

Geochemical Reactions of Na-montmorillonite in Dissolved scCO₂ in Relevance of Modeling Caprock Behavior in CO₂ Geological Storage

Zsuzsanna Szabó^{1,2*}, Csaba Hegyfalvi³, Ágnes Freiler-Nagy⁴, Beatrix Udvardi⁵, Péter Kónya⁶, Csilla Király⁷, Edit Székely³, György Falus¹

¹ Lithosphere Fluid Research Lab, Department of Petrology and Geochemistry, Institute of Geography and Earth Sciences, Faculty of Science, Eötvös Loránd University, H-1117 Budapest, Pázmány Péter sétány 1/C, Hungary

² MTA Premium Postdoctoral Research Program, MTA Office for Research Groups Attached to Universities and Other Institutions, Hungarian Academy of Sciences, H-1051 Budapest, Nádor u. 7., Hungary

³ Department of Chemical and Environmental Process Engineering, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1111 Budapest, Műegyetem rakpart 3., Hungary

⁴ CEMKUT Research & Development for the Cement Industry Ltd., H-1034 Budapest, Bécsi út 122-124., Hungary

⁵ KTI Institute for Transport Sciences Non-profit Ltd., H-1119 Budapest, Than Károly u. 3-5., Hungary

⁶ Department of Hydrogeology and Geochemistry, Mining and Geological Survey of Hungary, H-1143 Budapest, Stefánia út 14., Hungary

⁷ Geographical Institute, Research Centre for Astronomy and Earth Sciences, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45., Hungary

* Corresponding author, e-mail: zsszabo86@gmail.com

Received: 13 July 2018, Accepted: 06 December 2018, Published online: 18 March 2019

Abstract

One of the challenges of the present century is to limit the greenhouse gas emissions for the mitigation of climate change which is possible for example by a transitional technology, CO₂ geological storage. Clay minerals are considered to be responsible for the low permeability and sealing capacity of caprocks sealing off stored CO₂. However, their reactions are not well understood for complex simulations. This work aims to create a kinetic geochemical model of Na-montmorillonite standard SWy-2 supported by solution and mineral composition results from batch experiments. Such experimentally validated numerical models are scarce. Four 70-hours experiments have been carried out at atmospheric conditions, and with CO₂ supercritical phase at 100 bar and 80 °C. Solution samples have been taken during and after experiments and their compositions were measured by ICP-OES. The treated solid phase has been analyzed by XRD and ATR-FTIR and compared to in-parallel measured references (dried SWy-2). Kinetic geochemical modelling of the experimental conditions has been performed by software PHREEQC. Experiments and models show fast reactions under the studied conditions and increased reactivity in presence of scCO₂. Solution composition results cannot be described by the change of the uncertain reactive surface area of mineral phases. By considering the clay standard's cation exchange capacity divided proportionally among interlayer cations of Na-montmorillonite, the measured variation can be described on an order of magnitude level. It is furthermore indicated that not only the interlayer cations take part in this process but a minor proportion of other, structural ions as well, differently in the reference and scCO₂ environments.

Keywords

CO₂ geological storage, Na-montmorillonite, laboratory batch experiments, kinetic geochemical modeling, PHREEQC

1 Introduction

It is beyond doubt that human activity influences the climate system and that mitigating climate change requires reduction of greenhouse gas emissions [1]. The Paris Agreement [2] aims to keep global temperature rise well below 2 °C and pursue efforts for a 1.5 °C limit.

This "low-stabilization" scenario can only be reached by not only applying low, but also net negative emission technologies [3]. In the near-term, the only approach capable of making a major contribution to these seems to be the transitional technology of Carbon Capture and

Storage (CCS) [4] and its combination with bioenergy (BECCS) [3].

When CO₂ is to be stored in a potential deep geological reservoir, special attention must be paid to its low permeability seals, caprocks [5]. These rocks represent the physical barriers that could hinder the escape of injected supercritical CO₂ (scCO₂). Currently, it is not completely clear what factors (i.e. mineralogy, grain-size, cementation) are responsible for their retention capacity. It is assumed, however, that clay minerals play an essential role in the low permeability of these lithologies. It is crucial, therefore, to observe, understand and predict (model) how clays behave in the presence of reactive CO₂ which is in contact with [6] and present in the caprock both in dissolved and free phase [7, 8].

For the observation of mineral reactions induced by dissolved CO₂, one can either study natural analogues or conduct laboratory batch experiments. Despite of the drawbacks (for instance, the usually short laboratory time scales, non-natural solution compositions, variations in water / mineral ratio, the potential formation of experimental artefacts), these treatments and study of experimental solutions and solids are efficient to derive conclusions on long-term processes in CCS systems. With the possibility of "on-the-go" fluid sampling [9], these batch experiments can better support theoretical geochemical models due to the higher sensitivity of detecting solution than mineral composition changes and excluding the effect of reactor depressurization and cooling artefact formation in these samples. However, model validation by such experimental solution data is scarce. Also, there were only a few attempts made to couple any batch experimental results of soaked CCS caprocks with modeling [7, 10, 11]. Moreover, the number of experiments focusing especially on clay mineral reactions for the effect of dissolved CO₂ in pore water is very low since most clay studies have been conducted not specific to CCS [12] or in free phase scCO₂ [13–22].

Sendula et al. [9] studied illite, kaolinite and montmorillonite mixtures in scCO₂-saturated water. Their results indicated rapid and total dissolution of any traces of carbonates. The clay mixtures, initially containing montmorillonite, were more reactive than the sample of illite-kaolinite mixture. However, further results are needed to understand the behavior of cations, especially to gain data to be incorporated into geochemical models.

In present work batch experiments of pure SWy2 Namontmorillonite clay standard in scCO₂-saturated water with "on-the-go" solution sampling are carried

out and their data are used to fit the standard's kinetic PHREEQC model. Solution samples taken before and after reactor depressurization and cooling also provide information about expected artefacts in the solid samples in this and similar experimental works. Since the high pressure and temperature CO₂-experiments were prepared by mixing the clay with water at atmospheric conditions, additional reference experiments and modeling were performed in this ambient environment.

2 Materials and Methods

2.1 Materials

SWy-2 Namontmorillonite clay standard originates from Newcastle formation, County of Crook, State of Wyoming, USA. Na-montmorillonite is a swelling clay mineral belonging to the Smectite group. The standard's chemical composition and other basic information can be found online [23]. Montmorillonite structure is given as (Ca_{0.12}Na_{0.32}K_{0.05}) [Al_{3.01}Fe(III)_{0.41}Mn_{0.01}Mg_{0.54}Ti_{0.02}][Si_{7.98}Al_{0.02}]O₂₀(OH)₄, Ca²⁺, Na⁺ and K⁺ are interlayer cations.

The interlayer cations, and among them mostly the Na⁺ and Ca²⁺, are expected to be mainly responsible for the high cation exchange capacity (CEC) of the clay which equals to 76.4 meq (milliequivalent) for 100 g weight [23]. Based on the given stoichiometric equation the molar mass (*M*) is 549.07 g/mol and therefore, the CEC is calculated to be 0.42 in mol/mol units. Note that CEC of clays has been shown to decrease with decreasing pH [24, 25].

The specific surface area (SSA) of Na-montmorillonite is large, the N₂ area is given to be 31.82 ± 0.22 m²/g [23], but several even higher other data can be found in the literature. For example, SSA is mentioned to equal to 48 m²/g [26] and, with taking into account the interlayer region, also to 750 m²/g [27]. The RES³T database [28] goes as high as 898 m²/g SSA.

To use in experiments, pure, deionized water with less than 6.7 × 10⁻² μS/cm electric conductance was prepared in the laboratory of Mining and Geological Survey of Hungary by multiple distillation steps and filtering. For the acidification and therefore, stabilization of any solution samples taken, a 99:1 ratio mixture of the above deionized water and 68 % HNO₃ was used. In the CO₂-experiments Linde® CO₂ gas (> 99.5 %) was applied freshly distilled.

2.2 Experimental procedures and samples

2.2.1 Reference SWy-2 samples

During the experimental work, 8 reference samples have been prepared for the same analysis at the same time as

the treated samples. These aimed to represent the average mineral composition of the SWy-2 clay standard and to follow any time-sale changes of the analytical methods. These SWy2 samples were dried at 80 °C for 30 minutes and marked from *SWy-2-0a* to 0h.

2.2.2 Atmospheric batch experiments

Two repeats of atmospheric experiments were carried out in the laboratory of Mining and Geological Survey of Hungary. In a glass vessel, 1.6 g of SWy-2 was layered by the deionized water in multiple steps to reach approx. 35 water / mineral (mass) ratio. This ratio is highly increased compared to the natural, approx. 0.2 porosity/mineral ratio in caprocks however, necessary for homogenization and possibility to sample the solution.

The clay-water mix then was placed onto a magnetic stirrer for continuous mixing during the 70 hours (three days) experiments. The air temperature was 25 °C and the vessel was covered by a glass cap to decrease the evaporation of the water. At gradually increasing time intervals, fluid samples of 0.5 g were taken by a syringe from the top of the mixture. These samples were filtered through an attached membrane filter with pore diameter of 0.45 µm to remove solid particles and the pure solution drops with measured mass were added into a determined amount of stabilization solution. At the end of the experiments the solid material was separated from the rest of the solution on a glass filter dried at dust-free laboratory air for a week, then sent to analysis. The experimental conditions of these samples marked with names starting with *SWy2-ATM* are summarized in Table 1.

2.2.3 Dissolved scCO₂ batch experiment

Three successful high pressure and temperature experiments were carried out in the laboratory of Budapest University of Technology and Economics where

suitable reactor for dissolved scCO₂-treatments is available. Similarly to the atmospheric experiments, but in smaller proportions, about 0.35 g SWy-2 was layered by the deionized water in multiple steps to reach the 35 water / mineral ratio in a special glass vessel.

The layered sample then was placed onto a magnetic stirrer for mixing until homogenization was reached. The vessel exactly fits into the high pressure and temperature resistant reactor with the possibility of "on-the-go" fluid sampling, which schematic representation was published by Sendula et al. [9]. The reactor volume then was saturated by CO₂ and heated and pressurized up to reach 80 °C temperature and 100 bar pressure. This was a technically feasible pressure-temperature range close to the estimated conditions for potential local, Hungarian CCS caprocks in an earlier study [11]. During the 70 hours (three days) treatments the magnetic stirring of the water-mineral mixture was continued except at the time of "on-the-go" and post-experimental solution sampling. These were all filtered by a syringe attached membrane filter (0.45 µm) and added into the stabilization solution. The solid material was separated from the rest of the solution by a glass filter and/or drying on laboratory air in dust-free environment. The experimental conditions of these *SWy2-WCO2* samples (meaning treated in water and CO₂) are summarized in Table 1.

2.3 Applied analytical techniques

2.3.1 Mineral composition determination

The reference samples and the air dry treated samples were all analyzed by X-Ray Diffraction (XRD) and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) in the Mining and Geological Survey of Hungary. For XRD measurements a Philips® PW 1730 instrument and for ATR-FTIR analysis a Bruker® Vertex 70 with Bruker® Platinum single reflection diamond

Table 1 Treated SWy-2 samples, their experimental conditions and times of "on-the-go" fluid sampling. Water / mineral ratio is given as at the beginning of the experiments. In the case of scCO₂-experiments, solution samples have been taken also after depressurization and cooling, "post-exp."

Experiment and name of solid sample	SWy-2 treated in	Pressure (bar)	Temperature (°C)	Water / mineral ratio	Duration (hh:mm)	Fluid sampling times (hh:mm)
SWy-2-ATM-1	water at atmosphere	1	25	32.73	73:17	0:53, 2:35, 20:17, 44:17, 72:47
SWy-2-ATM-2				34.84	73:00	0:49, 2:28, 20:20, 44:20, 72:40
SWy-2-WCO2-3*	scCO ₂ -saturated water	100-105	80-85	35.03	76:20	2:00, 25:35
SWy-2-WCO2-4*				35.00	76:10	1:40, 29:10, 75:30, post-exp.
SWy-2-WCO2-6				34.43	69:35	0:30, 23:45, 69:00, post-exp.

*After experiments, SWy2-WCO2-3 and 4 samples have been simply dried on laboratory air for 3-4 weeks. Whereas,

SWy-2-ATM and SWy-2-WCO2-6 samples have been separated from the rest of the solution on a glass filter and dried on laboratory air for about a week.

ATR module and mercury-cadmium-telluride detector were used. Find more detailed description of these methods in Sendula et al. [9].

2.3.2 Solution composition determination

The Ca-, Mg-, K-, Na-, Fe-, Mn-, dissolved Si- and Al-concentrations (uncertainty 2-20 % for high and low concentrations) of experimental solution samples were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). For the measurements, a HORIBA Jobin Yvon® ULTIMA 2C instrument at the Mining and Geological Survey of Hungary was used. Further details can be found in Sendula et al. [9].

2.4 Kinetic geochemical modeling

Kinetic geochemical modeling was carried out in the PHREEQC 3.0 software [29] to describe the experimental results, among them, the solution compositions. The below described kinetic geochemical modeling methodology is a result of numerous test runs and following tuning of the PHREEQC model / code. The initial solution is pure water and the pressure and temperature is given as in experiments, 1 bar and 25 °C for atmospheric and 100 bar and 80 °C for scCO₂-experiments.

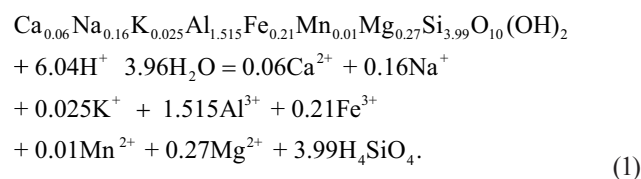
2.4.1 Gas phases

For all models a gas phase has been defined with either of the above given pressures and temperatures. The composition of the gas phase in atmospheric experiment modeling was specified to be 0.2095 bar O₂ and 0.0003 bar CO₂ based on these gases' partial pressures in air. The unreactive N₂ was not detailed among the constituents.

2.4.2 Mineral phases and their thermodynamic data

For all simulations the PHREEQC.DAT thermodynamic database was used. Thermodynamic data of Na-montmorillonite, however, is not included in this database. Therefore, the phase definition is taken from the LLNL.DAT with a few modifications.

To the original formula (Na_{0.33}Mg_{0.33}Al_{1.67}Si₄O₁₀(OH)₂) several other elements had to be added to be able to simulate all of the measured ionic concentrations (Ca-, Mg-, K-, Na-, Fe-, Mn-, Si- and Al). The new definition is based on the structure given for Na-montmorillonite in the SWy-2 clay standard [23], however, it excludes the minor amount of non-measured Ti. Furthermore, SiO₂ is represented as H₄SiO₄ for compatibility with PHREEQC.DAT. The reaction is therefore,



Note that the exact equilibrium constant (logK) of the given clay / reaction is not known and the models assume it to remain as in LLNL.DAT even though elemental composition changed. The latter modification (SiO₂ conversion to H₄SiO₄) is possible to take into account in the value of logK however; it does not seem to influence modeling results.

Besides Na-montmorillonite, the carbonate mineral dawsonite was also taken from LLNL.DAT. This is a potentially precipitating mineral in CO₂ geological storage environments [30, 31].

2.4.3 Mineral kinetic rates and specific surface areas

Kinetic dissolution and precipitation equations of mineral phases have been defined similarly to earlier works of the authors [11, 32], which modeling methodology is primarily based on a USGS report [33] and follows Hellevang et al. [34].

The equations in present study cover OH⁻ and HCO₃⁻-catalyzed mechanisms beside the neutral and H⁺-promoted reactions, if rate constants listed for 25 °C were available [33]. Calculation of rate constants to experimental temperature also follows above works [11, 32-34].

Kinetic rate definition code blocks were defined for all minerals in the standard (Na-montmorillonite, quartz, calcite and K-feldspar) and potential secondary minerals precipitating in experiments, such as Ca-montmorillonite, kaolinite, gibbsite, dawsonite, illite, dolomite, chlorite and anhydrite. For Na-montmorillonite the rate constants listed for montmorillonite, for Ca-montmorillonite listed for smectite and for illite listed for muscovite were used.

For all minerals, the largest SSA found in the RES³T database [28] has been used. For K-feldspar the orthoclase and for dawsonite the dolomite data were taken into account. In the definition of rates, SSA is converted into reactive SSA (RSA), which might be only a small portion of the total area. Several RSA scenarios were tested to fit the model on experimental data. Most important input parameters are at Mendeley Data [35].

2.4.4 Mineral composition and water / mineral ratio

PHREEQC models simulating rock-fluid interactions need the mineral composition of the rock as input data given in

mol/kgW (mol/kgH₂O) units. The original mineral composition of the SWy-2 standard (83 % Na-montmorillonite, 7 % quartz, 4 % calcite and 6 % K-feldspar, weight%) is determined based on the XRD measurements of the 8 reference samples. The weight% to mol/kgW calculation has previously been published [32] and it needs the porosity of the system. In the models of this work, the porosity was taken to be 97 % (volume%), which approximates the porosity in the experiments estimated from the 35 water / mineral ratio.

2.4.5 Cation exchange of Na-montmorillonite

The CEC of Na-montmorillonite in SWy-2 clay standard is 76.4 meq / 100 g [23] as described above. This was calculated to be 0.42 in mol/mol units (Section 2.1). However, the stoichiometric equation used in the model has been modified (Eq. (1)) and in this the *M* of Na-montmorillonite is 372.865 instead of 549.07 g/mol. Like this, the total CEC to be used in the model is calculated to be 0.285 mol/mol Na-montmorillonite.

Several thermodynamic ion exchange scenarios have been tested to fit the model on experimental data. The division was done primarily among interlayer cations proportionally to their amounts in the clay mineral structure. However, their charge had to be considered (for example Ca values were divided by two). Other scenarios, with including other ions, have also been tested.

3 Results and discussion

3.1 Experimental results

3.1.1 Measured "on-the-go" solution composition changes

During batch experiments, solution compositions sensitively changed due to standard-fluid interaction already starting at atmospheric conditions. These runs (SWy2-ATM) show K concentrations comparable to those of scCO₂ experiments (SWy-2-WCO₂) and Na concentrations in the same order of magnitude (Table 2). These are both cations in the interlayer space. All other ions (including Ca), though, show an increased reactivity at 80 °C, 100 bar and in the presence of scCO₂. Therefore, the preparation time on air before the reactor pressurization does not significantly affect these results.

3.1.2 Expected artefacts in the dissolved scCO₂-treated sample

At the end of high pressure and temperature rock-fluid experiments thermodynamically favored reactions change due to reactor depressurization and cooling and therefore, minerals may precipitate (or dissolve) by the time of solution sampling at atmospheric conditions. Comparison of solution compositions before and after stopping dissolved scCO₂-treatments allows identifying which minerals might be experimental artefacts, and not the results of the contact with CO₂. In this work, solid samples were not

Table 2 Measured "on-the-go" solution compositions in the experiments (Table 1). Concentration is given in mg/l and time (*t*) in hh:mm.

	<i>t</i>	Ca	Mg	K	Na	Fe	Mn	Si	Al
SWy-2-ATM	0:53	ND	0.16	7	61	0.21	0.01	2	0.07
	2:35	ND	0.19	11	86	0.02	0.01	3	ND
	20:17	ND	0.28	10	107	0.09	0.01	5	ND
	44:17	2.14	0.40	12	122	0.17	0.03	6	ND
	72:47	0.84	0.47	14	129	0.15	0.01	11	0.04
	0:49	ND	ND	2	39	0.07	0.01	1	0.14
	2:28	1.26	0.24	7	74	0.05	0.01	3	0.13
	20:20	ND	0.25	11	106	ND	0.01	5	0.04
	44:20	0.22	0.53	8	124	0.10	0.01	8	ND
	72:40	ND	0.69	13	127	0.18	0.01	13	ND
SWy-2-WCO ₂	2:00	73	18	17	348	9	0.65	99	20
	25:35	64	21	20	315	15	0.81	128	29
	1:40	61	17	15	279	9	0.52	85	26
	29:10	75	26	17	322	21	0.89	216	56
	75:30	65	20	17	276	23	0.85	142	48
	0:30	142	25	32	408	44	0.53	69	20
	23:45	105	21	31	369	24	0.76	58	6
	69:00	85	21	20	356	23	0.77	111	24

informative (see below), but artefacts might be detected in similar experiments of other authors.

Two pairs of last "on-the-go" and post-experimental solution samples were available and used for calculating the % change of ion concentrations presented on Fig. 1. Considering the systematically low % change of Al (around -90 %) and Si (around -50 %, Fig. 1) and their comparably high absolute ion concentrations presented in details later, the chemical composition of the experimental artefact will include primarily these two elements. These artifacts could be for example Al-oxides / hydroxides and amorphous silica. Additionally, minor amounts of Mg, Fe and K are expected to mineralize.

These findings partially overlap with previous experiences of the authors [29] reporting similar Al concentration drop and precipitation of boehmite (AlO(OH)) in some of the cooling experimental solution samples. The authors also note that saturation index (SI) changes in an equilibrium PHREEQC model, not detailed in present paper, also support Al- and Fe-oxides / hydroxide and amorphous silica precipitation as artefacts. It also indicates that kaolinite might form. This model uses the composition of an "on-the-go" solution sample at pressure and temperature conditions before and after stopping the reactor (conditions summarized in Table 1).

3.1.3 Mineral composition / structure changes

The analysis of XRD data, since new phases were not detected, focused on 3° to 11° 2Theta angles, which is the corresponding region to montmorillonite. These results are presented on Fig. 2. A systematic shift into two new peak positions can be observed. These analytical results of solid samples (Fig. 2), however, are determined by the post-experimental treatment, i.e., drying time (Table 1) and not the type of the batch experiment, atmospheric or scCO₂. Samples with short drying time (~ one week) display significant shift from the reference value (6° corresponding to $d_{001} = 14.9 \text{ \AA}$; 7.7° corresponding to $d_{001} = 11.47 \text{ \AA}$), whereas those with longer drying time (~ 34 weeks) fall in an intermediate position (7.2° corresponding to $d_{001} = 12.27 \text{ \AA}$) between reference values and those of short drying time. The measured d_{001} values for Na-montmorillonite are in agreement with the values reported as a function of integral hydration states, similar to the results of Sendula et al. [9].

ATR-FTIR peak positions / widths show similar changes to ATR-FTIR peak areas summarized in Table 3. A continuous change for the reference samples (from

SWy-2-0A to 0H) was detected what connects to the winter to summer sample transportation. Otherwise, the same effect of post-experimental treatment (short or long drying time, Table 1) can be only observed as on XRD data (Fig. 2).

3.2 Kinetic geochemical model fit

Measured solution compositions (Table 2) provide a sensitive experimental control of the geochemical models of

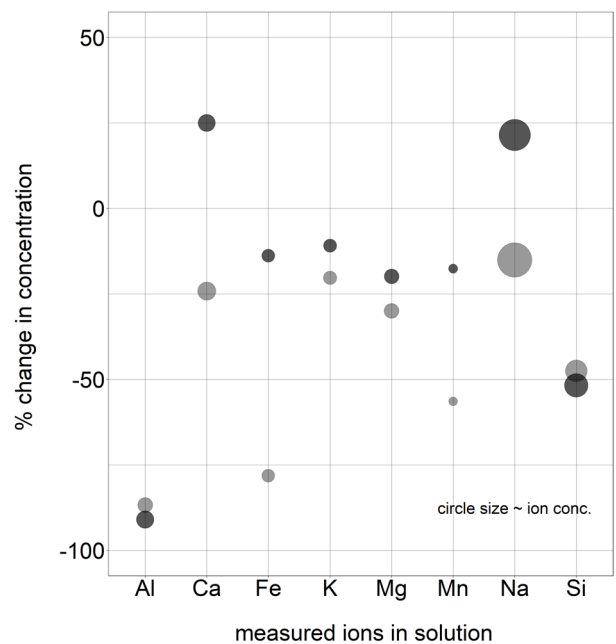


Fig. 1 Effect of reactor depressurization and cooling on solution composition in CO₂-experiments SWy-2-WCO2-4 (dark grey) and 6 (light grey). Uncertainty varies between 1 and 3 % (ICPOES).

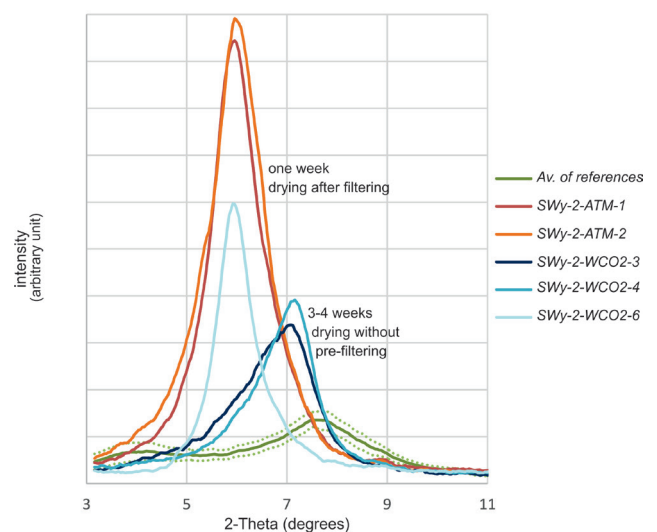


Fig. 2 Effect of post-experimental drying time (one week vs. 3-4 weeks) on XRD results of Namontmorillonite. The data of eight references are presented by their average and 95 % confidence interval.

Table 3 ATR-FTIR band areas corresponding to H₂O, H₂O, carbonates, silicates and quartz, respectively. From light to dark the values increase.

Wavenumber range [1/cm]	max:	3750	1740	1535	1250	818
	min:	2900	1540	1325	818	750
SWy-2	0A	18	0.71	0.17	49	0.60
	0B	8	0.29	0.16	39	0.55
	0C	9	0.32	0.17	41	0.59
	0D	23	0.93	0.28	45	0.56
	0E	31	1.26	0.25	66	0.61
	0F	35	1.49	0.18	71	0.60
	0G	29	1.22	0.20	51	0.57
	0H	27	1.14	0.25	53	0.56
SWy-2-ATM	1	52	2.50	0.15	77	0.55
	2	51	2.44	0.14	73	0.54
	3	40	1.86	0.23	72	0.64
SWy-2-WCO ₂	4	39	1.84	0.30	72	0.65
	6	55	2.62	0.00	76	0.56

Na-montmorillonite in air- and scCO₂-saturated water. After transforming mg/l data (Table 2) to mol/kgW, the goodness of model fit was possible to test by visualization in R. Several RSA and CEC scenarios have been run, their solution evolution is presented on Fig. 3 in comparison with measured data. The dissolution is always considered stoichiometric despite of the findings of Marty et al. [12], who reported the preferential release of Mg at 25 °C.

The interlayer cation (Ca²⁺, Na⁺ and K⁺, Section 2.1) concentrations in the atmospheric, SWy2-ATM experiments (Table 1) cannot be described solely by the change of RSA in the model and several orders of magnitude different values are predicted (ATM-noExch models, Fig. 3). By considering the clay standard's cation exchange capacity divided proportionally among interlayer cations, the measured variation can be reproduced on an order of magnitude level (ATM-(NaKCa)Exch models, Fig. 3). To gain the measured curve shapes for Na and K, cation exchange should be possibly defined also as a kinetic process, just like mineral dissolution and precipitation, however, suitable parameters are not known.

For the dissolved scCO₂-environment (SWy2-WCO₂), the reproduction of processes gets more complicated. Measured vs. modeled data indicates that not only the interlayer cations (Fig. 3) take part in ion exchange but a minor proportion of other, structural ions as well (WCO₂-(NaCaK0.4-4AlMgFeMn)Exch models, Fig. 3). This is mostly shown by Fe and Mn (Fig. 3). Taking into account CEC decrease with decreasing pH [24, 25], a minor improvement can be reached (WCO₂-0.75Exch models,

Fig. 3). Measured Si concentrations are higher than predicted by WCO₂ models (Fig. 3) probably due to its dissolution from the glass vessel in the reactor.

4 Conclusions

Batch experiments and kinetic geochemical models of this study primarily aimed to simulate the behavior of a selected clay mineral in CO₂ geological storage caprocks. Besides, a few technical conclusions were derived. One of them is that the detection of rock-fluid interactions is more sensitive by analyzing solution compositions than solid samples; XRD and ATR-FTIR data were primarily affected by the drying time of solid samples. Another drawback of solid samples is their potential contamination by experimental artefacts due to reactor depressurization and cooling. It was shown that these artefacts are expected to be mainly Al (e.g. boehmite) and Si containing phases.

Na-montmorillonite (SWy-2 clay standard) starts to react very fast already under atmospheric conditions but its reactivity highly increases when placed into CCS relevant conditions. The measured solution compositions could not be modeled by changing any of the dissolution parameters (e.g. RSA), but by considering the clay standard's cation exchange. With the combined approach, it was possible to simulate measured values on an order of magnitude level. In the atmospheric experiments dividing CEC proportionally among interlayer cations worked well in the models. However, when scCO₂ was present, data indicate that not only the main interlayer cations take part in cation exchange but a minor proportion of other ions as well. To better fit curve shapes probably the kinetic definition of ion exchange would be necessary.

The relevance of this experimentally validated definition of Na-montmorillonite was already shown by the more complex models of Szabó et al. [32]. Incorporation of CEC, based on this study, in their reactive transport simulations resulted in a very different and more representative prediction than earlier models.

Acknowledgement

This work was completed in the OTKA program (K-128120 for Gy. Falus) supported by the National Research, Development and Innovation Office of Hungary, in the ELTE Excellence Program (1783-3/2018/FEKUTSRAT) supported by the Hungarian Ministry of Human Capacities and in the GINOP-2.3.2-15-2016-00010 grant in the framework of the Széchenyi 2020 Plan, funded by the EU, co-financed by the ESIF. The work of Zs. Szabó was also

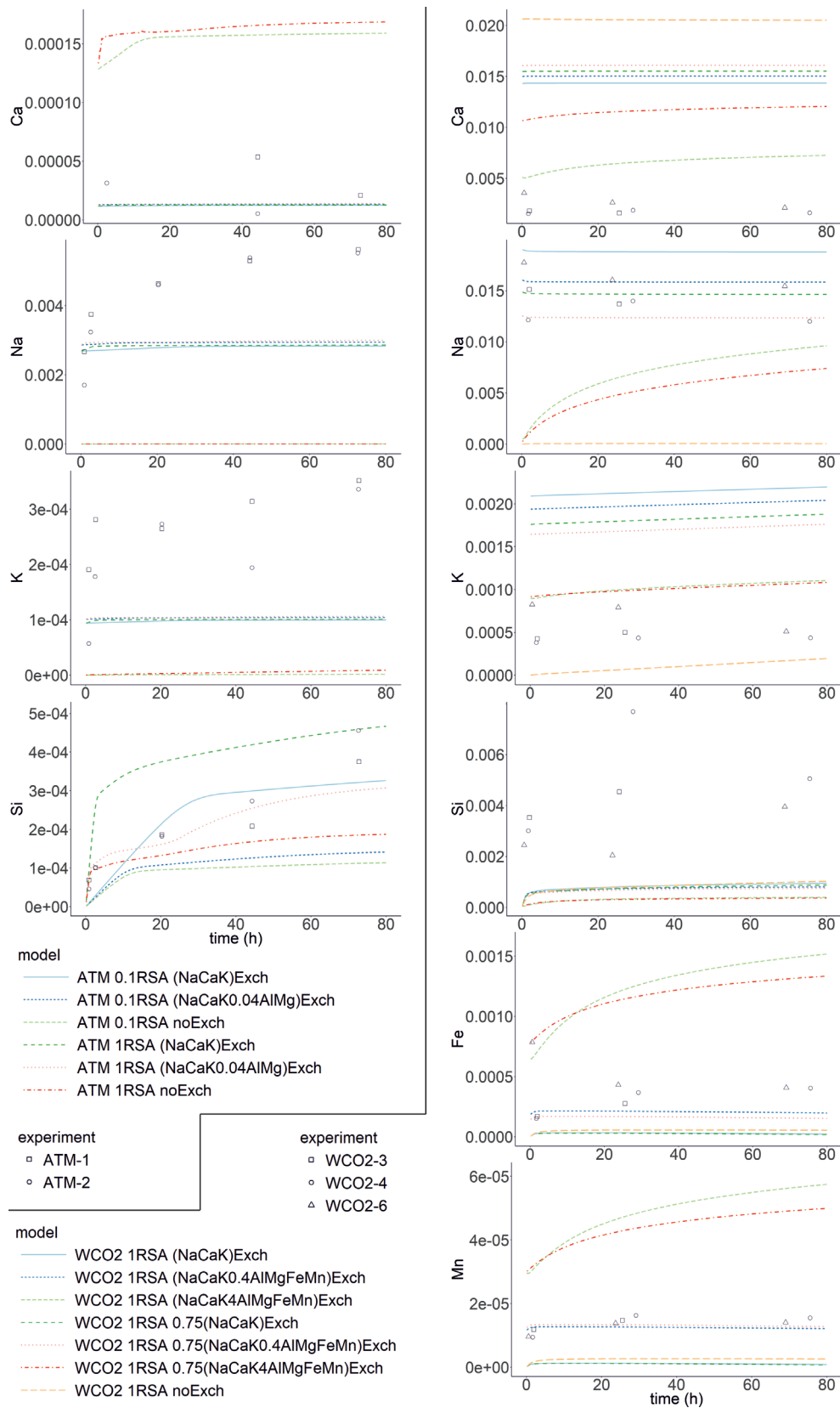


Fig. 3 Model fit on measured interlayer cation (Ca^{2+} , Na^+ and K^+) and Si concentrations [mol/kgW] in all batch experiments (Table 1 and 2) and on Fe and Mn concentrations in dissolved scCO_2 -batch experiments (*SWγ-2-WCO2*). *0.1-RSA* signs the proportion of SSA taken into account; *noExch* models do not consider CEC, *NaCaKExch* divide CEC proportionally among interlayer cations, *NaCaK0.4AlMgFeMnExch* extends the exchange processes to the 0.4-4 % of other ions; 0.75 decreases the total CEC to its 75 %.

funded by the MTA Premium Postdoctoral Research Program (Prémium_2017-13) of the Hungarian Academy of Sciences. The work of Cs Király was supported by the

FK-128230 OTKA grant. The authors thank the contribution of B.P. Szabó, Zs. Beke and Zs. Horváth.

References

- [1] Intergovernmental Panel on Climate Change (IPCC) "Summary for Policymakers", In: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., Midgley, P. M. (eds.) *Climate Change 2013: The Physical Science Basis: Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 1st ed., Cambridge University Press, New York, NY, USA, 2013, pp. 3-29.
- [2] United Nations Framework Convention on Climate Change (UNFCCC) "Article 21", In: *Adoption of the Paris Agreement*, FCCC/CP/2015/L.9/Rev.1, pp. 31–32, 2015.
- [3] Intergovernmental Panel on Climate Change (IPCC) "Summary for Policymakers", In: Edenhofer, O., Pichs-Madruga, R., Sokona, Y., Farahani, E., Kadner, S., Seyboth, K., Adler, A., Baum, I., Brunner, S., Eickemeier, P., Kriemann, B., Savolainen, J., Schlömer, S., von Stechow, C., Zwickel, T., Minx, J. C. (eds.) *Climate Change 2014: Mitigation of Climate Change: Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 1st ed., Cambridge University Press, New York, NY, USA, 2014, pp. 1–30.
- [4] European Academies Science Advisory Council (EASAC) "Carbon Capture and Storage in Europe", EASAC Secretariat, German National Academy of Sciences Leopoldina, Halle (Saale), Germany, EASAC Policy Report 20, 2013.
- [5] Kaldi, J., Daniel, R., Tenthorey, E., Michael, K., Schacht, U., Nicol, A., Underschultz, J., Backe, G. "Containment of CO₂ in CCS: Role of Caprocks and Faults", *Energy Procedia*, 37, pp. 5403–5410, 2013.
<https://doi.org/10.1016/j.egypro.2013.06.458>
- [6] Wang, X., Alvarado, V., Swoboda-Colberg, N., Kaszuba, J. P. "Reactivity of dolomite in water-saturated supercritical carbon dioxide: Significance for carbon capture and storage and for enhanced oil and gas recovery", *Energy Conversion and Management*, 65, pp. 564–573, 2013.
<https://doi.org/10.1016/j.enconman.2012.07.024>
- [7] Liu, F., Lu, P., Griffith, C., Hedges, S. W., Soong, Y., Hellevang, H., Zhu, C. "CO₂-brine-caprock interaction: Reactivity experiments on Eau Claire shale and a review of relevant literature", *International Journal of Greenhouse Gas Control*, 7, pp. 153–167, 2012.
<https://doi.org/10.1016/j.ijggc.2012.01.012>
- [8] Lu, J., Wilkinson, M., Haszeldine, R. S., Fallick, A. E. "Long-term performance of a mudrock seal in natural CO₂ storage", *Geology*, 37(1), pp. 35–38, 2009.
<https://doi.org/10.1130/G25412A.1>
- [9] Sendula, E., Páles, M., Szabó, B. P., Udvardi, B., Kovács, I., Kónya, P., Freiler, Á., Besnyei, A., Király, C., Székely, E., Szabó, C., Falus, G. "Experimental study of CO₂-saturated water – illite / kaolinite / montmorillonite system at 70-80 °C, 100-105 bar", *Energy Procedia*, 114, pp. 4934–4947, 2017.
<https://doi.org/10.1016/j.egypro.2017.03.1635>
- [10] Alemu, B. L., Aagaard, P., Munz, I. A., Skurtveit, E. "Caprock interaction with CO₂: A laboratory study of reactivity of shale with supercritical CO₂ and brine", *Applied Geochemistry*, 26(12), pp. 1975–1989, 2011.
<https://doi.org/10.1016/j.apgeochem.2011.06.028>
- [11] Szabó, Z., Hellevang, H., Király, C., Sendula, E., Kónya, P., Falus, G., Török, S., Szabó, C. "Experimental-modelling geochemical study of potential CCS caprocks in brine and CO₂-saturated brine", *International Journal of Greenhouse Gas Control*, 44, pp. 262–275, 2016.
<https://doi.org/10.1016/j.ijggc.2015.11.027>
- [12] Marty, N. C. M., Cama, J., Sato, T., Chino, D., Villiérás, F., Razafitianamaharavo, A., Brendlé, J., Giffaut, E., Soler, J. M., Gaucher, E. C., Tournassat, C. "Dissolution kinetics of synthetic Na-smectite. An integrated experimental approach", *Geochimica et Cosmochimica Acta*, 75(20), pp. 5849–5864, 2011.
<https://doi.org/10.1016/j.gca.2011.06.037>
- [13] de Jong, S. M., Spiers, C. J., Busch, A. "Development of swelling strain in smectite clays through exposure to carbon dioxide", *International Journal of Greenhouse Gas Control*, 24, pp. 149–161, 2014.
<https://doi.org/10.1016/j.ijggc.2014.03.010>
- [14] Galán, E., Aparicio, P. "Experimental study on the role of clays as sealing materials in the geological storage of carbon dioxide", *Applied Clay Science*, 87, pp. 22–27, 2014.
<https://doi.org/10.1016/j.clay.2013.11.013>
- [15] Giesting, P., Guggenheim, S., van Groos, A. F. K., Busch, A. "Interaction of carbon dioxide with Na-exchanged montmorillonite at pressures to 640 bars: Implications for CO₂ sequestration", *International Journal of Greenhouse Gas Control*, 8, pp. 73–81, 2012.
<https://doi.org/10.1016/j.ijggc.2012.01.011>
- [16] Hur, T.-B., Baltrus, J. P., Howard, B. H., Harbert, W. P., Romanov, V. N. "Carbonate formation in Wyoming montmorillonite under high pressure carbon dioxide", *International Journal of Greenhouse Gas Control*, 13, pp. 149–155, 2013.
<https://doi.org/10.1016/j.ijggc.2012.12.001>
- [17] Ilton, E. S., Schaefer, H. T., Qafoku, O., Rosso, K. M., Felmy, A. R. "In Situ X-ray Diffraction Study of Na⁺ Saturated Montmorillonite Exposed to Variably Wet Super Critical CO₂", *Environmental Science & Technology*, 46(7), pp. 4241–4248, 2012.
<https://doi.org/10.1021/es300234v>
- [18] Jeon, P. R., Choi, J., Yun, T. S., Lee, C.-H. "Sorption equilibrium and kinetics of CO₂ on clay minerals from subcritical to supercritical conditions: CO₂ sequestration at nanoscale interfaces", *Chemical Engineering Journal*, 255, pp. 705–715, 2014.
<https://doi.org/10.1016/j.cej.2014.06.090>

- [19] Krukowski, E. G., Goodman, A., Rother, G., Ilton, E. S., Guthrie, G., Bodnar, R. J. "FT-IR study of CO₂ interaction with Na⁺ exchanged montmorillonite", *Applied Clay Science*, 114, pp. 61–68, 2015.
<https://doi.org/10.1016/j.clay.2015.05.005>
- [20] Loring, J. S., Schaef, H. T., Thompson, C. J., Turcu, R. V., Miller, Q. R., Chen, J., Hu, J., Hoyt, D. W., Martin, P. F., Ilton, E. S., Felmy, A. R., Rosso, K. M. "Clay Hydration / dehydration in Dry to Water-saturated Supercritical CO₂: Implications for Caprock Integrity", *Energy Procedia*, 37, pp. 5443–5448, 2013.
<https://doi.org/10.1016/j.egypro.2013.06.463>
- [21] Romanov, V. N. "Evidence of irreversible CO₂ intercalation in montmorillonite", *International Journal of Greenhouse Gas Control*, 14, pp. 220–226, 2013.
<https://doi.org/10.1016/j.ijggc.2013.01.022>
- [22] Schaef, H. T., Loring, J. S., Glezakou, V.-A., Miller, Q. R. S., Chen, J., Owen, A. T., Lee, M.-S., Ilton, E. S., Felmy, A. R., McGrail, B. P., Thompson, C. J. "Competitive sorption of CO₂ and H₂O in 2:1 layer phyllosilicates", *Geochimica et Cosmochimica Acta*, 161, pp. 248–257, 2015.
<https://doi.org/10.1016/j.gca.2015.03.027>
- [23] The Clay Minerals Society "Source Clay Physical / Chemical Data", [online] Available at: www.agry.purdue.edu/cjohnston/sourceclays/chem.htm [Accessed: 13 July 2018]
- [24] Helling, C. S., Chesters, G., Corey, R. B. "Contribution of Organic Matter and Clay to Soil Cation-Exchange Capacity as Affected by the pH of the Saturating Solution", *Soil Science Society of America Journal*, 28(4), pp. 517–520, 1964.
<https://doi.org/10.2136/sssaj1964.03615995002800040020x>
- [25] Ma, C., Eggleton, R. A. "Cation Exchange Capacity of Kaolinite", *Clays and Clay Minerals*, 47(2), pp. 174–180, 1999.
- [26] Golubev, S. V., Bauer, A., Pokrovsky, O. S. "Effect of pH and organic ligands on the kinetics of smectite dissolution at 25 °C", *Geochimica et Cosmochimica Acta*, 70(17), pp. 4436–4451, 2006.
<https://doi.org/10.1016/j.gca.2006.06.1557>
- [27] Bradbury, M. H., Baeyens, B. "Porewater Chemistry in Compacted Re-Saturated MX-80 Bentonite: Physico-Chemical Characterisation and Geochemical Modelling", Paul Scherrer Institute (PSI), Villigen, Switzerland, PSI Bericht Nr. 02-10, 2002.
- [28] Helmholtz Zentrum Dresden Rossendorf (HZDR) "RES³T - Rossendorf Expert System for Surface and Sorption Thermodynamics", [online] Available at: www.hzdr.de/db/RES3T.queryData [Accessed: 13 July 2018]
- [29] Parkhurst, D. L., Appelo, C. A. J. "Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations", U.S. Geological Survey, Denver, Colorado, USA, Techniques and Methods 6-A43, 2013.
<https://doi.org/10.3133/tm6A43>
- [30] Király, C., Szamosfalvi, Á., Zilahi-Sebess, L., Kónya, P., Kovács, I. J., Sendula, E., Szabó, C., Falus, G. "Caprock analysis from the Mihályi-Répcelak natural CO₂ occurrence, Western Hungary", *Environmental Earth Sciences*, 75, article ID: 635, 2016.
<https://doi.org/10.1007/s12665-016-5399-6>
- [31] Hellevang, H., Aagaard, P., Jahren, J. "Will dawsonite form during CO₂ storage?", *Greenhouse Gases: Science and Technology, Special Issue: Geochemical reactivity in CO₂ geological storage sites*, 4(2), pp. 191–199, 2014.
<https://doi.org/10.1002/ghg.1378>
- [32] Szabó, Z., Gál, N. E., Kun, É., Szöcs, T., Falus, G. "Assessing effects and signals of leakage from a CO₂ reservoir to a shallow freshwater aquifer by reactive transport modelling", *Environmental Earth Sciences*, 77, article ID: 460, 2018.
<https://doi.org/10.1007/s12665-018-7637-6>
- [33] Palandri, J. L., Kharaka, Y. K. "A Compilation of Rate Parameters of Water-mineral Interaction Kinetics for Application to Geochemical Modelling", U.S. Geological Survey, Denver, Colorado, USA, prepared in cooperation with the National Energy Technology Laboratory – United States Department of Energy, Open File Report 2004-1068, 2004.
- [34] Hellevang, H., Pham, V. T. H., Aagaard, P. "Kinetic modelling of CO₂–water–rock interactions", *International Journal of Greenhouse Gas Control*, 15, pp. 3–15, 2013.
<https://doi.org/10.1016/j.ijggc.2013.01.027>
- [35] Szabo, Z. "SWy-2 PHREEQC model input parameters", 2018.
<https://doi.org/10.17632/vm7ngdxn35.1#file-c5f4d9c9-7a73-404e-8ee4-0a35f57163d7>