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Using gas geochemistry to delineate structural compartments and assess petroleum reservoir-filling directions: A Venezuelan case study

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ABSTRACT

Here we examined the light hydrocarbon and nitrogen content and isotopic signatures of eleven gaseous samples in order to evaluate lateral intra-reservoir continuity in a Venezuelan reservoir in the central area of Lake Maracaibo Basin. At least three single compartments, located in the northern-central and southern parts of the reservoir, are revealed by nitrogen concentrations showing clear step-like compositional breaks. The occurrence of step-breaks was also supported by the isotopic signature of individual hydrocarbon compounds in the range of C_1-C_4 alkanes. Samples presented only slight differences in N_2 and hydrocarbon gas compositions within the central and northern parts of the reservoir, and therefore it was not possible to infer structural barriers in coherence with the geological section. Some oil bulk parameters corroborate gradual changes that provide additional information on the reservoir-filling history, thus suggesting that the lateral physical–chemical equilibrium of fluids was not reached in this reservoir.

1. Introduction

Organic geochemistry has played a key role in hydrocarbon exploration in recent decades. In particular, the application of gas geochemistry to reservoir studies and production engineering has attracted considerable attention (Kaufman et al., 1990; Bazan, 1998; Levaché et al., 2000; among others). Several case studies have reported the use of oil and gas compositional variations to investigate reservoir compartmentalization (i.e., Schoell and Jenden, 1993; Hwang et al., 1994; Larter and Aplin, 1994; Holba et al., 1996; Beeunas et al., 1999; Tocco and Alberdi, 1999).

Reservoir geology and engineering are being integrated by means of new analytical techniques that provide information on the natural complexity of oils. For example, a novel complementary method based on Fourier Transform Infra Red (FTIR) spectroscopy was recently proposed (Permanyer et al., 2002) to determine crude oil reservoir compartmentalization. In addition, time-lapse geochemistry (TLG) technology was used for two reservoirs in the deep-water Gulf of Mexico to locate and study petroleum barriers, thus yielding valuable information about reservoir behavior (Milkov et al., 2007).

The study of low molecular-weight fractions ($<C_{15}$), and more recently gas fingerprints to evaluate the lateral and vertical continuity of reservoirs is based on the premise that light fractions from a single hydrocarbon column (continuous reservoir) have similar chemical compositions, whereas production from separate hydrocarbon columns (different sand/fault blocks) implies significantly different compositions (England et al., 1995). In this context, the use of gas isotopes to assess reservoir fluid heterogeneity has proved useful to further our understanding of reservoir connectivity (Rein and Schulz, 2007). The reasons for reservoir chemical and isotopic differences in discontinuous hydrocarbon columns are not fully understood and therefore a detailed study of each reservoir is required (Wavrek et al., 2001). Compositional similarities are thought to be the result of homogenization within the compartments after diffusion, convection (density-driven), and fluid–rock interactions have reached equilibrium (Smalley et al., 1994). England (2007) reviewed the applications of reservoir geochemistry from a reservoir engineering point of view and concluded that it is useful for addressing issues related to production allocation, reservoir compartmentalization, and the prediction of gravitational gradients. Beeunas et al. (1996) described in two reservoir sands without communication in the Gulf of Mexico

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a similar situation when compared to the present case study, determining carbon isotopic variations in methane, ethane, and propane.

It is also pertinent to note that nitrogen is one of the main non-hydrocarbon gas in many petroliferous basins (Jenden et al., 1988). Although nitrogen in natural gases is probably derived from organic matter in the sedimentary column (Rohrback et al., 1983), there are other subsurface nitrogen sources such as dissolved air in groundwater, mantle-derived N_2 in areas of recent magmatic activity, and N_2 released from metasedimentary rocks during metamorphism (Gold and Held, 1987; Krooss et al., 1993). While N_2 concentrations have been used mostly to allocate gas mixtures in storage containers (Schoell and Jenden, 1993), molecular nitrogen concentration in gases can also be applied to reservoir characterization (Ballentine and Sherwood Lollar, 2002). Consequently, there is growing interest in modeling N_2 generation (Littke et al., 1993). To date, most nitrogen studies have been done in gas-source rocks, such as coal or source rock containing humic organic matter (Clayton, 1997; among others); however, nitrogen generation from marine organic matter has received less attention (i.e., Kotarba and Nagao, 2008).

Given the preceding considerations, here we integrated diverse geochemical data with the aim to elucidate lateral intra-reservoir continuity in a Venezuelan reservoir (central sector of Lake Maracaibo Basin). For this purpose, we applied a relatively recent approach to integrate information about the compositional signatures of the C_1–C_4 alkanes and molecular nitrogen with isotopic analyses of individual hydrocarbons in gaseous samples. Furthermore, API gravities, V/Ni ratios and sulfur contents in sampled oils are also provided to complement and contrast data obtained from gases.

2. Petroleum exploitation context

The Maracaibo Basin is located in north-western Venezuela (Fig. 1a), an area comprising mainly the state of Zulia and also those of Falcón, Mérida, Táchira, and Trujillo. The Lake Maracaibo Basin (containing 700 oil-producing fields after drilling about 16,500 wells) covers an area of approximately 50,000 km^2, with an estimated sediment volume of 250,000 km^3 over a pre-Cretaceous basement (González de Juana et al., 1980).

The main petroleum source rocks in the study area are the Cenomanian–Campanian La Luna Formation (Erlich et al., 2000) and, to a lesser extent, the Aptian–Albian Apón Formation (Machiques Member), although other rock units also generate hydrocarbons (Talukdar et al., 1986). The Lake Maracaibo Basin

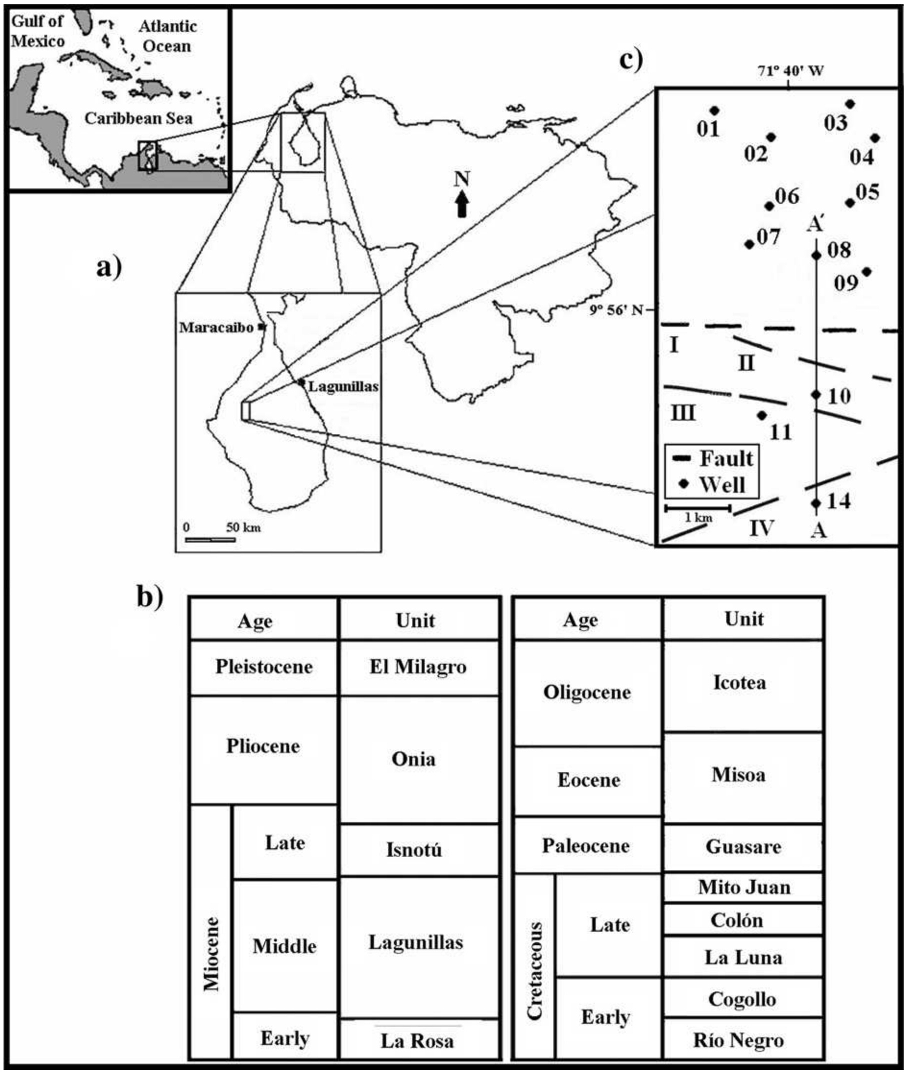

Fig. 1. a) Map of Lake Maracaibo in northwestern part of Venezuela; b) and c), respectively, stratigraphic column and sample locations in the study area.

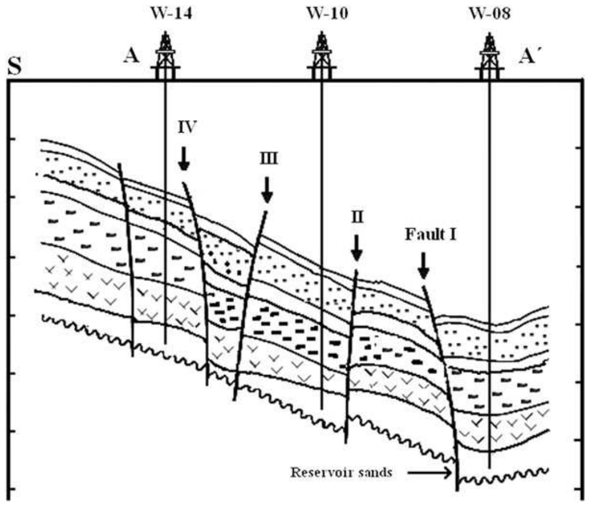

Fig. 2. North–south simplified A–A′ cross-section of the study area. It includes from bottom to top the Misoa, Icotea, La Rosa, Lagunillas, Isnotu and Onia Fms.

occupies the entire lake area (12,870 km^2 with water to an average depth of 100 ft) and the surrounding rolling hills. The major hydrocarbon accumulations are found in Eocene and Miocene deltaic sandstones (Talukdar and Marcano, 1994).

There are series of very large oilfields in the central sector of Lake Maracaibo Basin, including Lago-Lamar, Block I, Block II, Block V, and Ambrosio, among others. The stratigraphy of this sector consists of clastic sedimentary rocks of Miocene, Oligocene, Eocene, Paleocene and Cretaceous Age (see Fig. 1b). The main reservoir rocks are the Eocene Misoa Formation, as well as the Miocene Lagunillas and La Rosa formations (Parnaud et al., 1995).

3. Methodology

Eleven natural gas samples from nine oil wells (labeled between W-01 and W-09) and two gas-condensate wells (W-10 and W-11) were collected in sealed glass bottles by means of metal separators connected to two sealed cylinders in parallel in the well-head. Additionally, ten oil samples (W-01 to W-09, and W-14) were also collected and stored in glass jars prior to analysis. In both cases, a proper seal prevented the loss of light compounds and other possible sample alterations. Fig. 1c shows the sample collection sites in the study area.

All these producing wells are within the boundary of the study reservoir's area located in the Lama system fault zone. A secondary normal faulting (represented by "I", see Fig. 2) in this fault system would act as a sealing structure. This structural barrier must be considered, even though the displacement of the reservoir sands in the geological section does not seem to be high enough to interbed these sands with the over- and underlying beds in the stratigraphic framework. In the aforementioned section, each secondary fault is given a Roman numeral.

Analyses of compounds in gaseous samples were carried out in an HP-5890 Series II gas chromatograph with electronic pneumatic control. The multidimensional gas chromatography system includes switching valves, an HP-PLOT Q column (30 m length × 0.53 mm i.d.; oven temperature program of 45 °C for 6 min to 220 °C at 20 °C/min) to separate fixed gases and methane from the remaining alkanes, as well as an HP-PLOT MoleSieve 5A (30 m length × 0.32 mm i.d.; oven temperature program of 50 °C for 10 min to 120 °C at 10 °C/min) for separation of fixed gases and methane. Helium was used as the carrier gas. After elution of methane, the second column is bypassed. Ethane and higher alkanes elute from the first column to a flame ionization detector. Methane and fixed gases are quantified on a thermal conductivity detector. Relative standard deviations were below 0.8%.

Stable carbon and hydrogen isotope analyses of the individual compounds in the gas samples were performed repeatedly by gas chromatography-isotope ratio mass spectrometry using a GC/C III interface connected through a combustion reactor to a Finningan MAT Delta plus XL mass spectrometer. An Agilent 6890 series gas chromatograph equipped with a split–splitless capillary injector and a fused silica DB-1 capillary column (65 m length × 0.25 mm i.d.) was used. Gas samples were analyzed using a 100:1 split ratio injection system and the oven temperature program was 35 °C (hold for 2 min) to 300 °C at 4 °C/min rate and was then held constant for 30 min. Helium was used as the carrier gas. Individual compounds separated by GC were pyrolyzed to CO_2 and H_2 at 850 °C and 1440 °C, respectively. Isotope compositions of N_2 were determined by the same mass spectrometer after separation from the gas samples in a glass vacuum line using a trap held at -196 °C. The $^{13}C/^{12}C$, $^{15}N/^{14}N$ and D/H ratios are reported in "δ" notation. $\delta^{13}C$, $\delta^{15}N$ and δD refer to V-PDB, N-SVEC and SMOW standards for carbon, nitrogen and hydrogen stable isotope measurements. Reproducibilities for $\delta^{13}C$, $\delta^{15}N$ and δD values were better than ±0.3‰, ±0.5‰ and ±5‰ for the dataset.

The API gravity of each oil sample was measured by ASTM D-4052 procedure (ASTM, 2011) through a SBS-3500 specific gravity meter that uses oscillating U-tube technology. The sample is filled into a container to measure the frequency of oscillation, from which the density value is calculated. Also, sulfur percentages were determined by ASTM D-4294 method (ASTM, 2010) using an energy-dispersive X-ray Panalytical spectrometer (Axios model) equipped with a digital signal processor and dual multi-channel analyzer. Finally, we applied inductively-coupled plasma atomic emission spectroscopy through a Perkin–Elmer Optima 3000 spectrometer equipped with an automatic sampler for the

Table 1
Average aliphatic hydrocarbons ($<C_5$), argon, and nitrogen from W-01 to W-11 gas samples.

	W-01	W-02	W-03	W-04	W-05	W-06	W-07	W-08	W-09	W-10	W-11
Methane	75.00	67.10	75.50	75.00	62.39	59.76	48.77	27.97	66.98	60.20	73.12
Ethane	13.40	14.40	13.65	13.55	15.77	18.89	16.24	22.55	16.17	16.90	14.82
Propane	7.81	10.93	6.90	7.43	11.99	12.22	16.57	26.12	10.23	13.10	7.68
Isobutane	0.72	1.17	0.83	0.59	1.85	1.43	2.23	3.27	1.21	1.69	0.85
n-butane	1.74	3.35	1.75	2.14	4.12	3.99	7.85	10.76	2.99	4.50	1.77
Isopentane	0.35	0.90	0.40	0.41	1.17	0.79	2.25	2.43	0.67	1.06	0.45
n-pentane	0.42	0.78	0.55	0.42	1.44	1.33	2.76	2.88	0.76	1.22	0.50
Nitrogen	0.27	0.27	0.27	0.29	0.27	0.29	0.27	0.26	0.29	0.97	0.91
Argon	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002	0.002

Note: all data in molar percentages.

quantitative determination of V and Ni contents (ASTM D-5708; ASTM, 2005).

4. Results and discussion

4.1. Chemical and isotopic composition of gases

Molecular concentrations of methane, ethane, propane, *n*-butane, iso-butane, *n*-pentane, iso-pentane, nitrogen, helium and argon are shown in Table 1. Methane was the main component in the gas samples, ranging between 27.97 and 75.5% (average 62.9%).

The stable carbon isotopic compositions of the C_1–C_4 hydrocarbon compounds and hydrogen signature of methane for the gaseous samples are shown in Table 2. According to Schoell (1980), the $\delta^{13}C$ and δD ranges for methane in all samples indicate a thermogenic origin for this gas (Fig. 3a). Likewise, based on a Bernard diagram (Fig. 3b), $\delta^{13}C_1$ values over -55‰, uniform $\delta^{13}C_2$ data, and wetness values over 0.23, the natural gas samples could be classified as thermogenic gases generated from mature, sapropelic La Luna source rocks (Berner and Faber, 1988; Prinzhofer and Huc, 1995). Also, assuming that the $\delta^{13}C$ value of the La Luna kerogen is approximately -26‰ (Zumberge, 1984; Clayton and Bjoroy, 1994), and using the model proposed by Chung et al. (1988), the "natural gas plots" (r^2 values above 0.99; see Fig. 3c) confirm a nonexistent or scarce bacteriogenic methane fraction commingled with thermogenic methane (Rangel et al., 2003).

The molar concentrations of the C_1–C_4 alkanes indicate similar patterns, with two remarkable exceptions. Firstly, the W-08 sample showed an abnormally low value of methane content; in fact, in this well, a laboratory pressure test revealed a cylinder leak in coherence with chemical analysis, given that a notably lower concentration of methane, the major component, alters the relative concentration distribution pattern in the other organic compounds. An anomalous low concentration of methane was also noticed in W-07, but further pressure checking or geochemical analyses did not suggest anomalies in this well. However, as the gas-hydrocarbon sampling procedure is affected by production methods, pressure variation, and GOR (gas–oil ratio), changes in the pattern of this last well might be of circumstantial importance (Van Orsdal, 1990). These results confirm that it is not possible to obtain information about structural compartments using only the alkane ($>C_1$) compositions of the gas phase.

Nitrogen concentrations in gas samples at the well-head sampling sites provided valuable information. Gases from wells 10 and 11 showed molar nitrogen percentages (above 0.90%) four times higher than those from the other wells (values between 0.26 and 0.29%). These significant differences indicate that lateral composition is not equilibrated across the study reservoir. This chemically noteworthy step-like break could be indicative of the effect of geological barriers in molecular diffusion or convection, as discussed below.

Nitrogen is associated with the generation of high temperatures (Mingram et al., 2003), thus elevated concentrations of this gas are characteristic of a late hydrocarbon-pulse to the compartment

Table 2
$\delta^{15}N$ data (‰), δD (‰) in methane and $\delta^{13}C$ values (‰) in methane, ethane, propane, isobutane and n-butane for the gas samples.

	$\delta^{13}C_1$	$\delta^{13}C_2$	$\delta^{13}C_3$	$\delta^{13}iC_4$	$\delta^{13}nC_4$	δD	$\delta^{15}N$
W-01	−51.31	−39.93	−32.78	−29.77	−28.98	−209	−9.33
W-02	−49.02	−39.09	−32.63	−29.93	−28.96	−206	−9.29
W-03	−51.12	−40.58	−32.92	−29.60	−29.23	−209	−9.26
W-04	−50.90	−39.82	−32.61	−29.84	−29.16	−208	−9.10
W-05	−51.13	−39.64	−32.80	−29.72	−29.28	−209	−9.36
W-06	−50.91	−39.31	−32.75	−29.93	−29.21	−208	−9.14
W-07	−51.06	−39.16	−32.55	−29.73	−29.33	−208	−9.30
W-08	−51.56	−39.73	−32.83	−29.84	−29.46	−209	−9.40
W-09	−50.12	−38.52	−32.25	−29.66	−28.91	−207	−9.19
W-10	−48.43	−37.12	−31.44	−29.71	−28.46	−204	−8.84
W-11	−48.00	−36.55	−31.27	−29.67	−27.99	−204	−8.89

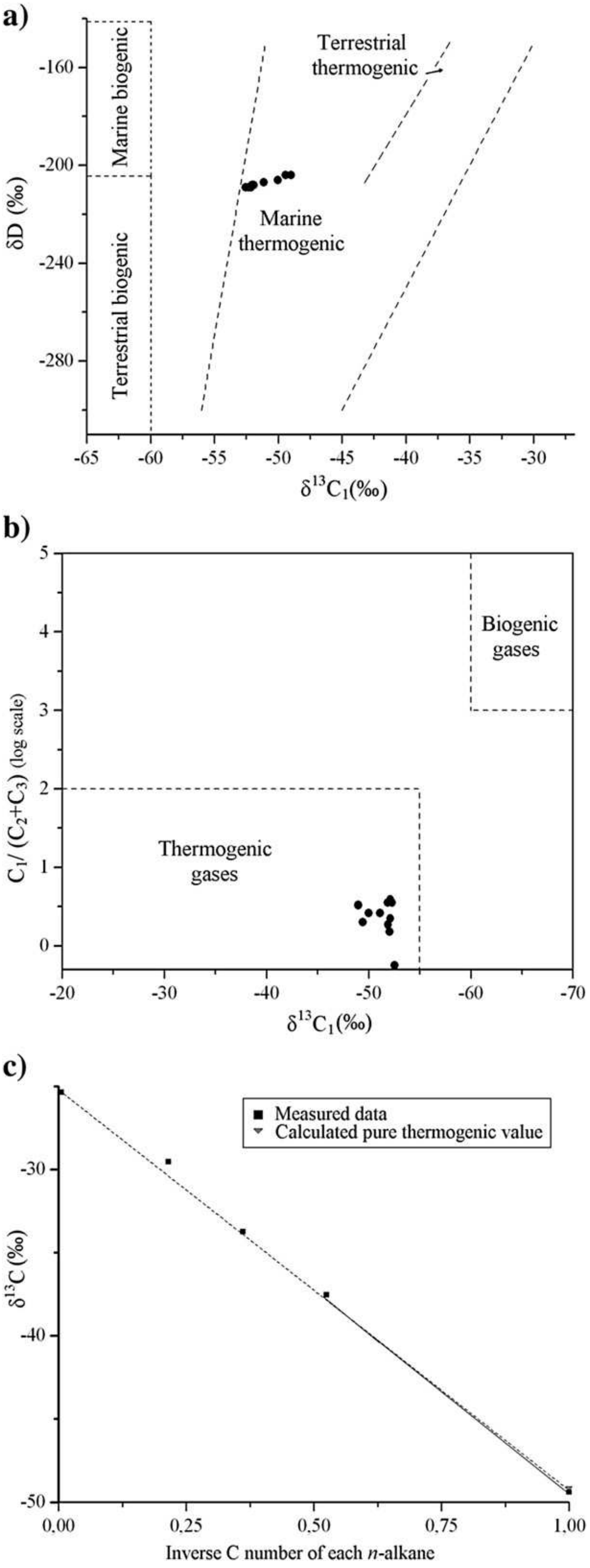

Fig. 3. a) and b), respectively, relationships of δD to $\delta^{13}C_1$ and of $\delta^{13}C_1$ to $C_1/(C_2 + C_3)$ for the studied gases; c) $\delta^{13}C$ vs. the inverse C number of individual C_1–C_4 *n-alkanes*.

without subsequent mixing with the rest of the study reservoir by diffusion or convection (Littke et al., 1995). Assuming a high average N_2/Ar ratio above 200 and $\delta^{15}N$ values about −9‰ in our case (Jenden et al., 1988; Zhu et al., 2000), the subsequent minimal or no contributions of magmatic, metamorphic or atmospheric N_2 lead us to infer that increasing concentrations of N_2 in the southern compartment are associated with increasing maturity levels in the source rock toward the south. In fact, these results are consistent with other data discussed in this study.

Methane showed a typically lighter carbon isotopic ratio on average than average $\delta^{13}C_2$, whereas the $\delta^{13}C$ patterns of C_1–C_4 alkanes ($C_1 < C_2 < C_3 < C_4$) were consistent with a regular Rayleigh "fractionation" model (Clayton, 1991). In particular, the isotopic compositions of methane and ethane from W-10 and W-11 presented differences of 2–3‰ with respect to the rest of the samples (see Table 2), thereby suggesting distinctive features. The gas correlation plot in Fig. 4 again shows a clear compositional change in the gases from the southern area when compared with mean values of the sample set from the central and northern parts, which had low $\delta^{13}C$ standard deviations (<1‰). In contrast, $\delta^{13}C$ for methane, ethane, propane, and *n*-butane in W-10 and W-11 were within experimental error range (0.2–0.3‰), thus indicating that these two samples belong to the same compartment. These results support the abovementioned chemical composition analyses (N_2) and indicate the presence of non-communicating reservoir compartments.

According to Lorant et al. (1998), isotopic data were also useful to hypothesize changes in the maturity levels of the samples. In fact, although all the gas samples analyzed fit within the oil window (see Fig. 5a showing a diagram with vitrinite reflectances), heavier $\delta^{13}C$ values for W-10 and W-11 may be related to increasing maturity levels in the source rock (Chung and Sackett, 1979), as reflected by increasing nitrogen values in the southern part of the reservoir. Secondary cracking or biodegradation in the reservoir compartments under study can be ruled out using the scheme of Prinzhofer et al. (2000), as indicated by the low C_2/C_3 ratios observed in all the gas samples (Fig. 5b).

Finally, natural gas data are described using star-diagrams applied to gas (also named Gastar diagrams by Prinzhofer and colleagues in 2000) to study the main processes (such as maturity, efficiency of accumulation or segregative migration) affecting the chemical and isotopic signatures of the samples. Eleven normalized geochemical parameters (C_1/C_2, C_2/C_3, iC_4/nC_4, $\delta^{13}C_1$, $\delta^{13}C_2$, $\delta^{13}C_3$, $\delta^{13}iC_4$, $\delta^{13}nC_4$, $\delta^{13}C_3$–$\delta^{13}C_2$, $\delta^{13}nC_4$–$\delta^{13}iC_4$, and $\delta^{13}C_2$–$\delta^{13}C_1$) were discussed through a method reported by Prinzhofer et al. (2000). All of these parameters were positively correlated with maturity, three (the isotopic ratios differences) were linked to the efficiency of accumulation, and another three (those involving methane) were strongly affected by migration. Fig. 6 shows the aforementioned data plotted in three star-diagrams. As expected, the W-10 and W-11 samples can be grouped, both registering the greatest degree of maturity (Fig. 6a). As already proposed, samples W-10 and W-11 represent a separate gas condensate reservoir compartment, which could be explained by differential entrapment of oil and gas.

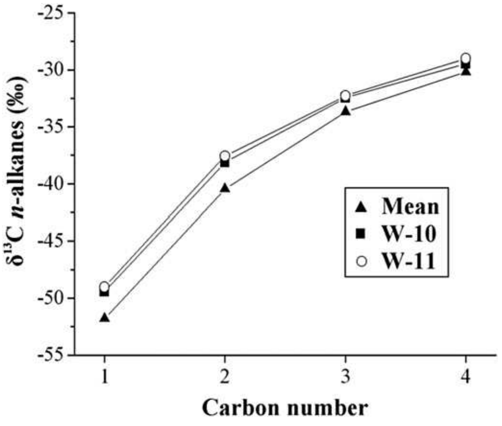

Fig. 4. $\delta^{13}C$ values (‰) in methane, ethane and propane from W-10, W-11, and the mean of the remaining sampled gases.

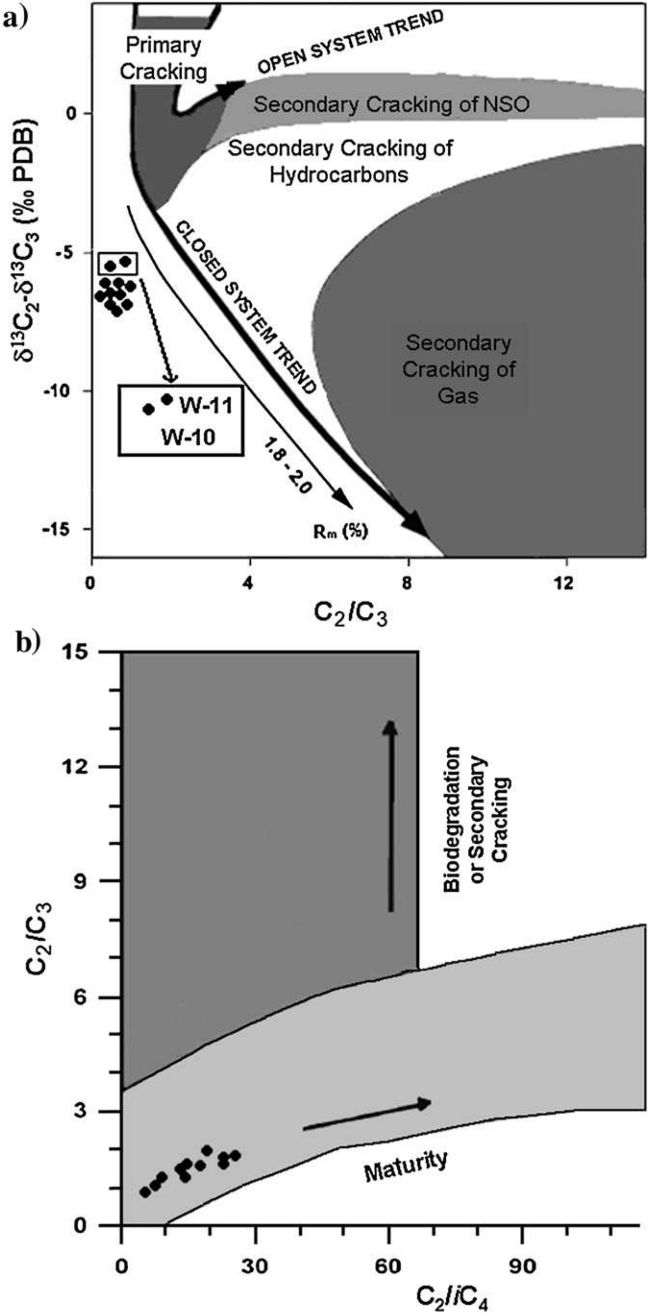

Fig. 5. a) and b), respectively, plots ($\delta^{13}C_2$–$\delta^{13}C_3$ vs. C_2/C_3) and (C_2/iC_4 against C_2/C_3) for the gas samples.

In addition, the geochemical differences of gaseous samples from the northern and central parts of the study reservoir support the notion of at least two oil compartments. Fig. 6b displays a series of natural gases (W-05 to W-09) with minor maturities, segregative fractionations and efficiencies of accumulation from the central part of the reservoir, as well as slight variations in these three processes. Although the differences between these five samples are

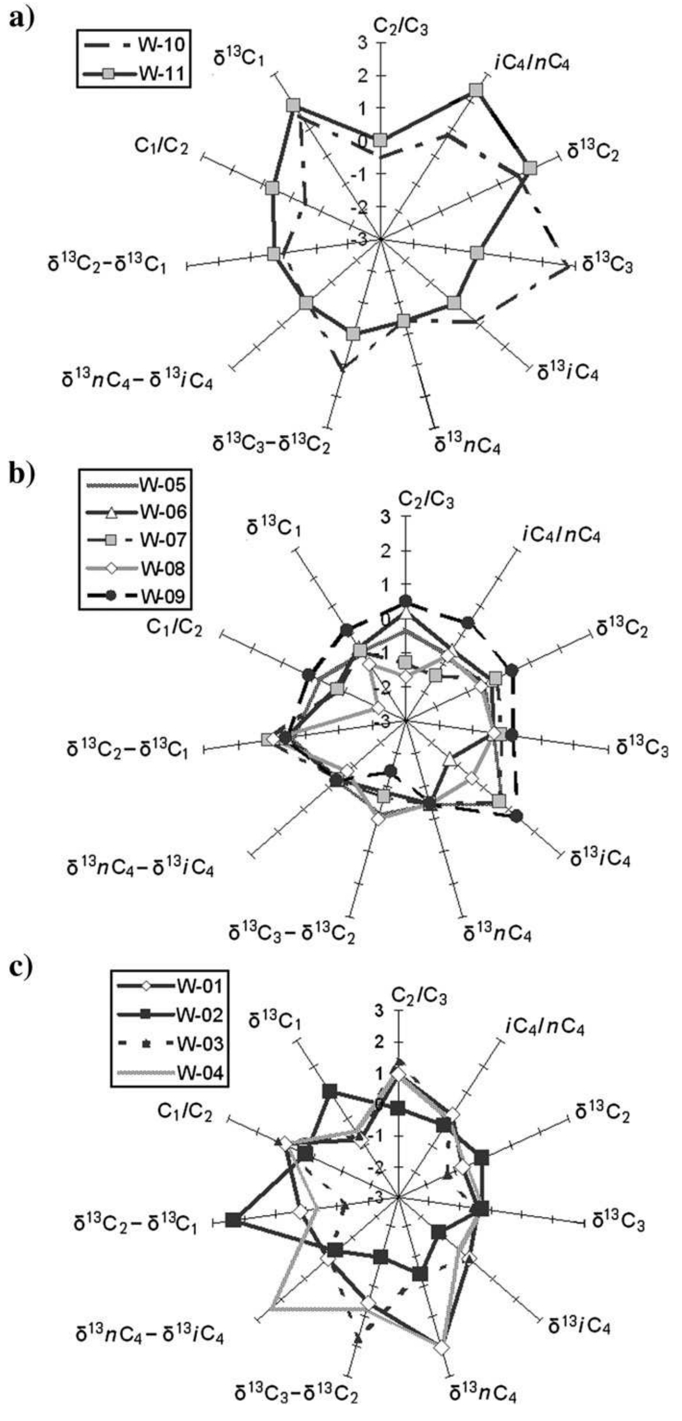

Fig. 6. a), b) and c), three normalized Gastar diagrams for the groups of gas samples coming from the studied reservoir. The scales are the same for all 11 axes of each diagram.

very close to analytical accuracy, a reasonable connectivity in the central part of the reservoir could be inferred from the C_1-C_4 hydrocarbon analyses, which reveal a somewhat inefficient convection mechanism for mixing the fluids in a large reservoir (approximately 40 km^2 of areal extension). Consequently, it is not possible to conclude complete fluid homogenization.

In contrast, Fig. 6c corresponds to the rest of the samples (gases W-01 to W-04) from the northern part of the reservoir and shows different behaviors; firstly, enhanced accumulation is observed, excluding W-01. Results for the W-02 sample showed compositional uniqueness; however, this feature is not enough to indicate a new single reservoir compartment or sub-compartment. Therefore, we cannot preclude that the hydrocarbon heterogeneities identified in Gastar diagrams are indicators of baffles and barriers to diffusion within the north-central part of the reservoir.

Table 3
Bulk geochemical data for the liquid samples.

	API	S	V	Ni	V/Ni
W-01	26.0	2.5	390	54	7.2
W-02	25.2	2.4	367	50	7.3
W-03	25.3	2.4	372	53	7.0
W-04	25.4	2.3	364	47	7.7
W-05	27.1	2.2	349	43	8.1
W-06	26.9	2.3	351	47	7.4
W-07	27.0	2.2	335	43	7.8
W-08	27.6	2.0	350	39	8.9
W-09	28.3	2.1	332	43	7.7
W-10	56.9	–	–	–	–
W-11	56.4	–	–	–	–
W-14	30.3	1.8	313	44	7.1

Note: V and Ni contents in ppm, sulfur ones in wt. %.

4.2. Petroleum bulk data heterogeneities

Results obtained for API gravity and sulfur content (Table 3) suggest intra-reservoir bulk lateral heterogeneity.

In this regard, the increasing API values of crude oils from the northeast to southwest may be attributable to the southward increase in maturity. Also, increasing maturity values from north to south may explain the southward decrease in the sulfur content of oils, which is possibly associated with lower concentrations of polar compounds (Peters et al., 2005). The V/Ni ratios above 7 (see Table 3) and sulfur content over 1% of the oils studied also pinpoint a carbonate source rock (La Luna Formation) deposited in an anoxic environment (Galarraga et al., 2008).

Consequently, this particular reservoir shows clear compositional trends from the northern to the southern part of the study area. The reservoir has a poor permeability (around 19 mD) and it is significantly long (11 km) and thin (16 m). These data can imply difficulties to obtain homogeneity of fluids (England et al., 1995). Computational simulation and/or detailed engineering monitoring should be used to examine possible stratigraphic transmissibility barriers in order to explain the fluid heterogeneities. On the basis of the data presented above, we propose that this area was filled from the south, meaning that the source rock was in the southern part of the study area. Less mature oils accumulated in the north and successive petroleum charges filled the southern sands.

5. Conclusions

The isotopic and compositional signatures of individual C_1-C_4 aliphatic hydrocarbon compounds and nitrogen concentrations in gases presented a marked step-break variation between W-10 and W-11 and the rest of the gaseous samples toward the north. Specifically, nitrogen concentrations showed a notable step-break between these two populations, thereby suggesting a sealing character associated with a secondary fault identified in the geological section.

On the basis of the gas analyses, the presence of structural barriers in the central and northern parts of the reservoir is possible, since certain analytical trends do not rule out a scenario of additional single compartments or sub-compartments. Reservoir simulation or detailed engineering monitoring is required to locate additional transmissibility barriers.

The sulfur contents and specific gravities of the oils sampled corroborated a north–south compositional trend within the anticline structure and adjacent compartments. Based on the integration of all the geochemical parameters available, we propose that these reservoirs were filled from the south.

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