Carbon isotope effects of methane transport through Anahuac Shale —a core gas study

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Abstract

Compositional data and stable isotope ratios are critical datasets for the study of hydrocarbon generation, expulsion, and migration. These geochemical parameters are also important for studies of leakage detection for geological carbon sequestration. Diffusion, gas-liquid partitioning and adsorption, the three most crucial processes to affect gas transport through shale and other low-permeability formations, are known to cause stable isotope fractionation. A considerable number of studies have been conducted on stable isotope fractionation associated with diffusion and gas-liquid partitioning. However, significantly fewer data are reported in the literature that specifically address adsorption carbon isotope effects. Moreover, adsorption isotope effects are rarely verified or seldom demonstrated in geologic systems. In this study, a shale core taken from the Anahuac Formation in Texas Gulf Coast, which overlies several Frio reservoirs, was analyzed for composition and stable isotope ratios of the residual gas. These

geochemical parameters are used to identify gas migration and associate transport mechanisms in the caprock formation. Gas samples extracted from the core contain alkane gas components (C1–C5) and show a systematic variation in carbon isotope ratios of methane along depth. An analytical model is proposed to interpret the observed carbon isotope trend on the basis of coupled processes of diffusion and adsorption. At a ratio of retardation of 0.99 between $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ (with $^{12}\text{CH}_4$ having a preferential bonding with the clay mineral) and a diffusion time of 1.5 Ma, the modeled curve fits well with observed upward increasing $\delta^{13}\text{C}_{\text{CH}_4}$ values. This study demonstrates the isotope effect of adsorption in a natural system and its importance in quantifying gas-migration rate and distance in low-permeability systems.

1. Introduction

Gas migration in shale and interactions between gas and rock components have significant implications for hydrocarbon expulsion and trapping. Hydrocarbon gas composition and its stable isotope ratios are important parameters that may be used to identify gas sources and migration pathways. Diffusion of a gas phase causes isotopic fractionation because the lighter isotopologues have a higher diffusivity compared to heavier isotopologues as a result of the reduced mass coefficient. The higher diffusivity of ^{12}C -methane compared to ^{13}C -methane, therefore, will result in a partitioning of the methane isotopologues and a diffusive front enriched in ^{12}C -methane will develop (e.g., Gunter and Gleason, 1971; Klimenko, 1976; Syngayevsky et al., 1978; Krooss and Leythaeuser, 1988, 1992; Pernaton et al., 1996; Prinzhofer and Pernaton, 1997). Diffusion experiments have demonstrated that the carbon isotope value of methane can be shifted up to 30‰ lower than the starting source of methane (Colombo et al., 1965, 1966; Syngayevsky et al., 1978; Fuex, 1980; Bondar, 1987; Pernaton et al., 1996; Prinzhofer and Pernaton, 1997). Both dry (Pernaton et al., 1996; Prinzhofer and Pernaton, 1997) and water-saturated shales (Zhang and Krooss, 2001) are capable of causing large carbon isotope fractionation during methane diffusion.

Transport models of isotope fractionation caused by gas diffusion are described by various authors (Zhang and Krooss, 2001; Schloemer and Krooss, 2004; Richter et al., 2006; Xia and Tang, 2012).

In addition to diffusion, gas adsorption onto clay minerals and organic matter can also lead to stable isotope fractionations. Unfortunately, very few experimental data are published that quantify adsorption carbon isotope effects for methane at temperatures relevant to reservoir conditions (Van Hook, 1967). Although several studies have documented adsorption isotope effects over a range of temperatures for deuterium substitution in methane (Bruner et al., 1966; Di Corcia and Liberti, 1970), only two studies have been identified that address potential chromatographic separation of $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ methane (Gunter and Gleason, 1971; Fuex, 1980). Both studies qualitatively identified inverse-isotope effects associated with adsorption onto dry chromatographic substrates, whereby the lighter $^{12}\text{CH}_4$ preferentially adsorbs to the substrate, thereby enriching the chromatographic front with $^{13}\text{CH}_4$. The experimental results of Fuex (1980) were conducted on a highly polar chromatography column (Porapak N, Waters Associates) that has a low affinity for adsorption of the nonpolar polar methane. With this column, Fuex (1980) measured a small 1.0‰ carbon isotope fractionation when he collected the first third of the methane chromatographic peak. Gunter and Gleason (1971) conducted a similar experiment using a more methane-sorptive 13A molecular sieve and measured much larger 10‰ carbon isotope fractionations for methane as a result of adsorption. It is difficult to compare these results for natural samples, although the suggestion is that adsorption may have only a small carbon isotope effect with an adsorption preference for the lighter $^{12}\text{CH}_4$ methane isotopologue. Even though chromatographic column separation of methane isotopologues is an extreme example of potential isotope effects because of the high surface areas and dry nature of the experiment compared to hydrated or water saturated geological substrates in nature, it demonstrates that an adsorption isotope effect may occur. Xia and Tang (2012) developed a continuum flow model coupling adsorption/desorption and diffusion processes to simulate isotope fractionation of natural gas related to transport in coal and shale. Several field studies have documented carbon isotope

fractionations between dissolved and adsorbed methane in near-surface rocks (e.g., Kettel, 1996). Their results show preferential $^{12}\text{CH}_4$ adsorption onto rocks with low permeability and high surface area. However, other studies that looked at surface methane fluxes found no evidence of isotope fractionation caused by adsorption (e.g., Klusman et al., 2000a; b). In cases of rapid transport or a high flux of light hydrocarbons from a reservoir to the surface, stable carbon isotope ratios for methane are believed to remain unchanged (Coleman et al., 1977; Klusman and Saeed, 1996).

Carbon isotope fractionation may also result from dissolution of gas-phase methane into an aqueous phase. The field-based study of Galimov (1967) attributes carbon isotope fractionation of methane (1‰ increase in $\delta^{13}\text{C}$ of methane over a 12 kilometer transport distance) to a preferential dissolution of $^{12}\text{CH}_4$ into water compared to $^{13}\text{CH}_4$. However, a later study by Harting et al. (1976) suggests that $^{13}\text{CH}_4$ has a higher solubility than $^{12}\text{CH}_4$ (by 0.06% at 293 K). Based on this study, a small yet measurable carbon isotope fractionation (+0.05%) was predicted resulting from different solubility (Bacsik et al., 2002).

In this study, we measure the gas composition and carbon-isotope ratios of methane in a newly acquired shale core directly overlying a gas reservoir in order to investigate potential gas migration and resulting carbon isotope effects. The objectives of this study are to (1) identify any evidence of historical natural gas migration in a shale formation and (2) determine gas-migration mechanisms on the basis of core gas composition and carbon isotope ratios.

2. Field geology and samples

The Frio Formation was deposited during the Oligocene as high volumes of sediment infill accumulated in the Gulf of Mexico through four delta systems (Galloway et al., 2000; Galloway, 2002, 2008).

Regional transgressive flooding occurred in the late Oligocene, the rate of sediment supply and accumulation decreased and the Frio depositional cycle terminated. The Anahuac marine shale was deposited across the Gulf margin after the termination of Frio depositional cycle. In downdip areas, the Anahuac Shale onlaps the Frio Formation and is overlain by progradational sandstones of the lower Miocene (Galloway et al., 1982a).

Core samples analyzed in this study were obtained from a 9.23-m (30.5-ft) shale core that was collected near the bottom of the Anahuac Formation from an oil field north of Lavaca Bay, Texas (Fig. 1). In the study area, the Anahuac Shale overlies a sand-rich axis of the aggradational Frio Greta barrier-strandplain system. Frio strata consist of several cycles of progradation that are separated by a transgressive marine shale, and are finally overlain by the Anahuac Shale.

Depth of the core ranges between 1488.95 and 1498.24 m. The top of the Anahuac Formation and the *Marginulina* Sand, the first underlying gas reservoir, are at 1389.28 m and 1519.12 m, respectively. The core is ~20.9 m above the top of the *Marginulina* reservoir. The core interval occurs at the beginning of a transgressive stage and contains dark-grey claystone and silt-rich claystone interbedded with very fine grained sandstone laminations, beds, and lenses locally (Fig. 2). It contains abundant fossils, erosive bases, ripple laminations, dewatering structures, and soft deformation features, and it is heavily bioturbated in places (Fig. 2). The core contains numerous elongated (up to 10-cm) dolomite/siderite nodules, most of which are present in the upper half of the core. Eleven core segments (~12 cm long) of claystone and silty claystone were selected from the core for various analyses.

3. Methodologies

The shale core was retrieved and immediately sealed in plastic bags after being removed from the core barrel in the field. Eleven core segments of ~12 cm long were then selected and subsampled from the core. These subsamples were wrapped in plastic film and aluminum foil and then dipped in melted wax three times to obtain a desirable seal before being transported to the laboratory. Air-tight IsoPak bags provided by Isotech Laboratories Inc. were used to capture evolved gas from the core specimens after the wax-preserved core samples were unwrapped and crushed. Approximately 200 cm³ of core chips from each sample was transferred into the IsoPak bags. Extra air was squeezed out of the bag by submerging the sample bag in water. Then the bags were quickly sealed by a dual-durometer field clip and three heat seals. After 2 days of degassing and equilibration, gas samples were extracted using a syringe through septa built into the IsoPak bags. The gas samples were analyzed by for composition and carbon isotope ratio of methane. Mineralogy and petrography of the rock samples were analyzed using X-ray diffractometer (XRD) and scanning electron microscope (SEM). Mercury intrusion capillary tests were conducted to provide pore throat size distribution and estimate porosity and permeability. The property of the organic matter in the samples was characterized by Rock-Eval pyrolysis.

3.1. Gas composition (GC)

Gas extracted from the IsoPak bags was analyzed using gas chromatography (Agilent Technologies GC system 7890A) to measure concentrations of C1–C5, CO₂, CO, H₂, N₂, O₂, and He. Each gas sample is a mixture of a small amount of intrinsic core gas and a larger amount of air left in the sample bags. Therefore, the major components of air such as nitrogen (N₂) and oxygen (O₂) constitute most gas samples. In the results, N₂ and O₂ concentrations were subtracted, and the rest of the component concentrations were normalized to 100%.

3.2. Carbon-isotope ratios

Carbon isotope ratios from methane evolved from shale samples in the IsoPak bags were measured using compound-specific isotope ratio mass spectrometry (IRMS). Briefly, methane was isolated from other gases and combusted to CO₂ in a 750°C reactor packed with copper oxide. Water generated from combustion was removed using a –20°C ethanol slurry trap, and CO₂ produced from the combusted methane was quantitatively collected on a liquid nitrogen (LN) cryotrap on a ThermoElectron GasBench II[®]. Prior to analysis, the LN trap was heated and the eluted CO₂ was further purified using a Nafion[®] water trap and a 25- × 0.32-mm Chrompak PoraPlot Q[®] fused silica GC column. Peak areas for CO₂ were measured for masses 44, 45, and 46 using a ThermoElectron[™] MAT 253 fixed-cup IRMS. An independently calibrated methane standard was also measured using the identical apparatus over a range of peak areas to account for potential analytical linearity. All reported sample peak areas were collected within a stable peak area range in which peak area–carbon-isotope linearity effects are insignificant. Carbon-isotope ratios are reported in standard per-mille notation with respect to $\delta^{13}\text{C}_{\text{vpdb}} = +1.95\text{‰}$ for NBS-19 calcite. Analytical precision for replicate sample analyses averaged $\pm 0.2\text{‰}$, which is consistent with replicate analyses of our internal methane standard over a range of concentrations that bracket the concentrations of actual samples.

3.3. X-ray power diffraction (XRD)

Bulk mineralogical analyses were conducted on 11 core samples using a random-powder X-ray diffraction (XRD) method. Samples were prepared following the procedures outlined in Hillier (1999). Core samples were disintegrated using a TEMA ball mill prior to wet grinding using a McCrone Micronizing Mill. The resulting slurry was sprayed through the heated chamber of a spray drier, and the dried powders were collected at the bottom of the chamber. XRD patterns were collected on a Bruker AXS D8 diffractometer and quantitative XRD analysis was conducted using Topas 3, a PC software program that is based on the Rietveld method (Bish, 1994). XRD analytical parameters can be found in Lu et al. (2011).

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167 Oriented slide samples were prepared on <2-μm clay-size fractions. Clay particles were deposited on
168 paper filters and mounted onto glass slides using a filter transfer method so that highly oriented
169 specimens could be obtained (Moore and Reynolds, 1997). Oriented slide samples were scanned from 4°
170 to 40° 2θ, accounting for 1.5 s per 0.015° step. Two separate scans were obtained for each sample: (1) in
171 an air-dried condition and (2) in an ethylene glycol-solvated condition. Detailed identification of clay
172 minerals in the clay-sized fraction was made following procedures given in Moore and Reynolds (1997).

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174 *3.4. Scanning electron microscopy (SEM)*

175 The argon-ion milling method was used to produce highly polished sample surfaces for SEM examination
176 so that nanometer-scale texture and pores might be resolved (Loucks et al., 2009). Polished sample blocks
177 were coated with 4-nm-thick iridium and examined using a field-emission SEM, an FEI Nova™
178 NanoSEM 430. Element distribution was mapped by two energy-dispersive X-ray spectroscopy (EDS)
179 detectors. EDS maps are rendered as false color images overlying SEM images to show chemical
180 composition, which indicates mineralogy.

181

182 *3.5. Mercury intrusion capillary pressure (MICP)*

183 Samples were analyzed using a Micrometrics AutoPore IV Mercury Porosimeter. Mercury intrusion
184 curves were obtained at pressure increasing to as much as 413 MPa (59,972.5 psi). Permeability is
185 estimated using the following equation (Swanson, 1981):

$$186 \quad K_{Calc.} = K_{air} = 399(S_b/P_c)_{max}^{1.691} \text{ (md)} \quad (1)$$

where S_b (mercury saturation) is the maximum value of the ratio of mercury saturation/mercury capillary pressure in pounds per square inch absolute (psia).

3.6. Rock-Eval pyrolysis

Eleven samples were analyzed for total organic carbon (TOC) content and Rock-Eval (RE) pyrolysis parameters at GeoMark Research Ltd. The RE pyrolysis method involves gradual heating of a small rock sample (Lafargue et al., 1998; Carrie et al., 2012). During the progressive heating process, three major pyrolysate fractions are obtained: (1) S1—the quantity of free hydrocarbon (mg hydrocarbons/g sample) in rock volatilized at 300 °C for 3 minutes, (2) S2—the quantity of heavier hydrocarbons derived from kerogen released between 300° and 550 °C at 25 °C/min, and (3) S3—CO₂ released from thermal cracking of kerogen between 300° and 390°C. On the basis of these parameters, the hydrogen index ($S2/TOC \times 100$) and the oxygen index ($S3/TOC \times 100$) can be determined so that properties of the organic matter can be assessed.

4. Results

4.1. XRD Mineralogy

Major clay minerals in the samples include discrete illite (average 31%), mixed-layer illite/smectite (average 18%), and kaolinite (average 10%) (Table 1). Total clay content varies between 52% and 68%, averaging 59% (Fig. 2). XRD analyses on clay-size fractions show that mixed-layered illite/smectite is R0 ordering with 10–30% of illite. Quartz, K-feldspar, plagioclase, and calcite are the other major mineral phases. Quartz content ranges from 11% to 19% (average 16%). XRD data of clay-size fractions show considerable amounts of quartz, suggesting that a large proportion quartz is clay size. Calcite abundance ranges from 5% to 11%, with an average of 8%. Pyrite is present in all samples, with a consistent abundance of between 2% and 3%.

4.2. Petrography and pore imaging

Backscattered secondary electron (BSE) images were acquired for documenting texture and differentiating mineral composition. EDS maps, which use false color to indicate presence of each element, were also obtained to overlap with SEM images. BSE images provide revealing information for lithologic and petrographic analyses (Fig. 3). Samples analyzed in this study with BSE and EDS generally contain abundant clay minerals and clay-sized particles with varying amounts of silt grains (Fig. 3). Besides the major clay minerals identified by XRD and SEM (illite, illite/smectite, and kaolinite), small amounts of chlorite were also detected by EDS analyses as matrix and silt-sized particles. Quartz, calcite, potassium feldspar, and albite make up most of the silt grains (Fig. 3). Calcite occurs mostly as shell fragments, foraminifera, and other fossils. Most calcite grains show severe dissolution pits and cavities (Fig. 3b, c), and calcite cements were occasionally observed as pore-filling minerals in fossil chambers (Fig. 3d). Pyrite is ubiquitously present in forms of framboids and, to lesser degree, single crystals (Fig. 4c, d). Trace amounts of anatase and dolomite were also observed. Dolomite usually occurs as rhombs tens of micrometers in size (Fig. 3b, d).

Degree of fabric alignment is generally higher in clay-rich samples. Silt grains in silt-rich claystone are usually less well aligned with direction of bedding and lamination (Fig. 3c, d). Abundance of silt grains varies on centimeter scales between beddings and laminations.

SEM images obtained from the ion-milled samples show texture and pores on a nanometer scale. Burial depth of the shale core is 1.5 km and therefore it is less compacted than those more deeply buried gas shales (e.g., Loucks et al., 2009, 2012; Milliken et al., 2012). Pores are abundant and large (up to tens of micrometers). Large primary pores are generally concentrated around rigid silt grains, especially when several large grains are in contact with one another (Fig. 4a). These pores are usually angular and are protected from compaction by the rigid silt particles (Schneider et al., 2011; Milliken et al., 2012).

Another major type of primary pore occurs as linear remnant space between clay platelets (Fig. 4b). These pores are up to several micrometers in length with apertures are on the order of nanometer widths.

Secondary pores that formed by calcite dissolution are common in calcareous shell fragments (Fig. 3b, c, 4c). These dissolution moldic pores, up to several micrometers in diameter, are highly concentrated in some fossil fragments. Body-cavity pores as primary fossil chambers are another important type of pore (Fig. 3c, d, 4d). Their diameters can reach over 10 micrometers, depending on the size of the faunal fossil grains. However, these large pores are generally isolated in fossil fragments by the surrounding clay matrix. Connectivity between pores appears limited by the pore network in the matrix.

4.3. MICP pore-size distribution and permeability

MICP results show that porosity of samples ranges from 7.3% to 15.8% (Fig. 5). The relatively high porosity is consistent with SEM observations. Permeability estimated from mercury-intrusion curves varies from 0.0006 to 0.0026 mD (Fig. 5).

Most samples show symmetric pore-throat size distribution and a similar size range (Fig. 6). Their modal pore-throat size is similar within a narrow range of 18–28 nm, although the SEM study shows abundant micrometer-sized pores in some samples. Apparently these larger pores around and within silt-sized particles are mostly isolated by the clay matrix or connected only by the small pore throats in clay matrix. Although local porosity can be high owing to preservation of primary pores or mineral dissolution, overall connectivity and accessibility of the large pores are limited by the nanopore system in the clay matrix.

4.4. Organic-matter characterization

TOC content is consistently low (<0.4%) in all samples (Fig. 2). Owing to the low TOC, only one sample yielded a T_{max} value of 430 °C, which indicates low maturity (below the oil-generation window). The

oxygen index is high, ranging from 125 to 232, whereas the hydrogen index is low (between 26 and 74) (Fig. 7). These indicators suggest that organic matter consists mostly of gas-prone Type III kerogen. No consistent correlations between organic-matter properties and depth can be seen. Free hydrocarbons released from the samples (S1) are low (average of 0.05 mg HC/g). Both TOC content and S1 show no correlation with depth (Fig. 2).

4.5. Gas Chromatography and carbon isotope analysis

GC analyses show that gases extracted from core shale samples in the IsoPak bags are composed mostly of methane, ethane, propane, i-butane, n-butane, and i- and n-pentane. No other components (CO₂, CO, H₂, or He) were detected (Table 2). Methane is the most abundant alkane with absolute concentration ranging from 24.7 to 294.6 ppm (average 69.7 ppm). i-butane is the second-most-abundant component (average 23.6 ppm), followed by propane (average 18.7 ppm). Concentrations of alkanes are much smaller in air than in core gas. For example, CH₄ concentrations in air are <2 ppm. Thus, the effect of mixing with the same gases present in air can be ignored in the context of this discussion.

Relative gas compositions for the gas equilibrated from the core samples after subtraction of air show large variations, such as 26.3%–69.9% of methane, 5.4%–12.5% of ethane, 5.2%–18.9% of propane, and 7.9%–22.8% of i-butane (Table 2). Such variations are large, given the small depth range in the core.

Carbon isotope compositions of methane across the core vary between –36.6‰ and –25.6‰ (Table 3). Plotted with respect to depth, $\delta^{13}\text{C}$ values show an upward-increasing trend (Fig. 8). The $\delta^{13}\text{C}$ values of the upper six samples have an average of –29.1‰, compared with –34.4‰ of deeper samples.

One gas sample was collected from the *Marginulina* reservoir, which immediately underlies the Anahuac Formation. This reservoir sample contains much higher percentage of methane (96.1% of the gas total, Table 2) than the caprock samples. Other minor components detected include ethane, propane, butane,

CO₂, and N₂. The carbon isotope composition of methane in this reservoir gas is −41.9‰, which is 5.8‰ lower than the lowest value of Anahuac core gas (Table 3). Gas samples from two other production wells that produce from the deeper *Greta* reservoir have similar carbon isotope ratios (−41.5‰ and −40.2‰). The *Greta* sandstone is ~30 m deeper than the *Marginulina* sandstone in the area, and they are separated by transgressive-marine shale 6–10 m thick.

5. Discussion

5.1. Sampling procedure

In this study, we define two potential types of gas in the shale caprock samples that may contribute to the total gas collected using the described gas collection method. One type is the ‘free’ pore gas that exists in interstitial pores between grains (*i.e.*, within the porosity). The second type is gas that is adsorbed to the surfaces of mineral and organic phases. It is not possible to distinguish between these two types since the gas sampling method used in this study is an equilibration technique that samples both the free pore gas and the surficially adsorbed gas. One concern is that any sampling procedure may affect the composition of the gas samples. For example, degassing of the core inevitably occurred as the core was extracted from the ground and pressure decreased, and as core samples were transferred, crushed, and loaded into the Isopak bags. Extreme caution was taken to minimize the exposure time of the core samples. The core was extracted to the surface and sealed in plastic bags for overnight transport to the laboratory facility and was exposed to air for <10 min for selection and wax preservation. Another exposure time of ~1 min occurred during transfer to the IsoPak sample bags. The short transfer times, coupled with the low permeability of the core, help minimize potential degassing. The low permeability of the core (0.6 to 2.6 μD) also makes it likely that the free gas trapped in the center of the shale core (diameter = 8.5 cm) would not have escaped through the tight matrix before the samples were crushed. The high concentration of alkanes collected in each IsoPak bag, and the correlation between carbon isotope value of methane and depth

suggests against significant sampling-induced distortion; however, we still caution that some amount of degassing may have occurred which could affect the reported stable isotope and compositional values. With regards to air contamination, the addition of alkanes from air is insignificant because concentrations in the samples are much higher than that of air (average >40 times greater). $\delta^{13}\text{C}$ of atmospheric methane varies seasonally within a small range of -47‰ to -48‰ (Quay et al., 1999), lower than those of core gas. Therefore, mixing with air would lead to a negligible decrease in $\delta^{13}\text{C}$ (average 0.5‰), which is not significant in context of this study and is not corrected in the results.

5.2. Source of core gas

Carbon isotope ratios of the core gas preserve a range of values between -36.6‰ and -25.6‰ (Fig. 8). Such a large difference in $\delta^{13}\text{C}$ is unlikely related to *in situ* methane production from organic matter for several reasons. Foremost, TOC in the core is consistently low, ranging between 0.22% and 0.29% (Fig. 2). Therefore, it is unlikely that significant accumulations of methane were produced *in situ*. In fact, only one sample contains sufficient organic matter to yield a T_{max} measurement of 430 °C in RE pyrolysis, suggesting maturity lower than the oil-generation window. Additionally, the quantity of free hydrocarbons (S1) measured by RE pyrolysis are low (average 0.05 mg HC/g) (Fig. 2), suggesting that the amount of hydrocarbon gas generated from *in situ* organic matter is limited.

The following two lines of evidence also argue against the large range in $\delta^{13}\text{C}$ being related to *in situ* methane production. The $\delta^{13}\text{C}$ of produced methane is dependent on the temperature of formation (*e.g.*, Schoell, 1983, 1984; James, 1990) and the $\delta^{13}\text{C}$ value of the source organic material (*e.g.*, Deines, 1980; Schoell, 1984; James, 1990). The small depth interval of the core ($\sim 9\text{ m}$) corresponds to a temperature difference of only $\sim 0.3\text{ °C}$ (Loucks et al., 1984). This temperature difference across the core interval is too

small to cause significant variations in methane carbon isotope value associated with organic maturity. The organic matter in the core consistently shows Type III characterization (Fig. 7), suggesting that the carbon isotope composition of the organic material should be consistent across the core interval. These observations along with the fact that there is no correlation between observed methane $\delta^{13}\text{C}$ values and sedimentary features, organic matter properties (TOC, S1, hydrogen index, and oxygen index), methane content, mineral composition, or clay abundance (Figs. 2, 7, and 9), strongly argue against the observed methane $\delta^{13}\text{C}$ values being related to variations associated with *in situ* production. In section 5.3 we present an alternative hypothesis to explain the observed trends in $\delta^{13}\text{C}$ of methane across the core interval.

5.3. Gas-transport model in shale

An alternative hypothesis to explain observed variations in methane $\delta^{13}\text{C}$ values along the Anahuac Shale core is that the gas sampled from the core is sourced from the underlying Marginulina gas reservoir and has been transported across the core interval. Transport of gas through low permeability rocks, such as the Anahuac Shale sampled here, is dominated by diffusion but will be affected by adsorption onto mineral and organic surfaces and dissolution into and exsolution out of aqueous phases such as formation water.

In this section we develop an analytical model to describe observed methane carbon isotope trends with respect to distance from reservoir gas (*i.e.*, decreasing depth). In the development of this model we consider six possible processes that may affect methane concentrations and/or its carbon isotope value: 1) mixing of multiple sources of methane (*i.e.*, thermogenic and/or biogenic), 2) microbial degradation, 3) advection, 4) diffusion, 5) adsorption, and 6) partitioning into an aqueous phase. As discussed above, the low organic content of the shale suggests that addition of *in situ* thermogenic methane across the shale caprock is unlikely. The addition of biogenic methane is also unlikely; biogenically derived methane is typically more depleted in ^{13}C than thermogenic methane (Whiticar et al., 1986; Schoell, 1988; Whiticar,

1990) and has correspondingly lower $\delta^{13}\text{C}$ values (*i.e.*, $< -50\text{‰}$). Because the carbon isotope values of methane in the shale caprock are greater than those of the gas samples collected from the underlying reservoirs, addition of biogenic methane could not explain the observed trends. For these reasons, the developed analytical model does not include mixing of multiple methane sources. Microbial degradation through methanotrophs, if active, will preferentially consume isotopically lighter methane and the residual methane will have a greater $\delta^{13}\text{C}$ value than the initial methane (Fuex, 1977; Coleman et al., 1981; Klusman et al., 2000a). Although microbial degradation of methane in the caprock could cause the $\delta^{13}\text{C}$ values of methane to be greater than the starting reservoir methane $\delta^{13}\text{C}$ value, we did not observe a trend whereby the concentration of methane decreased systematically with increasing $\delta^{13}\text{C}$ values of methane, as would be expected during active microbial degradation (Fig. 9). Also, the concentration of the oxidation product, CO_2 , is not elevated in the gas samples. We therefore do not include microbial degradation in our analytical model. The permeability of the shale is lower than 0.005 mD (Fig. 5), and therefore transport of methane is likely to be dominated by diffusion rather than advection. We therefore do not include advection in the model. Instead, we develop an analytical model that includes diffusion, adsorption and partitioning into an aqueous phase to describe the observed carbon isotope trends in the shale caprock.

The carbon isotope mass transport model is based on an analytical solution to Fick's second law of diffusion. Results from this model are compared to results using the isotope-specific diffusion model and diffusion coefficients for methane in water-saturated sedimentary rock presented by Zhang and Krooss (2001). Importantly, the form of the equation described here is identical to the form presented by Zhang and Krooss (2001), providing a means to compare parameters governing the transport of methane under different conditions. The critical difference is that Zhang and Krooss (2001) calculate effective diffusion coefficients for $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ in a water saturated experimental column whereas the equation described

here couples and differentiates diffusion and adsorption carbon isotope effects. Crank (1956) presents a solution to Fick's second law of diffusion for a constant concentration step function as:

$$C(x, t) = \frac{1}{2} C_o \cdot \operatorname{erfc} \left[\frac{x}{2\sqrt{D \cdot t}} \right] \quad (2)$$

Whereby $C(x, t)$ is the concentration at x = distance from a boundary with an instantaneous constant concentration (C_o), t = time since injection, and D = effective diffusion constant. Equation 2 is valid under the following boundary conditions: $C(0, t) = 0$ at $t < 0$, $C(0, t) = C_o$ at $t \geq 0$, and $C(\infty, t) = 0$ for all t . Here, adsorption is defined as a physiochemical partitioning between methane and a solid substrate. Although adsorption in this sense may be non-permanent and temporary, the effect of adsorption is to retard the mass transport of methane through the shale. In consideration of carbon isotope adsorption effects, the retardation factor reported here is between two isotopologues of methane: $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. The retardation coefficient (R) characterizes the adsorption process and is incorporated into Equation 2 by dividing the diffusion constant by the retardation coefficient:

$$C(x, t) = \frac{1}{2} C_o \cdot \operatorname{erfc} \left[\frac{x}{2\sqrt{(D/R) \cdot t}} \right] \quad (3)$$

Equation 3 is an analytical solution to a coupled diffusion-adsorption model. Dissolution of methane, or any gas, into an aqueous phase during gas transport has an analogous effect as adsorption onto a solid substrate in that the process slows down, or retards, the transport of a gas. In this way, the adsorption of methane onto a solid substrate or its dissolution into an aqueous phase cannot be distinguished analytically, and instead are both incorporated into the retardation factor. R is therefore the ratio of retardation factors between $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$. These retardation factors have not been measured empirically or calculated theoretically for $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ on geologically relevant materials. What remains poorly understood is the direction of stable isotope fractionation due to adsorption or dissolution.

As related to methane there is an apparent inverse isotope effect whereby $^{13}\text{CH}_4$ methane has a higher solubility and therefore preferentially dissolves in water compared to $^{12}\text{CH}_4$ methane (Harting et al., 1976) whereas $^{12}\text{CH}_4$ methane is shown to preferentially adsorb onto solid substrates compared to $^{13}\text{CH}_4$ (Gunter and Gleason, 1971; Fuex, 1980; Kettel, 1996). Therefore, the direction of the retardation factor (*i.e.*, greater than or less than 1) will depend on the dominance of either adsorption or dissolution. Carbon isotope effects associated with mass transport of methane are modeled by solving Equation 3 for each applicable methane isotopologue. For example, $\delta^{13}\text{C}$ of methane is modeled by simultaneously solving Equation 3 for $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$. The concentrations of these two methane isotopologues are converted to standard $\delta^{13}\text{C}$ notation where $R_{\text{sam}} = (^{13}\text{CH}_4)/(^{12}\text{CH}_4)$ and $\delta^{13}\text{C} = (R_{\text{sam}}/R_{\text{std}} - 1) \cdot 1000\text{‰}$.

In this study, x is the distance from the reservoir top (or the bottom of the caprock), and t is the time since gas emplacement in the reservoir (start of upward diffusion). The actual time of hydrocarbon emplacement in the Frio reservoirs is poorly constrained due to the large thickness and depth ranges of the source rocks in the region (Galloway, et al., 1982b). We chose three possible scenarios of 1Ma, 1.5Ma and 5Ma emplacement. In this model, the concept of emplacement represents that time (t_o) at which methane began diffusing into the shale caprock. We apply the effective diffusion coefficient of $2.98\text{E}^{-12} \text{ m}^2/\text{sec}$ for methane in a water saturated shale that is calculated by Zhang and Krooss (2001). In their study, the effective diffusion coefficient is measured from a water saturated single phase core flood-style diffusion experiment using methane saturated water at 90°C and 9MPa . The ratio of the effective diffusion coefficients (D^*) are calculated empirically using a least squares regression through measured cumulative methane carbon isotope ratios of methane collected from water eluted from the diffusion experiment by Zhang and Krooss (2001) to be $D^*_{^{13}\text{CH}_4}/D^*_{^{12}\text{CH}_4} = 0.9969$. This ratio of effective diffusion coefficients is identical to the ratio obtained by solving the binary diffusion coefficients for $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ in air from Fuller et al. (1966) using the same atomic diffusion volume each methane isotopologues of 24.42 and molar masses (g/mol) of 16.04 for $^{12}\text{CH}_4$ and 17.04 for $^{13}\text{CH}_4$. It appears, therefore, that the

ratio of the diffusivities for $^{13}\text{CH}_4$ and $^{12}\text{CH}_4$ are independent of the medium that methane is diffusing through; the ratio of isotopologue diffusivities of methane in water is the same as in air.

Illustrated in Fig. 10, the effect of diffusion alone cannot explain the observed shift in methane carbon isotope values through the shale from the starting value preserved in the reservoir. Diffusion alone tends to enrich the front of the chromatographic breakthrough with the lighter $^{12}\text{CH}_4$ isotopologue, which is opposite to that observed. The preferential adsorption of $^{12}\text{CH}_4$ on the shale material compared to $^{13}\text{CH}_4$, however, does provide a mechanism that can explain the observed results by enriching the chromatographic front in $^{13}\text{CH}_4$. The difference in adsorption affinity for $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ is not known, but as a starting point it is reasonable to suggest a ratio that is similar in magnitude to that observed for differences in diffusion constants between these isotopologues. The three solid curves illustrated in Fig.10 are constructed using a retardation factor of 0.99, which is slightly farther from 1.0 than the ratio of the effective diffusion coefficients between $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ (i.e., 0.9969). More quantified experiments on methane isotopologues adsorption are required, but the results presented here, which include the apparent preferential adsorption of the lighter $^{12}\text{CH}_4$ isotopologue during diffusion dominated transport is consistent with the observations of Kettel (1996). The magnitude of the results presented here, however, with a nearly 15‰ increase in $\delta^{13}\text{C}$ is contradictory to the conclusions suggested by Fuex (1980) and Xia and Tang (2012). Although Fuex (1980) does show qualitatively similar results for adsorption isotope effects, it is pointed out that in natural settings, these types of effects are rarely observed. Xia and Tang (2012) call upon experimental work, but develop a model suggesting that adsorption isotope effects fractionate methane in the same direction as dissolution isotope effects.

Another implication of the data presented here is that it argues against a large flux of methane through the Anahuac Shale. If permeability were high in the Anahuac Shale and either a higher effective diffusion

coefficient or advection occurred, one would expect the adsorption isotope effect to be overwhelmed and a more consistent carbon isotope value of methane to be preserved through the core. Therefore, these data may be used to determine the integrity of the caprock. In high-integrity caprocks where the flux of gas is low, one could expect to preserve adsorption or diffusion isotope effects depending on the mechanism of transport. The Anahuac Shale, which is not as compacted as more deeply buried shales, did not sustain a high flux of methane from the underlying Frio reservoir. Shale/mudrock formations, even though they may not be highly compacted, can offer sufficient sealing capacity in terms of preventing large-scale gas leakage. Hydrocarbon seepages and other leakage features are likely associated with conduits along faults, fracture networks, or caprock discontinuity.

6. Conclusions

A shale core was retrieved from the Anahuac Formation so that the mechanism of gas transport from the underlying reservoir into caprock could be studied. The Anahuac Formation is the regional seal for underlying oil and gas reservoirs of the Frio Formation. The core depth interval is between 1488.95 and 1498.24 m, and the shale core has relatively high porosity (7.3%–15.8%). The core contains an abundance of clay minerals (average 59%), which leads to low permeability in the range of 0.0006 to 0.0026 mD. TOC content is low across the core interval (<0.4%). *In situ* hydrocarbon generation in the formation is limited because free hydrocarbons released from rock (S1) during RE pyrolysis analyses are low (average of 0.05 mg HC/g).

Gas samples extracted from the core show large variations in carbon isotope ratios of methane from –36.6‰ to –25.5‰. The $\delta^{13}\text{CH}_4$ values of core gas are significantly higher than those of reservoir methane (–41.9‰) and increase upwards in the core interval. No correlated variations in core petrography or mineralogy were observed. Organic-matter properties suggest against *in situ* gas generation. We propose

that gas was sourced from the underlying hydrocarbon reservoirs and has intruded into the caprock. Isotopic variations were caused by coupled processes of diffusion and adsorption onto clay minerals. An analytical model is presented that includes potential isotope effects from diffusion and adsorption. With a retardation factor of 0.99 between $^{12}\text{CH}_4$ and $^{13}\text{CH}_4$ in shale and a diffusion time of 1.5 Ma, the calculated curve of the carbon-isotope ratio fits the data well. This study also suggests that the rate of transport of methane is slow and the Anahuac Formation is a sufficient seal, although relatively shallow.

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622

623 **Table 1**

624 XRD mineral composition of core samples.

625 **Table 2**

626 Composition of shale-core gas samples and their relative compositions after subtraction of air components.

627 Also included, compositions of three gas samples from underlying Marginulina and Greta reservoirs taken

628 from three production wells in field. Reservoir gas samples taken from three different production wells in

629 field (A-349, A-315, and A-482).

630 **Table 3**

631 Carbon isotope ratios of shale-core gas and reservoir gas.

632

633

Captions

Fig. 1. (left) Maps showing well locations (red star) and (right) gamma-ray log of study well. Core interval = red line by log. Well surface location: latitude, 28.794667; longitude, -96.606481.

Fig. 2. Sedimentary log of study core plotted along with mineral abundance of clay (illite, I/S, and kaolinite) and quartz + feldspar (Q+F), TOC content, and S1 (free hydrocarbons) of rock-eval pyrolysis.

Fig. 3. Back-scattered electron SEM images overlaid with EDS maps. (a) Claystone containing abundant clay minerals and silt grains of quartz (blue) and K-feldspar (pink). Sample depth 1495.61 m. (b) Silt-bearing, clay-rich mudstone. Silt grains include quartz (blue), K-feldspar (pink), calcite fossil fragments (red), and diagenetic dolomite rhomb (green). Sample depth 1494.30 m. (c) Mudstone containing abundant silt-sized quartz (blue), K-feldspar (pink), and calcite fossils (red). Foraminifera chambers partly filled with pyrite framboids (yellow). Sample depth 1489.05 m. (d) Laminations of silt-rich mudstone (upper right) and claystone (lower left). Sample depth 1489.05 m.

Fig. 4. Secondary electron SEM images on ion-milled samples. (a) Primary pores around quartz grains. Note that long cracks are caused by sample dehydration. Sample depth 1489.05 m. (b) Pores between clay aggregates (arrows). Sample depth 1492.99 m. (c) Dissolution-moldic pores in calcite grain. Sample depth 1492.10 m. (d) Millimeter-sized-pores in foraminifera chambers partly filled with pyrite and clay (arrow). Sample depth 1492.10 m.

Fig. 5. MICP porosity and calculated permeability.

Fig. 6. MICP Pore-throat size distribution showing mostly symmetric distribution. Modal pore-throat size falls within narrow range of 18–28 nm.

Fig. 7. Hydrogen index (HI) versus oxygen index (OI) (pseudo van Krevelen diagram) showing “classical kerogen-type maturation pathways.”

Fig. 8. Carbon isotope ratios of methane versus depth.

657 **Fig. 9.** Methane concentraton and clay abundance in rock versus carbon isotope ratio of methane in gas
658 samples.

659 **Fig. 10.** Caculated curves of methane carbon isotope ratio along transport path from sandstone reservoir
660 into overlying caprock. Dashed lines from diffusion-only models and black lines = coupled diffusion and
661 adsorption models. Squares = shale-core gas samples and circles = reservoir gas samples.

662

Table 1

Sample No.	Depth	Quartz	Calcite	Plagioclase	K-feldspar	Illite	Kaolinite	Pyrite	Anatase	I/S	I/S composition
	m	%	%	%	%	%	%	%	%	%	
1	1489.05	18.6	9.9	4.1	11.9	27.6	9.4	2.4	0.6	15.7	R0 illite (0.2)/Smectite
2	1490.03	18.7	10	4.7	11.8	29.4	8.7	2.4	0.6	13.7	R0 illite (0.2)/Smectite
3	1491.13	16.6	10.1	4.4	11.9	29.2	10.9	2.3	0.8	13.9	R0 illite (0.2)/Smectite
4	1492.1	17.5	7.5	3.2	11.5	31.2	9.8	2.5	0.6	16.2	R0 illite (0.2)/Smectite
5	1492.99	18.3	10.5	3.2	9.4	27.2	10.5	2.7	0.7	17.6	R0 illite (0.3)/Smectite
6	1494.30	11.1	4.1	2.4	11.4	27.8	7.8	2.7		32.8	R0 illite (0.2)/Smectite
7	1494.63	13.7	5.2	2.6	10.1	34.3	11.6	2.8	0.4	19.2	R0 illite (0.1)/Smectite
8	1495.61	12.6	10.7	2.5	8.1	34.6	11.9	2.8	0.6	16.3	R0 illite (0.2)/Smectite
9	1496.71	13.2	4.6	3.3	10.3	34.9	12.2	2.6	0.8	18.3	R0 illite (0.2)/Smectite
10	1497.19	18.4	5.2	4.3	12.9	30.1	9.1	2.1	0.6	17.3	R0 illite (0.2)/Smectite
11	1498.11	14.3	9.3	4.5	13.5	29.7	8.6	2.3	0.6	17.2	R0 illite (0.2)/Smectite
Average		15.7	7.9	3.6	11.2	30.5	10	2.5	0.6	18	R0 illite (0.2)/Smectite

Table 2

Sample No.	Depth m	C1 ppm	C2ane ppm	C2ene ppm	C3ane ppm	C3ene ppm	iC4 ppm	nC4 ppm	C4ene ppm	iC5 ppm	nC5 ppm	CO2 ppm	N2+O2 %
1	1489.05	81.93	8.82	0.00	10.49	0.00	15.92	6.77	0.00	3.98	3.37	0.00	99.99
2	1490.03	69.88	7.29	0.00	9.06	0.00	13.38	5.89	0.00	3.17	3.10	0.00	99.99
3	1491.13	24.67	4.79	0.00	2.91	0.00	10.29	5.56	0.00	4.38	3.46	0.00	99.99
4	1492.1	41.08	7.41	0.00	13.09	0.00	18.06	8.44	0.00	5.08	4.01	0.00	99.99
5	1492.99	294.63	31.47	0.00	30.21	0.00	33.32	15.58	0.00	8.66	7.47	0.00	99.96
6	1494.3	49.44	20.37	0.00	32.00	0.00	37.29	16.57	0.00	7.74	5.52	0.00	99.98
7	1494.63	30.74	13.05	0.00	21.88	0.00	25.88	12.90	0.00	6.52	5.07	0.00	99.99
7*	1494.63*	28.73	11.23	0.00	20.28	0.00	24.53	12.75	0.00	6.58	5.15	0.00	99.99
8	1495.61	84.21	24.04	0.00	26.99	0.00	31.26	14.25	0.00	6.61	4.91	0.00	99.98
9	1496.71	41.81	14.14	0.00	21.89	0.00	25.88	12.41	0.00	5.89	5.00	0.00	99.99
10	1497.19	57.93	13.37	0.00	22.80	0.00	28.22	10.33	0.00	4.58	3.60	0.00	99.99
11	1498.11	31.69	4.51	0.00	12.33	0.00	19.23	8.77	0.00	4.14	3.58	0.00	99.99
Average		69.73	13.37	0.00	18.66	0.00	23.60	10.85	0.00	5.61	4.52	0.00	99.99

Normalized by subtracting air

Sample No.	Depth m	C1 (%)	C2ane (%)	C2ene (%)	C3ane (%)	C3ene (%)	iC4 (%)	nC4 (%)	C4ene (%)	iC5 (%)	nC5 (%)	CO2 (%)	N2 (%)
1	1489.05	62.41	6.72	0.00	7.99	0.00	12.12	5.16	0.00	3.03	2.57	0.00	0.00
2	1490.03	62.52	6.53	0.00	8.11	0.00	11.97	5.27	0.00	2.84	2.77	0.00	0.00
3	1491.13	44.01	8.55	0.00	5.19	0.00	18.35	9.92	0.00	7.81	6.17	0.00	0.00
4	1492.1	42.27	7.62	0.00	13.47	0.00	18.59	8.69	0.00	5.23	4.13	0.00	0.00
5	1492.99	69.93	7.47	0.00	7.17	0.00	7.91	3.70	0.00	2.05	1.77	0.00	0.00
6	1494.3	29.27	12.06	0.00	18.94	0.00	22.07	9.81	0.00	4.58	3.27	0.00	0.00
7	1494.63	26.49	11.24	0.00	18.86	0.00	22.31	11.12	0.00	5.62	4.37	0.00	0.00
7*	1494.63*	26.29	10.28	0.00	18.56	0.00	22.46	11.67	0.00	6.02	4.72	0.00	0.00
8	1495.61	43.80	12.50	0.00	14.04	0.00	16.26	7.41	0.00	3.44	2.55	0.00	0.00
9	1496.71	32.92	11.13	0.00	17.24	0.00	20.37	9.77	0.00	4.64	3.94	0.00	0.00
10	1497.19	41.14	9.49	0.00	16.19	0.00	20.04	7.33	0.00	3.26	2.55	0.00	0.00
11	1498.11	37.61	5.36	0.00	14.63	0.00	22.83	10.41	0.00	4.92	4.25	0.00	0.00
Average		43.22	9.08	0.00	13.37	0.00	17.94	8.35	0.00	4.45	3.59	0.00	0.00

Reservoir Gas	Depth m	C1 (%)	C2ane (%)	C2ene (%)	C3ane (%)	C3ene (%)	iC4 (%)	nC4 (%)	C4ene (%)	iC5 (%)	nC5 (%)	CO2 (%)	N2 (%)
Marginulina rese	1520.56	96.06	1.28	0.00	0.18	0.00	0.11	0.04	0.00	0.02	0.01	1.83	0.47
Greta reservoir g	1546.25	94.15	3.01	0.00	0.62	0.00	0.20	0.21	0.00	0.11	0.08	2.20	0.55
Greta reservoir g	1545.64	87.04	2.96	0.00	0.89	0.00	0.33	0.33	0.00	0.17	0.12	9.13	1.14

*Duplicate sample

Table 3

Sample No.	Sample depth m	$\delta^{13}\text{C}$ methane ‰
1	1489.05	-27.53
1	1489.05	-27.99
2	1490.03	-31.84
2*	1490.03	-31.82
3	1491.13	-32.86
3*	1491.13	-32.99
4	1492.1	-25.55
4*	1492.1	-25.80
5	1492.99	-30.52
5*	1492.99	-30.46
5*	1492.99	-27.77
6	1494.3	-26.09
6*	1494.3	-26.58
7	1494.63	-32.72
7*	1494.63	-32.84
8	1495.61	-36.08
8*	1495.61	-36.64
8*	1495.61	-36.02
9	1496.71	-31.82
9*	1496.71	-31.77
11	1498.11	-35.81
11*	1498.11	-35.93
Marginulina reservoir gas (A349)	1514.86	-41.91
Greta reservoir gas (A-315)	1546.25	-41.47
Greta reservoir gas (A-482)	1545.64	-40.23

* Duplicate samples

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10