

**Stable isotope composition of CO<sub>2</sub> outgassed from cores of argillites :  
A simple method to constrain δ<sup>18</sup>O of porewater and δ<sup>13</sup>C of dissolved  
carbon in mudrocks**

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**Abstract**

Stable isotope characterization of porewater, and dissolved species, in mudrocks and argillaceous rocks is notoriously difficult. Techniques based on physical or chemical extraction of porewater may generate significant analytical artefacts. We report a novel, simple approach to determine the  $\delta^{18}\text{O}$  of porewater and  $\delta^{13}\text{C}$  of dissolved carbon in argillites. The method uses core samples placed in specifically-designed outgassing cells, sealed shortly after drilling and stored in well-controlled conditions. After 1-2 months,  $\text{CO}_2$  naturally outgassed by argillite porewater is collected, purified and analyzed for C and O isotopes. Porewater  $\delta^{18}\text{O}$  and dissolved carbon  $\delta^{13}\text{C}$  are calculated from  $\text{CO}_2$  isotope data using appropriate fractionation factors. This methodology was successfully applied to the Callovo-Oxfordian argillites, Bure, eastern Paris Basin, France, and the Opalinus Clay formation, Mont Terri, Switzerland. The main advantage of the approach is that it does not induce any major physical or chemical disturbance to the clay-water system investigated.

**Keywords :** stable isotopes, mudrocks,  $\text{CO}_2$ , porewater, dissolved carbon, Callovo-Oxfordian argillites, Opalinus Clay Formation

## 1. Introduction

Indurated clay-rich rocks, such as mudrocks, argillites and shales, are characterized by low permeabilities ( $10^{-14}$  to  $10^{-10}$   $\text{ms}^{-1}$ ) and low porosities (<15 vol. %). They constitute impermeable layers playing an important role in the hydrology and hydrogeochemistry of sedimentary basins, either as a source of water (water expelled due to compaction) or as a barrier to water flow (reservoir cap-rocks, aquitards...).

In the past decade, interest in the understanding of water-rock interactions in mudrocks and argillaceous materials has grown tremendously. This was driven, to a large part, by the confining properties of these rocks which makes them attractive for safe long-term underground disposal of radioactive wastes. In Europe, several research programs are in progress along this line, among which the international Mont Terri Project in Switzerland (Thury and Bossart, 1999; [www.mont-terri.ch](http://www.mont-terri.ch)) and the Andra HAVL-Argile Project in France (Lebon and Hoorelbeke, 2002; [www.andra.fr](http://www.andra.fr)). One major challenge of these research programs is to develop and validate reliable methodologies to improve knowledge of the nature of porewater present in argillites (Bath et al., 2001). Among other things, emphasis is placed on acquiring accurate stable isotope data (in addition to chemical data) for argillite porewater, in order to constrain water origin and extent of past/present water-rock interactions. Techniques based on physical or chemical extraction of porewater prior to isotopic analysis, including centrifugation, squeezing, leaching, distillation-lyophilisation, have been developed with variable success (among others, Walker et al., 1994; Araguas-Araguas et al., 1995; Moreau-Le Golvan et al, 1997). In a critical review of such methods, Sacchi et al. (2000) emphasized that porewater extraction from argillaceous rocks for chemical/isotopic analysis was not a trivial matter. Sacchi et al. (2000) further concluded that observed discrepancies between techniques were related to analytical artefacts in addition to

difficulties linked to the existence of different reservoirs of porewater (i.e., free water versus bound water).

In order to overcome this problem and derive accurate stable isotope data for porewater in argillites, methodologies not relying on porewater extraction must be used. Newly-developed techniques of direct equilibration (Hsieh et al., 1998; Koehler et al., 2000) and radial diffusion (Van der Kamp et al., 1996; Rübel et al., 2002) have been shown to hold great promises. In the direct equilibration technique, a wet (saturated) sample of argillite is placed in contact with CO<sub>2</sub> ( $\delta^{18}\text{O}$  determination) or H<sub>2</sub> ( $\delta\text{D}$  determination) gas, while in the radial diffusion technique, the argillite sample is placed in contact with a reservoir of distilled water of known isotopic composition. In the two approaches, the system is allowed to equilibrate isotopically, by isotope exchange through gas diffusion (direct equilibration) or water diffusion (radial diffusion). The isotopic composition of argillite porewater is derived from measurements performed on the added gas or water phase following thermodynamic equilibration.

In the present paper, we report a novel and simple alternative approach based on the isotopic analysis of CO<sub>2</sub> naturally released from porewater in cores of argillite under well-controlled conditions. The method was developed with the primary aim of avoiding any physical/chemical disturbance to the argillite sample that might affect porewater isotope composition. It provides indirect determination of  $\delta^{18}\text{O}$  of porewater and  $\delta^{13}\text{C}$  of dissolved carbon. The methodology is described below through its application to two argillite formations under consideration for underground disposal of radioactive waste : the Callovo-Oxfordian argillite of Bure, eastern Paris Basin, France and the Opalinus Clay Formation of Mont Terri, Switzerland. The results illustrate the validity and usefulness of the approach as an alternative to existing techniques.

## 2. Methodology

### 2.1. Outgassing cell and sample conditioning procedure

In order to recover gases naturally released by cores of argillites for chemical and isotopic analysis, outgassing cells able to accommodate relatively large core samples were specifically designed and manufactured (Fig. 1; Lassin et al., 2000). The outgassing cell is composed of a stainless-steel cylindrical container, 52 cm long and 11 cm diameter, which can be open in two halves by the middle in order to insert a core. Assembly and disassembly of the two flanged halves is done by fastening or releasing three mechanical locks positioned on the external side of the container. Air-tight sealing is achieved by use of an acrylic anaerobic gasketing/flange sealant (Loctite 638). The container is equipped with 1/4 inch tubing/fitting and a stainless-steel rotary valve (Sagana type) at each end, and with a pre-programmed pressure-temperature recording gauge (Keller Mano-record) at the top (Fig. 1). Precision of pressure and temperature measurements is  $\pm 3$  mbar and  $\pm 1^\circ\text{C}$ , respectively. The total internal volume of the cell approximates  $4000\text{ cm}^3$ , and permits to accommodate a maximum sample size of 45 cm length and 9 cm width. Maximum allowable pressure in the cell is 2 bar.

The core sample is placed in the outgassing cell at the drilling site as rapidly as possible after coring in order to minimize contact with atmosphere. A specific procedure was developed, that is briefly described below (further details can be found in Gaucher et al., 2001) :

1. The outer rim of the core is dry-sawed (using a diamond saw bench) to remove parts potentially contaminated by drilling fluid and reduce sample size to a 40-45 cm long segment of about  $7\times 7$  cm square section (Fig. 1).
2. The core segment is placed in the outgassing cell, which internal surface has been previously cleaned of all traces of dusty-oily deposits. In order to avoid clogging of the 1/4 inch tubing and valves, due to small particles breaking off the core during transport, cleansed silica wool is placed inside the cell at both ends prior to loading the core. A film

of acrylic sealant is deposited on the flange surfaces and the two cell-halves are assembled together and locked.

3. The assembled cell is flushed with dry N<sub>2</sub> (U grade, 99.995 % purity with CO<sub>2</sub> ≤ 50 vpm; H<sub>2</sub>O ≤ 5 vpm; O<sub>2</sub> ≤ 5 vpm) for 15-20 minutes at a pressure slightly greater than atmospheric pressure. This is done to remove air from the cell without applying intensive pumping which might remove significant water from the core. Following N<sub>2</sub> flushing, the cell is isolated and the sealant is allowed to solidify for about 30 minutes (sealant polymerization requires anaerobic conditions).
4. Once sealing is effective, the cell is pumped down to <math>10^{-2}</math> mbar in a few minutes. Dry N<sub>2</sub> is introduced in the cell again and pressure is adjusted to a final storage pressure ranging from 70 to 1000 mbar (see below). As an alternative to N<sub>2</sub>, helium gas (5.5 grade, 99.9995 % purity, CO+CO<sub>2</sub> ≤ 0.1 vpm; H<sub>2</sub>O ≤ 2 vpm; O<sub>2</sub> ≤ 0.5 vpm) can be used for storage conditioning.

Total duration of sample processing and conditioning typically takes one to a few hours (up to 4 hours) after core recovery. Actual contact with atmosphere, however, is limited to 2 hours or less. Back to the laboratory, outgassing cells are stored in an air-conditioned room at 20°C. If leakage is detected on a sealed cell after conditioning, the complete procedure is reiterated either in the field or in the laboratory. This situation occurred once in the set of experiments reported here (sample EST05444, see below).

## 2.2. Chemical analysis of released gas

Bulk chemical analysis of gas accumulating in the outgassing cell was performed periodically. Analyses were done on a Varian Star 3400 CX gas chromatograph (GC) in BRGM laboratories, equipped with a flame ionisation detector (FID) and using a Porapak injection column. The instrument and injection system were configured for analysis of small quantities of gas, with a detection limit of ca. 0.5 mbar of CO<sub>2</sub> at a minimum injection

pressure of 75 mbar. The volume of the injection loop and connection tubing being 1 ml, the volume of gas used for each GC analysis represents only a very small fraction (<0.06 %) of the total volume of gas present in the cell.

Although periodicity may vary from sample to sample, GC analysis was performed every two weeks in most cases, over a monitoring period ranging from 2 to 7 months. Quantities of CO<sub>2</sub> and light gaseous hydrocarbons (C1 to C6) were systematically determined. Other gases present include H<sub>2</sub>O vapor (released by core), N<sub>2</sub> and/or He (conditioning gas).

### 2.3. Collection and purification of released CO<sub>2</sub>

CO<sub>2</sub> gas is recovered from the outgassing cell by expansion in a vacuum line (Fig. 2) and purified by standard cryogenic techniques as follows. The outgassing cell is connected to the vacuum line via Swagelock fittings and a Nupro valve, and the line is evacuated to 10<sup>-4</sup> mbar. Gas accumulated in the cell is expanded in the vacuum line, then condensable compounds are trapped statically in a cold trap at liquid N<sub>2</sub> temperature (-196°C). Non condensable gases are pumped away. The cold trap is warmed to about -78°C by use of dry ice slush in order to release CO<sub>2</sub> while H<sub>2</sub>O remains frozen. Liberated CO<sub>2</sub> is transferred to a glass sample tube and further purified on active charcoals at room temperature (30-120 minutes at 20°C) in order to get rid of any traces of organics. The charcoal treatment was verified not to affect δ<sup>13</sup>C and δ<sup>18</sup>O of CO<sub>2</sub>, to within ±0.2 ‰, on several CO<sub>2</sub> gas standards (Girard et al. 2002a). Two different extraction/cryogenic procedures using different configurations of the vacuum line were tested to collect and purify CO<sub>2</sub> (Fig. 2). In the first procedure, referred to as "total recovery procedure", the total amount of CO<sub>2</sub> accumulated in the cell is collected through multiple, successive expansion and cryogenic cycles (up to 4 cycles). In the second procedure, referred to as "representative aliquot procedure", the gas accumulated in the cell is expanded and collected in a 0.5 litre expansion flask (one-shot expansion for 15 minutes), thereby providing a representative gas sample from which CO<sub>2</sub> is cryogenically separated. A detailed

step-by-step description of each of the two analytical procedures can be found in Girard et al. (2002a). In theory, the "total recovery procedure" allows a complete quantitative collection of CO<sub>2</sub> gas accumulated in the outgassing cell, ensuring no isotopic fractionation during the extraction process. In practise, however, it reveals difficult to warrant that 100% of CO<sub>2</sub> gas present in the cell has been extracted and collected because of the residual, above-background pressure remaining in the cell even after multiple extractions, which may be partly contributed by CO<sub>2</sub> (in addition to mainly residual degassing of H<sub>2</sub>O vapor). The "total recovery procedure" is time-consuming (several hours) and laborious, and results in a quasi total purge of the gas present in the outgassing cell. In contrast, the "representative aliquot procedure" is faster, more straightforward and more gentle to the gas-water-rock system since only a fraction (40-50%) of the gas present in the cell is removed. The fact, however, that only a split fraction of the gas present in the cell is extracted may introduce errors related to isotopic fractionation during gas expansion. The absence of such potential isotopic artefact was checked for in the course of this study, by performing multiple consecutive extractions of CO<sub>2</sub> aliquots from a single cell on the same day.

It was verified on separate blank cells that no measurable CO<sub>2</sub> is contributed by the experimental system and procedure (stainless steel, Loctite sealant, N<sub>2</sub>-He gas...).

#### *2.4. Stable isotope analysis of purified CO<sub>2</sub>*

The oxygen and carbon isotope composition of purified CO<sub>2</sub> gas was determined by standard Isotope Ratio Mass Spectrometry in the Stable isotope laboratory of BRGM, on a dual-inlet multicollection Finnigan Mat Delta S mass spectrometer. In the following,  $\delta^{13}\text{C}$  values are reported in ‰ relative to PDB standard and  $\delta^{18}\text{O}$  values in ‰ relative to SMOW standard. Conversion from PDB to SMOW scale was done according to the relation of Coplen et al. (1983). Analytical uncertainty on mass spectrometry measurements, based on repeated analyses of standards, is  $\pm 0.1$  ‰ for both carbon and oxygen isotopes. However, total

analytical uncertainty, taking into account extraction/purification treatment, is larger and can be estimated to be around  $\pm 0.5$ -1.0 % based on data acquired in this study (i.e., external reproducibility for repeated experiments, see below).

### 3. Samples

Samples investigated in this study come from two argillaceous formations presently under evaluation as prospects for underground storage of radioactive waste. Background information about the argillites is given below and relevant information about the samples is provided in table 1.

The first formation is the Callovo-Oxfordian argillite (COX) occurring in the eastern part of the Paris basin, France. This argillite formation constitutes the host strata for the experimental repository site of Andra (French National Agency for Nuclear Waste Management) at Bure, i.e., the so-called underground laboratory of Meuse/Haute Marne. The COX has been extensively studied, and an exhaustive compilation of geological, mineralogical and geochemical data can be found in the Andra technical report "Référentiel Géologique de Meuse/Haute-Marne" (Andra, 2001) and in Gaucher et al. (2003). The COX is a ca. 130 m thick marine formation, essentially composed of illite/smectite mixed-layer and illite clays (20-50%), quartz (22-36%) and calcite (23-40%), with minor admixtures of kaolinite, chlorite, dolomite, feldspar, pyrite, and traces of organic matter (<1%). Water content typically ranges from 5 to 8%. In the study area, the COX presently lies at depth varying between 350 and 550 m, and has not been submitted to temperatures greater than ca. 50°C. Four COX samples (EST05444, EST05525, EST05578, EST05640) were selected for this study. They were collected in September 2000 from the 423-477 m depth interval in well EST205. This well was specifically drilled using an oil-based mud in order to avoid contamination of core porewater by drilling fluids (Gaucher et al., 2003).

The second argillaceous formation used in this study is the Opalinus Clay Formation (OPA), occurring at Mont Terri, in the Swiss Jura, and constituting the host formation of the Mont Terri Rock Laboratory. Background information on the geology and geochemistry of this 160 m thick, marine shale of Aalenian age can be found in Thury and Bossart (1999), Degueldre et al. (2003) and Pearson et al. (2003). OPA mineralogy is similar to COX mineralogy, with a higher proportion of clays (45-75%), including illite, kaolinite, illite/smectite mixed-layers and chlorite, mixed with quartz (10-30%) and calcite (8-30%). Minor minerals include dolomite, siderite, ankerite, feldspars and pyrite, as well as traces of organics. Water content ranges from 3 to 8% (Rübel et al., 2002). Two OPA samples (MT7-1, MT7-2) coming from borehole BPC-1 (Pearson et al., 2003) were investigated in this study. This borehole was drilled upward in the New Gallery of the Mont Terri Rock Laboratory in March 2002 and under N<sub>2</sub> flushing to prevent porewater contamination.

The COX core samples, conditioned and stored in outgassing cells, were typically 40 x 7 x 7 cm in size (size slightly variable from sample to sample). This represents a volume of argillite of ca. 2000 cm<sup>3</sup>, containing about 100-200 ml porewater, and leaving a remaining volume of ca. 2000 cm<sup>3</sup> in the cell occupied by gas. The four COX samples were conditioned using N<sub>2</sub> gas. The two OPA core samples were smaller in size, typically 40 x 3 x 3 cm (i.e., 360 cm<sup>3</sup>), therefore, occupying a much smaller volume in the cell. One of them (MT7-2) was conditioned with He gas in replacement of N<sub>2</sub>.

#### **4. Analytical results**

##### *4.1. Chemical composition of released gases*

A detailed monitoring of the evolution of gas composition in the outgassing cells with time was performed as part of a larger study conducted by Lassin et al. (2000) and Gaucher et al. (2001, 2002) and focussed on chemistry of released gases. The later study used an extended set of COX and OPA cores totalizing 11 samples (including the 6 samples considered in this

study). Released gas composition was monitored for up to 13 months and outgassing cells were submitted to a number of purges and changes in storing conditions (temperature, nature and pressure of injected gas). The experimental strategy was primarily designed to determine partial pressure of CO<sub>2</sub> reflecting equilibrium with core porewater (following Henry's law), in order to derive porewater dissolved CO<sub>2</sub> in laboratory conditions and constrain the chemical composition of interstitial water in down-hole conditions. It is beyond the scope of this paper to discuss the details of chemical data gathered by Lassin et al. (2000) and Gaucher et al. (2001, 2002), and the reader is referred to the aforementioned technical reports for specifics. Only main conclusions and information pertaining to the six samples investigated for stable isotopes are reported below.

In all core outgassing experiments, similar observations were made with respect to the composition and evolution of released gases through time. A typical example is shown in figure 3, illustrating the following points. (Outgassed N<sub>2</sub> may also be significant but could not be analyzed in the study.)

1. Gas released by COX and OPA cores is essentially composed of CO<sub>2</sub> associated to trace amounts of light alkanes (methane, ethane, propane and butane).
2. Partial pressure of CO<sub>2</sub> in the cell increases progressively over one to two months after sealing and reaches a plateau value which remains steady for up to several months.
3. The same observations (as in points 1 and 2) are made when a cell is purposely purged and re-conditioned in the laboratory, i.e., submitted to a complete purge of accumulated gas by pumping and flushing with N<sub>2</sub> or He (no contact with atmosphere) and isolated anew. All other conditions being equal, the  $p\text{CO}_2$  returns to the same plateau value (within error) within a few to several weeks, even after up to four consecutive purges.

4. Plateau values of  $p\text{CO}_2$  recorded for the eleven COX and OPA samples investigated range from 1 to 10 mbar, i.e., one to two orders of magnitude greater than atmospheric  $p\text{CO}_2$  ( $\approx 0.35$  mbar).

In addition, in the course of the study by Lassin et al. (2000), it was verified on blank cells, i.e., cells containing no argillite but submitted to the same conditioning and outgassing procedure (same temperature and duration), that no measurable  $\text{CO}_2$  was contributed either from stainless steel parts, Loctite sealant, or  $\text{N}_2$ -He conditioning gas. Separate outgassing experiments conducted by Gaucher et al. (2001) also provided evidence that residues, if any, of oil-based drilling mud used for coring COX samples (well EST205) did not contribute significant  $\text{CO}_2$ .

All of the observations above, combined with stable isotope data reported below, indicate that  $\text{CO}_2$  released by the argillite cores is primarily contributed by porewater degassing under equilibrium conditions, with no significant contribution of atmospheric or bacteriogenic  $\text{CO}_2$  (Gaucher et al., 2001, 2002; Girard et al., 2002a, 2002b, 2003).

Regarding the samples selected for the isotope study, measured  $p\text{CO}_2$  ranges from about 6 to 10 mbar for COX and between 1 and 2 mbar for OPA (Table 1). These values are in the range of natural  $p\text{CO}_2$  ( $10^{-3}$  to  $10^{-1}$  bar) documented for confined aquifers in sedimentary sequences (Coudrain-Ribstein et al., 1998).

#### *4.2. Stable isotope composition of outgassed $\text{CO}_2$*

Three sets of  $\text{CO}_2$  extractions were carried out several months apart (May 2000, August 2000, January 2001) on the four COX samples, and one set (June 2002) on the two OPA samples.

Results are shown in figure 4 and tabulated in the appendix.

*COX samples* - The first set of  $\text{CO}_2$  extractions (May 2000) was done using the "total recovery procedure". No isotope data are reported for sample EST05525 because part of the gas was lost (mistakenly pumped away) during the extraction procedure, inducing isotopic

fractionation. Samples EST05444, EST05578 and EST05640 yielded consistent isotopic compositions of outgassed CO<sub>2</sub>, with  $\delta^{13}\text{C}_{\text{CO}_2}$  values ranging from -8.8 to -6.9 ‰ and averaging  $-7.6 \pm 1.0$  ‰, and  $\delta^{18}\text{O}_{\text{CO}_2}$  values between 34.6 and 34.9 ‰, averaging  $34.8 \pm 0.2$  ‰. The second (August 2000) and third (January 2001) sets of CO<sub>2</sub> extractions were performed using the "representative aliquot procedure", respectively three months and eight months after the first set of extractions. During the second set of extractions, samples EST05640 and EST05444 were submitted to two and three consecutive CO<sub>2</sub> extractions in order to assess reproducibility. Overall, measured  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  values are consistent for both extraction sets and all samples (Appendix), varying over 2.5 ‰ for  $\delta^{13}\text{C}_{\text{CO}_2}$  (-7.9 to -5.4 ‰) and less than 2 ‰ for  $\delta^{18}\text{O}_{\text{CO}_2}$  (34.6 to 36.3 ‰). Consecutive CO<sub>2</sub> extractions performed on a same sample on the same day (EST05444, EST05640) show no significant evolution of CO<sub>2</sub> isotopic composition. The good reproducibility of data obtained on consecutive extractions in a single day and five months apart on a same sample indicate that the "representative aliquot procedure" does not introduce any significant isotopic fractionation associated with gas expansion out of the cell into the vacuum line, hence validating the analytical procedure. The second and third extraction sets yield average isotopic compositions of  $\delta^{13}\text{C}_{\text{CO}_2} = -6.4 \pm 0.8$  ‰ and  $\delta^{18}\text{O}_{\text{CO}_2} = 35.5 \pm 0.5$  ‰ (n=11). These averages are similar, within error, to the averages calculated for the "total recovery procedure" (see above), further demonstrating the validity of the method. On a sample-per-sample basis, however, we note that the "total recovery procedure" tends to yield  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  values systematically lower (by ca. 1-2 ‰) than those obtained with the "representative aliquot procedure" (Appendix, Fig. 4). We suspect this may be related to CO<sub>2</sub> recovery being not-quite as complete as suitable in the former procedure. Indeed, because the "total recovery procedure" involves multiple cycles of expansion, freezing and thawing, opportunities for loss of small quantities of gas are greater

than in the "representative aliquot procedure". At present, isotopic compositions yielded by the later extraction procedure are therefore considered more accurate.

Average isotopic compositions of CO<sub>2</sub> outgassed from COX samples are compiled in table 2 on a sample basis.  $\delta^{18}\text{O}_{\text{CO}_2}$  values are identical within error, while  $\delta^{13}\text{C}_{\text{CO}_2}$  values show very minor variation (i.e., a 1.6 ‰ range).

*OPA samples* - The one set of CO<sub>2</sub> extractions performed on OPA samples was done using the "representative aliquot procedure". Because the two samples revealed contaminated by organic volatiles to a greater level than COX samples, extracted CO<sub>2</sub> was submitted to two consecutive longer (2 x 1 hour) charcoal treatments (see section 2). The two samples yielded identical  $\delta^{13}\text{C}_{\text{CO}_2}$  values of ca. -10 ‰, and slightly different  $\delta^{18}\text{O}_{\text{CO}_2}$  values around +30 ‰ (Table 2, Fig. 4).

## 5. Discussion

### 5.1. Lack of isotopic variation

The good overall consistency of  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  values determined for the different samples of a same argillite formation and at different times for a same sample reflects the great homogeneity, in space and time, of CO<sub>2</sub> outgassed by cores of the two argillites studied. This is indicative of a unique and a relatively large reservoir source of CO<sub>2</sub>, in agreement with its origin as core porewater degassing.

The small sample-to-sample variation, over a couple ‰ units, recorded in the data for each of the two formations (Table 2) is hardly significant considering our current estimate of total analytical error ( $\pm 0.5$ -1.0 ‰), except for  $\delta^{18}\text{O}_{\text{CO}_2}$  values of OPA cores which range over 2.5 ‰. At this time, we consider that most of this small variation is related to causes other than natural, including small differences in the conditions of sample processing/conditioning or in the history of events that affected the outgassing cell prior to the isotope study. For instance, the fact that sample EST05444 exhibits the lowest  $\delta^{13}\text{C}_{\text{CO}_2}$  of all COX samples may have to

do with the fact that it was affected by a leak (5 days after field conditioning) and was submitted to the greatest number of GC analyses (n=9; Gaucher et al., 2001). The extent to which such events might have affected core porewater is, however, unknown. Also, it is noticeable that the 3<sup>rd</sup> set of COX CO<sub>2</sub> extractions yields much more consistent  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  values than the 2<sup>nd</sup> set of extractions (see Appendix and Fig. 4), further suggesting that small variation may be largely related to quality of CO<sub>2</sub> extractions (resulting in a greater analytical uncertainty). Lastly, the observed difference in  $\delta^{18}\text{O}_{\text{CO}_2}$  for the two OPA samples may, or may not, have to do with MT7-2 being conditioned with He (instead of N<sub>2</sub>) at a higher pressure (980 mbar).

Regardless of whether these small sample-to-sample variations in the isotopic data are natural or artificial, they have no bearing on the interpretations and conclusions drawn below in terms of CO<sub>2</sub> origin. In contrast, the relatively large difference in oxygen and, to lesser extent, carbon isotope compositions exhibited by CO<sub>2</sub> outgassed from COX compared to OPA samples ought to reflect natural variation in relation with different geological settings and paleohydrological histories. This is further discussed below.

### *5.2. Origin of CO<sub>2</sub> and implication for isotopic characterization of porewater*

Average measured  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  for COX and OPA samples are plotted in  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  coordinates in figure 5, along with compositional fields for main natural sources of CO<sub>2</sub>, including atmospheric, magmatic, biotic-abiotic decay of organic matter and bacterial fermentation processes (Hoefs, 1980; Irwin et al., 1977). Published isotopic compositions for typical primary marine carbonates of Jurassic age (Veizer et al., 1999) and measured isotopic compositions of carbonate minerals (calcite, dolomite) occurring in the argillites studied (Gaucher et al., 2002; Girard et al., 2002a) are also plotted.

It can be seen in figure 5 that  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  measured for COX and OPA are not compatible with an atmospheric, magmatic or organic-matter-derived (bacterial or abiotic)

origin. Based on the location of data points between atmospheric and magmatic CO<sub>2</sub> endmembers, one might argue COX outgassed CO<sub>2</sub> represents a mixture of these two sources with a net predominance of atmosphere. This would imply major leakage of the four outgassing cells, in the same proportion since data points are tightly grouped together (Fig. 5). Such an event is highly unlikely and could not have been undetected. In addition, as indicated above and by Gaucher et al. (2002), the elevated *p*CO<sub>2</sub> exhibited by all samples excludes predominant contribution of atmospheric CO<sub>2</sub>. The possibility that outgassed CO<sub>2</sub> represents mixing of atmospheric and magmatic sources is, therefore, ruled out.

Outgassed CO<sub>2</sub> originating from degassing of core porewater, measured  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  values are best explained as reflecting equilibrium with interstitial water and dissolved bicarbonates (in situ pH is constrained to be around 7-8 in the two formations) in the argillites. The carbon isotope composition of dissolved bicarbonates ( $\delta^{13}\text{C}_{\text{diss-bicarb}}$ ) and the oxygen isotope composition of porewater ( $\delta^{18}\text{O}_{\text{water}}$ ) in isotopic equilibrium with outgassed CO<sub>2</sub> at 20°C (storage temperature, see above) can be calculated using appropriate fractionation equations. This was done using fractionation factors of Mook et al. (1974) for HCO<sub>3</sub>-CO<sub>2</sub> and of Brenninkmeijer et al. (1983) for CO<sub>2</sub>(g)-H<sub>2</sub>O(l). Using fractionation factors of Deines et al (1974) and Szaran (1997) for carbon isotopes, or those of Bottinga and Craig (1969) and Horibe et al. (1973) for oxygen isotopes would not change the results appreciably (to within  $\pm 0.3$  to  $0.4$  ‰). Results of the calculations are presented in figure 5 and lead to the following conclusions:

1. Calculated  $\delta^{13}\text{C}_{\text{diss-bicarb}}$  values are similar or close to that of seawater dissolved inorganic carbon ( $1 \pm 1$  ‰) and identical to those of marine carbonate minerals occurring in each of the two argillites (1 to 3 ‰ for COX and -1 to 0 ‰ for OPA). This unambiguously indicates an inorganic, marine origin of dissolved bicarbonates in core porewater, and further supports mineral equilibrium with carbonates present in the argillites.

2. Calculated  $\delta^{18}\text{O}_{\text{water}}$  values are markedly negative, around -6 ‰ for COX and around -11 ‰ for OPA, indicating a meteoric nature of porewater in the two argillite formations. This agrees well with the results of other works, based on different analytical techniques (squeezing, distillation, radial diffusion) and documenting a range of -6 to -4 ‰ for  $\delta^{18}\text{O}$  of COX porewater (France-Lanord and Guilemette, 2001) and -10 to -8 ‰ for OPA porewater (Rübel et al., 2002; Degueldre et al., 2003; Pearson et al., 2003).

The results above illustrate how valuable information can be readily gained from isotopic composition of  $\text{CO}_2$  outgassed by cores of argillite. In the particular case of COX and OPA argillites, conclusions drawn from calculated  $\delta^{13}\text{C}_{\text{diss-bicarb}}$  and  $\delta^{18}\text{O}_{\text{water}}$  values are in excellent agreement with what is known of the geological-geochemical context (Andra, 2001; Pearson et al. 2003). Constraints derived from the results of this study on the origin of porewater and dissolved carbon have important implications for the reconstruction and modelling of post-depositional processes and water-rock interactions that affected the two clay formations (Gaucher et al., 2001; Girard et al. 2002a, 2002b). One implication, for instance, is that the carbonate system in the studied rocks is primarily controlled by mineral equilibria, with no significant influence of  $\text{CO}_2$  putatively derived from organic matter. Another implication is that meteoric water was introduced in the argillites during post-depositional history and replaced original connate seawater. It is beyond the scope of the present paper to discuss these geochemical/geological issues, additional investigation being underway to gain further insight in vertical and lateral variability at field scale.

### 5.3. Accuracy of the approach

Indirect determination of  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^{13}\text{C}_{\text{diss-bicarb}}$  of argillite porewater following the approach described in this study is clearly associated to a significant uncertainty. The later cannot be evaluated quantitatively from the results reported herein alone. Factors prone to influence quality of results and uncertainty are reviewed below.

1. A first factor is potential contamination of porewater by drilling fluids during coring. From this stand point, it is advisable, as was done in this study, that drilling and coring be performed using oil-based mud or under dry atmosphere conditions (N<sub>2</sub> flush). In addition, it is highly recommended to remove the outer rim of the core, by dry sawing only, prior to loading in outgassing cell.
2. Another important factor is the duration of sample processing and conditioning in the field. Everything must be done to minimize contact with atmosphere and sample heating, in order to avoid significant loss of porewater by evaporation. Some CO<sub>2</sub> loss by diffusion out of the core during the few hours required for conditioning cannot be avoided. Based on the results of our study, it was estimated that CO<sub>2</sub> loss potentially occurring within the 1-2 hours conditioning would only affect the outmost few mm of the core, and would most likely not influence isotopic composition of porewater in a major way.
3. Any undetected leakage following cell sealing and subsequent contamination by air would certainly jeopardize quality of results.
4. The analytical uncertainty on  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  determinations is an important parameter that needs to be further evaluated. Cryogenic and active charcoal treatments are well mastered techniques, routinely used for CO<sub>2</sub> purification in many stable isotope laboratories. Fractionation might be introduced during expansion of the gas accumulated in the cell into the cryogenic line, due to sluggishness of transfer in the presence of abundant water vapor and/or organic compounds. In the case of COX and OPA samples, this was shown not to be a concern, in particular with the "representative aliquot procedure", but different samples may behave differently. At present, our results, combined with those of limited tests performed on CO<sub>2</sub> gas standards (Girard et al., 2002a), suggest that total analytical uncertainty on  $\delta^{13}\text{C}_{\text{CO}_2}$  and  $\delta^{18}\text{O}_{\text{CO}_2}$  determinations is in the range of  $\pm 0.5$ - $1.0$  ‰.

5. The calculated  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^{13}\text{C}_{\text{diss-bicarb}}$  are only as good as fractionation factors are. The error introduced by the choice of fractionation equation is evaluated to be on the order of  $\pm 0.3\text{-}0.4\text{ ‰}$  at the temperature of interest.

Vaporization of core porewater occurring in the outgassing cell after sealing is also an issue of concern. If significant vaporization takes place the isotopic composition of the remaining liquid porewater in the core may change appreciably, following a Rayleigh process. In the COX CO<sub>2</sub> extractions performed with the "total recovery procedure" the amount of water vapor expanded in the vacuum line (and collected aside from outgassed CO<sub>2</sub>) was on the order of 1 ml (Girard et al. 2002a), i.e. about 1% of the total amount of core porewater. A rapid calculation shows that isotopic fractionation associated with such vaporization would change the  $\delta^{18}\text{O}$  value of the remaining water by  $\approx 0.1\text{ ‰}$  only. In addition, this change will affect the  $\delta^{18}\text{O}_{\text{CO}_2}$  values of subsequent CO<sub>2</sub> extractions (not the first one). As a consequence, this process is not expected to be a major source of error as long as the amount of water vaporization remains of the order considered above.

Based on the above considerations, and provided sufficient care is taken during sample processing and conditioning, we conclude that isotopic composition of argillite porewater and dissolved bicarbonates can be constrained to within about 1 to 2 ‰ using the described methodology. In many instances, this is a sufficient level of accuracy to draw valuable conclusions as to the origin of interstitial water and dissolved carbon.

We are aware of a growing body of evidence supporting isotopic fractionation of porewater in clay-rich rocks in relation with partitioning in different compartments, including interlayer, bound and free water (France-Lanord and Sheppard, 1992; Hsieh and Savin, 1998; Sacchi et al., 2000 and references there-in). Our results do not provide any insight into this issue and, at present, it is assumed that outgassed CO<sub>2</sub> reflects isotopic equilibrium with bulk porewater.

The extent to which isotopic fractionation related to compartmentalization of porewater might be recorded in the isotopic composition of released CO<sub>2</sub> remains to be investigated.

The methodology reported in this study constitutes a relatively simple, straightforward way to characterize  $\delta^{18}\text{O}$  of porewater and  $\delta^{13}\text{C}$  of dissolved carbon in argillites. The main advantages are that 1) it does not require porewater extraction from cores by physical/chemical approaches as in most previously developed techniques, 2) it does not induce any kind of physical or chemical disturbance to the clay-water system (core) being investigated, and 3) it minimizes the time of contact between sample and atmosphere.

Provided sample processing/conditioning is carried out with sufficient care and promptness, reliable and valuable isotopic information can be derived from CO<sub>2</sub> naturally outgassed from cores of argillite in laboratory conditions. Application to COX and OPA argillites reported here clearly illustrate the usefulness of the methodology in hydrogeochemical studies of mudrocks such as reservoir cap-rocks and subsurface aquitards, in particular when limited core footage is available. One drawback of the method is that it does not give access to the hydrogen isotope composition of argillite porewater.

## **6. Conclusions**

A novel, simple methodology was developed to constrain the  $\delta^{18}\text{O}$  of porewater and the  $\delta^{13}\text{C}$  of dissolved carbon in argillaceous rocks. The approach is based on collecting, purifying and analyzing for C and O isotopes CO<sub>2</sub> naturally outgassed from cores under well-controlled conditions. A specifically-designed outgassing cell and a sample conditioning procedure were developed in order to achieve rapid storage of undisturbed (uncrushed) core samples in an inert atmosphere (N<sub>2</sub> or He) at the drilling site immediately after coring.

Monitoring chemical composition of released gas indicates that a constant partial pressure of CO<sub>2</sub>, resulting from porewater degassing, is reached within 1-2 months. The outgassed CO<sub>2</sub> reflects isotopic equilibrium with porewater and dissolved carbon.

The validity of the approach was demonstrated through application to the Callovo-Oxfordian argillites of Bure, eastern Paris Basin, France, and the Opalinus Clay formation, Mont Terri, Switzerland. It offers a valuable alternative to existing techniques requiring physical or chemical extraction of porewater prior to isotope analysis, that are impaired by potential introduction of undetected isotope fractionation. The main advantage of the method resides in the absence of any physical or chemical disturbance induced to the clay-water system being studied.

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## Appendix

Measured isotopic composition of CO<sub>2</sub> outgassed by cores of the Callovo-Oxfordian argillites (COX), eastern Paris Basin, and the Opalinus Clay Formation (OPA), Mont Terri. For COX samples, the 1<sup>st</sup> set of extractions (May 2000) was done with the "total recovery procedure", while the 2<sup>nd</sup> (August 2000) and 3<sup>rd</sup> (January 2001) sets used the "representative aliquot procedure". For OPA samples, all extractions were done with the "representative aliquot procedure".

Extraction date	Sample	Extraction #	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰ PDB)	$\delta^{18}\text{O}_{\text{CO}_2}$ (‰ SMOW)
COX - 1 <sup>st</sup> set				
May 2001	EST05444	05444-EXT1	-8.8	34.7
May 2001	EST05525	05525-EXT1	nd*	nd*
May 2001	EST05578	05578-EXT1	-7.1	34.6
May 2001	EST05640	05640-EXT1	-6.9	34.9
COX - 2 <sup>nd</sup> set				
August 2001	EST05444	05444-EXT2-A	-7.1	35.4
		05444-EXT2-B	-7.1	36.3
		05444-EXT2-C	-7.9	36.1
August 2001	EST05525	05525-EXT2	-5.7	35.5
August 2001	EST05578	05578-EXT2	-7.2	34.7
August 2001	EST05640	05640-EXT2-A	-5.4	35.5
		05640-EXT2-B	-5.7	35.2
COX - 3 <sup>rd</sup> set				
January 2002	EST05444	05444-EXT4	-6.7	35.8
January 2002	EST05525	05525-EXT4	-6.1	35.9
January 2002	EST05578	05578-EXT4	-5.6	35.2
January 2002	EST05640	05640-EXT4	-5.7	34.6
OPA				
June 2002	MT7-1	02G009	-10.2	29.0
June 2002	MT7-2	02G010	-10.5	31.5

\* : no data (see text)

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Table 1 : Relevant information on core samples and CO<sub>2</sub> outgassed from COX and OPA argillites used in the study.

Formation	Sample	Sampling date	Depth (m)	Conditioning gas and pressure	pCO <sub>2</sub> * (mbar)
COX	EST05444	14/09/00	424	N <sub>2</sub> at 72 mbar	10.0
	EST05525	15/09/00	448	N <sub>2</sub> at 72 mbar	5.7
	EST05578	16/09/00	461	N <sub>2</sub> at 72 mbar	8.5
	EST05640	17/09/00	477	N <sub>2</sub> at 72 mbar	9.7
OPA	MT7-1	21/03/00	7	N <sub>2</sub> at 250 mbar	1.6
	MT7-2	21/03/00	9	He at 981 mbar	1.3

\* : plateau value, see text

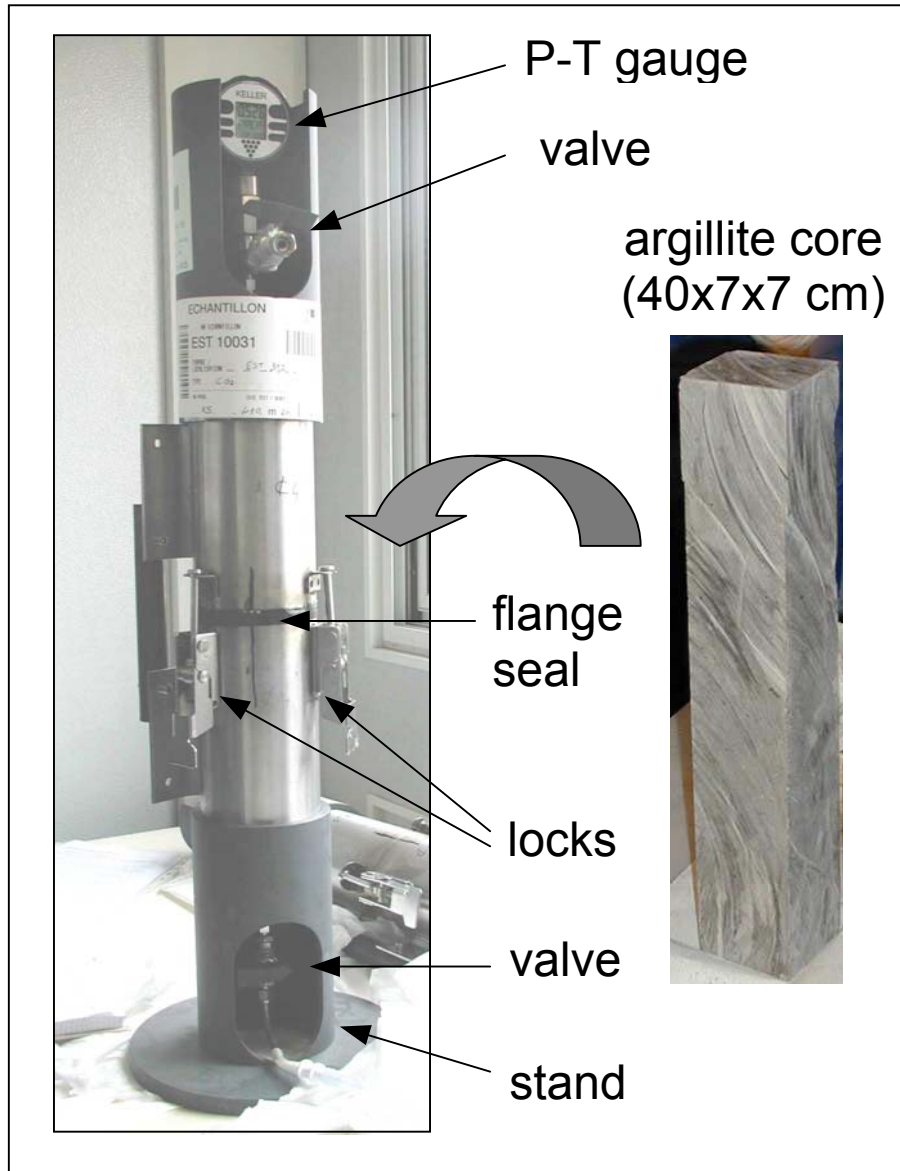
Table 2 : Average isotopic compositions of CO<sub>2</sub> outgassed from cores of COX and OPA argillites ("representative aliquot procedure" data only, see text).

Sample	Number of analyses	δ <sup>13</sup> C <sub>CO2</sub> (‰ PDB)	δ <sup>18</sup> O <sub>CO2</sub> (‰ SMOW)
EST05444	4	-7.2 ±0.5	35.9 ±0,4
EST05525	2	-6.7 ±0.8	35.3 ±0,8
EST05578	2	-5.7 ±0.1	35.4 ±0,2
EST05640	3	-5.6 ±0.2	35.1 ±0.5
MT7-1	1	-10.2	29.0
MT7-2	1	-10.5	31.5

**Figure captions**

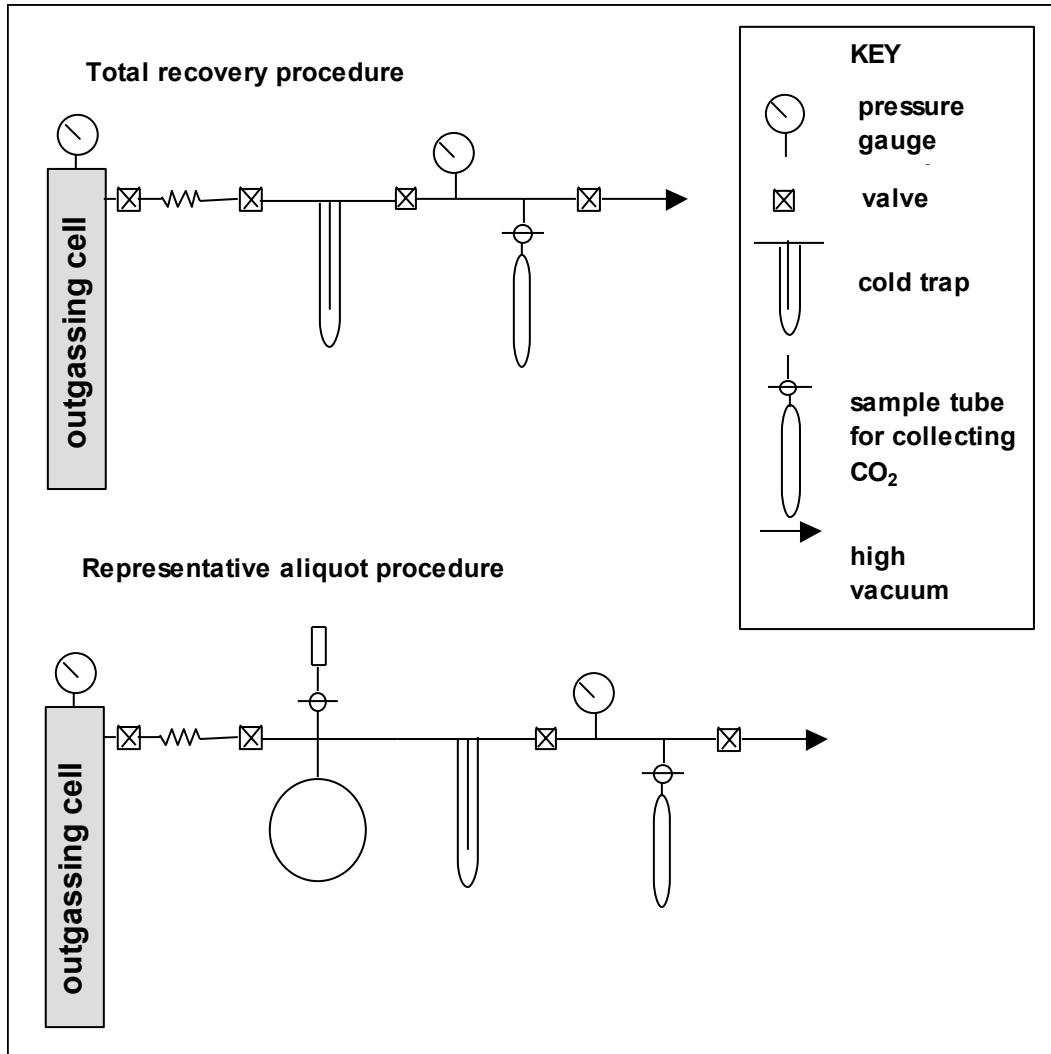
- Fig. 1 Photographs of an outgassing cell, showing the different components, and of an argillite core (COX sample) following dry-sawing of its external part prior to loading in the cell. Curved lines on core sides are saw marks. Core samples were usually not preserved as one piece during sawing. In many cases, the core broke into blocks (up to 5) which were piled up in the outgassing cell.
- Fig. 2 Sketch of the cryogenic vacuum line used for recovery and purification of CO<sub>2</sub> gas from outgassing cells. Slightly different configurations were used for the two different CO<sub>2</sub> extraction procedures (see text).
- Fig. 3 Typical time evolution of CO<sub>2</sub> partial pressure in the outgassing cell (GC data) as gas is released by argillite core (COX sample; Gaucher et al. 2001). Error on  $p\text{CO}_2$  measurements is evaluated to be  $\pm 20\%$  (Gaucher et al. 2001).
- Fig. 4 Stable isotope composition of CO<sub>2</sub> outgassed by COX and OPA argillites at 20°C (data in appendix). Open symbols are for "total recovery procedure" and filled symbols for "representative aliquot procedure" (see text). Symbols linked by a solid line are for extractions performed consecutively on the same sample in a single day.
- Fig. 5  $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$  plot showing measured isotopic compositions of COX (filled circles) and OPA (filled squares) outgassed CO<sub>2</sub>, and calculated isotopic compositions of porewater ( $\delta^{18}\text{O}_{\text{water}}$ ) and dissolved bicarbonates ( $\delta^{13}\text{C}_{\text{diss-bicarb}}$ ) for COX (filled triangles) and OPA (filled diamonds) interstitial water (see text). Measured isotopic compositions of solid carbonates (calcite and/or dolomite) occurring in each the two argillites (open circle and open squares) and compositional fields of main sources of CO<sub>2</sub> are also shown.

Fig. 1



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Fig. 2



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Fig. 3

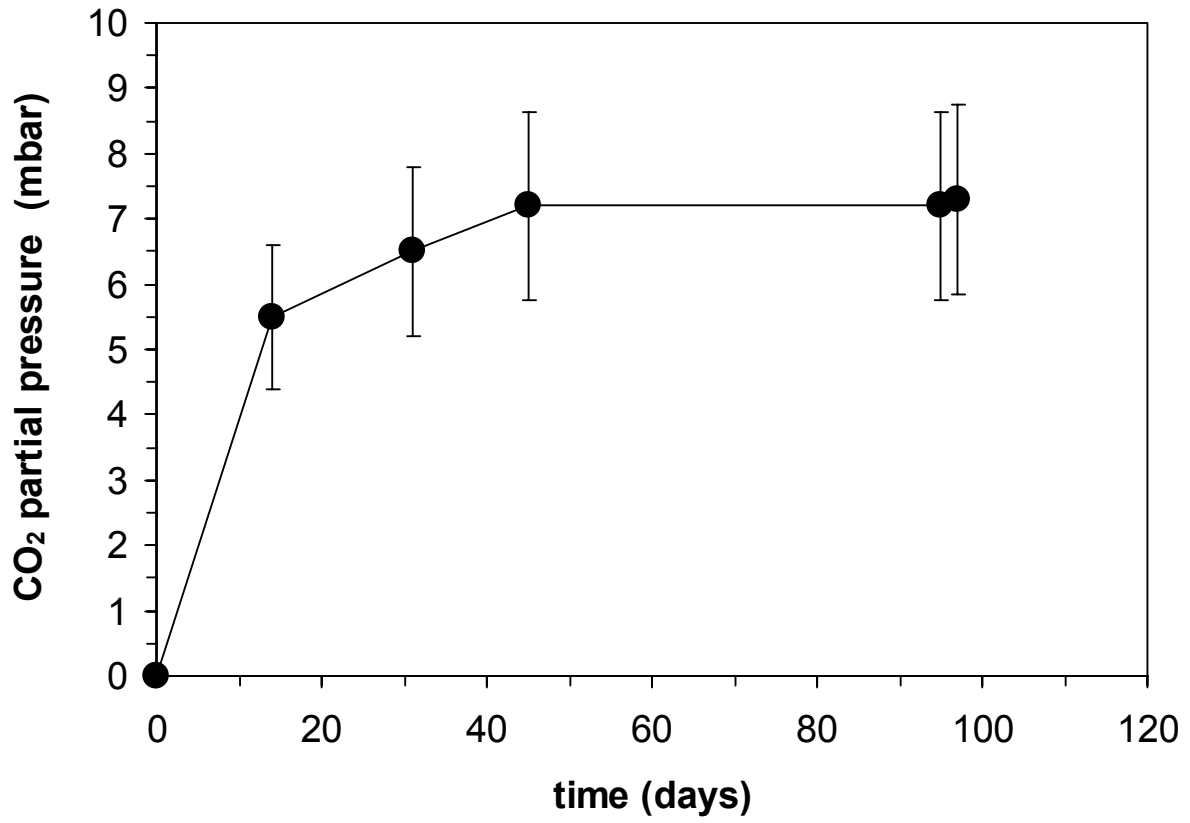
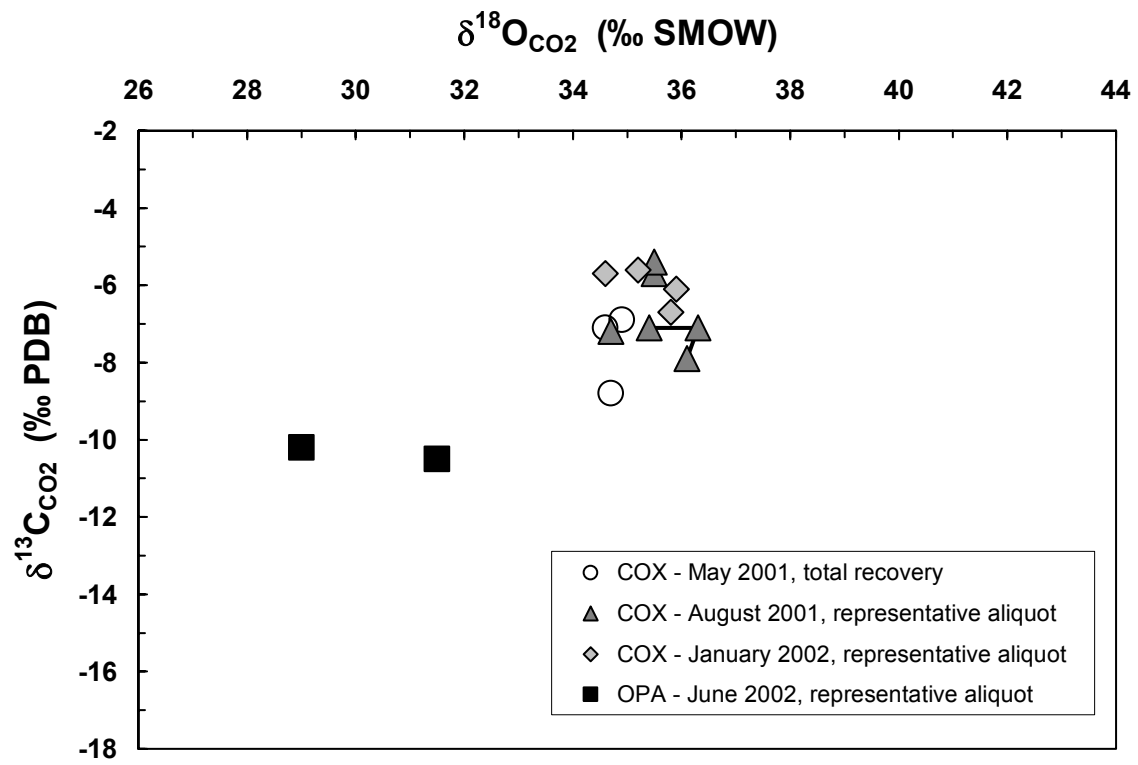
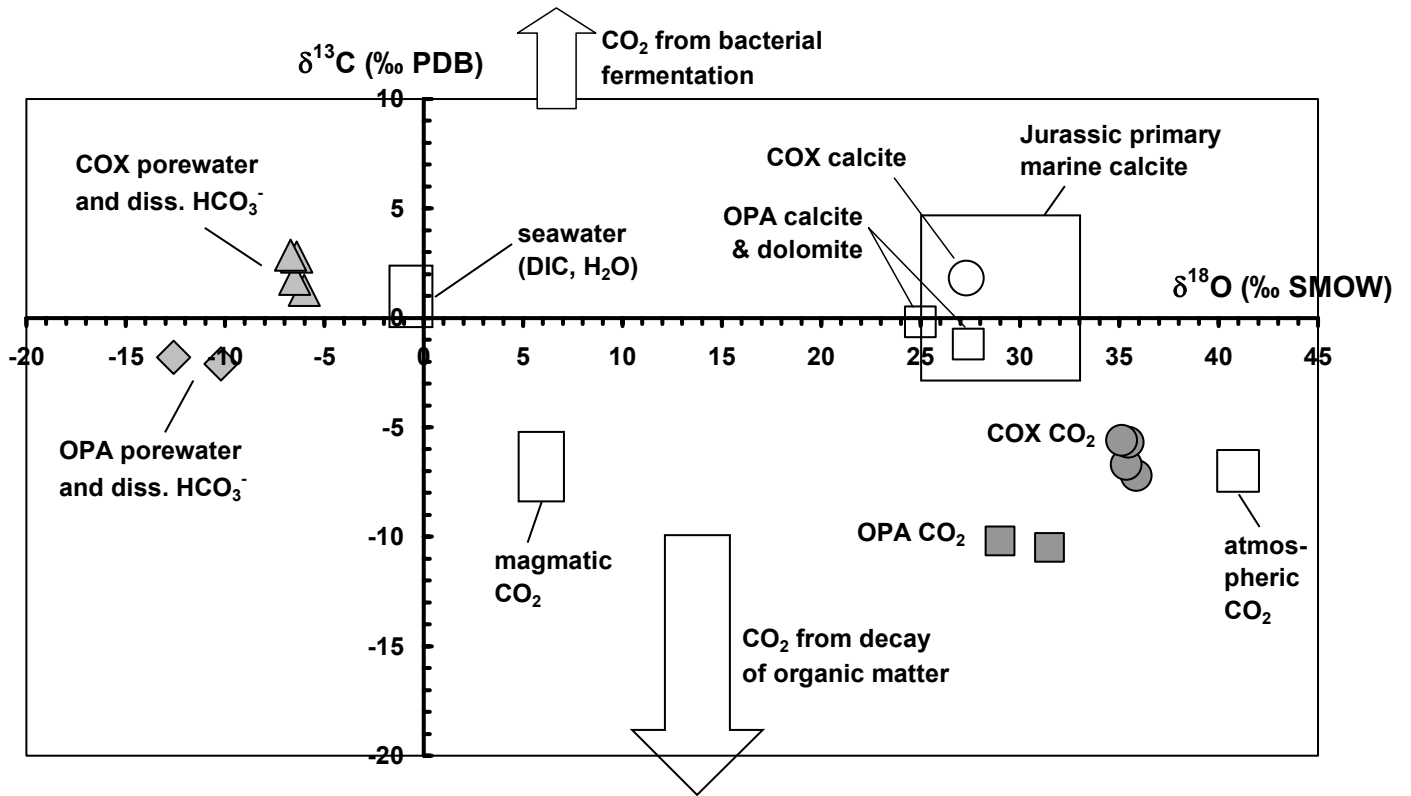


Fig. 4



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Fig. 5



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