RECONSIDERATION OF METHANE ISOTOPE SIGNATURE AS A CRITERION FOR THE GENESIS OF NATURAL GAS

INFLUENCE OF MIGRATION ON ISOTOPIC SIGNATURES

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RECONSIDÉRATION DE LA SIGNATURE ISOTOPIQUE DU MÉTHANE COMME CRITÈRE POUR LA GENÈSE DU GAZ NATUREL : INFLUENCE DE LA MIGRATION SUR LES SIGNATURES ISOTOPIQUES

Plusieurs expériences ont été réalisées dans le but d'étudier les conséquences isotopiques du transport par diffusion des gaz hydrocarbures au travers des roches sédimentaires. Associées à un modèle numérique, ces expériences de diffusion au travers d'une membrane d'argile reconstituée nous ont permis de corréler deux paramètres pétrophysiques du milieu de migration : la porosité et la diffusivité. D'importants fractionnements isotopiques ont été observés au cours de la diffusion du méthane et, à plus petite échelle, lors de la diffusion de l'éthane. Ces résultats remettent en cause le dogme actuel de la géochimie isotopique des gaz naturels qui stipule que la migration des gaz ne peut induire de fractionnements isotopiques. En conséquence, les méthodes de caractérisation génétique des gaz naturels utilisant la signature isotopique du méthane apparaissent comme insuffisantes.

RECONSIDERATION OF METHANE ISOTOPE SIGNATURE AS A CRITERION FOR THE GENESIS OF NATURAL GAS: INFLUENCE OF MIGRATION ON ISOTOPIC SIGNATURES

Experiments were performed in the purpose of studying the isotopic consequences of the diffusional transport of hydrocarbon gases through sediment rocks. Linked to a numerical model, these gas diffusion experiments through a shale porous plug allowed us to correlate porosity and diffusivity of the migration medium. Significant isotopic fractionations (carbon and hydrogen) of methane, and ethane at a lesser degree were observed. This is in contradiction with the actual dogma of isotope geochemistry of natural gases which claims that no fractionation occurs during gas migration. The genetic characterization of natural gases by using the isotopic signature of methane appears as an ambiguous method.

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NUEVOS ENFOQUES ACERCA DE LA SIGNATURA ISOTÓPICA DEL METANO COMO CRITERIO PARA LA GÉNESIS DEL GAS NATURAL : INFLUENCIA DE LA MIGRACIÓN SOBRE LAS SIGNATURAS ISOTÓPICAS

Se han llevado a cabo diversos experimentos con objeto de estudiar las consecuencias isotópicas del transporte por difusión de los gases de hidrocarburos a través de las rocas sedimentarias. En combinación con un modelo digital, estos experimentos de difusión a través de una membrana de arcilla porosa reconstituida, han permitido establecer la correlación de dos parámetros petrofísicos del medio de migración : la porosidad y la difusividad. Se han observado importantes fraccionamientos isotópicos durante el transcurso de la difusión del metano y, a escala más reducida, durante la difusión del etano. Tales resultados ponen en tela de juicio el dogma actual de la geoquímica isotópica de los gases naturales, dogma por el cual se estipula que la migración de los gases no puede provocar fraccionamientos isotópicos. Por consiguiente, cabe considerar que los métodos de caracterización genética de los gases naturales que utilizan la signatura isotópica del metano son insuficientes.

INTRODUCTION

In the past twenty years, isotope geochemistry of natural hydrocarbon gases has been based on the postulate that no fractionation occurs during gas migration (Fuex, 1980; Schoell, 1983). Some older work done by Soviet and Italian scientists (Galimov, 1967, 1975; Colombo *et al.*, 1968; Lebedev and Syngayevskiy, 1971), however claimed important isotopic shifts due to gas transports.

Convinced by the absence of fractionation during migration phenomena, most authors deduce that the isotopic and chemical variations observed in natural gases reflect mainly genetic processes (James, 1983; Schoell, 1983; Whiticar and Faber, 1986; Berner and Faber, 1987). Some researchers have designed different types of diagrams in which the carbon isotopic composition of methane is correlated to (1) the $C2_+$ concentration (chemical proportion of methane), (2) the hydrogen isotopic composition of methane and, if possible, (3) the carbon isotopic composition of ethane. These diagrams allow them to genetically characterize natural gases in terms of source, bacterial input and transformation ratio. Methane is always the common denominator of these plots because it is the only hydrocarbon gas formed through two different processes: bacterial activities and cracking of the organic matter (primary) or of the oil (secondary). These two processes cause a specific carbon isotopic signature for methane, thermogenic methane being heavier than biogenic methane. For example, in Figure 1, which represents one of these most famous diagrams in terms of $\delta D(CH_4)$ versus $\delta^{13}C(CH_4)$, the

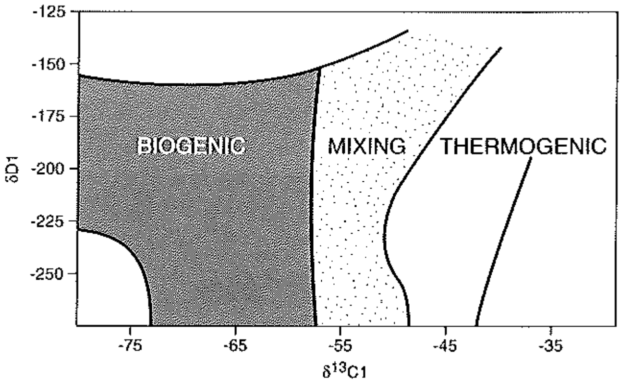


Figure 1

Gas field classification using the isotopic ratios of methane (Schoell, 1983).

two origins of methane can be distinguished. The intermediate values (between biogenic and thermogenic) are interpreted by the authors of the diagram as the result of a mixture between biogenic and thermogenic methane. With such a point of view, a geochemist then only needs to know the isotopic ratios ($\delta^{13}C$ and δD) of methane in order to understand the origin of natural gas accumulations. Furthermore, these authors believe that the post-genetic isotopic variations of natural gases would mainly result from mixing processes.

The objective of this article is to show that migration, with molecular diffusion, changes the isotopic composition of a gas. The diffusional transport is commonly accepted by the scientific community as an important mechanism of natural gas migration. Smith *et al.* (1971) consider that the loss of light hydrocarbons from reservoirs by diffusion to the surface of the earth is a major mechanism for depleting petroleum accumulations over geologic time. According to Krooss *et al.* (1992), there are three main gas migration mechanisms: (1) migration of a free-gas phase (darcy flow), (2) transport of dissolved gas in a dynamic aqueous phase and (3) diffusive transport through the water-saturated pore space of the caprock. The diffusive transport is the least efficient of the three mechanisms. However, this type of migration occurs throughout the entire history of a gas field as long as a concentration gradient across the caprock exists (Nelson *et al.*, 1995). Molecular diffusion can be considered in such terms as a migration process associated with the longevity of the reservoir.

Prinzhofer *et al.* (1995) have provided an example (Fig. 2) of two superimposed gas reservoirs where geologic and geochemical data may be interpreted as the result of a diffusion leakage. The lower reservoir consists in a carbonate reef whilst, the upper one is a sandy level. The caprocks are mainly shales, with some interbedded lenses of sandstone. The vertical distance between the two reservoirs is 300 m, and the depth of the lower reservoir is 1200 m. The chemical and isotopic compositions of four gas samples from the lower reservoir, and from the upper one have been measured. Besides hydrocarbons, the lower reservoir contains 24% of N_2 and 4% of CO_2, whereas the upper one is composed of 50% of N_2, 9% of CO_2, and 0.35% of H_2S. The upper reservoir consists of a very dry gas (0.02% C2, no measurable heavier compound), whereas the lower one contains 70.0 C1, 1.30 C2, 0.18 C3,

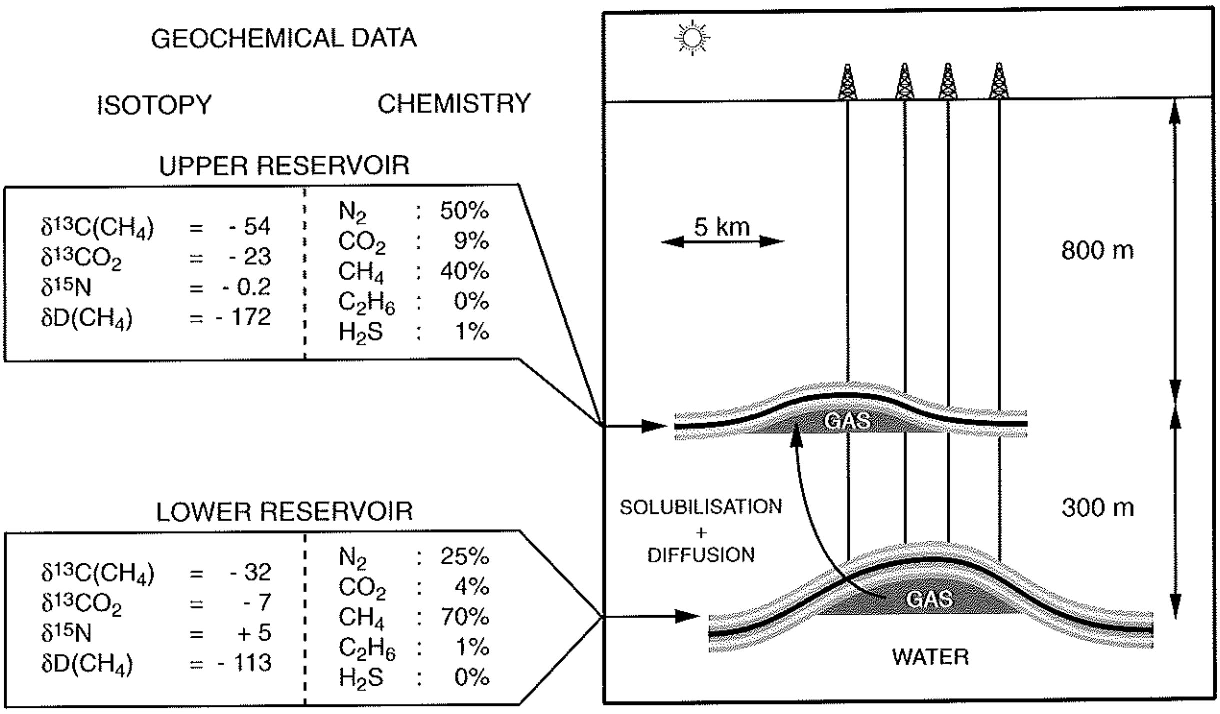


Figure 2

Schematic presentation of a gas field in a deltaic series (Prinzhofer *et al.*, 1995).

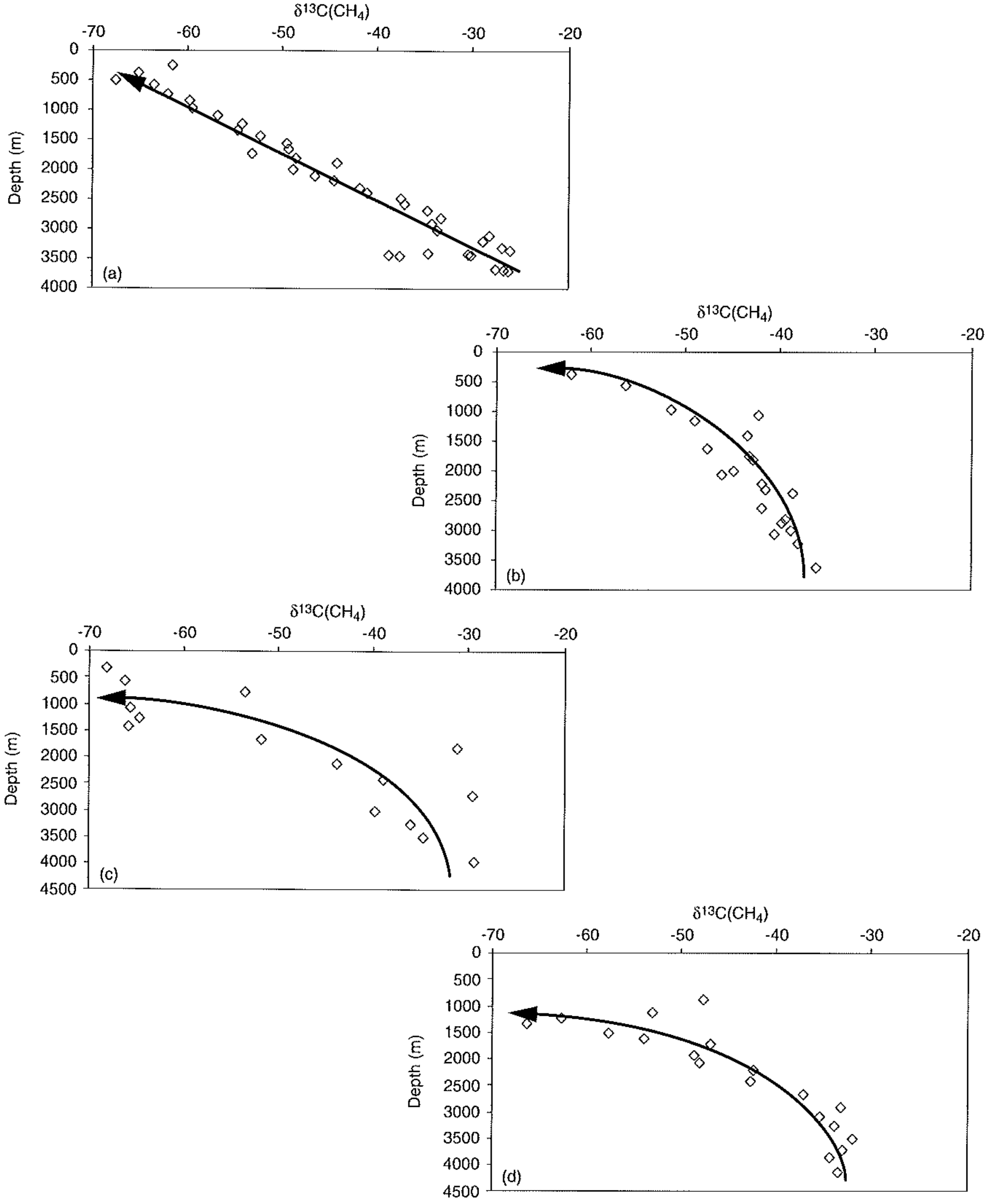


Figure 3

Examples of Head Space gases.

0.05 C4 and 0.01% C5. All isotopic signatures of the lower reservoir are heavier. The authors have interpreted these data as the result of a diffusive leakage of the lower up to the shallower reservoir. A quantitative model of dissolution/diffusion of the gases in water perfectly explains the chemical compositions of the two reservoirs. The isotopic lightness of the upper reservoir gases (gases resulting from the exudation of the deeper reservoir) is consistent with the diffusional model. Furthermore, Colombo (1968) and Galimov (1975) experimentally observed similar isotopic shifts: the migrated gas was enriched in light isotopes.

Another indication for isotopic fractionation are the isotopic ratios of gases collected above reservoirs during drilling, and sampled generally by the Head Space methodology. The carbon isotopic analysis shows that methane sampled from the shallower part of the wells is often lighter than that of the deeper zones (Fig. 3a, b, c, d). This means an enrichment in ^{12}C of methane from the caprock at the top of the reservoir to the surface of the earth. At the present time, this has been attributed to a mixing process between indigenous bacterial methane (generated by immature sediments) and varying quantities of thermogenic methane migrated from the reservoir (Ricchiuto, 1992). If isotopic fractionation occurs during gas migration, it would not be necessary to postulate a bacterial contribution in order to explain the isotopic distribution of methane in the wells.

We have thus elaborated an experimental methodology which associates experiments in laboratory supported by a mathematical model, in the aim of studying and quantifying the possible isotopic fractionations of natural hydrocarbon gas diffusing through sediment rocks (and especially through shales). By controlling the confining pressure, the porosity and the mineralogy of the shale (dry or impregnated with water), we will investigate the isotopic variations of both diffused gases and of the gases remaining in a reservoir.

1 METHODOLOGY

1.1 Principle of the experiment

1.1.1 Description of the device

We have built an experimental cell which is composed of three units (Fig. 4): a reconstituted argillaceous "membrane" and, on both sides, two gas reservoirs A and B. A gauge indicates the gas pressure in each reservoir. A system of sampling made up of two valves (1 and 2) separated by a small metallic tube, is connected to each reservoir.

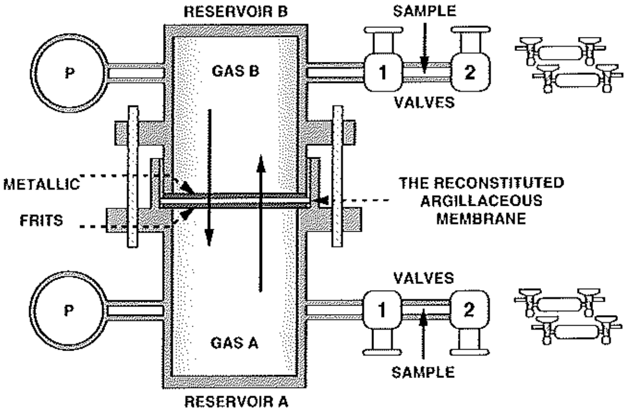


Figure 4

The cell diffusion.

1.1.2 The "membrane"

Our first task was the fabrication of the porous "membrane". We initially reconstituted an unconsolidated porous medium using argillaceous powder either with or without water. Held by two metallic frits in the middle part of the cell, the mixture was then packed to obtain an argillaceous mud (with water) or dry compact cake (without water). The measurement of the porosity of the compacted shale (Table 1) was done in two different ways, according to the presence, or absence of water in the membrane. We calculated it using the unconsolidated medium porosity and the decrease in thickness of the membrane during compaction. The porosity of the unconsolidated mud was determined from the amount of water and powder introduced in the aqueous argillaceous mixing. In the case of the dry medium, the porosity was determined by the relationship between the weight of powder introduced in the cell and its occupied volume, estimating the theoretical density of the shale.

1.1.3 The filling phase of the cell

After purging the cell (draining the air contained within the reservoirs), the two reservoirs A and B, separated by the compacted clay "membrane", were filled with two different gases. The initial gas confining

TABLE 1

The experimental factors

Factors	Experiment 1	Experiment 2	Experiment 3	Experiment 4
		RESERVOIRS		
Temperature	ambient	ambient	ambient	ambient
Pressure (bars)	5	50	52	6
Gas Species	C1-C2	N_2-C1	N_2-C1	N_2-C1
		POROUS MEDIA		
Thickness (mm)	3.5	1.5	1	8.5
Porosity (%)	60	33	37	30
Mineralogy	Bentonite 99%	Caprock Nigeria	Caprock Nigeria	Bentonite 99%
Water/Dry	Water saturated	Water saturated	Water saturated	Dry
Time	60 days	16 days	65 days	5 hours

pressures in each reservoir had to be identical in order to consider an initial gas flux through the shale only controlled by the concentration gradient of each gas, without any darcean flow. At the end of the filling phase, the two valves 2 were closed (valves 1 remaining open). We expected parts of gas A passing through the shale to reservoir B, and parts of gas B to migrate in the opposite direction.

1.1.4 The experimental factors

In this paper, we present four experiments with various changing parameters: gas species (CH_4, C_2H_6 and N_2 ultra-pure), gas pressure in the reservoirs (5, 6, 50 and 52 bars), porosity (30, 33, 37 and 60%), mineralogy of the shale (pure bentonite, natural shale), and presence or absence of water. All the experimental conditions are summarized in Table 1.

1.1.5 The sampling phases

In the course of the experiments, small aliquots of gases were sampled in the two reservoirs. We describe in this paragraph the procedure for one sampling. One or several glass containers (depending upon the pressure in the reservoir), previously pressure evacuated, were connected to valve 2 of each reservoir. In the same time, valve 1 was closed to trap within the metallic tube a representative aliquot of gases. Then, valve 2 was opened to transfer a part of the aliquot to the glass containers. Before closing valve 2, we waited for the homogenization of the gas sample in glass containers. Afterwards, valve 1 was opened in order to prepare the cell to the next sampling. The glass containers were then connected to either a Toepler line or a gas chromatograph in order to carry out chemical and isotopic analysis. In fact, this procedure of sampling is identical to the procedure of gas introduction in an isotopic mass spectrometer.

1.1.6 The analytical technique

For the purpose of chemical analysis of gas samples, we used a gas chromatograph (GC Varian Star 3600 Cx). A Toepler line, consisting of an oxidation oven (containing CuO and Cu_2O), a cold trap (with adjustable temperature from –196°C to +95°C), a reduction device (containing uranium) and at the end of the line a Toepler pump, was used to prepare each hydrocarbon gas species sampled from the diffusion cell for carbon and hydrogen isotopic analysis (Prinzhofer and Huc, 1995). Also, the Toepler line lets us separate methane and ethane by the use of the cryogenic trap.

From these measurements, we determined the ratios of (1) the migrated and (2) the remaining versus the initial gas amounts for each species. The initial amount of gas introduced in each reservoir was evaluated from the Ideal Gas equation, knowing the volume and the *(P, T)* conditions in the reservoir. Afterwards, we designed two types of diagrams in which (I) the ratio of migrated to initial gas amounts, and (II) the difference between the isotopic ratios of migrated and initial gases, were plotted versus time. These diagrams are called "migrated gas production" and "migrated gas isotopic fractionation", respectively.

1.2 Numerical model

In parallel to the experimental approach, we have developed a mathematical model (Schneider *et al.*, 1995) which simulates the transport of gas molecules in the cell. The gas migration in a porous medium is described by Fick's law:

$$\frac{\partial(\phi \times C_{m,i})}{\partial t} - \mathrm{div}\left(\phi \times \psi \times D_{m,i} \times \overline{\mathrm{grad}}(C_{m,i})\right) = 0$$

m	migration phase
i	species of the gas molecule
$C_{m,i}$	concentration of i in m
$D_{m,i}$	diffusion coefficient of i in m
ϕ	porosity of the porous medium
ψ	diffusivity of the porous medium.

This equation is consistent for a binary system if the pressure gradient between the two reservoirs does not become too important. This means that we have to choose two gas species which have the closest molar flows in the (P, T) conditions of the experiment: the molar flow of gas A (reservoir A) will approximately compensate for the countercurrent flow of gas B (reservoir B). Moreover, by using the sampling system, some gas aliquots may be sampled in the superpressured reservoir in order to restore the lowest pressure gradient between the two reservoirs.

Within the two reservoirs, the molecules diffuse in a gaseous phase (m = gaseous phase, $\Psi = 1$ and $\phi = 1$).

The reconstituted shale unit can be dry or saturated in water. In the water-saturated case, the pore spaces of the solid are filled with water, and the molecules thus diffuse through it. $D_{m,i}$ is the diffusion coefficient of gas species i in water (water contained in the porous medium). The solubility of molecules in water is calculated using "Henry's law" at low pressure:

$$\frac{x_g(P,T)}{x_g(P_0,T)} = \frac{P}{P_0}$$

x_g is the mole fraction solubility:

$$x_g = \frac{n_g}{n_g + n_w}$$

n_g and n_w being respectively the amount of dissolved gas (mol) and the amount of water (mol) in the reconstituted shale unit.

In this calculation, we use the following formula of the solubility:

$$\beta(P,T) = \frac{C_{w,i}}{C_{g,i}}$$

$C_{w,i}$	concentration of gas molecule i in water (mol/m^3)
$C_{g,i}$	concentration of gas molecule i in the gaseous phase (mol/m^3).

By considering the ideal gas approximation:

$$C_g = \frac{P}{R \times T}$$

R	ideal gas constant
T	temperature.

Moreover:

$$C_{w,i} = \frac{n_g}{V_w} \quad \text{and} \quad n_w = \frac{\rho_w \times V_w}{M_w}$$

V_w	volume of water in the reconstitued shale unit
M_w	water molar mass
ρ_w	water density.

So, we obtain a relationship between β (the solubility coefficient) and x_g (the mole fraction of gas in water):

$$\beta = \frac{\rho_w \times R \times T}{M_w \times P} \times \frac{x_g}{(1 - x_g)}$$

In the dry experiment case, two kinds of diffusion may occur: bulk phase diffusion and Knudsen diffusion. The first one can be described as managed by collisions between gas molecules. The second one can be defined as resulting from impacts of gas molecules with pore walls (if pore size is very low: a few tens of nanometers). In the bulk phase diffusion case, $D_{m,i}$ is the diffusion coefficient of gas species i in a gaseous phase m.

Preliminary tests shown that the time constants of gas diffusion within the two reservoirs A and B are negligible compared to the time between each sampling. Therefore, we consider the two gas reservoirs as homogeneous. The parameter controlling the gas transport is the migration speed of the gas molecules χ_i through the porous medium:

$$\chi_i = \frac{\phi \times \psi}{e} \times p_0 \tag{1}$$

$p_0 = D_{w,i} \times \beta_i$	diffusive permeability of gas molecule i in pure water
$p_0 = D_{g,i}$	diffusion coefficient of gas molecule i in a gaseous phase
ψ	diffusivity
ϕ	porosity of the porous medium
e	thickness
β_i	solubility coefficient of gas molecule i in water
$D_{w,i}$	diffusion coefficient of gas molecule i in water
$D_{g,i}$	diffusion coefficient of gas molecule i in gaseous phase.

The diffusive permeability values (defined by Krooss and Leythaeuser, 1988) were computed using the thermodynamical equations of the solubility and diffusion coefficients in pure water (β_i: Hayduk, 1982; Battino, 1987; Fogg and Gerrard, 1990) ($D_{w,i}$: Hayduk and Laudie, 1974). The theoretical diffusion coefficient of gas in a gaseous phase ($D_{g,i}$) was calculated using the Chapman and Enskog equation (Reid *et al.*, 1988).

Apart from the solubility and diffusion coefficients, χ_i is a function of three migration factors depending on the geometry of the membrane (Ψ, ϕ, e). Porosity ϕ and thickness e can easily be measured. Diffusivity Ψ is linked to the tortuosity and is characteristic of the internal geometry of the porous medium. We cannot measure it directly, but calculate its value from equation (1).

For each gas species, we adjusted the model on the experimental "migrated gas production" and "migrated gas isotopic fractionation" curves (definitions § 1.1). The fit of the "migrated gas production" curves was first obtained by adjusting χ_i of the predominant isotope (for example $^{12}CH_4$). The migration speed of this isotope is looked upon as the effective migration speed of the gas species (C1). Secondly, we calibrated χ_i of the other isotope, present only in trace amount ($^{13}CH_4$ and $\{^{12}CH_3D + {}^{12}CH_2D_2 + {}^{12}CHD_3 + {}^{12}CD_4\}$) in order to fit the "migrated gas isotopic fractionation" curves. We define the notion of migration isotopic fractionation $\delta\chi_i$ of the gas species using the usual delta notation:

$$\delta\chi_i = \left(\frac{{}^{a}\chi_i}{{}^{b}\chi_i} - 1 \right) \times 1000$$

in water-saturated medium

$$\delta\chi_i = \left(\frac{{}^{a}D_{w,i} \times {}^{a}\beta_i}{{}^{b}D_{w,i} \times {}^{b}\beta_i} - 1 \right) \times 1000 \qquad (2)$$

in dry porous medium

$$\delta\chi_i = \left(\frac{{}^{a}D_{g,i}}{{}^{b}D_{g,i}} - 1 \right) \times 1000 \qquad (3)$$

a heavy isotope of gas *i*

b light isotope of gas *i*.

2 RESULTS

It should be specified that the main goal of these series of experiments was the control of possible isotopic fractionation during gas migration. However, the information on the gas flux involved in each of our experiments has important geologic implications. Even if the correlation between migration speed and petrophysical parameters of the porous medium should be treated extensively in future studies, we already present the first constraints applicable to geologic conditions.

For each diffusion experiments through a water saturated medium (1 to 3), we chose gas compounds which are characterized by the nearest theoretical diffusive permeabilities ($D_{w,i}.\beta_i$) in pure water in the (P, T) conditions of the experiment, in order to limit the increase of a pressure gradient between the reservoirs A and B, due to different migration speeds of the two gases (experiment 1: CH_4-C_2H_6 ; experiments 2 and 3: CH_4-N_2).

Two kinds of argillaceous powder were used: an artificial bentonite (purity 99%) (experiments 1 and 4), and a natural shale from a Nigerian reservoir caprock (experiments 2 and 3). The porosity values of the shale membranes after compaction (see § 1.1.2 The "membrane") were respectively 60%, 33%, 37% and 30% for experiment 1 to 4.

2.1 Flux of migrated gas

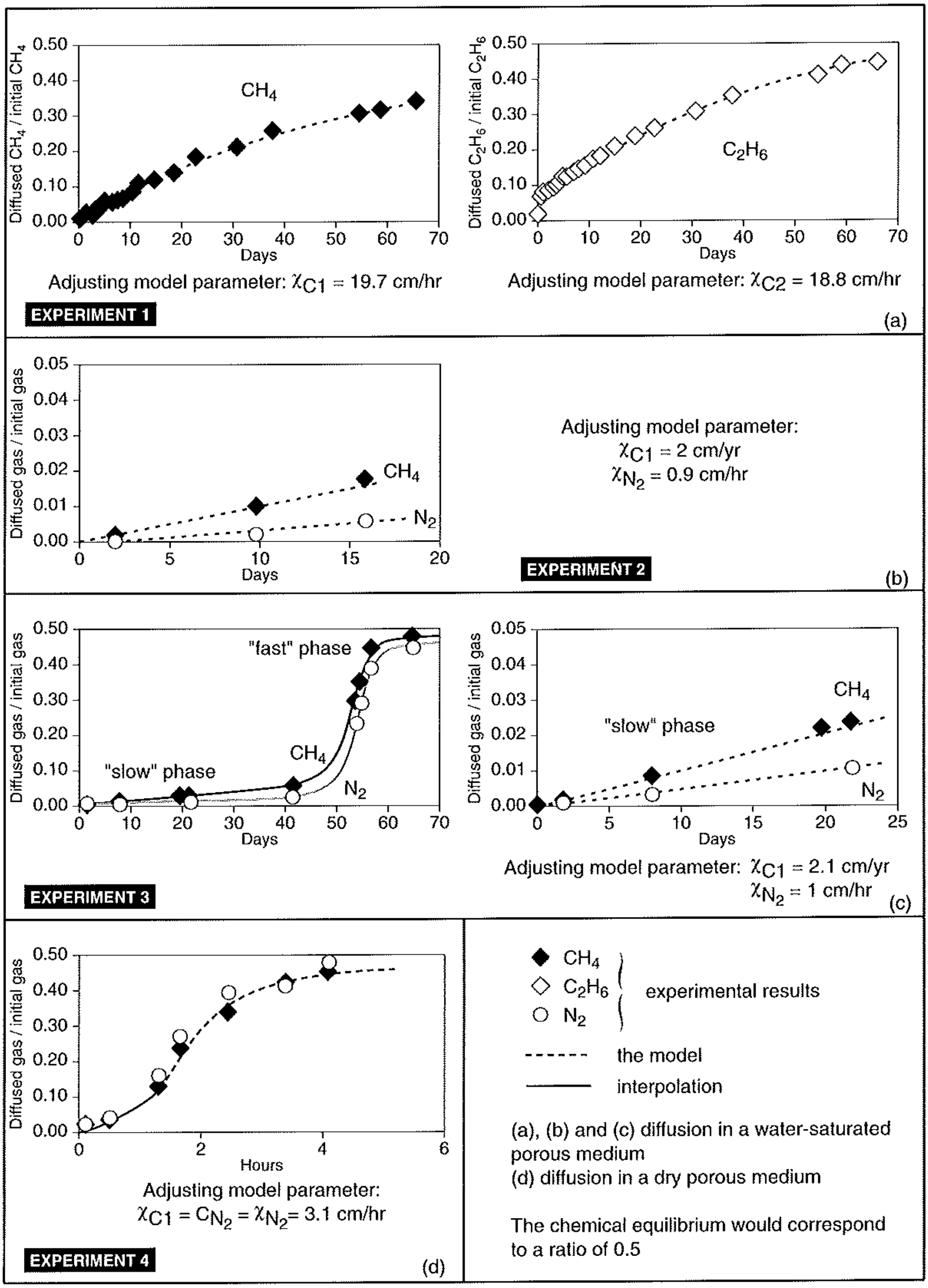
The results are classified depending upon the wet or dry conditions of the porous medium. Figures 5a to 5d correspond to experiments 1 to 4 respectively and represent the "migrated gas production" curves. As previously explained (§ 1.2), we adjusted χ_i of the predominant isotope in order to fit the "migrated gas production" curves. This enabled us to estimate the value of the effective migration speed of the gas species through the porous medium, and from the equation (1), to calculate the value of the diffusivity Ψ of the porous medium.

2.1.1 Wet porous media (experiments 1, 2 and 3)

Experiment 1 (Fig. 5a)

Five bars of methane and ethane were introduced into the reservoirs A and B, respectively. In a time span of two months, we sampled from each reservoir twenty one gas aliquots.

Results indicate that a solubility-diffusion process can explain the ethane and methane migrations as shown with the correct fit of the "migrated gas production" curves. Quantitatively, the model gives us



Adjusting model parameter: χ_{C1} = 19.7 cm/hr

Adjusting model parameter: χ_{C2} = 18.8 cm/hr

Adjusting model parameter:
χ_{C1} = 2 cm/yr
χ_{N_2} = 0.9 cm/hr

Adjusting model parameter: χ_{C1} = 2.1 cm/yr
χ_{N_2} = 1 cm/hr

Adjusting model parameter:
$\chi_{C1} = C_{N_2} = \chi_{N_2}$= 3.1 cm/hr

(a), (b) and (c) diffusion in a water-saturated porous medium
(d) diffusion in a dry porous medium

The chemical equilibrium would correspond to a ratio of 0.5

Figure 5

"Migrated hydrocarbon gas production" curves.

the effective migration speeds of methane χ_{C1} and ethane χ_{C2} respectively 19.7 cm/y and 18.8 cm/y. The values of the diffusivity of the porous medium calculated from the equation (1) are respectively 0.6 or 0.5 for methane and ethane. The difference between these two values is not significant because of uncertainties on (1) the determination of ϕ the porosity of the migration medium and (2) the measurement of e the thickness of the compacted shale "membrane". Diffusivity is a parameter linked to the internal geometry of the porous medium and it does not depend upon the migrating gas species.

Experiment 2 (Fig. 5b)

The initial gas pressure in experiment 2 was set at fifty bars. The gas species introduced into the two reservoirs A and B were respectively methane and nitrogen. In the sixteen days of the experimental procedure, three representative aliquots of gas were collected in each reservoir.

Here again, the correct fit of the model on the experimental results indicates that the methane and nitrogen migrations through the porous medium obeys the Fick's law. The obtained effective migration speeds are about 2 cm/y for methane and about 0.9 cm/y for nitrogen which correspond for these two gases (near to the experimental uncertainties) to a medium diffusivity value of 0.06.

The experiment was stopped one month after it started, because of an experimental set back: the two gas reservoirs were homogeneized, evidence of a failure in the role of the shale membrane. We voiced the hypothesis of a drying of the porous medium. For this reason, experiment 3 was performed with a greater proportion of water in the migration medium.

Experiment 3 (Fig. 5c)

Therefore, experiment 3 differs from the previous one by a larger porosity (see Table 1). During this experiment which lasted sixty five days, nine samples were collected.

As we can see on Figure 5c, this experiment comprises two migration stages: a "slow" phase which lasts five weeks and a "fast" one during the last month of the experiment. The fits of the model on the first phase (nitrogen and methane) are perfectly correct. This indicates that methane and nitrogen migrate by diffusion through the water-saturated medium during the first month of the experiment. The model gives us the effective migration speed values of 2.1 cm/y for methane and 1 cm/y for nitrogen. From the equation (1) the calculated diffusivity value of the porous medium for these two gases is 0.04.

The second stage of production is faster than the first one: the ratio between the two effective migration speeds (corresponding to the two stages) is approximately 200. The changing flow rate is most likely the result of a gas connection between the two reservoirs caused by either the formation of preferential ways of migration through the argillaceous "membrane" or because of the partial drying of the porous medium. Therefore, during this "fast" phase the gas migration process could be considered as a combination between the diffusion in water, and the diffusion in gaseous phase and/or Knudsen diffusion. Considering the theoretical diffusive permeability of methane in water ($D_{w,C1}.\beta_{C1}$ = 14 cm^2/y) and its diffusion coefficient in nitrogen gas ($D_{N_2,C1}$ = 14 m^2/y), the preferential gas way in the shale cannot be more than 0.14% of the total surface of the "membrane".

It seemed to us essential for the understanding of this experiment to carry out a diffusion experiment of methane through a dry porous medium (experiment 4). As we will see in § 2.2, the isotopic behavior of methane during experiments 3 and 4 will allow us to confirm this hypothesis of bi-diffusion.

2.1.2 Dry porous medium

Experiment 4 (Fig. 5d)

Methane and nitrogen were respectively introduced into the reservoirs A and B with an initial pressure of six bars. In five hours time, seven aliquots of gases were sampled from each reservoir.

In this experiment, Knudsen diffusion may take a part in the migration of the two gases. The superimposition of the two migrated gas curves (nitrogen and methane) indicates that the flow of nitrogen is the same as the countercurrent flow of methane. The first hour is characteristic of a transitory rate of flow: the concave part of the curve indicates an accelerated movement of gas molecules up to a steady state of diffusive flow representing by the convex zone. The effective diffusion speed of the two gases (nitrogen and methane) is found to be 3.1 cm/h in the steady state part of the experiment. The diffusivity value is 0.06.

2.1.3 The diffusivity factor Ψ of the porous media

The equation (1) gives us the relationship between the measured gas migration speed in the porous medium, and the theoretical migration speed χ_0 of gas in a medium only constituted by water or gas (in agreement with the wet or dry experiments):

$$\chi_i = \phi \times \psi \times \chi_0 \tag{4}$$

$$\chi_0 = \frac{p_0}{e}$$

$p_0 = D_{w,i} \times \beta_i$ diffusive permeability of gas molecule i in pure water

$p_0 = D_{g,i}$ diffusion coefficient of gas molecule i in gaseous phase.

The values of χ_i and χ_0 are summarized in Table 2.

TABLE 2

Experimental and theoritical migration speeds of hydrocarbon gases

Experiment	1		2		3		4
Gas species	C1	C2	C1	N_2	C1	N_2	C1 & N2
χ_i (cm/y)	19.7	18.8	2	0.9	2.1	1	3.1 cm/h
χ_0 (cm/y)	53.1	58.9	94.5	48.6	140	72.8	157.6 cm/h

These gas diffusion experiments, linked to a numerical model, enable us to determine the diffusivity Ψ of the porous medium whose the experimental values are summarized in Table 3.

TABLE 3

Diffusivity values of porous media

Experiment	1		2		3		4
Gas species	C1	C2	C1	N_2	C1	N_2	C1 & N_2
ψ	0.6	0.5	0.06	0.06	0.04	0.04	0.06

Whatever the migration phase (water or gas), the character of the porous medium is described by the ratio of χ_i/χ_0 ($\Psi \cdot \phi$). A diagram has been designed in which this ratio is correlated with the porosity. Data from experimental work of Chen (1973) are plotted with our values (Table 4) in the same diagram (Fig. 6). The variation of the diffusivity factor versus porosity may be interpreted in terms of percolation thresholds. The first decrease of the diffusivity would correspond to the first percolation threshold, which is the connection of both solid and fluid networks. The second decrease of the diffusivity (corresponding to the secondary percolation threshold) would coincide with the loss of the fluid connectivity.

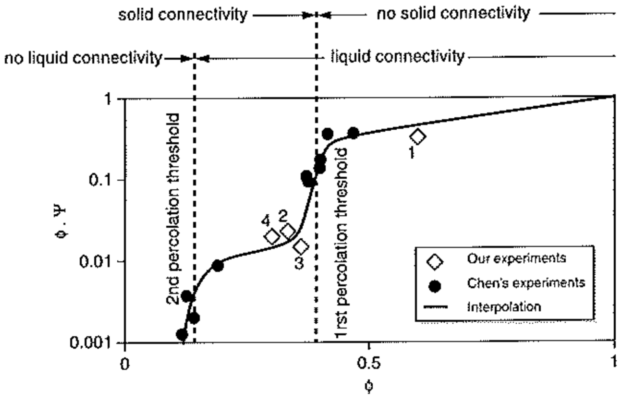


Figure 6

Variation of ($\phi \cdot \Psi$) versus ϕ of the medium.

TABLE 4

(Porosity·diffusivity) versus porosity

Experiment	ϕ	$\phi \cdot \psi$
1 (C1)	0.6	0.37
1 (C2)	0.6	0.32
2 (C1)	0.33	0.021
2 (N_2)	0.33	0.019
3 (C1)	0.37	0.015
3 (N_2)	0.37	0.014
4 (N_2 & C1)	0.3	0.019
Chen 1	0.396	0.138
Chen 2	0.467	0.376
Chen 3	0.414	0.364
Chen 4	0.399	0.172
Chen 5	0.374	0.102
Chen 6	0.371	0.119
Chen 7	0.141	0.002
Chen 8	0.117	0.001
Chen 9	0.127	0.004
Chen 10	0.191	0.009

The correlation between porosity and diffusivity (using the concept of percolation thresholds) enables us to predict the effective migration speed of gas molecules through a porous medium knowing the porosity of the medium.

2.2 Isotopic evolutions of hydrocarbon migrated gases

In the following section dealing only with hydrocarbon isotope interpretation, the term "source" corresponds to the isotopic value (carbon or hydrogen) of the initial introduced hydrocarbon gas. For experiment 2, no isotopic analysis has been made.

2.2.1 Carbon isotope

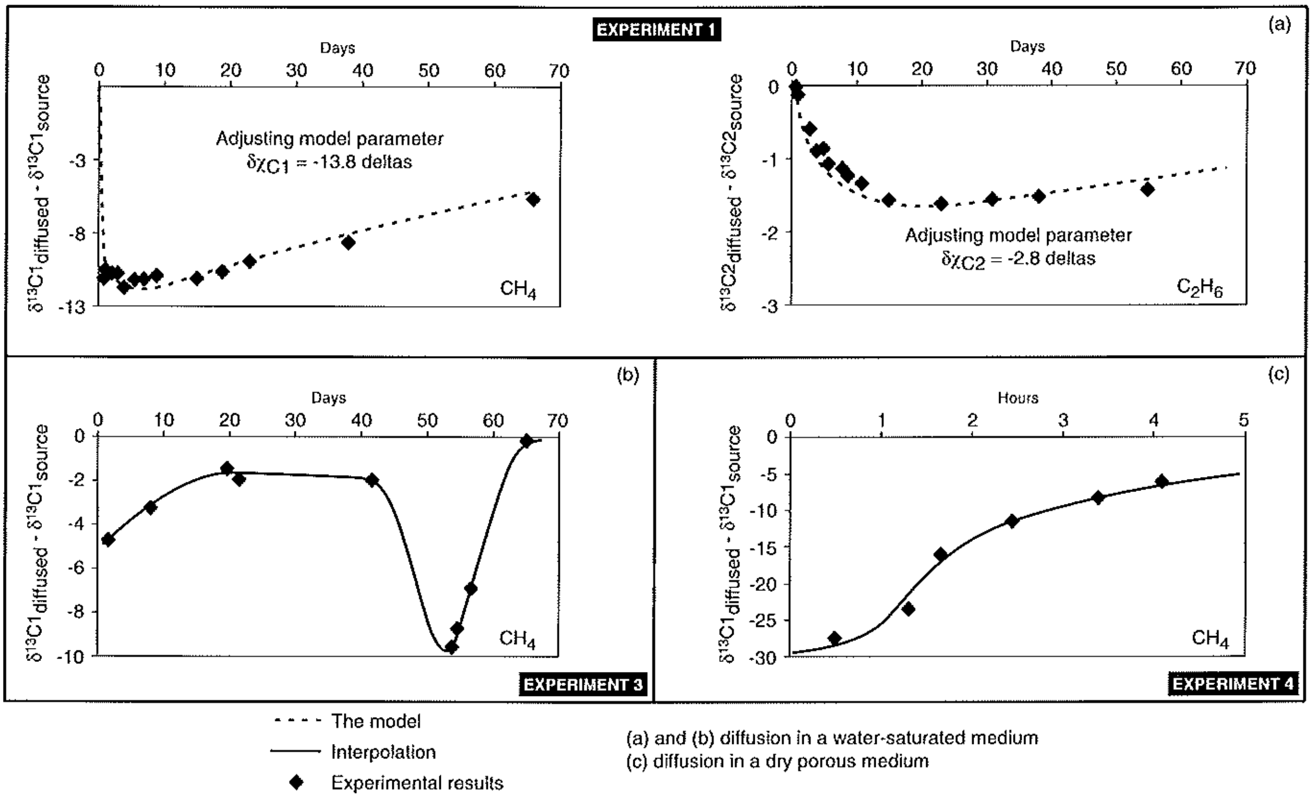
Figures 7a to 7c correspond to results of experiments 1, 3 and 4, respectively. They illustrate the carbon fractionations of diffused hydrocarbon gases as a function of time. From the migration speed value of the predominant isotope (^{12}C) obtained by fitting the "migrated gas production" curve, we calibrated the migration speed of the other isotope (^{13}C) in order to fit the curves on Figure 7. This permitted us to determine the migration isotopic fractionation of the gas species $\delta\chi_i$ (equations 2 and 3).

Water-saturated porous media (experiments 1 and 3)

Experimental data plotted on Figures 7a and 7b show that the carbon of diffused gases is always isotopically lighter than that of the source. Indeed, the carbon fractionation of methane changes by –5 to –11 deltas from the source as it diffuses through a water-saturated medium. The fractionation for ethane is –2 deltas. From the literature, such lightening of $\delta^{13}C$ of methane would be interpreted as the result of a mixing process between biogenic and thermogenic methane. Clearly our experiments present evidences in contradiction to the earlier postulate that no fractionation occurs during migration processes (Fuex, 1980). Each experiment will be examined in details in the following paragraph.

– *Experiment 1* (Fig. 7a): the carbon isotopic behavior of diffused methane and ethane can be attributed to the simple difference of isotope migration speeds as shown with the correct fit of the carbon isotopic evolution curves on the figure. According to the model, the carbon migration fractionations for methane and ethane are respectively $\delta\chi_{C1} = -13.8$ deltas and $\delta\chi_{C2}$ –2.8 deltas.

The two associated processes occurring during the gas molecule migration in the water-saturated medium are the solubility and the diffusion. In order to estimate the possible influence of the solubility process on the migration isotopic fractionation, a dissolution experiment of methane in water was performed. A bottle of methane under 60 bars was connected to a small metallic container filled with water (V = 1 cm^3). We waited for equilibrium (3 weeks) before isolating the metal container. Then, this container was connected to a vacuum line in order to sample, quantify and measure



(a) and (b) diffusion in a water-saturated medium
(c) diffusion in a dry porous medium

Figure 7

"Migrated hydrocarbon gas carbon isotopic fractionations" curves.

the $\delta^{13}C$ and δD of the dissolved methane in water. At first, the amount of dissolved methane (measurement 57 µmoles) in the volume of water (1 cm^3) was consistent with the theoretical solubility coefficient of methane at these *(P, T)* conditions. Secondly, no isotopic shifts (carbon and hydrogen) were detected between dissolved methane and the source. The solubility process does not seem to fractionate in a quantifiable way. Galimov (1975) and Fuex (1980) had once also performed dissolution experiments to measure possible isotopic fractionation. Their result slightly differed, as they measured a small but significant fractionation (Galimov: +0.2 deltas; Fuex: +0.4 deltas). This may be explained by the design of their experiment, where no equilibrium was reached and where they added a diffusional effect to the solubility effect.

In the absence of fractionation by solubilisation, equation (2) becomes:

$$\delta\chi_i = \left(\frac{^{a}D_{w,i}}{^{b}D_{w,i}} - 1\right) \times 1000 = \delta D_{w,i} \quad \text{in water-saturated medium} \qquad (5)$$

Instead of speaking about a migration fractionation, we introduce the notion of diffusion coefficient fractionation $\delta D_{w,i}$. It corresponds to the ratio between the effective diffusion coefficients of the isotopes.

As is well known, the fractionation of gases, generated during diffusion processes in a gaseous phase, depends upon the isotope masses (for instance the separation procedure for ^{235}U-^{238}U used by the nuclear industry). By considering gas molecules as punctual masses (ideal gas approximation), the coefficient of isotope separation is equivalent to the square root of their masses:

$$\left.\frac{^{a}D_{g,i}}{^{b}D_{g,i}}\right) = \sqrt{\frac{m_b}{m_a}} \qquad (6)$$

This would give about 30 per mil fractionation for two carbon isotopes of methane.

In aqueous solutions, the relationship is more complicated. According to Galimov (1975), the ratio of the diffusion coefficients to the square root of the reverse mass ratio is proportional:

$$\left.\frac{^{a}D_{w,i}}{^{b}D_{w,i}}\right) \approx \sqrt{\frac{m_b}{m_a}}$$

Looking at our experiment, a possible interaction of the methane molecules with water will increase the masses m_a and m_b and reduce the pure methane fractionation. This may be written, as water (apart from gas molecules) is the only possible mobile molecule in the porous medium:

$$\left.\frac{^{13}D_{w,C1}}{^{12}D_{w,C1}}\right) = \sqrt{\frac{m_{H_2O} + m_{^{12}C1}}{m_{H_2O} + m_{^{13}C1}}} = \frac{\delta\chi_{C1}}{1000} + 1$$

where m_{H_2O} is the mass of water structurally associated to a methane molecule. The numerical application of this formula is straightforward because we know all the other terms. We obtain: $m_{H_2O} = 19.48$, a mass approaching that of one water molecule (18). If we apply this formula to ethane diffusion, $\delta\chi_{C2} = -2.8$ deltas, we obtain that ethane diffuses in the water-saturated porous medium escorted by eight water molecules.

– *Experiment 3* (Fig. 7b): the interpretation of this experiment is more complex because two production phases are observed (see § 2.1.1, Experiment 3). Figure 7b shows that the migrated methane is lighter than the source from –5 deltas (at the beginning) to –2 deltas (at the end of the "slow" phase). Afterwards, a drastic increase of fractionation (until about –10 deltas lighter than the source) appears, which corresponds precisely to the beginning of the "fast" phase. This might be the result of the process of methane diffusion through preferential gas ways in the shale previously discussed in paragraph 2.1.

As we will see in the next paragraph, the diffusion of methane in a dry porous medium produces a significant isotopic fractionation.

Dry porous medium

– *Experiment 4* (Fig. 7c): in experiment 4, methane diffuses through the pore spaces of the dry medium. We obtain a large initial carbon isotopic fractionation, of about –30 deltas lighter than the methane source. In the course of the experiment, the carbon isotopic ratio of diffused methane nears toward the source value.

In fact, the initial fractionation represents the rate of the effective diffusion coefficients between the two isotopes, $^{12}C1$ and $^{13}C1$. A numerical application of equation (6), using the masses of $^{12}C1$ and $^{13}C1$ (16 and 17 respectively) gives a theoretical fractionation between the two isotopes as –29.9 deltas. It is interesting to note that the same value has been found experimentally.

Diagram $\delta^{13}C$ (diffused methane) – $\delta^{13}C$ (source) *versus F*

In order to compare the carbon isotopic behavior of diffused methane of the three experiments (1, 3 and 4), we have designed a diagram in which the difference between the carbon isotopic ratio of diffused methane and the source is plotted versus the progress (F) of experiment (Fig. 8). F is the ratio of the diffused methane to the final methane amount (when equilibrium is reached).

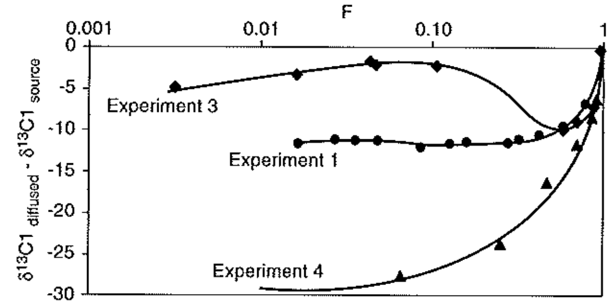


Figure 8

Comparison carbon isotopic fractionation of diffused methane between experiments 1, 3 and 4.

The most relevant information from this diagram, is at the beginning ($F \leq 0.1$) of the experiments 1 and 3. The discrepancy, between the initial isotopic fractionations (experiment 1: –11 deltas; experiment 3: –5 deltas) could result from an adsorption phenomenon, more important and visible during experiment 3. This may also be caused by the nature of argillaceous powder used, or by the different compaction of the clay membrane, which gives in experiment 3 a higher surface of contact between gas and clay (Table 1).

A similar trend of diffused methane at the ending of experiments 3 and 4 (superimposition of the two curves) is noted. This confirms the hypothesis of bi-diffusion during the "fast" phase of experiment 3.

2.2.2 Hydrogen isotope

Figures 9a to 9c correspond to experiments 1, 3 and 4, respectively and illustrate the hydrogen isotopic fractionation of diffused hydrocarbon gases as a function of time.

At first glance, the isotopic fractionation of the hydrogen of diffused gas appears to be more complex than for the carbon fractionation. As a matter of fact, the model cannot correctly fit the curves, as the δD values of diffused methane cross the source value. Therefore, the hydrogen fractionation of diffused gases involves other processes not well understood, and does not seem to be only a result of solubilisation and diffusion.

Water-saturated porous media

– *Experiments 1 and 3:* for the two experiments 1 and 3 (Fig. 9a and 9b), we observe a similar isotopic trend of the hydrogen of diffused methane: an initial heaviness of about +30 deltas then, in the course of the experiments hydrogen becomes lighter than the source.

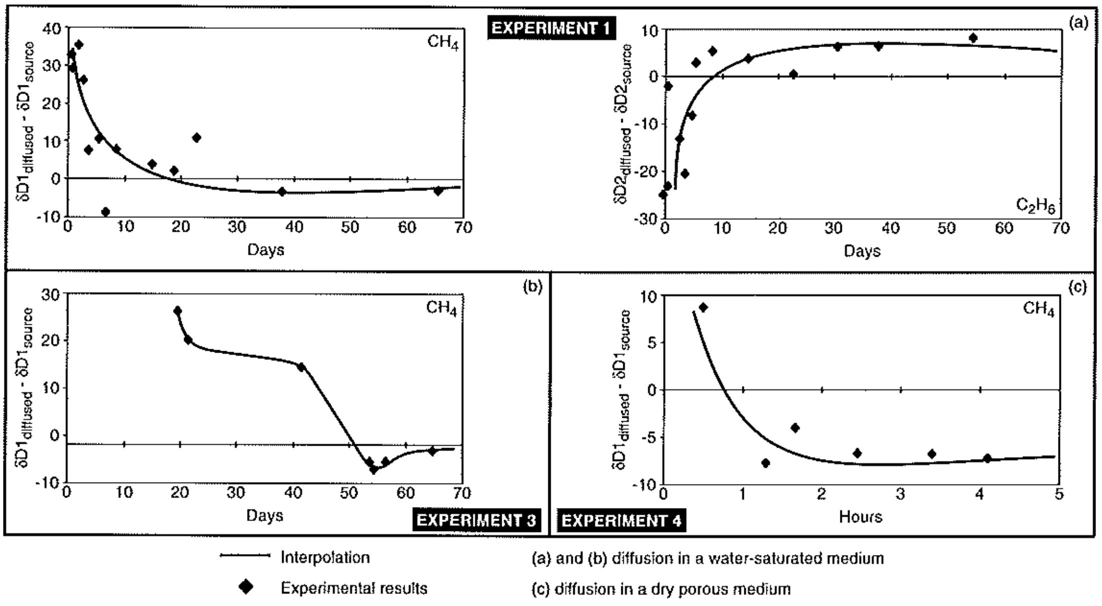


Figure 9

"Migrated hydrocarbon gas hydrogen isotopic fractionation" curves.

The comparison between carbon and hydrogen behavior of diffused methane indicates, at the beginning of the diffusional process, an opposite fractionation trend: diffused carbon is lighter than the source, whereas hydrogen is heavier. A similar opposite isotopic fractionation was observed during adsorption phenomena of methane on coal: the carbon isotopic fractionation of adsorbed methane was studied by Lebedev and Syngayevskiy (1971), Colombo *et al.* (1970), and Friedrich and Jüntgen (1972) whereas Constabaris *et al.* (1960) noted the opposite isotopic behavior of hydrogen.

In Figure 9a, we see that ethane δD values exhibit an opposite isotopic behavior than methane.

Dry porous medium

– *Experiment 4 (Figure 9c):* methane diffusing through the dry porous medium behaves for hydrogen isotopically in the same fashion than methane diffusing in water saturated medium: an initial heaviness then a lightness.

Diagram δD (diffused methane) – δD (source) *versus F*

Figure 10 represents the hydrogen fractionation of diffused methane ($\delta D1_{diffused} - \delta D1_{source}$) versus the progress of the experiments. The superimposition of the three curves (experiments 1, 3 and 4) indicates a similar process operating in the hydrogen isotopic fractionation. From the fact that the wetness or dryness of the porous medium does not seem to act upon the hydrogen behavior, we conclude that water does not play a major role in the hydrogen isotopic segregation of diffused methane. Apart from water, the porous medium is constituted by argillaceous grains.

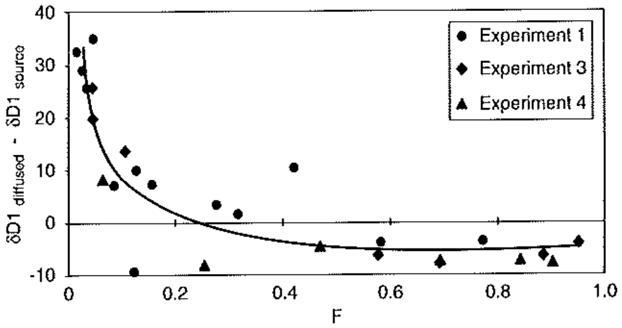


Figure 10

Comparison hydrogen isotopic fractionation of diffused methane between experiments 1, 3 and 4.

Therefore, we suggest that the hydrogen fractionation results from some interactions with the solid.

The initial heaviness of hydrogen of diffused methane appears as the most consistent observation. As the electronic cloud of deuterium is smaller than the ^1H electronic cloud, CH_3D would interact less than CH_4 with the solid of the porous medium.

CONCLUSION

Our experiments show that the migration of gases by diffusion through a dry or wet porous medium induces significant isotopic segregations. Whatever the diffusional phase, diffused gases are always enriched in ^{12}C.

Indeed, methane diffusing through a dry porous medium is affected by a large isotopic fractionation of –30 per mil. In water-saturated conditions, gas migrates by solubilisation and diffusion in an aqueous phase. As solubilisation induces negligible fractionation, the only mechanism of isotopic separation is the diffusion. The isotopic fractionations observed for methane in the course of water-saturated experiments (–11 and –5 per mil) even though highly significant, is smaller that in dry experiments. This is interpreted as the result of the migration of the gas linked to variable amounts of water molecules. Moreover, if the porosity of the medium is small, some retention phenomena caused by the solid may have an effect on the mobility of this migrating molecular system.

Concerning the hydrogen isotopic data, the heaviness of diffused methane may result from a higher speed of CH_3D molecules as their sizes are smaller than CH_4's ones.

In any event, the diffusion as a migration process through sedimentary rocks involves a significant modification of the original isotopic signature of methane. This means that the isotopic signature of methane in a field is not always linked directly to the chemical mechanisms of its genesis. To illustrate this fact, we have plotted in a (δD1 versus $\delta^{13}C1$) diagram our isotopic results of diffused methane (Fig. 11). From a thermogenic source, methane affected by diffusional processes presents an isotopic signature in the range of biogenic or mixed biogenic-thermogenic gases. The isotopic composition of methane cannot be used as a criterion of genetic charaterization of natural gases on account of its possible variability resulting from post-genetic processes. We consider that a better characterization of natural gases should first involve the chemical and isotopic study of the $C2_+$ fraction, as suggested by Prinzhofer and Huc (1995), and quantified by Lorant *et al.* (1996). This first study would give reliable information on the genetic processes, without any significant post-genetic fractionation. Methane isotopic signatures would then be useful to deconvoluate the possible biogenic and post-genetic events, as its thermogenic characterization would be deduced from the $C2_+$ study.

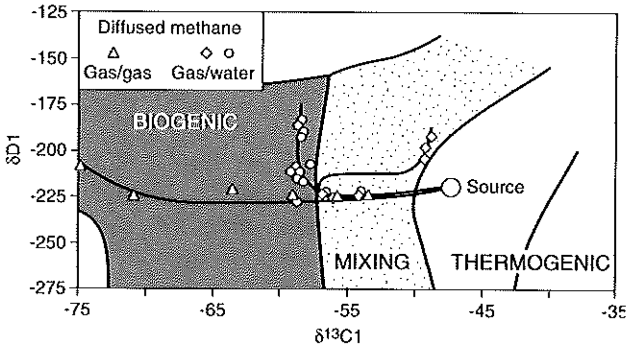


Figure 11

Experimental isotopic results of the diffused methane plotted in a (δD1 versus $\delta^{13}C1$) diagram of "genetic characterization" of natural gases.

To conclude, we should keep in mind that gas accumulations are dynamic systems on spatial as well as time scales. For this reason, the various isotopic signatures of hydrocarbon gases should be considered as the results of kinetic and physicochemical processes which take place either near the source rock (genetic mechanisms) or in the reservoir (post-genetic phenomena).

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