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ARTICLE

Shale gas plays, Neuquén Basin, Argentina: chemostratigraphy and mud gas carbon isotopes insights

Análise quimioestratigráfica e dos isótopos do carbono em mud gas aplicados à exploração do shale gas, Bacia Neuquén, Argentina

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ABSTRACT: In order to enhance the knowledge of shale objectives from Vaca Muerta and Los Molles Formations in the Neuquén Basin, Argentina, chemostratigraphic and mud gas carbon isotope analyses were performed in two wells from Agua del Cajón and Salitral oilfields (ADC-1016 and NqSa-1148). Geochemical data show restricted levels in both cases to perforate and produce. In ADC-1016 well, Lower Los Molles Formation looks like the most suitable play to be produced. At El Salitral oilfield (NqSa-1148), the best remarkable Vaca Muerta-Quintuco objectives are associated with authigenic elements, in limited horizons. Enhancement of the Quintuco reservoir by deep circulating fluids (thermobaric reservoir) is suggested. Carbon isotope analysis reveals complex processes that affected the gas composition. Addition of microbial methane, biodegradation of ethane-propane and mixing of gases has been recognized. Isotope reversals and presumed water reforming of hydrocarbons have been registered associated with overpressure for Lower Los Molles Formation in the ADC-1016 well, which is pointed out as the most promising shale play in the area. Vaca Muerta gases at Agua del Cajon ADC- 1016 well are associated with the homonymous source. El Salitral 1148 well shows that primary isotope composition in gases from Vaca Muerta shale play and Quintuco reservoir could be associated with a Lower Los Molles source, an aloctonous charge related with the main structures of the area.

KEYWORDS: Neuquén Basin; Carbon isotopes; Reversal; Natural gas.

RESUMO: *A fim de aumentar o conhecimento dos objetivos do shale gas das Formações Vaca Muerta e Los Molles, na Bacia Neuquén, Argentina, foram realizadas análise quimioestratigráficas e dos isótopos do carbono em mud gas correspondentes a dois poços dos campos petrolíferos Agua del Cajón e Salitral (ADC-1016 e NqSa-1148). Os dados geoquímicos mostraram níveis restritos em ambos os casos para perfurar e produzir. No poço ADC-1016, a Formação Los Molles inferior aparece como a mais adequada a ser produzida. No campo petrolífero El Salitral (NqSa-1148), os objetivos mais notáveis nas Formações Vaca Muerta-Quintuco estão associados a elementos autigênicos, em horizontes limitados. É sugerida a melhora do reservatório Quintuco por fluidos da origem profunda (reservatório termobárico). A análise dos isótopos do carbono revela processos complexos que afetaram a composição do gás. A adição de metano microbiano, biodegradação de etano-propano e mistura de gases foi reconhecida. As reversões dos isótopos e suposta reforma dos hidrocarburos por água foram registradas em associação à sobrepressão para a Formação Los Molles inferior no poço ADC-1016, o que é assinalada como a locação do objetivo mais promissor da área. Os gases da Formação Vaca Muerta em Agua del Cajón estão associados com a fonte homônima. O poço El Salitral 1148 mostra que a composição isotópica primária em gases da Formação Vaca Muerta e o reservatório Quintuco podem ser associados com a fonte da Formação Los Molles inferior, uma carga alóctona relacionada com as principais estruturas da área.*

PALAVRAS-CHAVE: *Bacia Neuquén; Isótopos de carbono; Inversão; Gás natural.*

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INTRODUCTION

Natural gas demand has pushed the exploitation of shale gas accumulations in Argentina, where the most promising sources are in the Neuquén Basin. Knowledge of sources and operating processes are critical in order to understand and evaluate the resources. Inorganic geochemistry and molecular–isotopic characterization of gases on source rocks are key tools for a better comprehension, focusing on exploration objectives and evaluation of their potential for gas generation.

In order to characterize and identify sources of gas in deep and shallow wells looking for shale plays at the Huincul Dorsal, a pilot project to analyze the geochemistry of cutting and mud gas isotope compositions was carried out in two wells from Agua del Cajón and El Salitral oilfields. Samples from different levels and objectives were processed to identify the most promising horizons in a deep well (ADC-1016, Agua del Cajón oilfield, Los Molles shale objective) and in a shallow well (NqSa-1148, El Salitral oilfield, Vaca Muerta-Quintuco shale objective).

GEOLOGICAL SETTING

The Neuquén basin is located in west-central Argentina, on the eastern side of the Andes. It extends along Neuquén, southern Mendoza, southwest La Pampa and northern Río Negro provinces. It is a triangular shaped basin of approximately 125,000 km^2, bounded on the west by the Andean folded belt and partially controlled on the south by a major east-west trending wrench fault (Huincul Dorsal, Fig. 1). The generalized stratigraphic column is shown in Figure 2. Numerous references can be cited, and we select a few of them, which summarizes the main geological features. Early contributions were: Bodenbender (1889), Keidel (1913), Windhausen (1914), Keidel (1925), Groeber (1929, 1938) and Weaver (1931). Many others deserve a citation, but we select Stipanicic (1969), Rolleri (1978), Digregorio (1979), Ploskiewicz *et al.* (1984), Legarreta & Gulisano (1989), Uliana & Legarreta (1993), Gulisano & Gutierrez Plemling (1994), Ramos (1978), Urien & Zambrano (1994), Vergani *et al.* (1995), Veiga *et al.* (2005), Ramos *et al.* (2011), Mosquera *et al.* (2011).

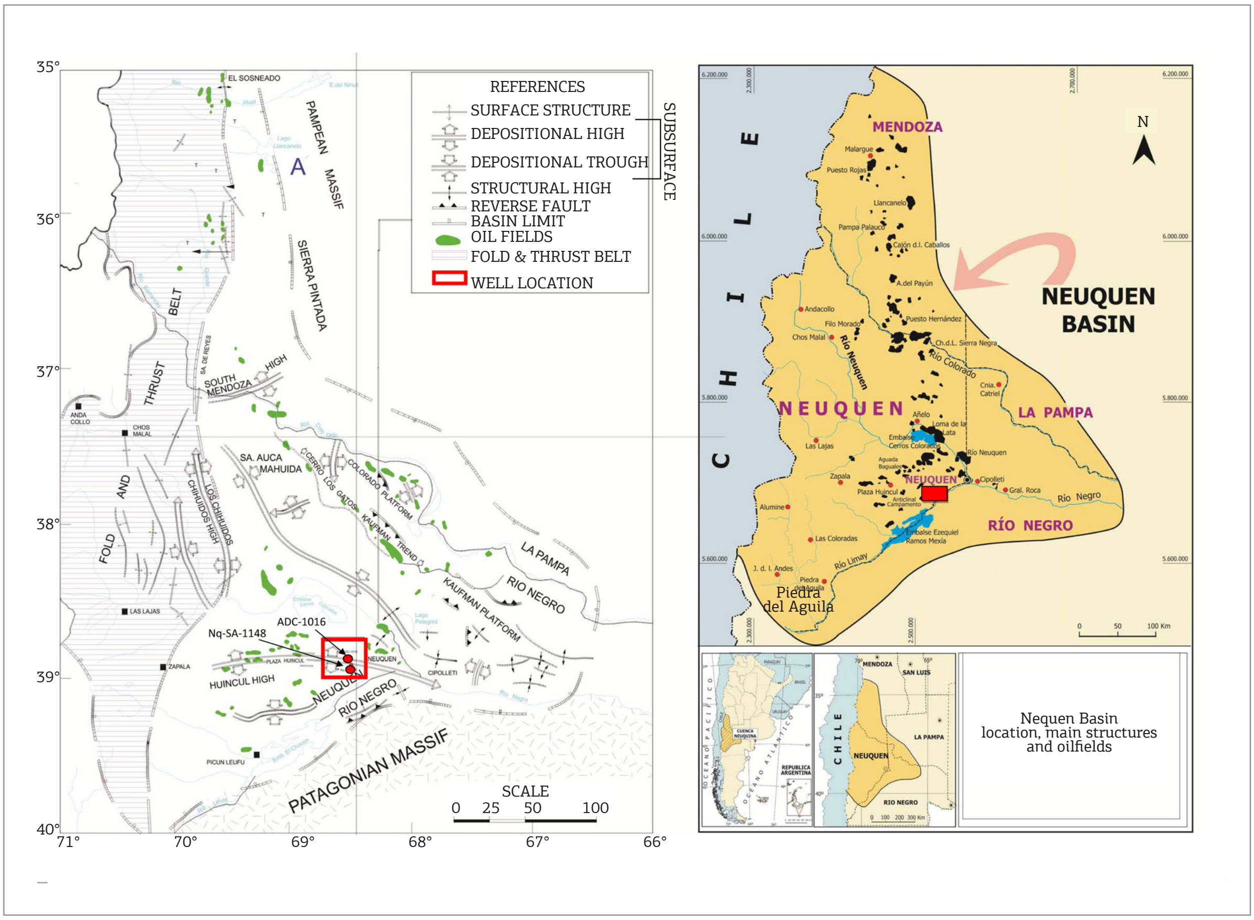

Figure 1. Neuquén Basin. Location, main structures, oilfields and analyzed wells.

Sedimentation in the basin started during Late Triassic and it was strongly controlled by the extensional rifting. In Late Jurassic-Early Cretaceous, the basin went through a period of back-arc subsidence associated with the evolution of a magmatic arc along the western margin of Gondwana. Clastic deposits include alluvial, fluvial, shallow-marine, deltaic and lacustrine sediments while the transition to more regional subsidence during Early Jurassic times resulted in shallow-marine facies (Veiga *et al*. 2005).

During Late Cretaceous, the Neuquén region was a retro-arcforeland basin, thick units of post-orogenic red beds were deposited and towards the end of the Cretaceous continental sedimentation was widespread. The sedimentary section was subsequently covered by discontinuous Cenozoic sediments, which were affected by the Andean deformation. The tectonic movements of Jurassic and Paleogene age created many structural traps, which, with the presence of very important stratigraphic traps, have controlled the commercial accumulations of oil and gas in the basin.

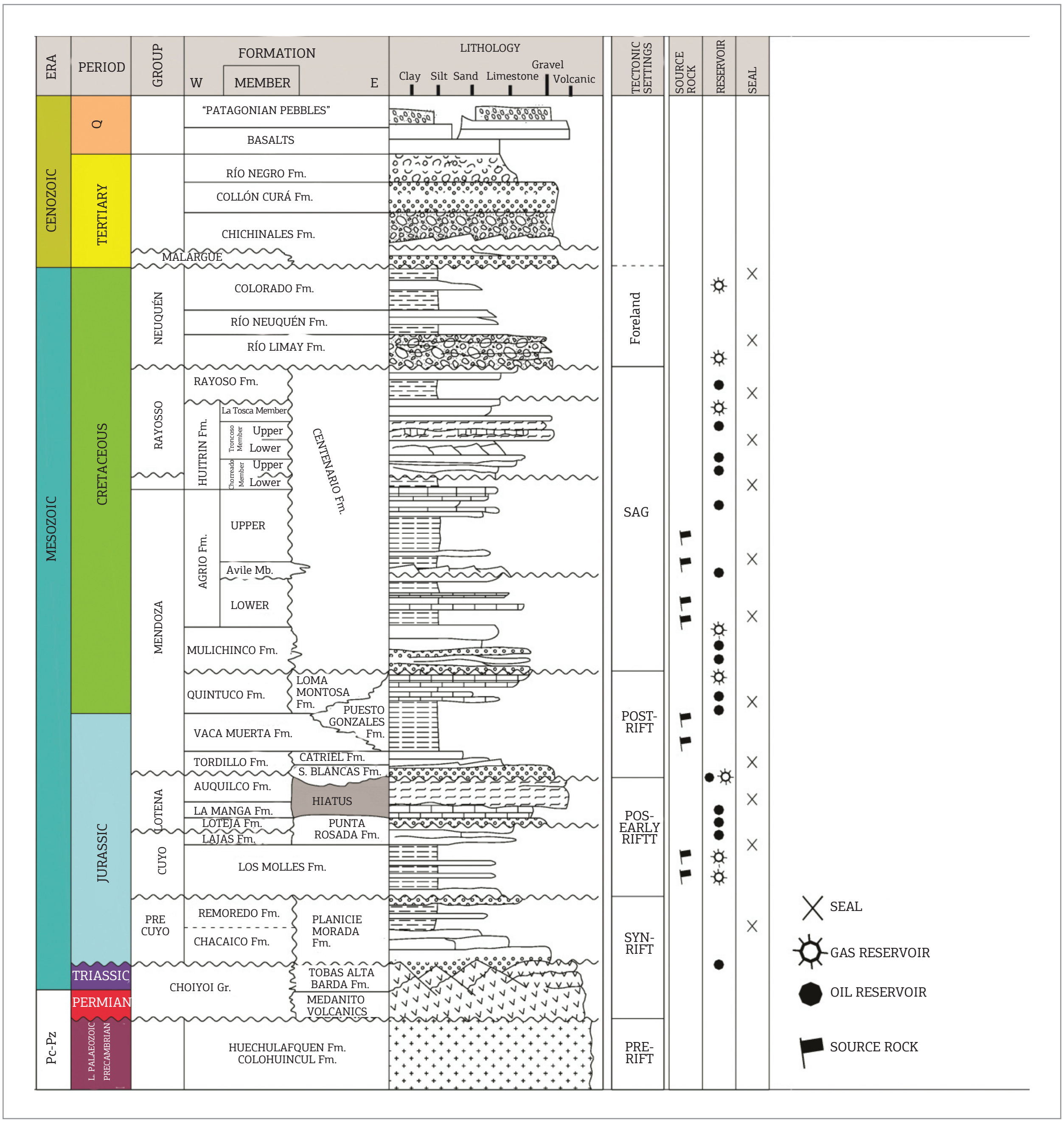

Figure 2. Neuquén Basin. Generalized stratigraphic column.

The sedimentary fill of the Neuquén Basin encompasses marine and no-marine siliciclastic, carbonates and evaporites.

The Jurassic sandstones of the Lotena, Punta Rosada, Tordillo and Sierras Blancas Formations, together with the Late Jurassic-Early Cretaceous limestones in the Quintuco and Loma Montosa Formations, are the main reservoirs with commercial value.

The black shales of Los Molles, Vaca Muerta and Agrio Formations are very prolific source rocks for oil, condensate and gas throughout the basin (Cruz *et al*. 1999, 2002, Villar *et al*. 2005).

Average depth of reservoirs is between 2,000 and 2,900 m below the surface. Average oil gravity varies between 29.5 and 33.2º API.

The black shales of Los Molles Formation (which could reach thickness of over 1,000 m) were deposited during the Early Jurassic marine transgression. The total organic cabon (TOC) of these shales varies between 1 and 6%. The kerogen type is II and III. The petrographic analysis of kerogen suggest that it is a mixture of marine and terrestrial organic matter, gas/oil prone. The thermal maturity of this formation varies according to its position in the basin. In general, for an intermediate position in the basin, its lower part could be over mature, while its upper part could still be within the oil window.

Vaca Muerta Formation consists of basinal marine black shales, shelf marine sandstones, marls and limestones with a bituminous section in its lower part. TOC varies from 3 to 8%, vitrinite reflectance (%) from 0.8 to 2, hydrogen Index 400 – 800 mg HC/g TOC; the kerogen type is I-II and IIS in marginal areas (Legarreta & Villar 2011). From the values found in different parts of the basin, the thermal maturity of this formation is located within the oil window, except near the depocenter of the basin.

The Mulichinco Formation is stratigraphically above Vaca Muerta Formation and consists of distal shelf black shales, limestones and sandstones. TOC values vary between 1.3 and 2.4%, and the kerogen is Type II. Thermal maturity varies, depending on its position in the basin, between immature and over mature.

The Agrio Formation is divided in two members. The Lower Member has two intervals with black shales. The lower one is associated with the Vaca Muerta-Mulichinco hydrocarbon system, while the upper one would form an independent hydrocarbon system, associated with the Avilé Member as reservoir. The black shales of the Lower Member of the Agrio Formation are characterized as very good source rocks. The kerogen is Type II, of marine bacterial-algae origin, deposited in an anoxic environment, with minor terrestrial organic matter supply. The TOC values vary between 1 and 3.5%. Average values of HI and OI are 200 mg HC/g TOC and 20 mg CO_2/g TOC. Thermal maturity varies, changing with the location in the basin, from immature to mature (late oil stage).

The Upper Member of the Agrio Formation is a potential source rock. It is formed of bituminous black shales and minor limestones of marine shelf environment. TOC values vary between 1 and 2%, with peaks up to 3.5%. The organic matter is amorphous, sapropelic, of algae origin, with minor terrestrial influence (kerogen type II to II-III). HI and OI values are 100 – 300 mg HC/g TOC and 27 mg CO_2/g TOC. Thermal maturity varies from mature to immature (0.6 – 0.8 % Ro).

Numerous shale intervals, in almost all levels of the Jurassic, Cretaceous and Tertiary sedimentary section, are efficient seals, together with the evaporitic levels of the upper part of the Tábanos, Auquilco, Huitrin and Rayoso megasequences.

In several fields, the unconformities at the base of some of the megasequences also act as seals. Some seals can be normal, and reverse faults generated during Middle and Upper Tertiary times. On the other hand, in other fields, the seal is provided by variations in the permeability within the same formation.

A large variety of traps occur in the Neuquén basin: structural, stratigraphic and a combination of both. Over 50% of the commercial oil discovered in the basin was trapped in stratigraphic or combined traps. Presently, it can be said that most of the structures have already been drilled. Some of the largest fields, like Loma La Lata, are stratigraphic traps, and there are other localities that could potentially be favorable for this type of traps, like the area at the south of the Colorado River, and south and north of the Huincul Dorsal. (Pangaro *et al*. 2002, 2006). Magmatism has played a sometimes disregarded key role in the basin evolution and oil generation, but for the studied wells the influence of volcanic activity is not considered relevant.

METHODOLOGY

Cutting samples (3 m spacing) submitted from the wells were washed, rinsed and cleaned at DTP Laboratories (ISO 17025 Laboratory) for quantitative Energy Dispersive X-Ray Fluorescence (EDXRF), using a Shimadzu 720 instrument. Samples were milled with a Spex mixing miller and sieved through mesh 200. The powdered samples were pressed to form a pill without addition of agglutinant and then measured in vacuum. Precision for major, minor and trace elements is in the order of 3%. Gas samples were collected at the wellhead during drilling (location in Fig. 1) in aluminum Isotubes through a proprietary by pass device, and were analyzed for molecular composition at DTP Laboratories by Gas chromatography – Flame ionization detector (GC-FID). Carbon isotopes were measured by Geoisochem Laboratories using GC-IRMS standard techniques. Carbon isotopic compositions of molecular organic compounds are reported relative to Vienna - Peedee Belemnite (V-PDB) standard. Precision for individual components in the molecular analysis are ±2% and ±0.1‰ for $\delta^{13}C$. Results are shown in Table 1 and Table 2 for both molecular – isotope analysis. XRF data can be requested to the authors, due to the sampling interval and number of analysis involved (>400).

DISCUSSION

Inorganic geochemistry

In the last decades, inorganic geochemical data have been shown that bulk rock geochemical data can provide chemostratigraphic correlation and can be linked with other parameters like total organic cabon, brittleness, redox conditions and 3D modeling of petrophysical parameters, which are critical to constrain reservoir characteristics (i.e.: Ratcliffe *et al.* 2006, Pearce *et al.* 1999, 2010, Hildred *et al.* 2011). The ability to identify the most promising and richest (perforating) zones within the shale is derived from the geochemical data to mineralogy, and it is possible for shale objectives to estimate real reserves on a more confident and correlatable basis.

Agua del Cajon oilfield – ADC-1016 Well

In this site, the interval Precuyo-Lajas Formation was sampled, with emphasis in the source rock. We will summarize the obtained information, focusing in the objectives of the pilot test. The section, represented in Figure 3, shows the variation of SiO_2, Al_2O_3 and CaO. Lithology is deduced from chemical analysis, after Herron (1988) and Spalletti *et al.* (2014).

Table 1. Isotope analysis.

Well	$\delta^{13}CC_1$	$\delta^{13}CC_2$	$\delta^{13}CC_3$	$\delta^{13}CCO_2$	$\delta^{13}C_2$-$\delta^{13}C_3$	Unit	Depth
NqSa 1148	-26,7	-27,1	-26,5	-9,5	-0,6	Quintuco Fm.	1348
NqSa 1148	-54,8	-28,5	-27,8	-11,7	-0,8	Quintuco Fm.	1407
NqSa 1148	-35,2	-26,6	-26,8	-10,5	0,2	Quintuco Fm.	1422
NqSa 1148	-50,3	-24,4	-25,7	-9,3	1,3	Quintuco Fm.	1425
NqSa 1148	-43,7	-28,1	-27,3	-11,9	-0,8	Vaca Muerta Fm.	1437
NqSa 1148	-57,1	-24,4	-26,6	-13,5	2,2	Vaca Muerta Fm.	1452
ADC 1016	-48,7	-37,3	-32,8	-16,7	-4,4	Vaca Muerta Fm.	2280
ADC 1016	-49,6	-38,0	-33,6	-13,3	-4,4	Vaca Muerta Fm.	2321
ADC 1016	-50,5	-37,4	-33,1	-9,6	-4,3	Vaca Muerta Fm.	2330
ADC 1016	-54,3	-36,2	-32,8	-13,8	-3,4	Vaca Muerta Fm.	2360
ADC 1016	-48,4	-36,0	-32,3	-13,5	-3,7	Lajas Fm.	2614
ADC 1016	-33,8	-31,3	-30,5	-16,0	-0,8	Lajas Fm.	3489
ADC 1016	-32,2	-32,2	-29,0	ND	-3,1	Lajas Fm.	3674
ADC 1016	-35,5	-32,5	-28,3	-15,8	-4,2	Lajas Fm.	3685
ADC 1016	-37,9	-28,7	-28,2	ND	-0,5	Los Molles Fm.	3826
ADC 1016	-32,7	-28,4	-28,4	-14,1	-0,1	Los Molles Fm.	3900
ADC 1016	-31,1	-26,3	-29,5	-15,9	3,2	Los Molles Fm.	4003
ADC 1016	-32,8	-25,9	-27,1	-16,2	1,2	Los Molles Fm.	4105
ADC 1016	-41,0	-27,3	-22,5	ND	-4,8	Precuyo Gr.	4133
ADC 1016	-35,1	-26,6	-23,2	-15,0	-3,5	Precuyo Gr.	4223
ADC 1016	-40,0	-25,9	-20,9	ND	-5,0	Precuyo Gr.	4233

ND: Not determined.

Table 2. Molecular analysis (GC-FID).

Well	C1%	C2%	C3%	iC4%	nC4%	iC5%	nC5%	
NqSa 1148	64,0	8,5	8,8	2,7	6,9	3,5	5,6	100,00
NqSa 1148	66,2	7,3	9,2	2,2	7,7	2,7	4,7	100,00
NqSa 1148	72,7	6,0	6,9	1,9	6,2	2,4	4,0	100,00
NqSa 1148	74,6	7,6	6,1	1,6	4,6	2,1	3,4	100,00
NqSa 1148	47,4	11,4	14,4	3,6	13,7	3,1	6,4	100,00
NqSa 1148	73,7	6,5	6,6	1,9	5,3	2,5	3,7	100,00
ADC 1016	74,2	12,0	7,8	1,0	3,2	0,7	1,2	100,00
ADC 1016	72,7	12,8	8,3	1,0	3,4	0,6	1,2	100,00
ADC 1016	69,9	13,5	9,4	1,2	3,9	0,8	1,4	100,00
ADC 1016	71,6	12,7	8,4	1,1	3,8	0,8	1,5	100,00
ADC 1016	79,4	12,2	6,0	0,7	1,4	0,2	0,2	100,00
ADC 1016	58,3	21,5	12,9	2,8	4,5	<q.l.	<q.l.	100,00
ADC 1016	96,4	2,7	0,5	0,2	0,1	<q.l.	<q.l.	100,00
ADC 1016	53,3	18,5	17,0	2,9	8,2	<q.l.	<q.l.	100,00
ADC 1016	97,2	2,2	0,3	0,2	0,1	<q.l.	<q.l.	100,00
ADC 1016	96,2	3,0	0,5	0,2	0,1	<q.l.	<q.l.	100,00
ADC 1016	97,6	2,0	0,3	0,1	0,1	<q.l.	<q.l.	100,00
ADC 1016	73,5	23,6	2,0	0,3	0,7	<q.l.	<q.l.	100,00
ADC 1016	97,7	1,9	0,2	0,1	0,0	<q.l.	<q.l.	100,00
ADC 1016	98,1	1,6	0,2	0,1	0,0	<q.l.	<q.l.	100,00
ADC 1016	98,6	1,2	0,1	0,0	0,0	<q.l.	<q.l.	100,00
Well	**C1/C2**	**C1/C2+C3**	**C2/C3**	**i/nC4**	**i/nC5**	**C2/iC4**	**Unit**	**Depth (m)**
NqSa 1148	7,53	3,70	0,97	0,40	0,63	3,10	Quintuco Fm.	1348
NqSa 1148	9,05	4,01	0,80	0,28	0,58	3,35	Quintuco Fm.	1407
NqSa 1148	12,10	5,66	0,88	0,31	0,60	3,17	Quintuco Fm.	1422
NqSa 1148	9,85	5,44	1,23	0,35	0,61	4,75	Quintuco Fm.	1425
NqSa 1148	4,17	1,84	0,79	0,26	0,48	3,18	Vaca Muerta Fm.	1437
NqSa 1148	11,39	5,65	0,99	0,35	0,67	3,47	Vaca Muerta Fm.	1452
ADC 1016	6,21	3,76	1,54	0,32	0,57	11,81	Vaca Muerta Fm.	2280
ADC 1016	5,69	3,44	1,53	0,28	0,55	13,20	Vaca Muerta Fm.	2321
ADC 1016	5,17	3,05	1,44	0,30	0,55	11,70	Vaca Muerta Fm.	2330
ADC 1016	5,64	3,39	1,51	0,28	0,51	11,96	Vaca Muerta Fm.	2360
ADC 1016	6,53	4,38	2,03	0,49	0,86	18,37	Lajas Fm.	2614
ADC 1016	2,71	1,69	1,66	0,62	N/D	7,67	Lajas Fm.	3489
ADC 1016	35,35	29,65	5,20	2,00	N/D	13,00	Lajas Fm.	3674
ADC 1016	2,88	1,50	1,09	0,35	N/D	6,34	Lajas Fm.	3685
ADC 1016	45,18	38,93	6,22	1,67	N/D	11,20	Los Molles Fm.	3826
ADC 1016	31,96	27,62	6,36	1,42	N/D	15,96	Los Molles Fm.	3900
ADC 1016	49,71	43,65	7,21	1,37	N/D	20,15	Los Molles Fm.	4003
ADC 1016	3,11	2,87	12,03	0,40	N/D	88,18	Los Molles Fm.	4105
ADC 1016	50,93	45,39	8,19	3,14	N/D	19,73	Precuyo Gr.	4133
ADC 1016	62,02	56,06	9,41	1,15	N/D	28,61	Precuyo Gr.	4223
ADC 1016	79,06	71,57	9,56	3,88	N/D	25,29	Precuyo Gr.	4233

Chemostratigraphic analysis reflects a clear contrast between the Precuyo Unit and Los Molles Formation. The contrast can be determined by main inflexions not only in major elements as Si and Al but also in Mo, Zn, V and Ni (Fig. 4). In Los Molles Formation, two chemostratigraphic units are clearly distinguished: Lower Los Molles Formation (LLM) and Upper Los Molles Formation (ULM, Fig. 4). Change in the content in authigenic elements like Mo, V, Zn and S identify the LLM from the ULM. Transition between ULM and Lajas Formation (LF) is not clear, except for the amplitude of the geochemical variations and the general trends from 3,800 md. We suggest that this is probably the real contact between Los Molles Formation and Lajas Formation, and that the previously presumed location (around 3,500 md) was inappropriate due to the fact it was based on well log observations. Total gas concentration

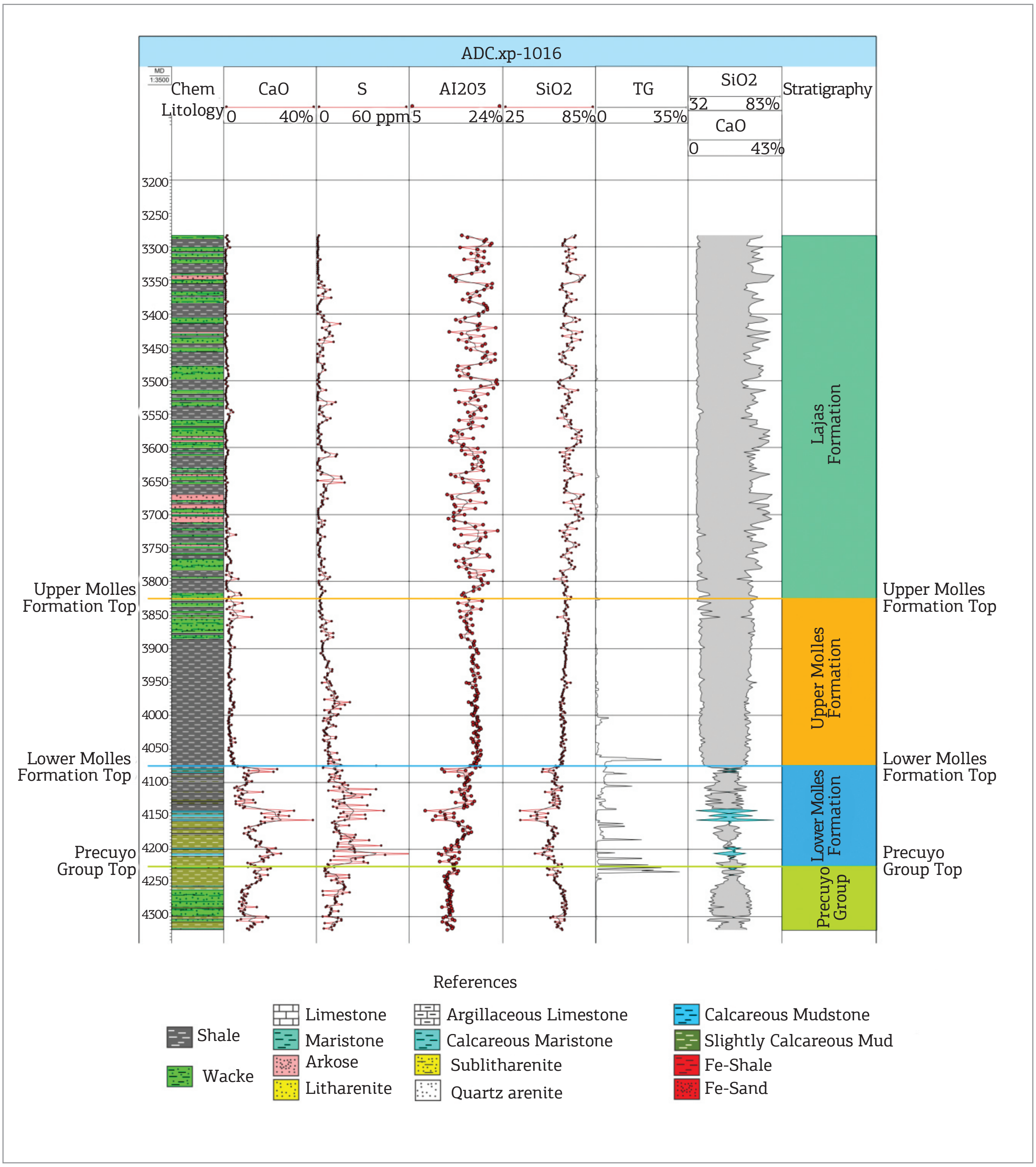

Figure 3. Well ADC-1016. Chemostratigraphic logs (major elements), Total mud gas and formations.

and overpressure is detected in LLM. Figure 4 shows the enrichment in authigenic elements like Mo and Zn, associated with total gas peaks. In our criteria, it is a first order correlation at least for Lower Molles and shows the most promising producing levels. Precuyo units (PC) and ULM also show gas peaks, but they are no associated with geochemical anomalies.

El Salitral oilfield –NqSa-1148

NqSa-1148 is a shallow well, and, in this case, the geochemical and isotope analysis were focused in the presumed source rock (Vaca Muerta Formation) and reservoir (Quintuco Formation.). Additional geochemical data from lower (Lajas Formation.) and upper units (Centenario Formation) were also considered.

For Vaca Muerta Formation, chemolithology suggests the alternance of shales and calcareous mudstones, reflecting the transgressive character of the unit. The section showed in Figures 5 and 6 reflects increasing anomalies in authigenic elements like Mo, associated with euxinic levels. Accompanying anomalies in Ni, V and S reflect the transition between anoxic-oxic conditions in a timescale detectable by the data (Tribovillard *et al.* 2006). Quintuco Formation, limited by an inflexion in S and V values, shows the higher contents of calcium, with remarkable positive magnesium anomalies in the middle of the section assigned to dolomite replacement. Maximum total gas contents are associated with Mo maximum for Vaca Muerta Formation and Mg maximum in the case of Quintuco Fm. We suggest that the latter case could be related with deep fluids ascent,

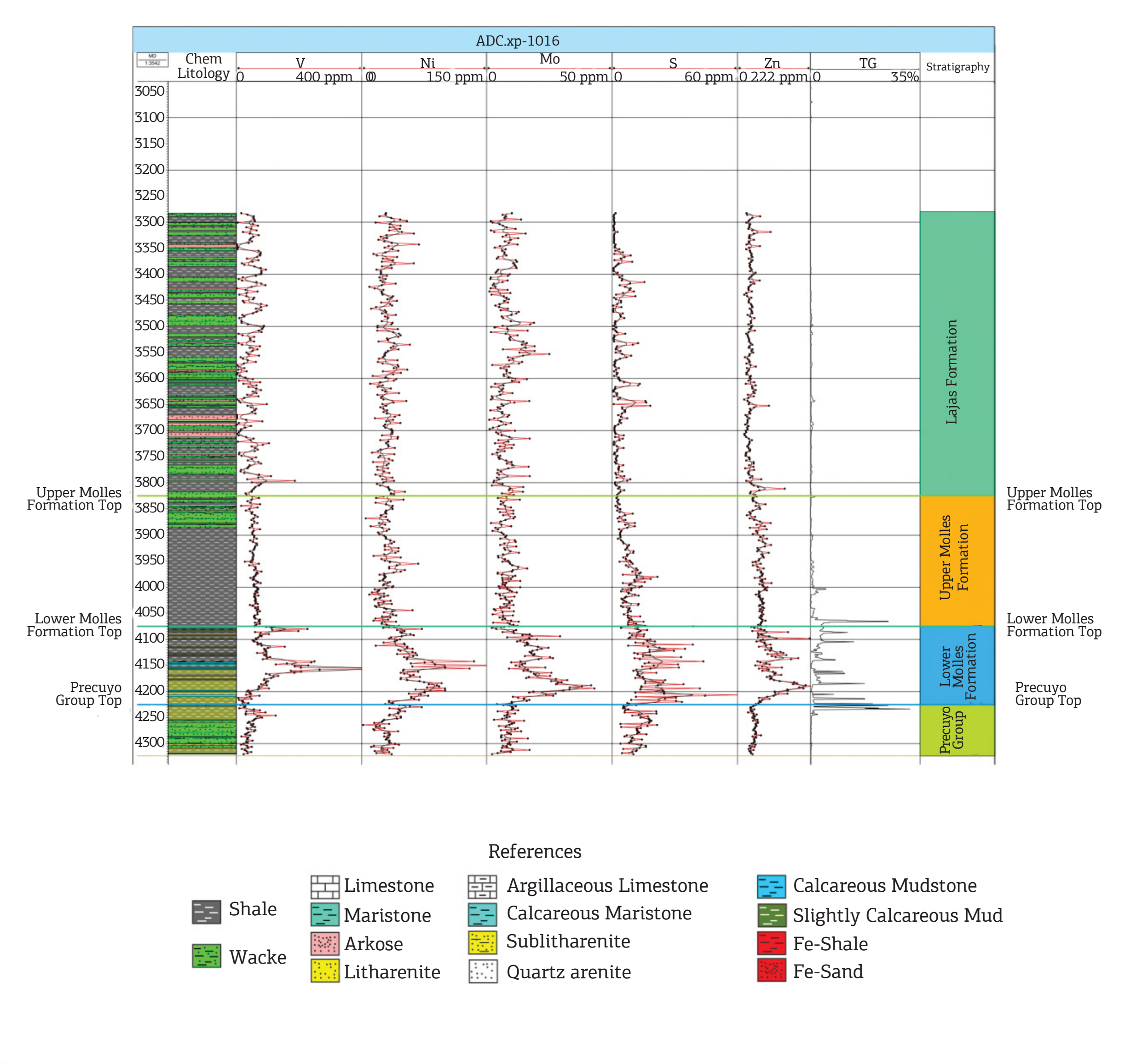

Figure 4. ADC-1016 well. Chemostratigraphic logs (authigenic trace elements) and total mud gas.

replacement and circulation (thermobaric reservoir?), due to the evidences of limited reservoir enhancement observed in near wells. Centenario Fm. displays a marked increment in siliciclastic components, with higher values of Si and Al, except for a short Ca-rich interval at the base.

Carbon isotopes

During the late XX century, the geochemistry of natural gas has received attention from different empirical and theoretical points of view and has supported important advances (Stahl 1973, Schoell 1980, 1983, James 1983, Chung *et al.* 1988, Clayton 1991, Behar *et al.* 1992, Berner *et al.* 1995, Tang & Schaufer 1994, Whiticar 1994, Tang & Jenden 1995, Rooney *et al.* 1995, Price & Schoell 1995, Lorant *et al.* 1998, Tang *et al.* 2000, Prinzhofer *et al.* 2000, Zhang 2013). Most data reflect a sequence of decreasing carbon isotopic compositions from methane $\delta^{13}C$to butane $\delta^{13}C$. However, since many years ago, isotope reversals were detected in deep wells (Jenden *et al.* 1993, Laughrey & Baldassare 1998, Wavrek *et al.* 1999, Hechem *et al.* 2003, Burruss & Ryder 2003), and different explanations have been suggested to be theoretically possible, including gas mixing, abiotic

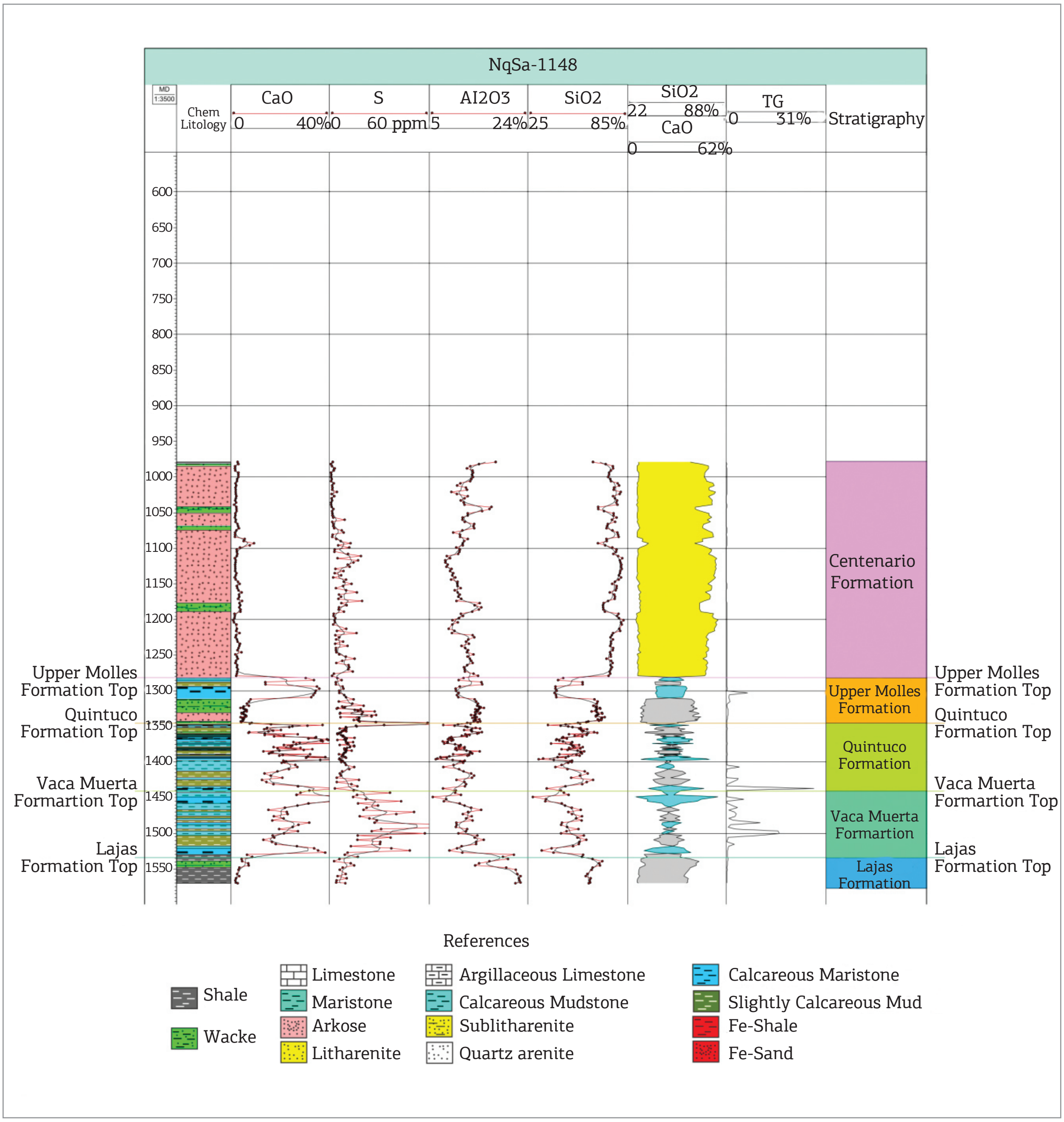

Figure 5. NqSa -1148 well. Chemostratigraphic logs (major elements), Total mud gas and formations.

sources, different levels of maturity, Rayleigh fractionation, late stage generation of methane and a combination of all or part of these processes (James & Burns 1984, Krouse 1988, Chung *et al.* 1988, Jarvie *et al.* 2007, Prinzhofer 2008, Behar *et al.* 2010, Burrus & Laughrey 2010, Schoell 2011, Tilley & Muehlenbachs 2013). These data have contributed to evaluate new and not well known resources.

Carbon isotopes were interpreted on the basis of well-known graphic plots. In the Schoell plot (Fig. 7) it is visible that all gases can be classified as thermogenic gases with variable degrees of maturity, mixing with biogenic gases and secondary processes like bacterial oxidation. Bernard plot (Fig. 8) identifies those gases associated with Vaca Muerta and Los Molles sources in both wells. Some anomalies on heavy isotopes ($\delta^{13}CC_1$) in gases from Lajas Formation, Quintuco Formation and Los Molles Formation shown in the Bernard Diagram could be explained as product of oxidation. Vaca Muerta and Los Molles source rocks generate gas that must be classified as wet, and Los Molles gases are drier than the Vaca Muerta ones. Precuyo gases in the Bernard Diagram are close to LM gases, associated with a kerogen Type II trend.

The normal trend in the Whiticar diagram (Fig. 9) is defined by the solid line that can also be related for vitrinite reflectance equivalence; also is useful to determine the reason for the different anomalies. In the $\delta^{13}CC_1$ –$\delta^{13}CC_2$ diagram, it can be recognized the bacterial methane contribution for gases from Quintuco Formation, Vaca Muerta Formation (NqSa-1148, ADC-1016), Lajas Formation (NqSa-1148) and Precuyo (ADC-1016), and the existence of methane oxidation for most samples of Lajas Formation, Los Molles Formation and Precuyo (ADC-1016). Only one sample of Quintuco Formation is in the methane oxidation field for Nq-SA 1148 field.

The $\delta^{13}CC_2$ – $\delta^{13}CC_3$ diagram (Fig. 10), less sensitive to the bacterial contribution, reflects the existence of biodegradation for PC samples and thermogenic gas mixing in the case of ADC-1016 well (Los Molles) and Sa 1148 well

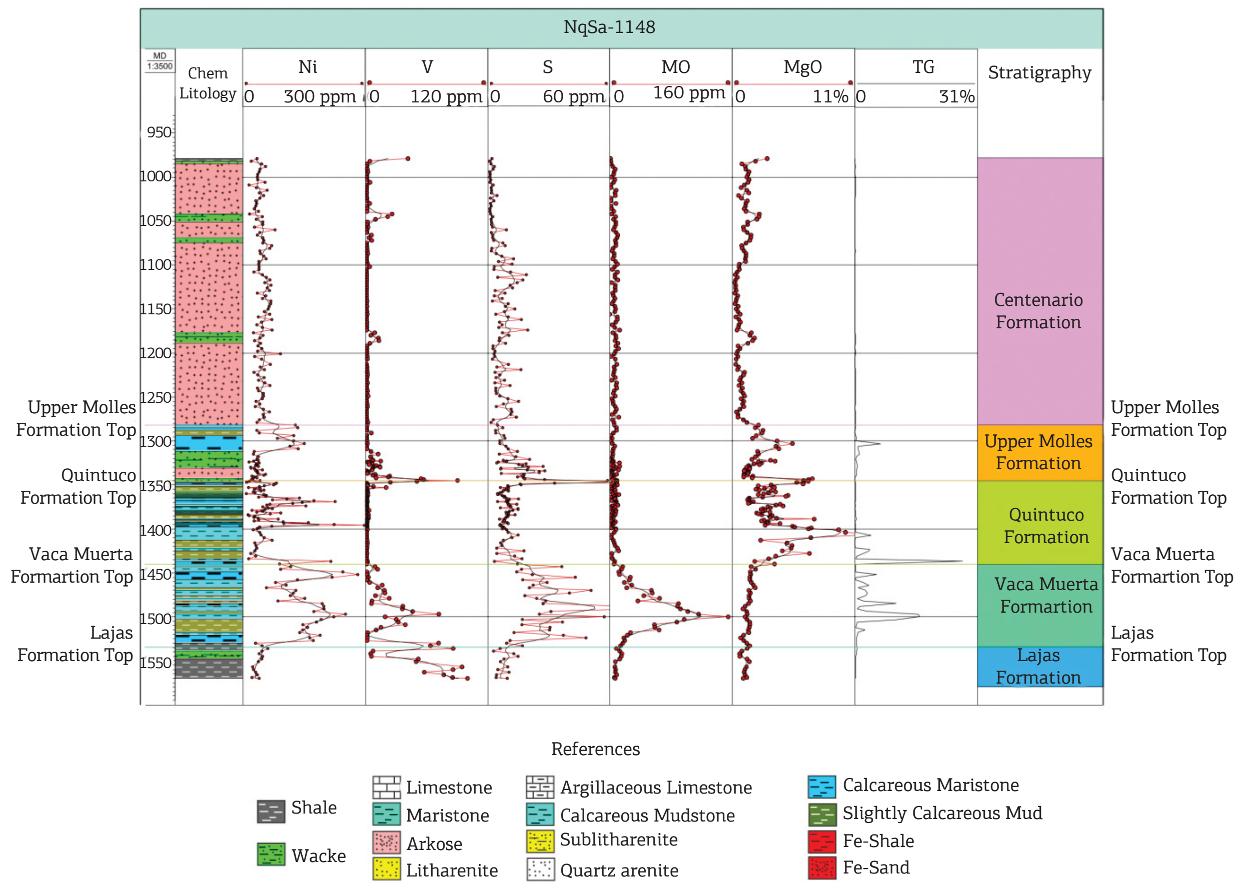

Figure 6. NqSa -1148 well. Chemostratigraphic logs (authigenic trace elements) and total mud gas.

(Vaca Muerta and Quintuco Formations). The samples display evidence of mixing of either thermogenic or microbial gas. In spite of microbial addition of methane, microbial consumption of C_2 and C_3 and mixing of gases, as a first approach, the Whiticar line can give us an idea of thermal maturity shown as vitrinite reflectance. The data is in agreement with the presumed thermal history for the different units at the Huincul Dorsal.

It is necessary to make a distinction between gas generated from primary cracking of kerogen from those generated by the secondary cracking of crude oil or secondary gas cracking (in situ reservoir process). The premise of the Lorant *et al.* (1998) plot is that the ethane/propane ratio remains constant during primary cracking, whereas it increases rapidly during secondary cracking. Ethane minus propane carbon isotopes tend towards zero with increasing

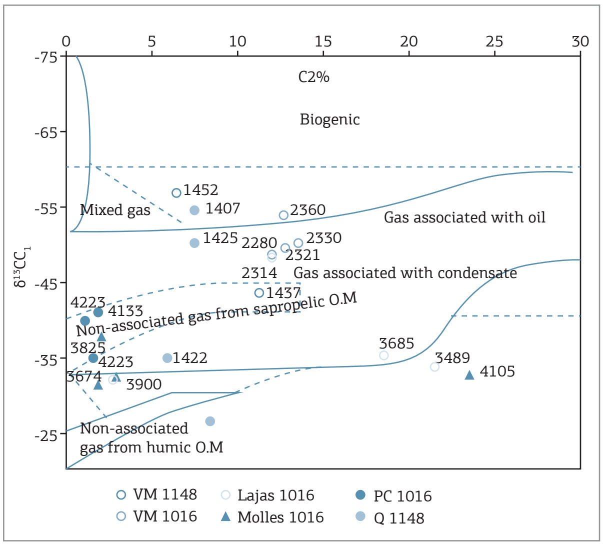

Figure 7. Schoell plot. Key: VM: Vaca Muerta Fm.; Lajas: Lajas Fm.; Molles: Los Molles Fm.; PC: Precuyo Group; Q: Quintuco. 1016: ADC-1016 well; 1148: El Salitral 1148 well. Numbers: MD.

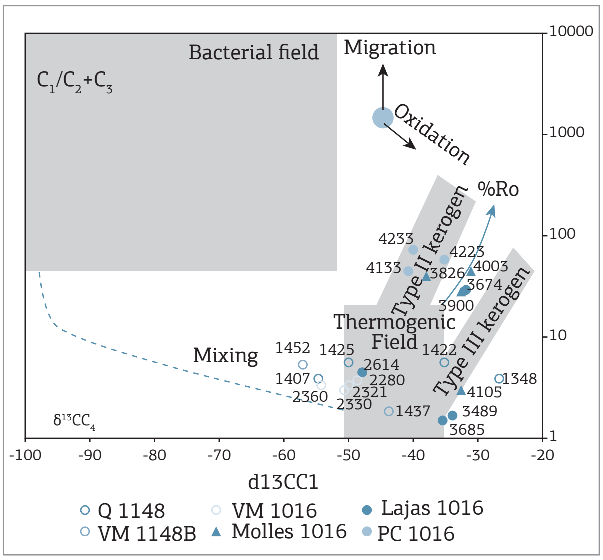

Figure 8. Bernard plot. Key: VM: Vaca Muerta Fm.; Lajas: Lajas Fm.; Molles: Los Molles Fm.; PC: Precuyo Group; Q: Quintuco. 1016: ADC-1016 well; 1148: El Salitral 1148 well. Numbers: MD.

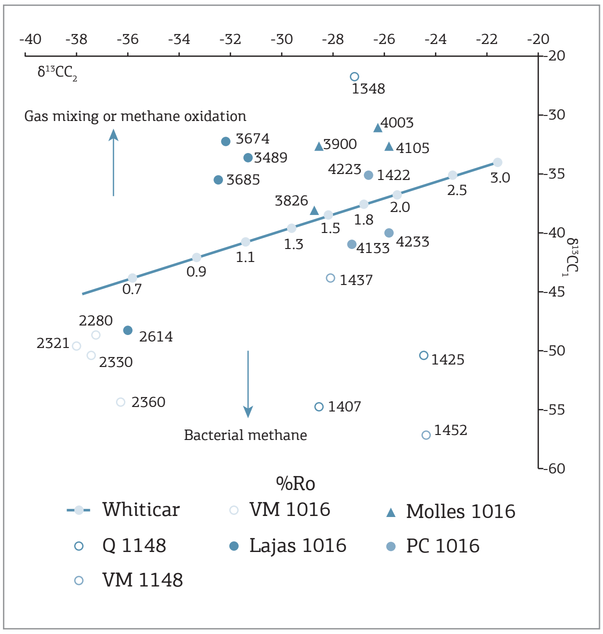

Figure 9. Whiticar plot. Key: VM: Vaca Muerta Fm.; Lajas: Lajas Fm.; Molles: Los Molles Fm.; PC: Precuyo Group; Q: Quintuco. 1016: ADC-1016 well; 1148: El Salitral 1148 well. Numbers: MD.

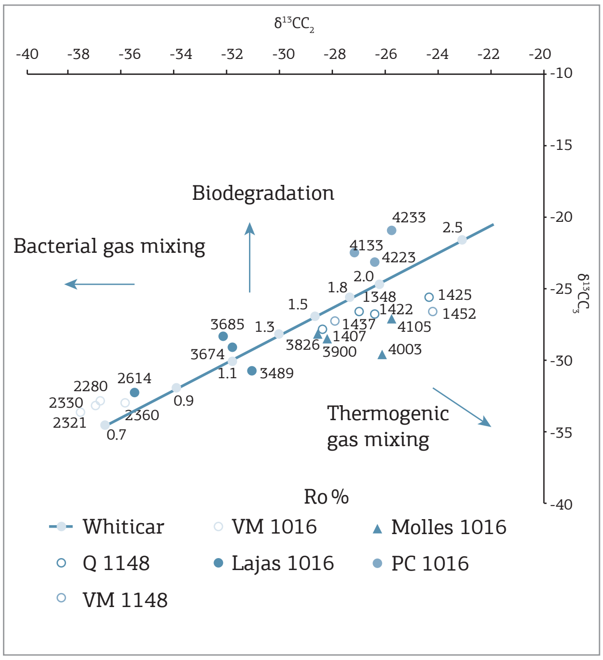

Figure 10. Whiticar plot. Key: VM: Vaca Muerta Fm.; Lajas: Lajas Fm.; Molles: Los Molles Fm.; PC: Precuyo Group; Q: Quintuco. 1016: ADC-1016 well; 1148: El Salitral 1148 well. Numbers: MD.

maturity in primary cracking, but it is not the case for secondary cracking of oil. Figure 11 reflects that most samples from de Sa 1148 well (VM and Q) can be associated with a primary cracking, together with VM gases of ADC-1016. Los Molles gases are located far from a normal trend, suggesting the existence of oil cracking and residual oil as source. Precuyo gases show evidences of secondary cracking of gas, and all samples are close together.

The pattern of C_1-C_3 carbon isotopes (Natural gas plot or Chung Plot) for gas analysis on samples from ADC-1016 well, corresponding to LLM, ULM, PC, LF and Vaca Muerta (VM) units is shown in Figure 12. All the groups can be identified and characterized. Precuyo Group gases show the most enriched values on $\delta^{13}CC_2$ and $\delta^{13}CC_{3,}$ with variable contributions of biogenic methane. The intersections with the Y-axis indicate anomalous high values, and this can be related with the origin of PC gases. Deeper and over pressurized part of Los Molles Formation shows isotope reversals in 4003 – 4118 depths. This is the first time (at least, published) that these reversals are found in the Huincul Dorsal, associated with an over pressurized section. This fact has been detected in other shale prospects from Northern Hemisphere and also recognized in Vaca Muerta shale wells (DTP Labs, *unpub*.). Usually, these anomalies accompany the most productive wells, and this is a case that confirms the rule. Overpressure and associated increase in temperature are linked to secondary cracking and isotope reversal

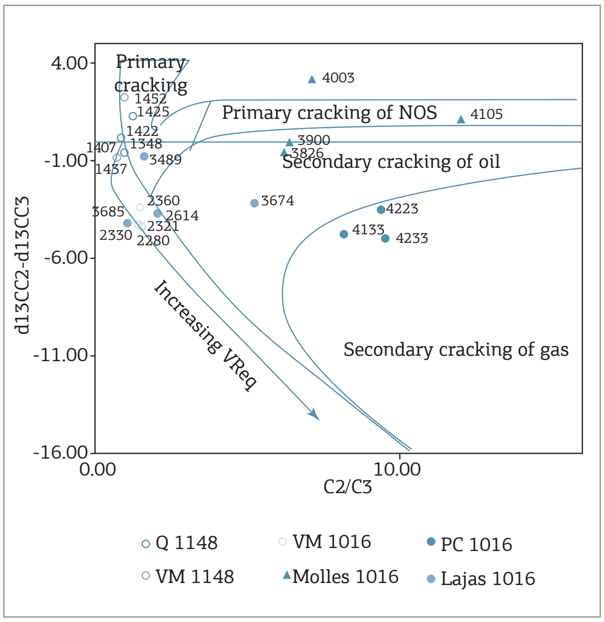

Figure 11. Lorant *et al.* plot, 1998. Key: VM: Vaca Muerta Fm.; Lajas: Lajas Fm.; Molles: Los Molles Fm.; PC: Precuyo Group; Q: Quintuco. 1016: ADC-1016 well; 1148: El Salitral 1148 well. Numbers: MD.

(Zumberge *et al.* 2009, 2012), process that results in the presence of a "reservoir" filled with dry gas (Chatellier *et al.* 2011). Water-reforming of high-mature organic matter coupled with Fischer-Tropsch process is a possible mechanism for shale gas generation, as suggested by Tang & Xia (2010a,b). This is also consistent with the isotope reversal detected.

The existence of processes like hydrocarbon reforming and water participation suggested by Tang & Xia (óp.cit.) and Zumberge *et al.* (2012) can explain the $\delta^{13}C$ enrichment trend associated with C_2% diminution that can be seen in Figure 13. The $\delta^{13}CCO_2$ become heavier until 7.6% C_2 and then reverses to more negative values. This observation

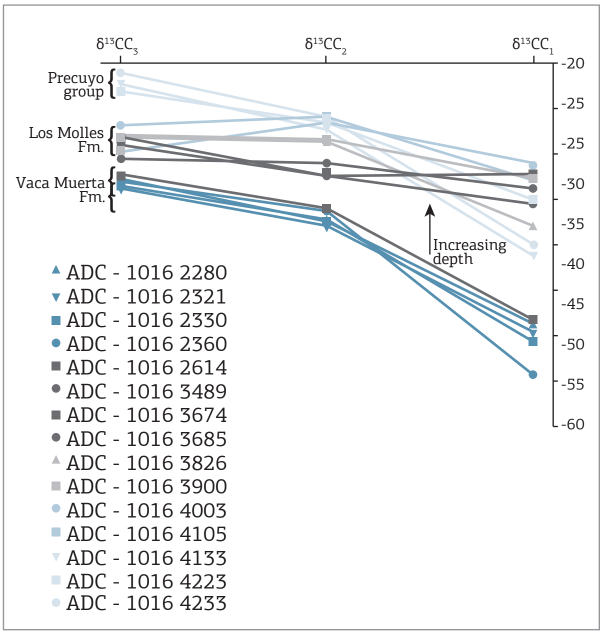

Figure 12. Natural gas plot (Chung Plot) for ADC-1016 well, with potential sources.

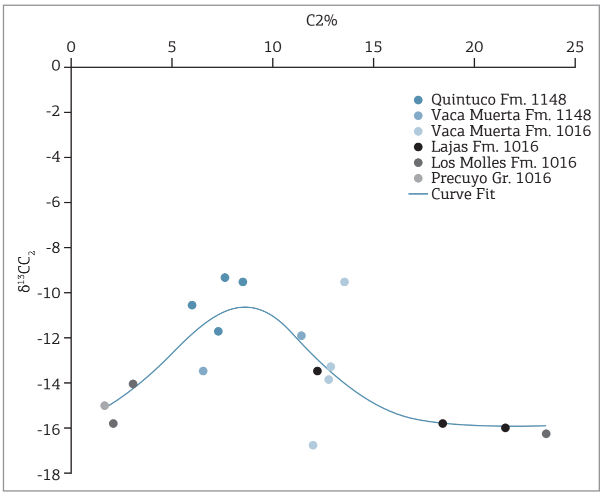

Figure 13. Correlation between $\delta^{13}CCO_2$ – C_2%. Sample depth indicated.

could be linked with Tang & Xia (óp.cit.) two stage reaction scheme, involving H_2 and CO_2 by water reforming in the first step. Data on isotope composition of co-produced shale water and maturity in the Neuquén basin show a variation trend compatible with this process (Ostera, unpub. data).

ULM presents less enriched carbon isotope compositions, although reach almost equal values for C_2 and C_3. Lajas Formation presents a less evolved trend. As a whole, LMF and LF present similar compositions, indicating Los Molles source for the sampled interval 3489 – 4105 md. However, a sample belonging from 2614 md shows a clear contribution from VM source, which has been sampled at interval 2280 – 2360 md. In this case, the composition reflects a contribution of biogenic methane and an evolution in accordance with the registered thermal maturity for VM in the area and the probable characteristics of the source rock.

From the same well, Isotope composition of Los Molles Formation is, as it could be expected, very different from Vaca Muerta source. Gas analysis from levels 2280 – 2360 md reflect that Vaca Muerta gases show lower maturity compared with Los Molles Fm. In both cases, isotope analysis adjust to theoretical calculated evolution by isotope modeling, although with limitation for Los Molles gases, which in our opinion reflect the process complexity (oil cracking) and supply and mixing of more mature gases added to Lower Los Molles from deeper sources (Fig. 14). Extreme values are shown in Precuyo Unit. In such case, we propose the possibility of an evolved source rock, with associate gas cracking.

For Sa-1148 well, data on carbon isotopes for Vaca Muerta and Quintuco Formations reflect a marked increase on C_2-C_3 isotope ratios compared with the ADC-1016 well data, and a relevant biogenic contribution (Fig. 12). Shale gas

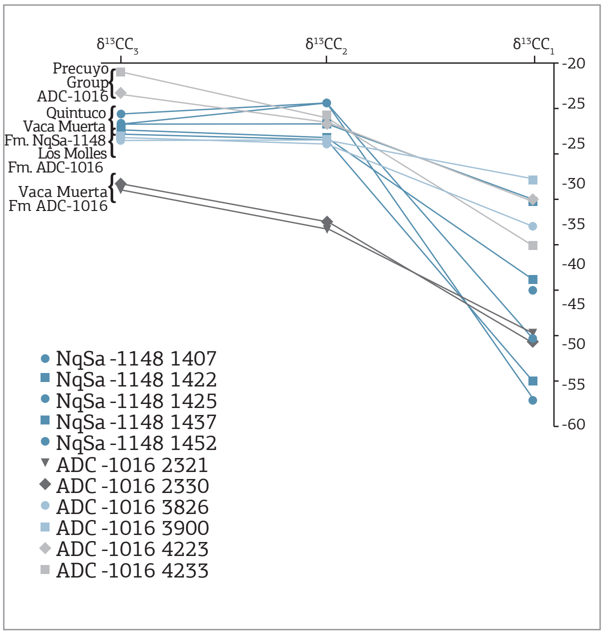

Figure 15. Natural gas plot, NqSa.-1148 well samples. Representative samples for ADC-1016 are also.

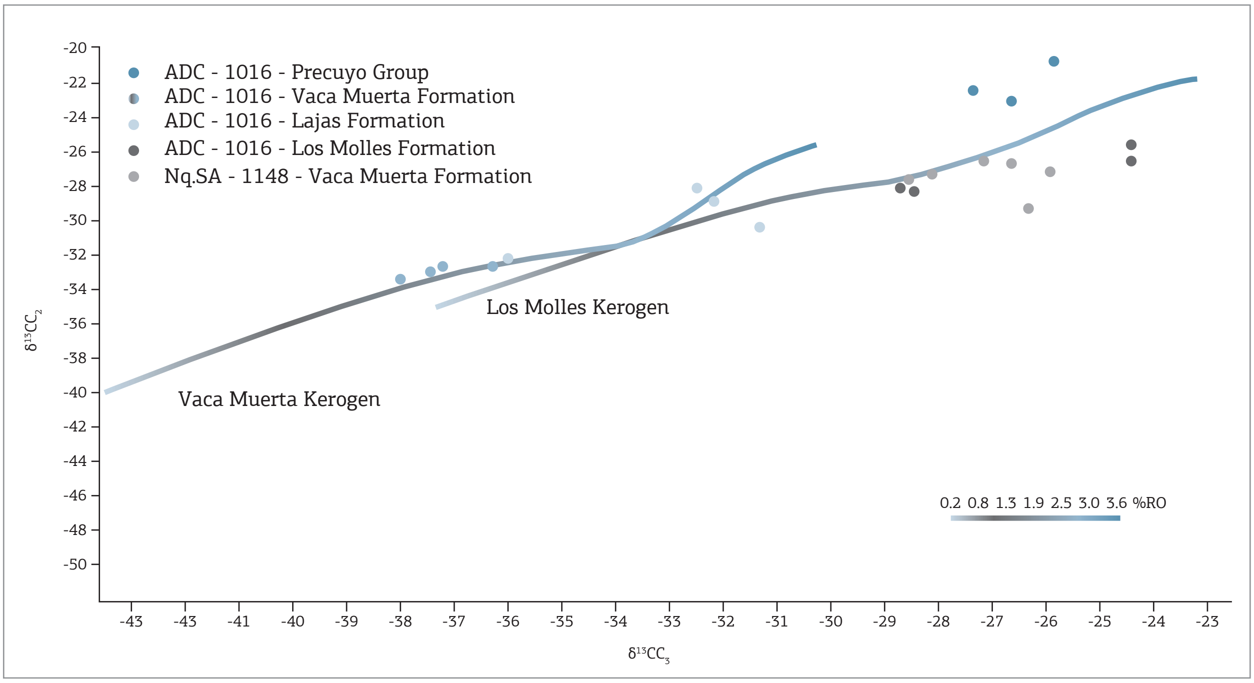

Figure 14. Theoretical isotope evolution and gas analysis for Vaca Muerta Kerogen and Los Molles Kerogen in the Huincul Dorsal at well location $\delta^{13}CC_2$- $\delta^{13}CC_3$. Modelled using GOR-Isotopes™ software, accumulated gas.

plays use to have heavier compositions, due to the differential adsorption of isotopes on organic matter. Shale gas from Vaca Muerta (DTP unpub. data) typically is enriched in ^{13}C and many times shows isotope reversals. However, this effect alone is not considered responsible of isotope compositions. The pattern of isotope evolution can be linked with another source rock (Los Molles Fm.), recharging the reservoirs and overwhelming and overprinting the gas content of Vaca Muerta Formation, due the overlapping of values shown in Figure 15. Although other interpretation could be possible, in this case, we think that gas coming from Los Molles Formation through main structures related with the Huincul Dorsal could be the ultimate source for this gas. Such source agrees with the theoretical evolution shown in Figure 14. This assumption is in accordance with structural, geophysical and geological evidences, which reflect the existence of deep structures in the Huincul Dorsal with the ability to act as migration pathways for gases coming from more evolved source rocks. Detected vertical migration pathways, which represent expulsion of primary gas from Los Molles source rock, have been identified by shallow gas clouds. This gas migrates through the relatively low maturity Vaca Muerta oil prone source, causing expulsion of oil from Vaca Muerta (Conolly & Garcia 2010) and giving this particular isotopic fingerprint.

CONCLUSIONS

Geochemical study of ADC-1016 and Sa-1148 at the Huincul Dorsal led to the recognition of the main formational units and revealed that shale objectives have restricted levels in order to perforate and produce. In the case of Los Molles shale play (well ADC-1016), only Lower Los Molles Formation seems to have appropriate conditions to be produced. At El Salitral oilfield (Sa-1148 well), the most interesting Vaca Muerta - Quintuco objectives are associated with authigenic elements. They have also delimited horizons at the shale objective and reservoir. Enhancement of the Quintuco reservoir by deep circulating fluids suggests the possibility of a thermobaric reservoir. Carbon isotope analysis on wells of the Huincul Dorsal (Agua del Cajon and Salitral oilfields) reveals complex processes that affected the gas composition of shale and conventional plays. Addition of microbial methane, biodegradation of ethane-propane and mixing of gases has been recognized. Although there are evidences for deeper objectives, like Precuyo Group at Agua del Cajón oilfield, the data reveal overmature conditions and gas cracking for this source on the basis of isotope compositions. Isotope reversals have been registered associated with overpressure for Lower Los Molles Formation in the ADC-1016 well, and water reforming is proposed on the basis of the presented evidence. This suggests that Lower Los Molles Formation could be the most promising shale play in the area. At Agua del Cajon ADC-1016 well, Vaca Muerta gases are well correlated with the accepted homonymous source. El Salitral 1148 well shows that primary isotope composition in this shale play and associated reservoirs is overwhelmed by an aloctonous charge, related with the main structures of the area and associated with a probable Lower Los Molles source.

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