Gas-bentonite interactions: Towards a better understanding of gas dynamics in Engineered Barrier Systems

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ABSTRACT

Bentonite is a common backfill material used in Engineered Barrier Systems (EBS) for radioactive waste disposal. Its thermal, hydraulic, and chemical properties have been extensively studied. However, empirical evidence on the interactions with the free gas phase present in its pore space under conditions close to those prevailing in deep geological repositories (i.e., exposure to multiple gas species at temperature and humidity conditions close to those of freshly backfilled EBS) is scarce. This limits the prediction/assessment of the evolution of the gas composition in EBS. Here we present the outcome of laboratory experiments targeting such gas-bentonite interactions using two different types of bentonite (Italian bentonite; Wyoming bentonite) being exposed to atmospheric air in sealed stainless-steel vessels. The results indicate that gas sorption on bentonite can occur at repository-like conditions and is likely to play a significant role in the overall gas dynamics in the backfill of EBS. Drying of both bentonites was shown to partly re-activate their CO_2 sorption capacity during a subsequent re-hydration phase. Furthermore, the grinding of Wyoming bentonite resulted in the generation of new pyrite surfaces that significantly enhanced O_2 removal from the free gas phase by oxidation. Our initial investigations call for more systematic and extensive series of laboratory experiments in order to quantitatively constrain the different processes involved in gas-bentonite interactions.

1. Introduction

Deep geological repositories are the preferred option for radioactive waste disposal in most countries. Indeed, deep geological repositories provide the capability to isolate radioactive waste in stable geological formations over long timescales with no obligation to actively maintain the respective facilities for future generations.

However, several safety-relevant criteria need to be considered and evaluated. The behavior of gases is one of the important factors in the safety assessment of deep geological repositories, as different gas species are expected to be produced, consumed, and transported is such underground systems. This can potentially affect the performance of the host rock and the Engineered Barrier System (EBS) by changing their state conditions. For instance, excessive pressure build-up within EBS could compromise their integrity (Norris et al., 2013). Consumption of molecular oxygen by interaction with clay materials on the other hand is considered to be beneficial since it will reduce corrosion of the metal canisters encapsulating the waste (Wersin et al., 1994). However, the variety of gas production and consumption processes (Diomidis et al., 2016) as well as the complexity of the partitioning of volatiles within different repository compartments make the prediction of gas dynamics in and around deep repositories a notoriously challenging task.

From this point of view, gas measurements in laboratory or in field experiments can provide direct observations supporting the identification and characterization of the relevant processes affecting gas composition in EBS. Insights on the gas dynamics based on empirical evidence provide key information to guide modeling exercises leading to more realistic scenarios.

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Over the last years, a few laboratory experiments as well as in-situ monitoring programs started to provide data and tentative interpretations on gas evolution in EBS-like environments, such as the observation of O_2 depletion in bentonite backfills which were linked in one case to aerobic copper corrosion (Birgersson and Goudarzi, 2018), and in another case both to abiotic processes and oxigen consumption by methane-oxidizing bacteria (Svemar et al., 2016). Other long-term in-situ experiments identified changes to the reactive gas spectrum in the EBS pore space as being primarily catalysed by metal corrosion and degradation of organic matter from the EBS installation (Férnandez and Giroud, 2016).

In the only in-situ study including monitoring of noble gases in the EBS pore space (the Fullscale Emplacement (FE) experiment in the Mont Terri underground rock laboratory, Switzerland; Müller et al., 2017), gas exchange with the surrounding host rock could be demonstrated, both constraining the gas evolution in the EBS over time as well as indicating that gas sorption on the bentonite backfill is a potential factor to be considered in order to explain the observed changes in gas composition (Giroud et al., 2018; Tomonaga et al., 2019). Sorption of gases on clays has been well studied in the fields of natural gas exploration, carbon storage, industrial applications (porosity measurement, chemical gas separation) but only in a limited manner in the context of radioactive waste disposal (e.g., Gregg and Sing, 1982; Gadikota et al., 2017; Song et al., 2017; Truche et al., 2018).

All these studies make the case that the composition of volatiles within an EBS strongly depends on the specific conditions of the investigated system and various physical and biogeochemical aspects need to be considered to attain a comprehensive and integral understanding of the gas dynamics. However, gas-clay interactions under common ambient or repository-like conditions are not yet well constrained. In order to provide further empirical evidence and stimulate the scientific discussion on such interactions, based on the experience gained during the investigation on the gas dynamics in the FE experiment (Giroud et al., 2018; Tomonaga et al., 2019), we performed laboratory experiments targeting gas sorption and reaction potential using two different types of bentonite. The first bentonite type was Wyoming bentonite, the second bentonite type was Italian bentonite. Both bentonites have been considered as potential backfill materials for deep geological repositories in different countries (Kiviranta et al., 2018, for more details on the bentonites refer to the Methods section).

The experiments were conceived as an initial study to identify and characterize the interactions between a gas phase (i.e., atmospheric air) and the bentonite confined within sealed stainless-steel vessels. As the stainless-steel vessels can safely be considered chemically inert within the context of the experimental parameters and timeframe, any changes in the composition of the gas phase (i.e., the vessel headspace) could be related to the presence of the clay materials. The synchronous measurements of multiple gas species (i.e., He, Ar, Kr, N_2, O_2, CO_2, and CH_4) provided a comprehensive overview on the gas composition in order to constrain the gas dynamics and evolution in the sealed stainless-steel vessels and allowed exclusion of possible experimental artifacts (e.g., leakage). The outcome of our laboratory experiments represents a further step towards a better understanding of gas dynamics in EBS and the discrimination of processes relevant for model optimization and validation.

2. Methods

2.1. Bentonite samples

Following bentonite samples were provided and were investigated: Italian bentonite and Wyoming bentonite. Wyoming corresponds to the bentonite used in previous laboratory experiments (Giroud et al., 2018), but with a coarser grain size. The grain size of the Italian bentonite is roughly estimated to be about 0.1–2 mm while the one of the Wyoming bentonite is approximately 0.1–1 mm. Both bentonite materials display

a high smectite content of 80–85 wt %; the exchanger composition is dominated by Ca–Mg and Na for the Italian bentonite and the Wyoming bentonite, respectively (Kiviranta et al., 2018; Kumpulainen et al., 2021). The water content of the bentonite samples "as-received" is estimated to be approximately 15 wt % for the Italian bentonite and 10 wt % for the Wyoming bentonite (see Experiment D). It should be noted that such water content refers to the wet weight of the samples.

2.2. Gas measurement system

Fig. 1 summarizes the analytical setup used to measure gas species in our laboratory experiments (for further details refer to the work by Brennwald et al., 2016). The system allows the quantification of the partial pressures of He, Ar, Kr, N_2, O_2, CO_2, and CH_4 in gaseous and aqueous matrices with an analytical uncertainty of approximately 1–3 %. Uncertainties lower than this typical range are likely to be underestimated. Bearing in mind that the bentonites in their original state could potentially trap large amounts of CH_4, the respective measurements were performed on the Faraday cup detector (i.e., less sensitive compared to the electron multiplier detector used to determine e.g. He and Kr). Thus, the CH_4 analyses were not tailored to air-like CH_4 concentrations and the respective results should not over-interpreted. Our laboratory trials did not target H_2 although the applied analytical setup is in principle suitable for tracking the H_2 evolution (Tomonaga et al., 2019). The gas was collected through a capillary pressure reduction system into a vacuum chamber, where its composition was analyzed using a quadrupole mass spectrometer (Stanford Research Systems RGA-200). Calibration of the measurements was done using a gas calibration bag (Linde, Plastigas) filled with atmospheric air (Ozima and Podosek, 1983) at an ambient pressure of ∼ 960 mbar (Tomonaga et al., 2019).

The capillary inlet of the mass spectrometer system was connected to the outlet of a VICI® six port selection valve. The inlets of the valve were connected to a) the gas calibration bag, b–c) two stainless steel vessels containing the bentonite samples, and d) a sealed port for residual gas (blank) determination. Inlets between the two positions connecting the vessels were sealed airtight and used to evacuate the dead volume of the valve before each measurement and, hence, limit cross-contamination between different inlet positions.

Each vessel used to host the bentonite samples in our experiments consisted of a stainless-steel cylinder (inner volume: approx. 160 cm^3). The two DN40 open ends of the cylinder were sealed by o-ring seals kept tight with an aluminum chain. The bottom was sealed with a blind flange and the top with a DN40 to Swagelok 1/4" adapter connected by a Swagelok 1/4" to 1/16" adapter to the capillary of the MS system.

The analytical protocols foresaw six major steps: i) a calibration with atmospheric air (from the gas calibration bag), ii) the determination of residual gas intensities after evacuation of the system set on the sealed port (30′), iii) measurement of the gas composition in the vessel containing the Italian bentonite, iv) evacuation of the capillary inlet system set on the sealed port located between the ports connected to the sample vessels (30'), v) measurement of the gas composition in the vessel containing the Wyoming bentonite, and vi) a second calibration with atmospheric air. Each calibration, blank, or sample measurement consisted of 20 readings on the Faraday cup detector (for CH_4, N_2, O_2, Ar, and CO_2) and 40 readings on the electron multiplier detector (for He and Kr).

Before each measurement, the detectors of the mass spectrometer underwent a warm-up cycle to constrain sensitivity drifts. The total gas pressure, monitored by sensors (gas-type independent absolute pressure transducers with an accuracy of 0.08 % BSL, i.e., Best Straight Line) connected to the vessels, was used to support the determination of the gas composition (i.e., to constrain the absolute gas partial pressures of the measured species) as well as to correct total pressure changes resulting from the gas removal necessary for the analyses. For the data processing refer to Brennwald et al. (2016).
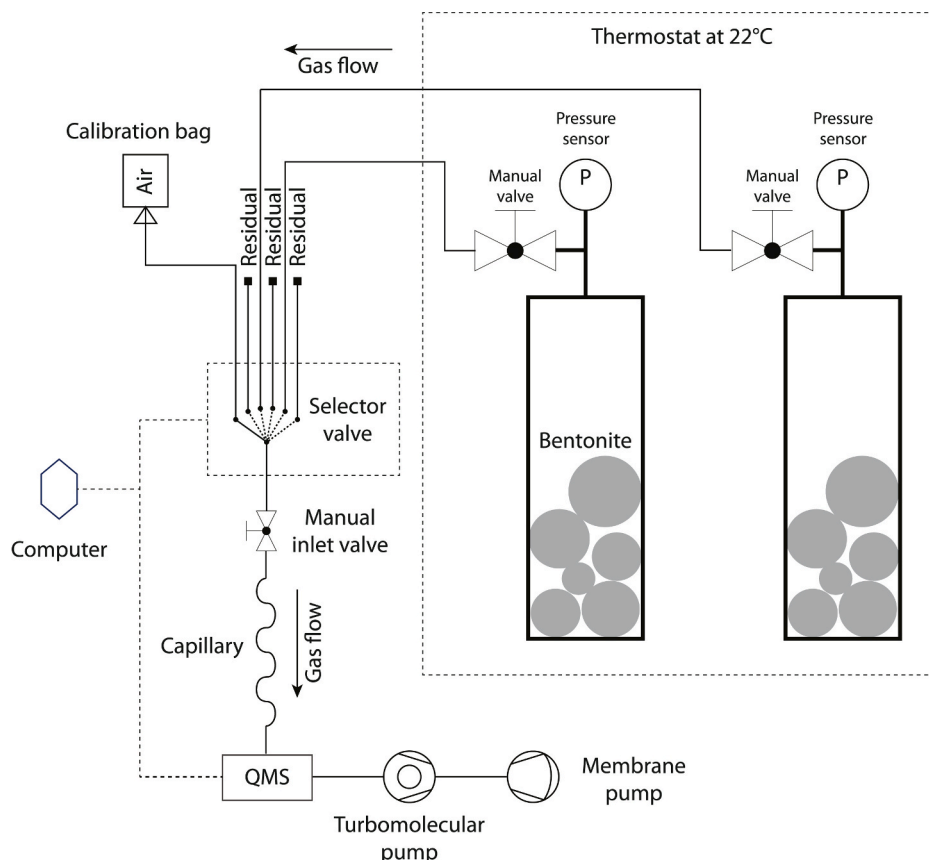
Fig. 1. Schematic overview of the mass spectrometer system used for the laboratory experiments (miniRUEDI; www.gasometrix.com; Brennwald et al., 2016; Giroud et al., 2018). The inlet selector valve and the quadrupole mass spectrometer (QMS) were (remotely) controlled by a computer.

It should be noted that potential interactions between gases and the used vacuum components were assessed by monitoring the total pressure and the gas composition in empty control vessels over almost two weeks. As the total pressure and the gas composition did not change significantly, we concluded that the none of the adopted parts composing the vessels affected the gas phase.

2.3. Experiment description

Four different series of experiments were conducted as specified in the following subsections. All experiments, lasting from 12 days up to almost two months, were performed in a thermostat at a constant temperature of 22 °C. A summary of the conditions prevailing upon starting the experiments is given in Table 1.

2.3.1. Experiment with untreated bentonite (A)

This experiment targeted the parallel and synchronous measurement of the gas composition in two airtight stainless-steel vessels: one vessel containing Italian bentonite and the other vessel filled with Wyoming

bentonite "as-received" (i.e., untreated bentonites as delivered by the producers, about 180 g in each vessel). The gas composition (initially reflecting the one of atmospheric air) was determined in the gaseous headspace above the bentonite materials. The experiment provided initial information on the dynamics between gas phase and clay mineral phase, allowing optimization of the analytical protocols for the subsequent experiments.

2.3.2. Experiment with untreated bentonite under controlled RH (B)

This experiment was performed almost as Experiment A. The only difference was that the relative humidity (RH) was kept constant at ~75 % by placing a small vial with a saturated NaCl solution into the vessels. Experiment B was conducted in order to assess if the (further) hydration of the clay minerals affects the gas dynamics. The absence of a conditioning of the bentonite materials under the targeted RH was intentional and mimicked the early stages of an EBS where the backfill material is exposed to increasing RH over time due to the re-saturation by humidity from the host rock.

Table 1

Summary of the initial conditions of the experiments conducted with Italian and Wyoming bentonite aliquots. For the first two experiments (A and B), the bentonite was inserted in the vessels with no treatment (i.e., "as-received"). For Experiment C the bentonites were ground and for Experiment D they were subsequently dried. The water content refers to the wet weight of the samples at the beginning of the experiments.

Experiment	T [°C]	Gas phase RH [%]	Aliquots ground	Aliquots dried	Water content Italian [wt %]	Water content Wyoming [wt %]
A	22	∼ 55	no	no	∼ 15	∼ 10
B	22	∼ 75	no	no	∼ 15	∼ 10
C	22	∼ 75	yes	no	∼ 15	∼ 10
D	22	∼ 75	yes	yes	0	0

2.3.3. Experiment with ground bentonite under controlled RH (C)

This experiment was similar to Experiment B but performed with finely ground bentonite aliquots to investigate the relation between the production of new mineral surfaces and gas emission/removal.

To this end, both bentonite samples were ground under inert gas conditions (N_2) using a Retsch Planetary Ball Mill PM 100 down to grain sizes of less than 200 μm. The Italian bentonite was ground in aliquots of about 50 mL for 22 min at 253 rpm using eight grinding balls. Wyoming was ground in aliquots of 50 mL for 18 min at 253 rpm using five grinding balls.

To enhance the overall sensitivity with regards to the gas dynamics (compared to Experiments A and B), solid glass beads were then used to minimize the headspace volume in the vessels (i.e, due to the reduced headspace, the resulting changes in gas composition were more pronounced than in the previous experiments). The glass beads had a diameter of about 2 mm and were solid. Significant chemical or physical interactions between the glass beads and the gas phase in the vessels were not expected.

2.3.4. Experiment with ground and dried bentonite under controlled RH (D)

This experiment was like Experiment C but using dried bentonites. Experiment D aimed to analyze the relation between gas sorption/consumption and the degree of clay interlayer hydration (thus, the RH might have been subject to fluctuations during the initial phase of the trial).

The ground bentonite aliquots of Experiment C were dried in an oven under atmospheric air at 100 °C for eight days. Thus, the water vapor and other gases emitted from the heated bentonite samples were mostly lost to the atmosphere. From the difference of the weights measured before (182 g for each bentonite; i.e., the wet weight) and after drying, the water content of the Italian bentonite (dry weight: 155 g) and the

Wyoming bentonite (dry weight: 163 g) was estimated to be 15 wt % and 10 wt %, respectively. After drying, the two samples were sealed in stainless-steel vessels with vials containing a saturated NaCl solution. For the whole duration of the experiment (i.e., about one month), the bentonites were exposed to the moisture of the NaCl solution.

3. Results and discussion

The experiments were carried out between December 2018 and July 2019. The results are summarized in Table 2 and Fig. 2. It should be noted that the results are reported as the shares of the initial partial pressures normalized to the total pressure (i.e., the relative change; see Table 2). This notation has the advantage to remove the effects due to swelling of the bentonite materials (i.e., when exposed to the moisture from the salt solution used to control the RH in most of the experiments). On the other hand, only a limited assessment of what happens with an individual gas species is possible, as the respective share is inferred in conjunction with all other gas species at a given time.

The uncertainties for N_2, O_2, and Ar are much lower than expected uncertainties (i.e., 1–3 %, Brennwald et al., 2016) and appear to be underestimated. Lower uncertainties result from a lower scattering of the readings for the individual measurements. However, such lower uncertainties are not representative for the usual performance of the analytical system. In the following we discuss the respective results considering such typical uncertainties as reported in Brennwald et al. (2016).

3.1. Experiment with untreated bentonite (A)

The experiment with untreated bentonite aliquots lasted for ∼ 12 days. The RH was not actively controlled but it is roughly estimated to be around 55 % immediately after closure of the vessels (based on

Table 2
Results of the experiments with Italian and Wyoming bentonite aliquots reported as the shares of the initial partial pressures (i.e., the relative change) normalized to the total pressure (i.e., $[p_i(t)/p_{tot}(t)]/[p_i(t_0)/p_{tot}(t_0)]$ where p_i is the partial pressure of gas i, p_{tot} is the total pressure, t is the time of the measurement, and t_0 is the time of the first measurement for the respective experiment) determined during the measurement of the gas composition under a controlled temperature of 22 °C. Uncertainties of the gas measurements are given at the 1σ level.

Bentonite	Time [d]	CH_4	N_2	O_2	Ar	CO_2	He	Kr
Experiment A - Untreated bentonite								
Italian	0.0	1.00 ± 0.05	1.000 ± 0.003	1.000 ± 0.003	1.000 ± 0.003	1.00 ± 0.01	1.00 ± 0.02	1.00 ± 0.02
	4.2	1.01 ± 0.05	1.000 ± 0.003	1.000 ± 0.004	1.007 ± 0.005	1.03 ± 0.01	1.04 ± 0.02	1.03 ± 0.02
	8.4	1.04 ± 0.05	0.993 ± 0.005	1.026 ± 0.005	1.005 ± 0.005	1.09 ± 0.01	1.07 ± 0.02	1.01 ± 0.02
	12.5	1.01 ± 0.06	0.995 ± 0.004	1.017 ± 0.005	0.998 ± 0.005	1.09 ± 0.01	1.07 ± 0.02	1.08 ± 0.02
Wyoming	0.0	1.00 ± 0.06	1.000 ± 0.004	1.000 ± 0.003	1.000 ± 0.004	1.00 ± 0.02	1.00 ± 0.02	1.00 ± 0.02
	4.2	1.07 ± 0.06	0.996 ± 0.004	1.016 ± 0.005	1.019 ± 0.005	0.89 ± 0.02	1.04 ± 0.02	1.03 ± 0.02
	8.4	1.02 ± 0.05	1.000 ± 0.004	0.999 ± 0.004	1.002 ± 0.004	0.81 ± 0.01	1.07 ± 0.02	1.01 ± 0.02
	12.5	1.04 ± 0.06	1.005 ± 0.004	0.984 ± 0.005	0.983 ± 0.005	0.76 ± 0.02	1.03 ± 0.02	1.03 ± 0.02
Experiment B - Untreated bentonite under controlled RH								
Italian	0.0	1.00 ± 0.07	1.000 ± 0.003	1.000 ± 0.003	1.000 ± 0.003	1.0 ± 0.1	1.00 ± 0.02	1.00 ± 0.02
	13.9	1.05 ± 0.08	0.997 ± 0.004	1.013 ± 0.005	0.996 ± 0.003	1.1 ± 0.2	1.20 ± 0.02	1.12 ± 0.02
Wyoming	0.0	1.00 ± 0.07	1.000 ± 0.004	1.000 ± 0.004	1.000 ± 0.003	1.0 ± 0.1	1.00 ± 0.02	1.00 ± 0.02
	13.9	0.98 ± 0.08	1.002 ± 0.003	0.996 ± 0.005	0.979 ± 0.004	0.5 ± 0.1	1.03 ± 0.02	1.02 ± 0.02
Experiment C - Ground bentonite under controlled RH								
Italian	0.0	1.00 ± 0.05	1.000 ± 0.003	1.000 ± 0.003	1.000 ± 0.005	1.00 ± 0.01	1.00 ± 0.03	1.00 ± 0.02
	55.7	0.87 ± 0.05	1.009 ± 0.005	0.964 ± 0.003	1.011 ± 0.004	1.54 ± 0.01	0.97 ± 0.03	0.98 ± 0.02
Wyoming	0.0	1.00 ± 0.04	1.000 ± 0.004	1.000 ± 0.003	1.000 ± 0.003	1.00 ± 0.01	1.00 ± 0.02	1.00 ± 0.02
	55.7	1.01 ± 0.05	1.032 ± 0.005	0.877 ± 0.004	1.046 ± 0.005	0.62 ± 0.01	1.09 ± 0.03	1.06 ± 0.02
Experiment D - Ground and dryed bentonite under controlled RH								
Italian	0.0	1.00 ± 0.07	1.000 ± 0.004	1.000 ± 0.002	1.000 ± 0.005	1.00 ± 0.04	1.00 ± 0.02	1.00 ± 0.02
	14.6	1.07 ± 0.07	0.997 ± 0.005	1.013 ± 0.003	1.012 ± 0.005	0.53 ± 0.04	1.00 ± 0.02	1.09 ± 0.03
	22.6	0.97 ± 0.06	1.003 ± 0.004	0.989 ± 0.003	1.020 ± 0.005	0.52 ± 0.04	0.93 ± 0.03	1.06 ± 0.03
	34.6	0.96 ± 0.06	0.997 ± 0.004	1.008 ± 0.003	1.043 ± 0.005	0.52 ± 0.04	0.95 ± 0.02	1.09 ± 0.03
Wyoming	0.0	1.00 ± 0.06	1.000 ± 0.003	1.000 ± 0.002	1.000 ± 0.004	1.00 ± 0.06	1.00 ± 0.03	1.00 ± 0.02
	14.6	0.96 ± 0.06	1.000 ± 0.004	1.000 ± 0.003	1.001 ± 0.004	0.75 ± 0.04	0.95 ± 0.02	1.00 ± 0.03
	22.6	0.91 ± 0.06	1.009 ± 0.004	0.968 ± 0.003	1.007 ± 0.005	0.61 ± 0.05	0.91 ± 0.02	1.03 ± 0.02
	34.6	0.87 ± 0.06	1.001 ± 0.005	0.995 ± 0.002	1.032 ± 0.005	0.73 ± 0.06	0.96 ± 0.02	1.07 ± 0.02
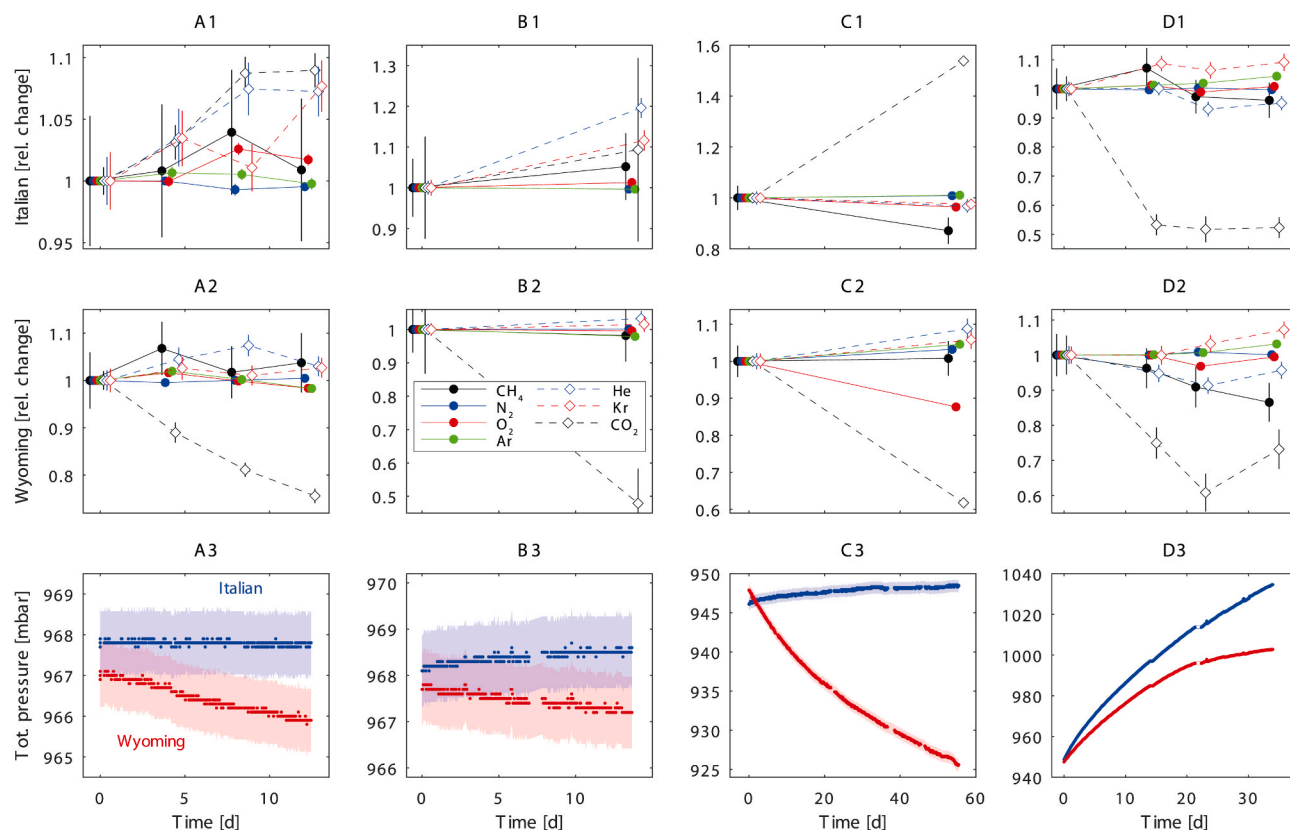
Fig. 2. Results of the experiments with Italian and Wyoming bentonite aliquots. Capital letters A–D in the subplot titles refer the different experiments as described in the introductory section. The two upper panel rows report the shares of the initial partial pressures (i.e., the relative change) normalized to the total pressure (i.e., $[p_i(t)/p_{tot}(t)]/[p_i(t_0)/p_{tot}(t_0)]$ where p_i is the partial pressure of gas i, p_{tot} is the total pressure, t is the time of the measurement, and t_0 is the time of the first measurement for the respective experiment) determined during the measurement of the gas composition under a controlled temperature of 22 °C. Vertical lines indicate the uncertainties of the gas measurements at the 1σ level. The lowest panel row reports the measured total pressures (blue/red shaded areas indicate the uncertainty ranges).

temperature and RH readings from a nearby weather station).

CH_4, N_2, and Ar concentrations did not change significantly in the vessel containing Italian bentonite (Fig. 2, panel A1). The time series implies slight O_2 partial pressure increase of less than 2 % that, however, lies within the typical uncertainty range of the used analytical setup (i.e., about 1–3 %) and does not seem to be significant. Moreover, considering the experimental setup, the production of O_2 would hardly be justifiable. Indeed, the total pressure remained virtually constant over the duration of the experiment (Fig. 2, panel A3). The He, CO_2, and Kr concentrations increase slightly by ~ 8 % implying that these gases are emitted from the Italian bentonite. ^{4}He is produced by the decay of U and Th within the mineral matrix and can accumulate in the pore space over geological time scales. CO_2 is known to be dissolved in the clay interlayer water from the initial carbonate content and to be enriched with respect to bulk water due to enhanced solublilities (Gadikota et al., 2017). At this stage we cannot explain the Kr enrichment within the Italian bentonite but, based on the analytical setup, it cannot be ascribed to atmospheric contamination during the experiment. Most likely the Kr excess is of non-atmospheric origin and was entrapped after/during clay deposition or during the bentonite production process (i.e., from geogenic or anthropogenic sources). The release of these species indicates that gas partitioning between the Italian bentonite and the atmosphere is not yet at equilibrium and the mineral structure of the Italian bentonite still preserves previously acquired gases.

The gas composition in the headspace of the vessel containing Wyoming bentonite evolved considerably over time (Fig. 2, panel A2). At the end of the experiment CO_2 is strongly depleted (about −25 %). Similarly to the Italian bentonite, He and Kr concentrations slightly increased (3 %) suggesting emission of these gases from the bentonite.

Although the origin of Kr remains unclear, it is worth to note that a Kr excess has been observed in the FE experiment (Tomonaga et al., 2019) where the same bentonite has been used as backfill material. However, a direct linkage to our experiments would be highly speculative, as Kr in the FE experiment might also originate from past or ongoing activities at the Mont Terri rock laboratory. Ar and O_2 concentrations appear to be slightly depleted with respect to their initial values. The total pressure decreases over time suggesting gas removal (Fig. 2, panel A3). The results for Wyoming seem to be in agreement with previous experiments conducted with similar clay material (Giroud et al., 2018) which indicated substantial gas sorption onto this material. It should be noted that the experiments in Giroud et al. (2018) involved heating of a vessel containing Wyoming bentonite for 1 day at 100 °C. A potential explanation was that the 1-day-long heating step removed a share of the adsorbed water molecules from the mineral surfaces leaving free active sorption sites that were subsequently occupied by other gas species. The absence of a He and Kr concentration decrease in Experiment A might imply that the bentonite sorption capacity for these gas species is already depleted.

These initial observations indicate that untreated bentonite materials can carry different gas signatures that in turn lead to different interactions with the gas phase in the vessel headspace. Processes involved in the bentonite production are likely to play a major role in adding/removing such signatures, but can hardly be tracked.

3.2. Experiment with untreated bentonite under controlled RH (B)

The results of this experiment are summarized in Fig. 2, panels B1–B3. The changes in gas composition over time are similar to the

temporal trends observed for the first experiment with untreated bentonite (Fig. 2, panels A1 and A2).

The high RH seems to foster the swelling of the Italian bentonite (i.e., swelling of the bentonite caused the reduction of volume available for the free gas phase leading to higher gas pressures; see Fig. 2, panel B3). Indeed, clay minerals are well known to undergo significant volume increases in response to water uptake in the clay mineral interlayers (i.e., interlayer water sorption). Within a closed system (i.e., the vessels used in our experiments) such solid phase volume increase results in a decrease of the volume of the respective gaseous phase and, thus, in an increase of the total gas pressure. As the interlayer water density can be significantly lower compared to the density of bulk water (Appelo, 2013), a transfer of water molecules from the vial containing the salt solution into the interlayer pore space of the bentonite sample may induce the bulk bentonite volume change required to produce the observed total pressure increase. The occurrence of swelling is supported by the outcome of Experiment A, where no NaCl solution was inserted in the vessel and, thus, no additional water (besides the water vapor present in the headspace) could be sorbed on the untreated Italian bentonite.

The large uncertainty affecting the CO_2 concentration of the Italian bentonite does not allow identification of significant changes over time (e.g., in relation to the sorption of water). The measured concentration, however, is the same as the one of Experiment A suggesting also CO_2 degassing and implying that the total CO_2 amount in the bentonite grains is (much) higher than the amount that can be dissolved in the interlayer water even considering the additionally sorbed water. The concentrations of He and Kr increase by 20 % and 12 %, respectively, confirming the emission of these gases from the bentonite as observed in Experiment A. On a highly speculative level, the higher He and Kr concentrations compared to those of Experiment A might imply that the diffusion/emission of these gases is fostered in a more swelled clay material.

The total gas pressure for the Wyoming bentonite decreased slightly (Fig. 2, panel B3). Such decrease, being somewhat lower than observed in Experiment A, suggests also some swelling of the Wyoming bentonite. A slight decrease in the Ar and O_2 concentrations (although a decrease of 2 % might be significant only for Ar at best) and a slight increase in He (3 %) and Kr (2 %, but not significant) is in line with the outcome of Experiment A. The CO_2 loss for the Wyoming bentonite (about -50 %; Fig. 2, panel B2) is similar (i.e., within a factor of two) to Experiment A (Fig. 2, panel A2).

3.3. Experiment with ground bentonite under controlled RH (C)

The results of this experiment are shown in Fig. 2, panels C1–C3. The laboratory trial lasted for approximately 55 days until the total pressure change in one of the vessels exceeded 2 % (i.e., to ensure that potential concentrations changes even for a major gas such as O_2 would be at least similar to the typical experimental uncertainties).

The CO_2 concentration in the vessel filled with the Italian bentonite increased for more than 50 % (Fig. 2, panel C1). He, Kr, and O_2 concentrations slightly decreased by about 2–3 % (although only the change for O_2 is statistically significant). The observed changes in gas concentrations imply that the grinding of the Italian bentonite likely fostered the gas exchange between the bulk mineral phase and the free gas phase in the stainless-steel vessel. Indeed, the large CO_2 excess already present in the Italian bentonite (see Experiments A and B) was emitted more rapidly. As the mineral grains in Experiment C were smaller, the (diffusive) escape path for CO_2 from the center to the surface of the grains became shorter allowing faster CO_2 release into the vessel headspace. The potential removal of the chemically inert He and Kr might imply that sorption is partly controlling the evolution of the gas composition (Giroud et al., 2018). However, as Ar does not seem to be affected (by sorption), final conclusions cannot be drawn.

The grinding of the Wyoming bentonite affected the respective gas composition in the vessel headspace quite differently. The concentrations

of non-reactive gas species increased (roughly: He $\sim$ 9 %, Ar $\sim$ 5 %, and Kr $\sim$ 6 %). Obviously these gases, already present in the bentonite, were released during the experiment (Fig. 2, panel C2). CO_2 decreased by almost -40 % which is in the range of the previous experiments (i.e., from -25 % down to -50 %). This indicates that the Wyoming bentonite was not hosting a large CO_2 excess as observed for the Italian bentonite and that its CO_2 sorption capacity was not completely depleted. Remarkably, up to $\sim$ 12 % of the initial O_2 was removed most likely as the result of oxidation of newly formed ("fresh") pyrite surfaces (Wersin et al., 1994). The slight decrease in the O_2 concentration in the vessel containing the Italian bentonite could also imply reaction with a minor amount of pyrite (Kumpulainen et al., 2021). Additional sorption of O_2 on these new surfaces cannot be confirmed by our measurements, as Ar (i.e., a gas species with similar physical properties as O_2) would be expected to show a similar behavior. However, the presence of sorption cannot be fully excluded, as it might be counteracted to some degree by the Ar emission from the bentonite material enhanced by grinding.

Furthermore, we cannot exclude that microbial respiration might be partly involved in the O_2 removal observed for both bentonites. However, considering the outcome of all other experiments (i.e., showing a CO_2 increase but no O_2 decrease), the effect of microbial activity (if any) seems to be negligible.

3.4. Experiment with ground and dried bentonite under controlled RH (D)

The results of this experiment carried out over a time span of about one month are shown in Fig. 2, panels D1–D3.

Because both aliquots were dried, the two bentonites started to swell immediately after being exposed to the moisture from the saturated salt solution resulting in total pressure increases as shown in Fig. 2, panel D3. In principle, the observed total pressure increases could be also the result of the production of gas species not quantified by our experimental setup (e.g., H_2). This is, however, very unlikely (or at least not significant), as the previous experiments show total pressure increases being almost two orders of magnitude smaller compared to the total pressure increases of Experiment D. Thus, a remarkable production of non-measured gases only for Experiment D does not seem reasonable.

According to the limited total pressure changes observed for both bentonites in Experiments A and B and the minor pressure changes for the Italian bentonite in Experiment C, the water content of the clay materials used in the previous experiments seems to be close to saturation. Thus, the water content determined in Experiment D is likely to be only slightly higher compared to the water content of the samples "as-received" (i.e., 15 wt % for the Italian bentonite and 10 wt % for the Wyoming bentonite; see Section 2.3.4).

Compared to Experiment C, O_2 consumption is not observed for the Italian bentonite and is strongly reduced for the Wyoming bentonite. It is to be expected that oxidation reactions were facilitated by the presence of moisture in Experiment C and that the subsequent drying process may already have oxidized and thus passivated (part of) the newly generated pyrite surfaces prior to run Experiment D.

Ar and Kr concentrations increase, indicating release of these gases from the bentonites (see also Experiment C). The absence of a He increase indicates that previously acquired He excess substantially degassed from the bentonites during the drying procedure. Indeed, He has a higher diffusion coefficient compared to Ar and Kr and, thus, is expected to be removed from the bentonite grains faster than the other gas species. As mentioned in the initial part of the Results and Discussion section, the chosen normalization of the measured partial pressures to the total pressure implies that total pressure changes produced by one (or more) gas species can affect other gas species in the opposite way. In Experiment D, the positive Ar concentrations changes resulted in an apparent negative shift of the He concentrations which should not be over-interpreted.

Despite the overall total pressure increases, the CO_2 concentrations clearly decrease for both bentonite samples (Fig. 2, panels D1 and D2). It

should be noted that the atmospheric partial pressure of CO_2 (less than 0.4 mbar) is more than two orders of magnitude smaller compared the total pressure changes resulting from the bentonite swelling in the sealed vessels (up to about 90 mbar). Therefore, CO_2 removal hardly contributes to the total pressure changes. In the case of the Italian bentonite, the CO_2 concentration decrease indicates that the CO_2 excess previously present in the bulk clay material (i.e., both mineral matrix and interlayer water; see Experiment C) was removed by heating (i.e., by degassing the bentonite). This observation indicates that CO_2 sorption, at least in the case of the Italian bentonite, is strongly dependent on the initial saturation state of the bentonite. Enhanced dissolution in the interlayer pore water, as shown by molecular dynamics modeling (Gadikota et al., 2017), may play a major role in the observed CO_2 removal. However, the rather constant CO_2 concentrations after about 14 days suggest that such removal is not linearly dependent on the amount of sorbed water. This could be related either to changes in solubility due to the increasing amount of water layers hosted by the mineral matrix or to other interactions with the mineral phase controlling the CO_2 removal.

4. Conclusions

Our laboratory experiments indicate that gas sorption on bulk bentonite (in this context understood as interaction with both the mineral matrix and the interlayer water) occurs at repository-like conditions and are in line with the findings of laboratory-scale and full-scale experiments for radioactive waste disposal (Giroud et al., 2018; Tomonaga et al., 2019). The experiments support the hypothesis that sorption can affect the overall gas budget in the backfill of the EBS. However, both bentonite types used in the experiments seemed to be already rather exhausted in terms of their gas sorption capacity (in their original state, i.e., "as-received"). This is most likely the result of a considerably long exposure (i.e., between bentonite production and our experiments) to a free gas phase allowing gases to occupy the available sorption sites. Such a free gas phase could possibly (but not necessarily) reflect atmospheric air or air-like conditions (e.g., in storage facilities or within the packaging used to ship the bentonites).

Slight concentration increases of He and possibly other noble gases suggest that these gas species are released from the investigated bentonites. Thus, these gases can be considered as part of the original gas signature already present in the clay materials prior to the execution of our experiments. However, the origin of noble gases in the bulk bentonites cannot be fully explained. Future work might specifically target the noble-gas signature of the chosen backfill materials (i.e., by means of precise isotope measurements using static mass spectrometry).

The Italian bentonite seems to entrap significant amounts of CO_2 which can be easily released from the clay material (especially when the respective clay material is finely ground). Such release needs to be considered when analyzing the gas dynamics and assessing the safety in close and low-permeability environments such as those foreseen for radioactive waste disposal. According to our experiments, the timing of production, storage, and processing (e.g., grinding or heating) of the bentonite can directly affect the amount of gases released in an EBS after its emplacement.

After grinding, the Wyoming bentonite showed consumption of considerable amounts of O_2 most likely related to pyrite oxidation. As grinding produced very small grains, it appears reasonable that pyrite crystals present in the bentonite were effectively broken, leading to the generation of new mineral surfaces prone to reaction with O_2. Our results support earlier findings (Birgersson and Goudarzi, 2018) indicating that untreated commercial pyrite-bearing bentonites are not effective O_2 scavengers, presumably because the originally reactive surfaces were already oxidized (Jerz and Rimstidt, 2004). For the Italian bentonite, only a minor O_2 consumption after grinding was observed. As this clay material contains almost no pyrite, this supports the hypothesis of pyrite oxidation being responsible for O_2 consumption in the vessel hosting Wyoming bentonite.

Drying of the bentonite samples potentially re-activated the CO_2 sorption capacity during a subsequent re-hydration phase. At this stage it is not possible to assess to which extent the same behavior can also be expected for other gas species. To address this issue, long-term experiments (i.e., beyond the time required for bentonite to completely equilibrate with the chosen RH – which was most likely not attained in our experiments lasting for up to two months) would be needed. Furthermore, the effect of temperature (e.g., by adding a heat source to the experimental vessels) on the behavior of O_2 and other gases could be looked into (Birgersson and Goudarzi, 2018; Giroud et al., 2018). Within the context of future experiments, monitoring the evolution of H_2 and other safety-relevant gas species would contribute to the overall understanding of the gas-clay interaction.

Declaration of competing interest

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

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