CO2 partial pressure in clayrocks: a general model

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ABSTRACT: An initial geochemical characterization of clayrocks is needed in order to evaluate their feasibility for use as caprocks or host formations for greenhouse gas storage or nuclear waste disposal facilities, respectively. In this context, a method was developed for the measurement of CO_2 partial pressure in clayrock pore water. The PCO_2 was systematically acquired using core samples obtained from underground laboratories located at 4 locations in Europe. The isotope ratios (C, O) of the gas and of the carbonate minerals were also obtained. The stable isotope ratios limit the possible origins of the CO_2 to a thermodynamic equilibrium between aqueous solution species and the diagenetic carbonate minerals (calcite, dolomite), and a Mg-aluminosilicate.

1 INTRODUCTION

The geochemistry of clayrocks is of current interest in the context of development of facilities for nuclear waste (radwaste) disposal and greenhouse gas storage. The low permeability and porosity of these rocks allow very good confinement of both radwastes and $CO_{2(g)}$. In both cases, long term safety is a critical parameter for their public acceptance and this safety assessment is generally developed with the help of transport/chemistry modelling. These models require a clear understanding of the initial geochemical conditions in the selected clayrocks. Indeed, such knowledge is the starting point of research on the long-term evolution of materials used in the context of nuclear disposal (nuclear glass, steel, concrete, engineered clay barrier, etc.) or for geological gas storage (metallic casing of old and new boreholes, cement filling, etc.). On the other hand, the low permeability of clayrocks makes them extremely difficult to recover undisturbed water samples by classical pumping tests in boreholes from the surface. Many problems have been identified and in particular, the degassing of the solutions is extremely difficult to avoid, eliminating the possibility of measuring *in situ* CO_2 partial pressure (PCO_2).

A direct method of measurement of PCO_2 on clayrock core samples was developed at BRGM over the last decade. Pioneering attempts were made in the Mont Terri underground rock laboratory (URL) (Switzerland) (Lassin et al. 2003) and the effort was continued in France in the Meuse/Haute Marne URL of Bure (Girard et al. 2005). The method makes possible the measurement of CO_2 partial pressure and isotopic (C, O) composition, as well as the concentrations of other gases (light hydrocarbons). More recently, data were also obtained from the Tournemire URL in the south of France and from the Mol URL in Belgium. The PCO_2 values obtained at the 4 sites show an interesting convergence. Furthermore, the isotopic composition of the gas phase allows us to strongly constrain the plausible hypotheses concerning its origin. That is why a synthesis of these data appears to be valuable as it reinforces the understanding of the thermodynamic equilibria governing the carbonate system in clayrocks as recently demonstrated for one site (Gaucher et al. 2009).

2 MATERIALS AND METHODS

2.1 *Degassing cell and analytical procedure*

A metallic degassing cell was specifically designed to accommodate relatively large core samples. The core samples were placed in the degassing cell immediately after coring in order to minimize atmospheric contamination. After several cycles of alternately flushing of the cell with an inert gas (N_2, Ar, or He) and drawing a vacuum to remove the atmospheric gas, the cells were sealed to allow degassing of the core till stabilization of the gas composition. This stabilization took between two months and one year. Gas pressure and tempera-

ture were monitored during this period, and bulk chemical analyses of gas accumulating in the degassing cell were periodically performed on a Varian Star 3400 CX gas chromatograph. The quantities of CO_2 and light gaseous hydrocarbons were systematically determined at a known pressure, allowing gas partial pressure to be calculated. Recently, a concomitant measurement of the relative humidity has been introduced in order to verify that the PCO_2 measurement is performed near the water saturation of the core samples.

2.2 *Stable isotope analysis*

At the end of the gas composition measurement phase, the CO_2 fraction was recovered from the degassing cell by expansion into a vacuum line and purification by standard cryogenic techniques. Active charcoal treatment was used in order to remove any traces of organics. The O and C isotope composition of purified CO_2 gas was determined by standard Isotope Ratio Mass Spectrometry on a dual-inlet multi-collection Finnigan mat Delta S mass spectrometer. (See details in Girard et al. 2005).

Calcite, dolomite and siderite were selectively dissolved by reaction of approximately 400 mg of bulk rock with 100% phosphoric acid. Calcite was extracted first at 25.2°C for 4 h, dolomite (and ankerite) were extracted next at 100°C for 1 h, and finally siderite was extracted at 150°C for 2 h (Rosenbaum & Sheppard 1986). The resulting CO_2 samples obtained in this way were analyzed for their isotopic compositions using our Finnigan-Mat Delta S mass spectrometer.

The results are reported in δ units relative to the SMOW for oxygen and PDB for carbon. Reproducibility was ± 0.2‰ for oxygen and carbon.

2.3 *Core Samples*

2.3.1 *Mont Terri URL (Jura, Switzerland)*

The URL is located in the Opalinus Clay (Aalenian – i.e. early Middle Jurassic). The overall amount of clay material varies from 28% to 93% depending on the rock lithology and contains mainly illite, illite/smectite, kaolinite, and chlorite. Other components include quartz, calcite, dolomite, siderite, pyrite, micas, feldspars, celestite and organic C (1%). The salinity of the pore water is roughly one third that of seawater (Pearson et al. 2003). Four boreholes drilled in the laboratory have produced core samples for PCO_2 measurements. For the first two boreholes (A6, BGS2), the drilling fluid was air. The BPC1 and the BPCC boreholes were drilled with $N_{2(g)}$.

2.3.2 *Bure URL (Meuse/Haute Marne, France)*

The URL is located at roughly 500 m depth in the Callovian-Oxfordian formation (Middle / Late Jurassic). The mineralogy is very similar to that of the Opalinus Clay except for the absence of kaolinite in the upper part of the formation (Gaucher et al. 2004) and a more dilute pore water salinity (10 to 100 mmol of Cl). The samples come from 4 deep boreholes drilled from the surface (EST205, EST211/212, EST312, EST322) and from 4 boreholes (PAC) drilled from within the URL under $N_{2(g)}$ atmosphere.

2.3.3 *Tournemire URL (Aveyron, France)*

The URL is located in a century-old disaffected railroad tunnel and is located in the upper Toarcian marls in southern France. A deep borehole (PH4-250 m) allowed collection of 4 samples from the upper Toarcian and 2 others from the lower Toarcian. The mineralogical composition of this formation is again similar to the two first URLs (Boisson et al. 2001), the lower Toarcian being richer in carbonates and having a roughly 10 times higher organic content of 10%. The Toarcian marls are very indurate with an average water content of less than 4%, i.e. about two times lower than those of the Bure and Mont Terri clayrocks. The pore water salinity ranges from 40 to 200 mmol/l for the whole Toarcian sequence (Trémosa et al. 2010).

2.3.4 *Mol URL (Antwerp, Belgium)*

The URL was constructed in the Boom Clay formation (Rupelian – i.e. lower Oligocene). Again, the mineralogy is quite similar to that of the others. The formation has a significantly higher porosity and pyrite and organic matter contents reaching 5%. The pore water is dilute with a Cl concentration around 1 mmol/l (de Craen et al. 2004).

3 RESULTS

3.1 *Partial pressure of CO_2*

Table 1. Range of partial pressures of CO_2 $\{\log_{10}(PCO_2[bar])\}$ obtained at Mont Terri, Bure, Tournemire & Mol URLs.

URL	Age	Number of sample	Min	Max
Mont Terri	Aalenian	7	-3.07	-2.12
Bure	Callovo-Oxf.	33	-3.01	-2.00
Tournemire	Upper Toarc.	3	-2.44	-1.86
Tournemire	Low Toarc.	1		-2.19
Mol	Rupelian	2	-2.33	-2.15

Figure 1 illustrates the degassing of a core sample coming from a deep borehole in the Bure URL area. After 60 days, the partial pressure of CO_2 is stabilized at a constant value of

$\log_{10}(PCO_2[bar]) = -2.17$. Minimum and maximum values obtained from the different sites are compiled in Table 1. Considering the different sampling campaigns, the lowest values ($\log_{10}(PCO_2[bar]) < -2.5$) are linked to partially dried samples. The maximum values are found for the Upper Toarcian of Tournemire and attributed to a partial and accidental oxidation of CH_4 during the degassing phase. CH_4 is present in this formation at high values around $\log_{10}(PCH_4[bar]) = -1.5$ (source rock of hydrocarbons). By considering these limitations, an equilibrium range of $\log_{10}PCO_2$ between -2.5 to -1.9 may be considered for these clayrocks.

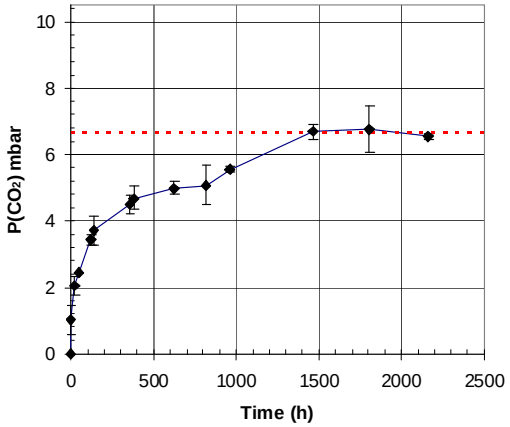

Figure 1 Example of CO_2 degassing in the degassing cell. Sample from the Meuse/Haute-Marne URL (EST312 10273). $\log_{10}(PCO_2[bar]) = -2.17$ at 90 days and for a relative humidity of 95%.

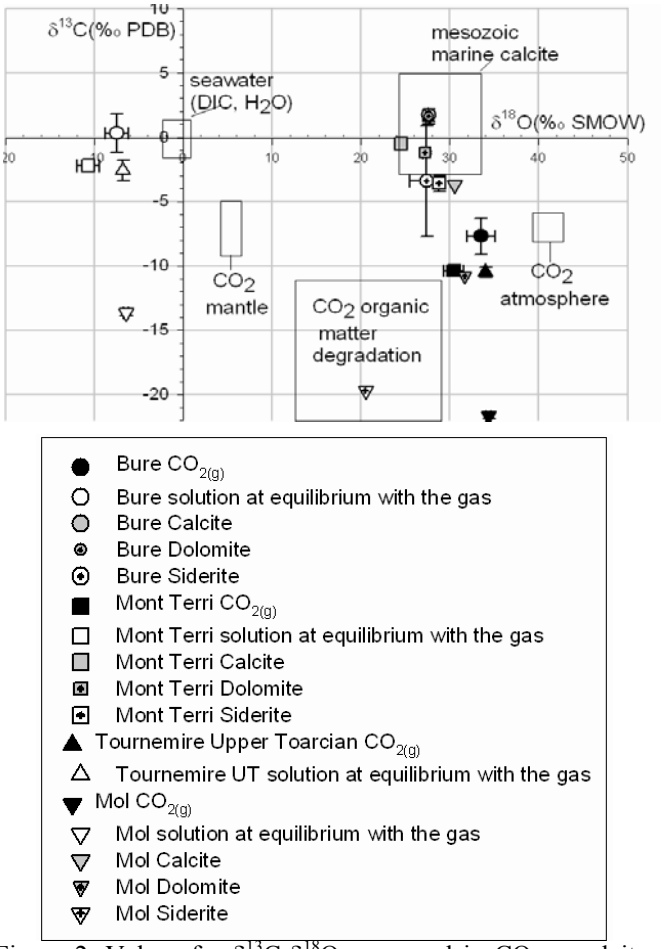

Figure 2. Values for $\delta^{13}C$-$\delta^{18}O$ measured in $CO_{2(g)}$, calcite, dolomite and siderite and calculated for the corresponding pore water at equilibrium with the $CO_{2(g)}$. Compositional fields of main sources of CO_2 are also shown.

3.2 *C, O isotopes in gas and carbonate minerals*

Average $\delta^{13}C$-$\delta^{18}O$ values obtained for $CO_{2(g)}$ for the 4 sites are plotted in Figure 2, along with compositional fields for the main natural sources of CO_2 including atmosphere, earth's mantle, and biotic-abiotic decay of organic matter. Published isotopic composition for typical primary marine carbonates of Jurassic age (Veizer et al. 1999) and measured isotopic composition of carbonate minerals (calcite, dolomite, siderite) at the 4 sites are also plotted.

Figure 2 shows that the $\delta^{13}C$-$\delta^{18}O$ values for $CO_{2(g)}$ obtained for the 4 sites are inconsistent with an atmospheric, magmatic, or organic matter origin. The high CO_2 partial pressures obtained exclude a significant atmospheric, contamination which in turn can not be considered as a mixture end-member. Measured $\delta^{13}C$-$\delta^{18}O$ values for $CO_{2(g)}$ are best explained by equilibrium with the pore water and dissolved bicarbonate species. The values for $\delta^{13}C$-$\delta^{18}O$ for pore waters at equilibrium with the degassed CO_2 were calculated at 25°C (storage temperature) using appropriate fractionation factors proposed by Mook et al. (1974) for $HCO_{3(l)}$-$CO_{2(g)}$ and by Brenninkmeijer et al. (1983) for $H_2O_{(l)}$-$CO_{2(g)}$.

The calculated $\delta^{18}O_{water}$ values are markedly negative, between -6.5‰ for Mol and -11‰ for Mont Terri indicating a meteoric origin of pore waters for the 4 clayrocks in agreements with previous studies.

The calculated $\delta^{13}C_{diss\text{-}bicarb}$ values are close to that of seawater for the different sites (between 1‰ to -4‰) except for Mol where the values are very low (-13,8‰). The comparison with the data obtained for the carbonate minerals is very interesting and the Mol study can be considered a demonstrative case study. Indeed, at Mol the $\delta^{13}C_{diss\text{-}bicarb}$ is between those of dolomite and siderite (closer to that of dolomite (-11‰)) and quite different from the value for calcite (-3.7‰). The situation is the same at Mont Terri but with a lower dispersion of the $\delta^{13}C$ values measured for carbonate minerals. For Bure, the calcite and dolomite have very similar $\delta^{13}C$ signatures (1.7‰ ± 0.5 and 1.6‰ ± 0.6) but the $\delta^{13}C_{diss\text{-}bicarb}$ values are a little lower (0.3‰ ± 1.5) than those values and are also in between dolomite and siderite. It should be noticed that in the rare cases in which the $\delta^{13}C$ of the diagenetic calcites have been measured, their values are closer to those of the diagenetic dolomites and lower than those of the primary calcites.

4 DISCUSSION AND CONCLUSION

The results of the recent study of pore water chemistry by modelling at the Bure site (Gaucher et al. 2009) suggest that the carbonate system is regulated by the presence of calcite, dolomite and chlorite type Mg-clay minerals. The participation of Mg-clay minerals in carbonate system regulation for sedimentary rocks was previously proposed by Coudrain-Ribstein and Gouze (1993). The PCO_2 modelled by Gaucher et al., (2009) for the Bure pore water ranging from -2.6 to -1.8 (log_{10}, bar) depending on the clay minerals considered (and the corresponding thermodynamic data). This range can be compared to the value of -1.9 determined on a free water produced from a dedicated borehole at Bure URL (Vinsot et al. 2008). In the present synthesis, we have observed that, for 4 clayrocks of different ages and different chemical environments, the measured partial pressures are in the same range and tend to converge towards a set of values between -2.5 and -1.9, thus indicating that the PCO_2 is regulated by a closely related mineralogical sequence.

The results of the stable isotope study demonstrate that the partial pressure of CO_2 is internally regulated by equilibrium between the dissolved bicarbonate species and the carbonate minerals. Furthermore, in this study it has been possible to determine precisely the nature of these minerals. Indeed, the $\delta^{13}C_{diss\text{-}bicarb}$ of the different samples is more related to an equilibrium with the diagenetic carbonates (dolomite, probably secondary calcite and in a lesser extent siderite) rather than with the primary calcite.

Thus it is possible to consider that in clayrock containing the same paragenesis as for the 4 sites studied and at a temperature around 20°C, the partial pressure of CO_2 should be around -2.00 (log_{10}, bar). The chemical equilibria explaining this value are governed by an assemblage of calcite, dolomite and Mg-clay minerals. Lastly, the $\delta^{13}C$ values indicate that amongst the identified carbonates, the secondary phases are the most reactive.

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