This can be explained by a significant change in the surface charge of the
18 goethite after CO₂ intrusion, assuming that surface charge is strongly dependent on pH, as is
19 widely described in the literature (e.g. 27, 34 and references therein) and on the understanding
20 that the Cu and Cd speciation in solution remains unchanged in the presence of goethite when
21 CO₂ is intruded into the system (see Table 1). In our study, the pH (measured ex-situ) changes
22 drastically when CO₂ is intruded into the system (Fig. 2b). In this context, the intrusion of
23 CO₂ could create a positive charge on the goethite, enabling the re-sorption of available
24 dissolved anions in the interacting solution. Finally, a slight release of Fe (<2mg/L) was
25 measured prior to CO₂ intrusion, indicating slight dissolution of the goethite, and Fe was no

1 longer detected in the interacting solution (<0.1 mg/L, “minimum value in our calibrating
2 curve”) when CO_2 was intruded into the system (Fig. 2b). This is in agreement with the
3 literature, in the fact that the goethite is stable over a broad range of pH values (from 3 to
4 13.5) at ambient temperature (35, 36) as also verified by equilibrium Phreeqc calculations.

5

6 Calcite as an aquifer mineral analogue

7 In a similar way to the goethite scenario, Figure 3 summarizes five different adsorption
8 experiments now using pure calcite as adsorbent. The respective pH profiles and an average
9 Ca-concentration profile can be also consulted in Figure 3b. The adsorbed/remobilized
10 amounts for all the ions investigated were also normalized with respect to the available
11 surface area in the calcite system ($3\text{g}\cdot 7\text{m}^2/\text{g}$). Here, the major result is the fast, strong
12 sorption of Cd(II) and Cu(II) onto/into the calcite. The ex-situ monitoring of pH and Ca
13 concentration in the interacting solution (Fig. 3b) suggests that slight dissolution of calcite
14 enhances the sorption of cadmium and copper (heavy metals) as claimed earlier by Limousin
15 (37) for cadmium in particular. We also note that CO_2 intrusion into the calcite system has no
16 significant effect on the Cd(II) and Cu(II) already sorbed. This means that dissolution of the
17 calcite, i.e. the release of Ca from the calcite into the interacting solution as a result of CO_2
18 intrusion, was dissociated from potential remobilization of sorbed Cd and Cu as might be
19 speculated at first sight. On the other hand, the oxyanions investigated (Se(IV), Se(VI) and
20 As(III)) were only slightly adsorbed on the calcite, if the values are compared with those for
21 the sorbed amounts of Cd(II) and/or Cu(II) (Fig. 3a). We also note that arsenite As(III) and
22 selenate Se(VI) were completely remobilized from the calcite when CO_2 was intruded into the
23 system. Conversely, a more complex behavior was observed in the case of selenite Se(IV); in
24 fact, a given amount of dissolved Se(IV) was re-adsorbed on the calcite by CO_2 intrusion. In
25 this way, the decrease in pH resulting from CO_2 intrusion plays an important role with regard

1 to the surface charge of a given mineral, the chemical speciation of dissolved elements (partial
2 protonation of selenite from SeO_3^{2-} to HSeO_3^- : see Table 1) and possibly the surface
3 complexation process (25). It should be noted that the decrease in pH can be significantly
4 moderated/buffered by the dissolution of carbonate minerals (e.g. calcite) as illustrated in
5 Figures 2a (goethite system) and 3a (calcite system). This pH buffering capacity can be
6 envisaged in freshwater aquifers because these underground layers generally contain
7 carbonate minerals. Numerical simulations have been successfully used to quantify this pH
8 buffering capacity in groundwater in response to CO_2 leakage from deep geological storage
9 (7).

10 Goethite-calcite composite as an aquifer mineral analogue

11 Five supplementary adsorption/release experiments are reported in Figure 4, but, in this case,
12 a goethite-calcite composite was used as adsorbent. The pH profile for each adsorption/release
13 experiment and release of Fe and Ca by dissolution of goethite and calcite, respectively, are
14 also reported in Fig. 4b. As indicated in the previous cases, the adsorbed/remobilized amounts
15 of the ions investigated were normalized with respect to the available surface area in the
16 goethite-calcite system ($3\text{g}\cdot 90\text{m}^2/\text{g}$). In a similar way to the calcite system, fast, strong
17 adsorption of Cd(II) and Cu(II) onto the goethite-calcite was measured. However, the kinetic
18 behavior was reversed. For example, Cd was adsorbed in the first 10 minutes when pure
19 calcite was used as adsorbent and its adsorption was considerably retarded in the case of the
20 goethite-calcite system (see Fig. 3a and 4a). This was probably due to different textural
21 properties between pure calcite (nanosized) and calcite contained in the composite (sub-
22 micrometric) (31-32). On the basis of the results obtained with the calcite system, we assume
23 that such high adsorption is controlled preferentially by the calcite contained in the composite.
24 Additionally, these two adsorbed heavy metals were scarcely perturbed by CO_2 intrusion into
25 the system; this is in complete agreement with the calcite system (Fig. 3a and 4a). Concerning

1 the so-called oxyanions, a given proportion of residual dissolved selenite Se(IV) was
2 reabsorbed onto the goethite-calcite composite by CO₂ intrusion. Conversely, adsorbed
3 arsenite As(III) was partially remobilized from the goethite-calcite composite. This is in
4 agreement with the calcite and goethite systems. The selenate Se(VI) ion was slightly
5 adsorbed on the calcite and/or goethite before and/or after CO₂ intrusion into the system (Fig.
6 2a and 3a). This highly mobile ion had not presented any adsorption affinity with the goethite-
7 calcite composite (Fig. 4a). Finally, mineral dissolution could be intensified by CO₂ intrusion
8 in this way; we assumed that the goethite contained in the composite was extremely stable in
9 the conditions investigated because the Fe concentration measured in the solution was less
10 than 0.1 mg/L, the “minimum value in the calibrating curve”. Conversely, significant Ca
11 concentration was measured in the interacting solution and this was intensified by CO₂
12 intrusion, reaching about 340mg/L at the end of the experiment (48h) (Fig. 4b). As mentioned
13 above, calcite dissolution may moderate the decrease in pH and such dissolution is not related
14 directly to the remobilization of adsorbed heavy metals (e.g. Cd and Cu).

15

16 Competitive adsorption/remobilization of binary metal(loid) ions

17 For competitive adsorption/remobilization of binary metal(loid) ions using goethite-calcite
18 composite as adsorbent, two ions were arbitrarily combined as follows: As(III)-Se(IV),
19 As(V)-Se(VI) or Cd(II)-Cu(II). These three independent experiments are reported in Figure 5.

20 *Cd(II)-Cu(II) competition:* All available copper in the solution (about 50 mg/L) was adsorbed
21 more rapidly than the available cadmium (unfilled circle profiles in Figure 5). The same
22 kinetic behavior was observed in the case of single metal(loid) ion solutions (Fig. 4a). This
23 suggests insignificant competitive adsorption between Cu and Cd using goethite-calcite
24 composite. However, CO₂ intrusion into the system created slight remobilization of adsorbed
25 Cu. This is in disagreement with a single metal(loid) ion solution in the case of the goethite-

1 calcite system. Such disagreement could be explained if all the adsorption sites on the
2 available calcite were saturated with Cd and Cu, and the liberated Cu therefore comes from
3 the goethite, as observed in the pure goethite system when CO₂ is intruded (Fig. 2a).

4 *Se(IV)-As(III) competition:* Clearly, arsenite As(III) is adsorbed on the goethite-calcite
5 composite in preference to the selenite Se(IV) ion (unfilled star profiles in Figure 5).
6 However, CO₂ intrusion into the system reactivates the adsorption of residual dissolved
7 Se(IV). Conversely, adsorbed As(III) is partially remobilized from the goethite-calcite
8 composite. CO₂ intrusion was observed to have a similar effect in the case of single Se(IV)
9 and As(III) ion solutions (Figure 4a).

10 *Se(VI)-As(V) competition:* Arsenate As(V) was strongly adsorbed on the goethite-calcite
11 composite. Conversely, insignificant adsorption of selenate Se(VI) was measured in the
12 conditions investigated (unfilled triangle-down profiles in Figure 5). Surprisingly, CO₂
13 intrusion into the system led to re-adsorption of residual dissolved As(V) on the goethite-
14 calcite composite while As(III) was remobilized in all the other cases investigated. This can
15 be explained in terms of chemical speciation in the solution because arsenate remains partially
16 protonated before and after injection of CO₂ (dominant species H₂AsO₄⁻: see also Table 1)
17 while arsenite is completely protonated from H₂AsO₃⁻¹ to H₃AsO₃⁰ when CO₂ is intruded into
18 the system.

19 In conclusion, this simple experimental study provides further specific insights into the
20 remobilization/re-adsorption of Se(IV), Se(VI), Cd(II), Cu(II), As(III) and As(V) caused by
21 CO₂ intrusion into an equilibrated mineral-ion solution system. This has direct implications
22 for CO₂ leakage from deep geological formations and its possible intrusion into freshwater
23 aquifers. CO₂ intrusion into a given aquifer has been directly associated with the release
24 and/or remobilization of trace elements via mineral dissolution and/or desorption. In the
25 present study, we demonstrated that the remobilization of trace elements as a result of CO₂

1 intrusion is not a universal physicochemical effect. In fact, goethite and calcite, two minerals
2 frequently found in aquifers, can successfully prevent the remobilization of adsorbed Cu(II),
3 Cd(II), Se(IV) and As(V) if CO₂ is intruded into a drinking water aquifer. Moreover, a
4 decrease in pH resulting from CO₂ intrusion can reactivate the adsorption of Se(IV) and
5 As(V) if goethite and calcite are sufficiently available in underground layers. Our results also
6 suggest that the adsorption of cadmium and copper could be promoted by calcite dissolution.
7 In this way, adsorbed Cd(II) and Cu(II) on calcite are not remobilized when CO₂ is intruded
8 into the system, but it intensifies calcite dissolution, which plays a buffering role. On the other
9 hand, arsenite As(III) is significantly adsorbed on goethite, but is partially remobilized by
10 CO₂ intrusion. Finally, our results confirm the low or even insignificant adsorption affinity of
11 selenate Se(VI) with calcite and/or goethite. The latter oxyanion is reputed to be a very highly
12 mobile element in natural oxic environments.

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1 **References**

- 2 (1) Allwood, J. M.; Cullen, J. M.; Milford, R. L. Option for achieving a 50% cut in
3 industrial carbon emissions by 2050. *Environ. Sci. Technol.* **2010**, 44, 1888-1894.
- 4 (2) Knauss, K. G.; Johnson, J. W.; Steefel, C. I. Evaluation of the impact of CO₂, co-
5 contaminant gas, aqueous fluid and reservoir rock interactions on the geological
6 sequestration of CO₂. *Chem. Geol.* **2005**, 217, 339-350.
- 7 (3) Friedmann, S. J. Geological carbon dioxide sequestration. *Elements*, **2007**, 3, 179-184
- 8 (4) IPCC (Intergovernmental Panel on Climate Change), *Climate Change 2007: Climate*
9 *Change Impacts, Adaptations and Vulnerability*, 2007.
- 10 (5) Bachu S. CO₂ storage in geological media: role, means, status, barriers to deployment.
11 *Prog. Energy Combust. Sci.* **2008**, 34, 254-273.
- 12 (6) Kharaka, Y. K.; Cole, D. R.; Hovorka, S. D.; Gunter, W. D.; Knauss, K. G.; Freifeld,
13 B. M. Gas-water-rock interactions in Frio formation following CO₂ injection:
14 Implications for the storage of greenhouse gases in sedimentary basins. *Geology*,
15 **2006**, 34, 577-580.
- 16 (7) Zheng, L.; Apps, J. A., Zhang, Y.; Xu, T.; Birkholzer, T. On mobilization of lead and
17 arsenic in groundwater in response to CO₂ leakage from deep geological storage.
18 *Chem. Geol.* **2009**, 268, 281-297.
- 19 (8) Rempel, K. U.; Liebscher, A.; Heinrich, W.; Schettler, G. An experimental
20 investigation of trace element dissolution in carbon dioxide: Applications to the
21 geological storage of CO₂. *Chem. Geol.* **2011**, 289, 224-234.
- 22 (9) Montes-Hernandez, G.; Pironon, J. Hematite and iron carbonate precipitation-
23 coexistence at the iron-montmorillonite-salt solution-CO₂ interfaces under high gas
24 pressure at 150 C. *Appl. Clay Sci.* **2009**, 45, 194-200.

- 1 (10) Montes-Hernandez, G.; Sarret, G.; Hellmann, R.; Menguy, N.; Testemale, D.;
2 Charlet, L.; Renard, F. Nanostructured calcite precipitated under hydrothermal
3 conditions in the presence of organic and inorganic selenium. *Chem. Geol.* **2011**, 290,
4 109-120.
- 5 (11) Noiriel, C.; Renard, F.; Doan, M. L.; Gratier, J. P. Intense fracturing and
6 fracture sealing induced by mineral growth in porous rocks. *Chem. Geol.* **2010**, 269,
7 197-209.
- 8 (12) Kaszuba, J. P.; Janecky, D. R.; Snow, M. G. Experimental evaluation of mixed
9 fluid reactions between supercritical carbon dioxide and NaCl brine: Relevance to the
10 integrity of a geologic carbon repository. *Chem. Geol.* **2005**, 217, 277-293.
- 11 (13) Chopping, C.; Kaszuba, J. P. Supercritical carbon dioxide-brine-rock reactions
12 in the Madison Limestone of Southwest Wyoming: An experimental investigation of a
13 sulfur-rich natural carbon dioxide reservoir. *Chem. Geol.* **2012**, 322-323, 223-236.
- 14 (14) Bickle, M.; Chadwick, A.; Huppert, H. E.; Hallworth, M.; Lyle, S. Modelling
15 carbon dioxide accumulation at Sleipner: Implications for underground carbon
16 storage. *Earth Planet. Sci. Lett.* **2007**, 255, 164-176.
- 17 (15) Zheng, L.; Apps, J. A.; Zhang, Y.; Xu, T.; Birkholzer, T. Reactive transport
18 simulations to study groundwater quality changes in response to CO₂ leakage from
19 deep geological storage. *Phys. Procedia*, **2009**, 1, 1887-1894.
- 20 (16) Wang, S.; Jaffe, P. R. Dissolution of a mineral phase in potable aquifers due to
21 CO₂ releases from deep formations; effect of dissolution kinetics. *Energy Convers.*
22 *Manage.* **2004**, 45, 2833-2848.
- 23 (17) Humez, P.; Audigane, P.; Lions, J.; Négrel, P.; Lagneau, V., Tracking and CO₂
24 leakage from deep saline to fresh groundwaters: development of sensitive monitoring
25 techniques. *Energy Procedia*, **2011**, 4, 3443-3449.

- 1 (18) Vong, C. Q.; Jacquemet, N.; Picot-Colbeaux, G.; Lions, J.; Rohmer, J.; Bouc,
2 O. Reactive transport modeling for impact assessment of a CO₂ intrusion on trace
3 elements mobility within fresh groundwater and its natural attenuation for potential
4 remediation. *Energy Procedia*, **2011**, 4, 3171-3178.
- 5 (19) McGrath, A. E.; Upson, G. L.; Caldwell, M. D. Evaluation and mitigation of
6 landfill gas impacts on cadmium leaching from native soils. *Ground Water Monit.*
7 *Remed.*, **2007**, 27, 99-109.
- 8 (20) Smyth, R. C.; Hovorka, S. D.; Lu, J.; Romanak, K. D.; Partin, J. W. C.; Yang
9 W. C. Assessing risk to fresh water resources from long term CO₂ injection-laboratory
10 and field studies. *Energy Procedia*, **2009**, 1, 1957-1964.
- 11 (21) Little, M. G.; Jackson, R. B. Potential impacts of leakage from deep CO₂
12 geosequestration on overlying freshwater aquifers. *Environ. Sci. Technol.*, **2010**, 44,
13 9225-9232.
- 14 (22) Lu, J. M, Partin, J. W.; Hovorka, S. D.; Wong, C. Potential risks to freshwater
15 resources as a result of leakage from CO₂ geological storage: a batch-reaction
16 experiment. *Environ. Earth Sci.*, **2010**, 60, 335-348.
- 17 (23) Zheng, L.; Apps, J. A.; Spycher, N.; Birkholzer, J. T.; Kharaka, Y. K.;
18 Thordsen, J.; Beers S. R.; Herkelrath, W. N.; Kakouros, E.; Trautz, R. C. Geochemical
19 modeling of changes in shallow groundwater chemistry observed during the MSU-
20 ZERT CO₂ injection experiment. *Int. J. Greenhouse Gas Control* **2012**, 7, 202-217.
- 21 (24) Trautz, R. C.; Pugh, J. D.; Varadharajan, C.; Zheng, L.; Bianchi, M.; Nico,
22 P.S.; Spycher, N. F.; Newell, D. L.; Esposito, R. A.; Wu, Y.; Dafflon, B.; Hubbard, S.
23 S.; Birkholzer, J. T. Effect of dissolved CO₂ on shallow ground water system: A
24 controlled release field experiment. *Environ. Sci. Technol.* **2013**, 47, 298-305.

- 1 (25) Wolthers, M.; Charlet, L.; Van Cappellen, P. The surface chemistry of divalent
2 metal carbonate minerals. *Am. J. Sci.* **2008**, 308, 905-941.
- 3 (26) Paquette, J.; Reeder, R. J. Relationship between surface structure, growth
4 mechanism, and trace element incorporation in calcite. *Geochem. Cosmochem. Acta.*
5 **1995**, 59, 735-749.
- 6 (27) Aquino, A. J. A.; Tunega, D.; Haberhauer, G.; Gerzabek, M. H.; Lischka, H.
7 Acid-base properties of a goethite surface model: A theoretical view. *Geochem.*
8 *Cosmochem. Acta.* **2008**, 72, 3587-3602.
- 9 (28) Cornell, R. M.; Schwertmann, U. *The Iron Oxides*; VCH: Weinheim,
10 Germany, **1996**.
- 11 (29) Ozdemir, O., Dunlop, D. J. Intermediate magnetite formation during
12 dehydration of goethite. *Earth Planet. Sci. Lett.* **2000**, 177, 59-67.
- 13 (30) Montes-Hernandez, G.; Beck, P.; Renard, F.; Quirico, E.; Lanson, B.; Chiriac,
14 R.; Findling, N. Fast precipitation of acicular goethite from ferric hydroxide gel under
15 moderate temperature (30 and 70 C degrees). *Cryst. Growth Des.* **2011**, 11, 2264-
16 2272.
- 17 (31) Montes-Hernandez, G.; Daval, D.; Chiriac, R., Renard, F. Growth of nanosized
18 calcite through gas-solid carbonation of nanosized portlandite particles under
19 anisobaric conditions. *Cryst. Growth Des.* **2010**, 10, 4823-4830.
- 20 (32) Montes-Hernandez, G.; Renard, F.; Chiriac, R.; Findling, N.; Ghanbaja, J.;
21 Toche, F. Sequential precipitation of a new goethite-calcite nanocomposite and its
22 possible application in the removal of toxic ions from polluted water. *Chem. Eng. J.*
23 **2013**, 214, 139-148.
- 24 (33) Parkhurst, D. L.; Appelo, C. A. J. Users guide to PHREEQC (version 2) – A
25 computer program for speciation, batch reaction, one dimensional transport and

1 inverse geochemical calculations. *US Geological Survey Water-Resources*
2 *Investigation report 99-4259*. **1999**, 312pp.

3 (34) Gaboriaud, F.; Ehrhardt, J. J. Effects of different crystal faces on the surface
4 charge of colloidal goethite (α -FeOOH) particles. *Geochem. Cosmochem. Acta*. **2003**,
5 67, 967-983.

6 (35) Schwertmann, U.; Cornell, R. M. *Iron oxides in the laboratory: Preparation*
7 *and Characterization*; VCH: Weinheim, Germany, 1991.

8 (36) Dzombak, D. A.; Morel, F. M. M. Surface complexation modelling: hydrous
9 ferric oxide. Wiley **1990**, 416 pp.

10 (37) Limousin, G.; Gaudet, J. P.; Charlet, L.; Szenknect, S.; Barthès, V.; Krimissa,
11 M. Sorption isotherms: A review on the physical bases, modelling and measurement.
12 *Appl. Geochem.* **2007**, 22, 249-275.

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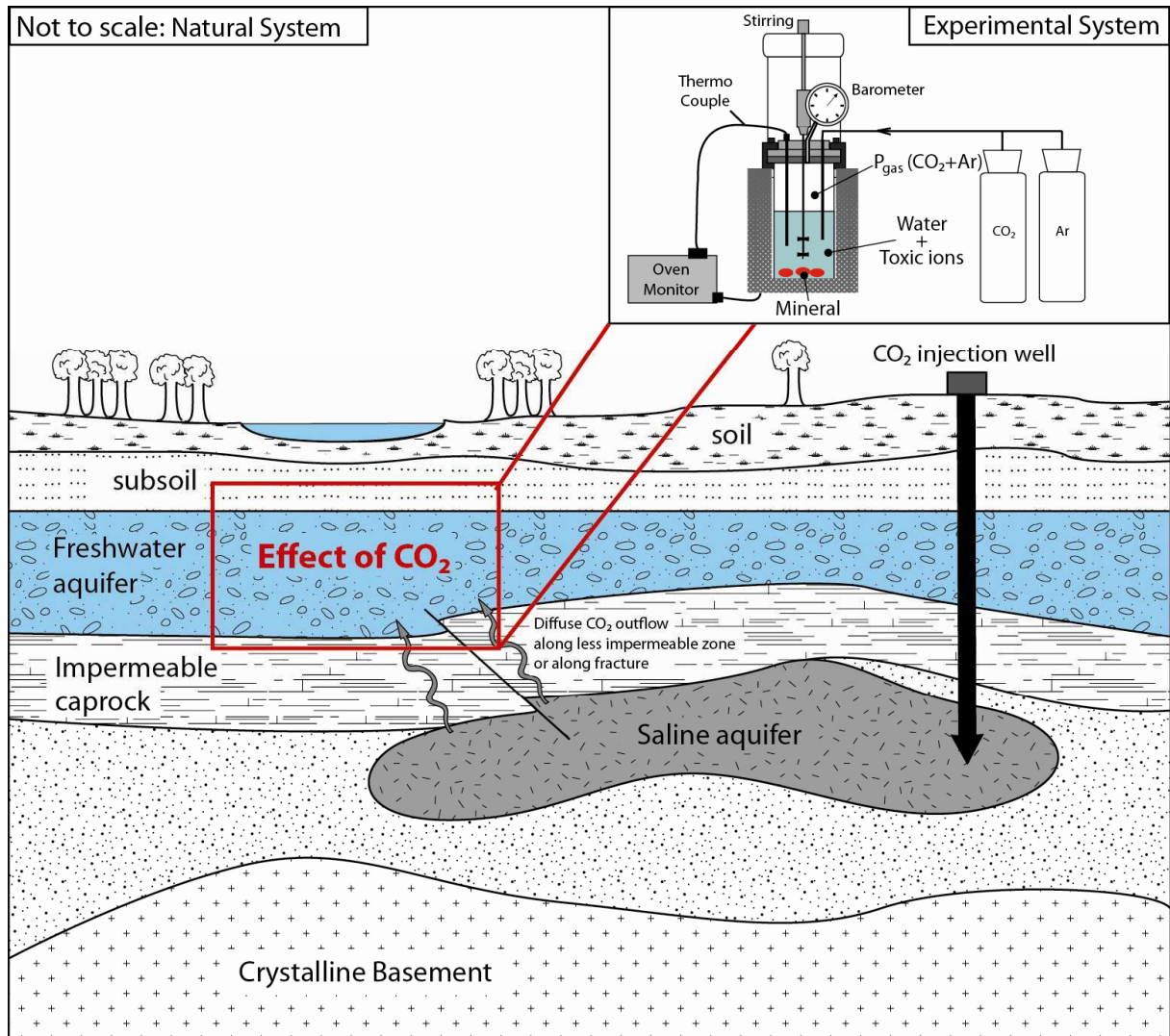
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1 Table 1. Dominant species and pH in suspensions prior to and after CO₂ injection into the
 2 system. These values were determined by using Phreeqc numerical simulations with an
 3 element initial concentration of 50 mg/L and 8 bar of CO₂ in the system.

Soluble Salt	Mineral	pH		Dominant Species (>98%)		pH		Dominant Species (>98%)
		Phreeqc ¹	Ex-situ ^a			Phreeqc ²	Ex-situ ^b	
NaAsO ₂	Calcite	10.324	9.91	H ₂ AsO ₃ ⁻	After CO ₂ intrusion within system	4.04	6.29	H ₃ AsO ₃ ⁰
NaAsO ₂	Goethite	10.235	9.87	H ₂ AsO ₃ ⁻		3.981	5.25	H ₃ AsO ₃ ⁰
Na ₂ SeO ₃ ·5H ₂ O	Calcite	10.06	9.33	SeO ₃ ⁻²		4.244	6.25	HSeO ₃ ⁻
Na ₂ SeO ₃ ·5H ₂ O	Goethite	9.323	9.25	SeO ₃ ⁻²		4.196	5.38	SeO ₃ ⁻²
Na ₂ SeO ₄	Calcite	10.05	8.26	SeO ₄ ⁻²		3.6	6.28	SeO ₄ ⁻²
Na ₂ SeO ₄	Goethite	7.035	8.18	SeO ₄ ⁻²		3.463	5.52	SeO ₄ ⁻²
Cd(NO ₃) ₂ ·4H ₂ O	Calcite	9.678	6.44	Cd ⁺²		3.708	6.25	Cd ⁺²
Cd(NO ₃) ₂ ·4H ₂ O	Goethite	6.763	6.40	Cd ⁺²		3.438	6.14	Cd ⁺²
CuCl ₂ ·2H ₂ O	Calcite	7.702	5.72	Cu ⁺² (51%) CuO (49%)		4.357	6.32	Cu ⁺²
CuCl ₂ ·2H ₂ O	Goethite	5.499	5.54	Cu ⁺²		3.439	6.23	Cu ⁺²
Na ₂ HAsO ₄ ·7(H ₂ O)	Calcite	11.291	8.32	H ₂ AsO ₄ ⁻		4.08	6.24	H ₂ AsO ₄ ⁻
Na ₂ HAsO ₄ ·7(H ₂ O)	Goethite	11.291	8.28	H ₂ AsO ₄ ⁻		4.038	5.50	H ₂ AsO ₄ ⁻

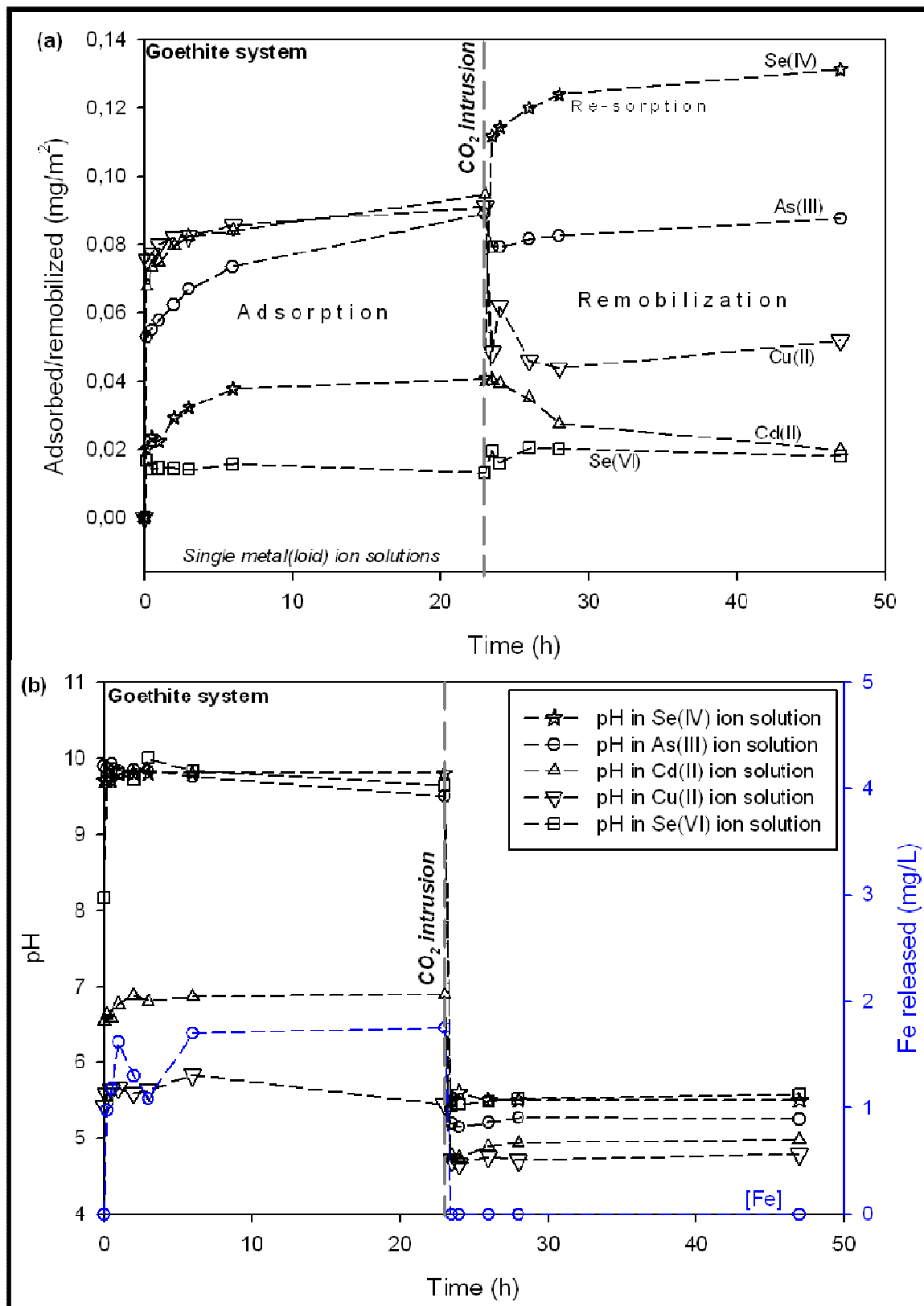
4 ¹ Equilibration between ion solution and mineral prior to CO₂ injection; ^a pH measured ex-situ at 20°C in the
 5 mother solution; ² Equilibration between ion solution and mineral after CO₂ injection; ^b pH measured ex-situ at
 6 20°C at the end of the experiment (after 48h).

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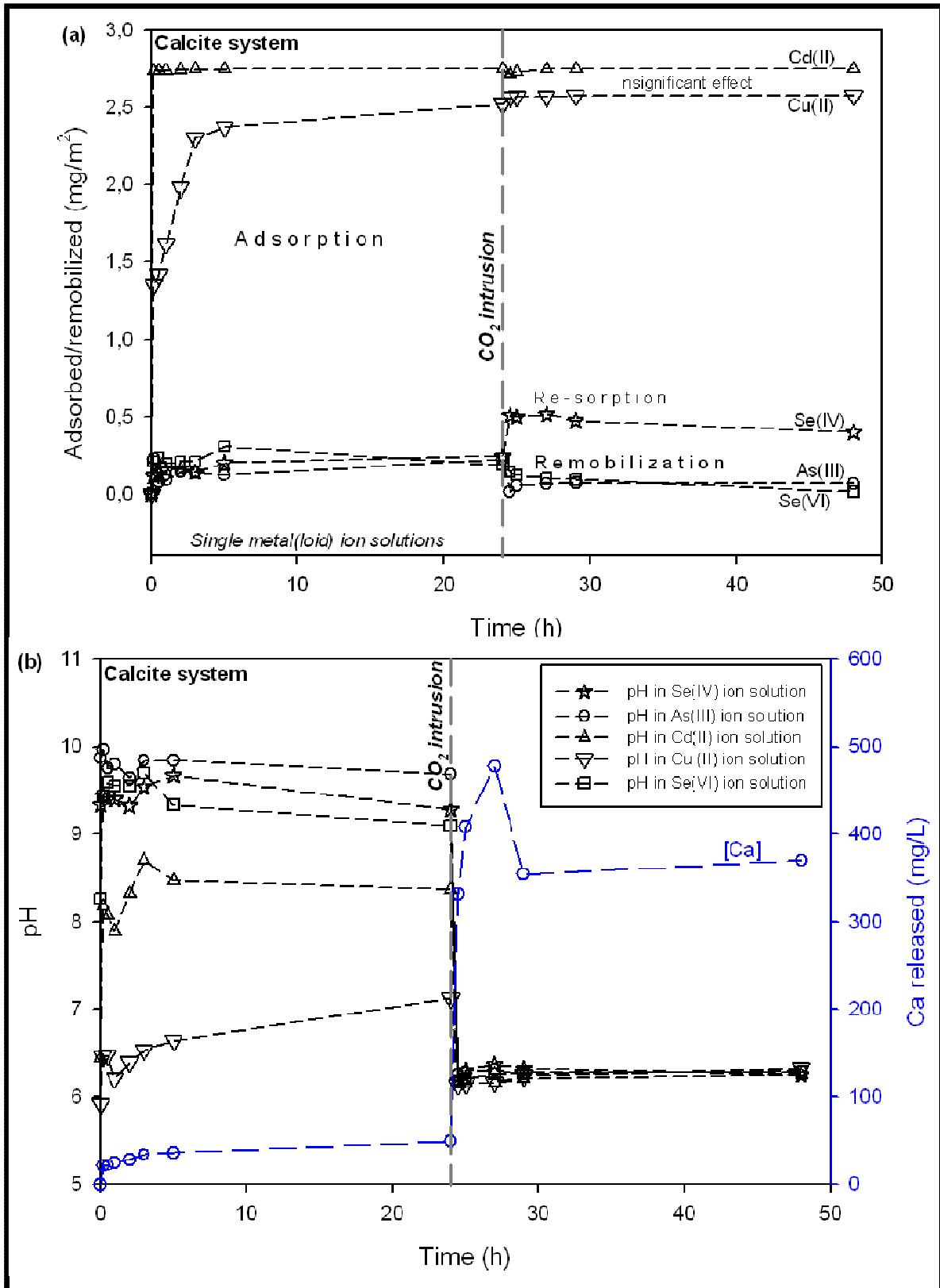


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Figure 1. Schematic representation of CO₂ leakage from deep geological storage, focusing in red on the present study: “experimental assessment of CO₂-mineral-toxic ions interactions in a simplified potable aquifer”.

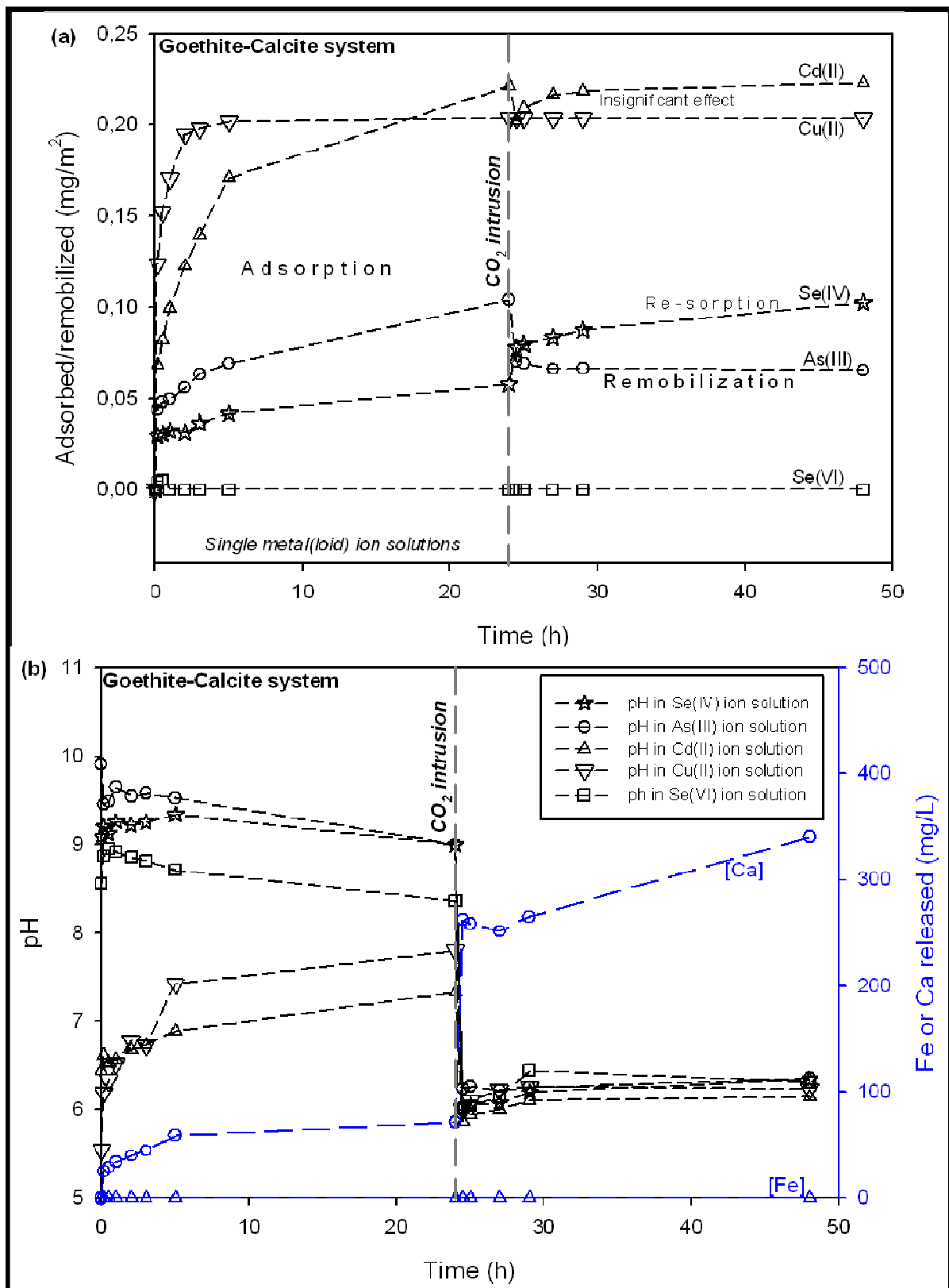


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 2 **Figure 2.** (a) Kinetic adsorption behavior of a single metal(loid) ion on goethite and effect of
 3 CO₂ intrusion into the system. (b) pH profiles before and after CO₂ intrusion. In all
 4 experiments, a similar initial ion concentration (about 50mg/L) was used and the
 5 adsorbed/remobilized amount of each element was normalized with respect to the initial
 6 available surface area (3g*130m²/g).



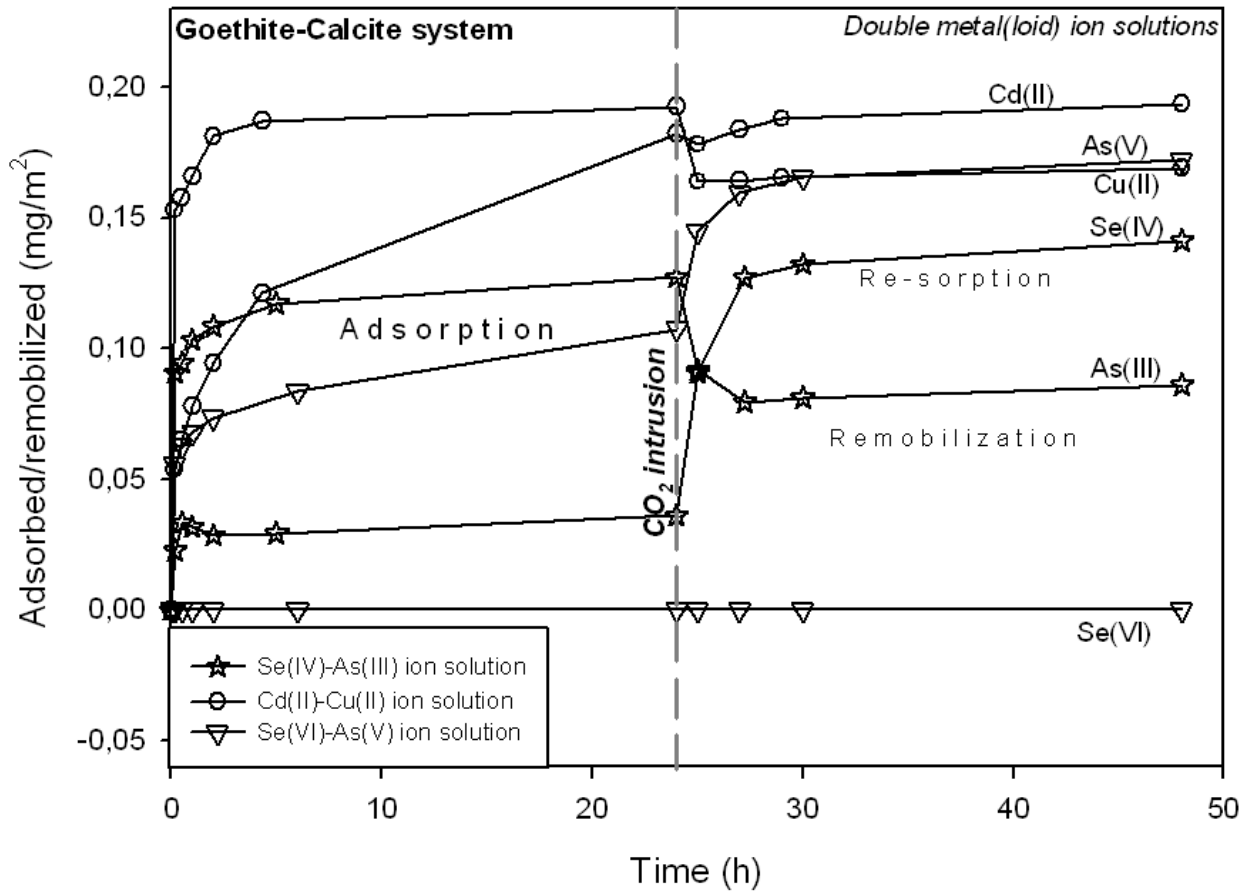
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2 **Figure 3.** (a) Kinetic adsorption behavior of a single metal(loid) ion on calcite and effect of
 3 CO₂ intrusion into the system. (b) pH profiles and average [Ca] profile before and after
 4 CO₂ intrusion. In all experiments, a similar initial ion concentration (about 50mg/L) was
 5 used and the adsorbed/remobilized amount of each element was normalized with respect
 6 to the initial available surface area (3g*7m²/g).



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 2 **Figure 4.** (a) Kinetic adsorption behavior of a single metal(loid) ion on goethite-calcite
 3 composite and effect of CO₂ intrusion into the system. (b) pH profiles and average
 4 [Fe] and [Ca] profiles before and after CO₂ intrusion. In all experiments, a similar
 5 initial ion concentration (about 50mg/L) was used and the adsorbed/remobilized
 6 amount of each element was normalized with respect to the initial available surface
 7 area (3g*90m²/g).

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8 **Figure 5.** Competitive adsorption/remobilization of binary metal(loid) ions by using goethite-
9 calcite composite as adsorbent. Two ions were arbitrarily combined as follows: As(III)-
10 Se(IV), As(V)-Se(VI) or Cd(II)-Cu(II). A similar initial ion concentration (about 50mg/L for
11 each element) was used and the adsorbed/remobilized amount was normalized with respect to
12 the initial available surface area (3g*90m²/g).