

## **Geochemical Characterization of Heavy Oil Accumulations on the Northeastern Margin of the Neuquén Basin, Argentina**

Martín F. Cevallos, Edmundo N. Marot, Hernán Paponi

Petro Andina Res. Ltd., Maipú 1210 4-P (ACT1006) Buenos Aires, Argentina

[martin.cevallos@petroandina.com](mailto:martin.cevallos@petroandina.com), [nicolas.marot@petroandina.com](mailto:nicolas.marot@petroandina.com), [hernan.paponi@petroandina.com](mailto:hernan.paponi@petroandina.com)  
and

Héctor Villar

GeoLab Sur S.A., Italia 1616 (1602DOF), Florida-Buenos Aires, Argentina

[Hector.Villar@geolabsur.com](mailto:Hector.Villar@geolabsur.com)

### **Summary**

One of the key issues related to heavy oil development is understanding the variation of API gravity and viscosity. Direct measurements are usually difficult (mainly for viscosity) and provide limited information regarding genesis of the hydrocarbons. Geochemistry has been used effectively to characterize heavy oil pools, and data collection at early stages of development is the key to addressing depletion strategies.

Recent heavy oil discoveries and their development by Petro Andina in the Northeastern margin of the Neuquén Basin (Mendoza and La Pampa Provinces, Central-Western Argentina) motivated an intensive rock and fluid characterization project. At early development stages, the lack of good analogies in the country forced the company to base reserves assessments and reservoir performance on inappropriate analogs, lab studies and incipient pilot projects. This is way fluid sampling for geochemical characterization began in the exploration phase and it is still ongoing.

In the studied areas, hydrocarbon pools are mainly in stratigraphic traps, where truncation and pinch-out are the key elements on updip edges. The main reservoirs are unconsolidated sandstones of the Centenario Formation (Hauterivian), deposited in a marginal marine to fluvial environment. Petrophysical properties are very good, with 30% average porosity and permeability ranging from 0.5 to 3 Darcies. The arid paleoclimate of the region and the predominance of siltstones and shaly sands in the shallower formations, resulted in a thick vadose zone causing a “naturally under pressured regime”. The main pay zone is at an average depth of 600 meters (Figure 1(a)).

There is an overall vertical distribution of hydrocarbon types along the preserved Cretaceous section. The deeper reservoirs, the carbonate-siliciclastic mixture of the Loma Montosa Formation, host the lighter oils, with 30 °API and 2500 GOR. The main pay zone is in the Centenario Formation and it accounts for 99% of the producing reserves and has oil gravities averaging 19° API (range 15 to 20° API), viscosities ranging from 250 - 700 cP at reservoir conditions. The shallowest hydrocarbon pools are hosted by the Neuquén Group (Upper Cretaceous), which are mainly saturated with methane (6 - 30 % molar CO<sub>2</sub>) and isolated oil lenses below a poorly defined GOC (poorly sampled, preliminary around 15 °API, but lower gravities are inferred). Formation water has being intensively sampled from the main pay zone (Centenario Formation)

and sparsely for other units, showing geographic and vertical compositional variations. There is a general salinity decrease from East to West and from deeper to shallower reservoirs that could be linked to meteoric water source and or oil migration entry point.

### Geochemical Characterization

The oils of the study area are typically biodegraded but still bear the unaltered biomarker fingerprints of the basinal organic facies of the Vaca Muerta shales, considered the most prolific hydrocarbon source unit of the Neuquén Basin. Their geochemical signature is largely consistent with a siliciclastic marine source enriched in algal organic matter, deposited under moderately anoxic conditions. According to biomarker isomerization ratios and other maturity-dependant parameters such as the degree of thermal cracking of triaromatic steranes, the oils are thermally mature and have been generated close to the peak oil phase. This infers lateral migration in the order of 40-60 km from the hydrocarbon kitchen located to the South-Southwest of the producing area, according to the known present-day maturity trends known for the Vaca Muerta in this region of the basin.

The biodegradation of the oils varies from very light to, moderate. The first level (API around 30-34°) characteristically occurs in the deepest reservoir layers (Base of Lower Centenario Member and Loma Montosa Formation) where the oils have experienced either no alteration or mild to significant alteration of light ends plus occasional mild alteration of mid-range paraffins. The second level (API in the range 15-20°) is ubiquitous in the intermediate reservoir layers (Lower and Upper Centenario), where the oils are usually depleted in n-paraffins and isoprenoids. Both saturate and aromatic biomarkers are generally not affected by the biodegradation process; in particular, 25-norhopanes, typical indicators of advanced biodegradation in some oils, have not been detected in the data. The unique groups of compounds that show significant variability to allow monitoring the level of biodegradation through the entire alteration range are two- and three-ring aromatic hydrocarbons, specifically naphthalenes, dibenzothiophenes and phenanthrenes (compare with Larter et. al., 2006). These compounds show a general decrease of their concentrations with increasing oil degradation, encompassing stages where paraffins and isoprenoids have been severely altered and are no longer useful for assessment of the alteration progress, and where biomarker fingerprints remain in their original form. In addition, variations in the relative distributions of methylphenanthrenes and dibenzothiophenes allow the application of specific compound ratios that parallel the overall concentration decrease.

Although the work to determine the geochemical patterns in relation to oil biodegradation trends in the area is still in a preliminary phase, some examples that illustrate the core of the current results can be offered. Figure 2 shows the decrease of naphthalenes, dibenzothiophenes and phenanthrenes in oil samples extracted from a continuous core through a sandstone reservoir interval of approximately fifteen meters, where the deepest layers are the closest to the water contact. Whereas the gas chromatography (GC) study of the extracted oil shows a monotonous *Unresolved Complex Mixture* (UCM) pattern deprived of n-alkanes and isoprenoids in all samples, the gas chromatography-mass spectrometry analysis (GCMS) of the aromatic fractions shows the decline in the concentration of the aromatic compounds when the evaluated samples approach the water contact, that is, when the biodegradation progress is more efficient.

A second example related to the change in the relative proportions of individual compounds within each aromatic group is provided by Fig. 1(b) for four oils of a distinctive biodegradation level, in which several transformations are outstanding: massive decrease of naphthalenes; dramatic drop of phenanthrene and increase in 9-methylphenanthrene; decrease of dibenzothiophene and 4-methyldibenzothiophene. Biomarker patterns (tricyclic and pentacyclic terpanes, steranes, aromatic steroids) of the oils show no significant change with increasing biodegradation.

Overlying gas accumulations present a composition impoverished in C<sup>13</sup> content suggesting that the gas origin is not completely thermogenic, compared to the majority of the gas produced from this formation in the basin. It is interpreted that the gas is a combination of thermogenic gas migrated from the gas window and biogenic gas associated with “in situ” oil biodegradation.

Formation water composition has geographic and vertical variations. There is a general salinity decrease from East to West and from deeper to shallower reservoirs. Highest salinities are found in conventional reservoirs in the deepest areas (70,000 – 90,000 ppm Cl<sup>-</sup>eq). In the Centenario Formation, the highest salinity exists to the east (45,000 ppm Cl<sup>-</sup>eq), and in the lower member of the formation; salinity decreases to 29,000 ppm Cl<sup>-</sup>eq as you move west in the same member. In the upper member of the formation, to the west, the lowest salinity exists in the Centenario Formation (12,000 ppm Cl<sup>-</sup>eq). In addition, formation water presents an abnormal bicarbonate concentration that could be another by-product of the oil biodegradation. Lowest salinities correspond to the Neuquen Group, the shallowest Formation in the areas, where salinity varies from 8,000 to 2,000 ppm Cl<sup>-</sup>eq.

## **Conclusions**

The oil gravity distributions show heaviest API's in the shallowest pools, where exposure to biodegradation increases. The level of biodegradation has been determined by analyzing mass chromatograms of aromatic hydrocarbon fraction. The unique groups of compounds that show significant variability to allow monitoring the level of biodegradation through the entire alteration range are two- and three-ring aromatic hydrocarbons, specifically naphthalenes, dibenzothiophenes and phenanthrenes

In the main producing zone, the Lower Centenario Member shows increasing biodegradation toward the base of the zone. Maximum bacterial activity is inferred to be occurring at the Oil/Water contact in each individual reservoir.

The origin of the extended shallow gas accumulation that overlay the oil pools (Neuquén Group) is interpreted as a combination of thermogenic gas migrated from the basin center and biogenic gas associated with “in situ” oil biodegradation. Thin Centenario top seals were enough to trap the liquid fraction, but allowed gas to leak to shallower traps.

Salinity and composition gradients of the formation water are correlative with oil gravity trends. The lowest salinities coincide with the heaviest oil API's. Abnormally high bicarbonate content observed on the top of the Centenario Fm might be a by-product of biodegradation.

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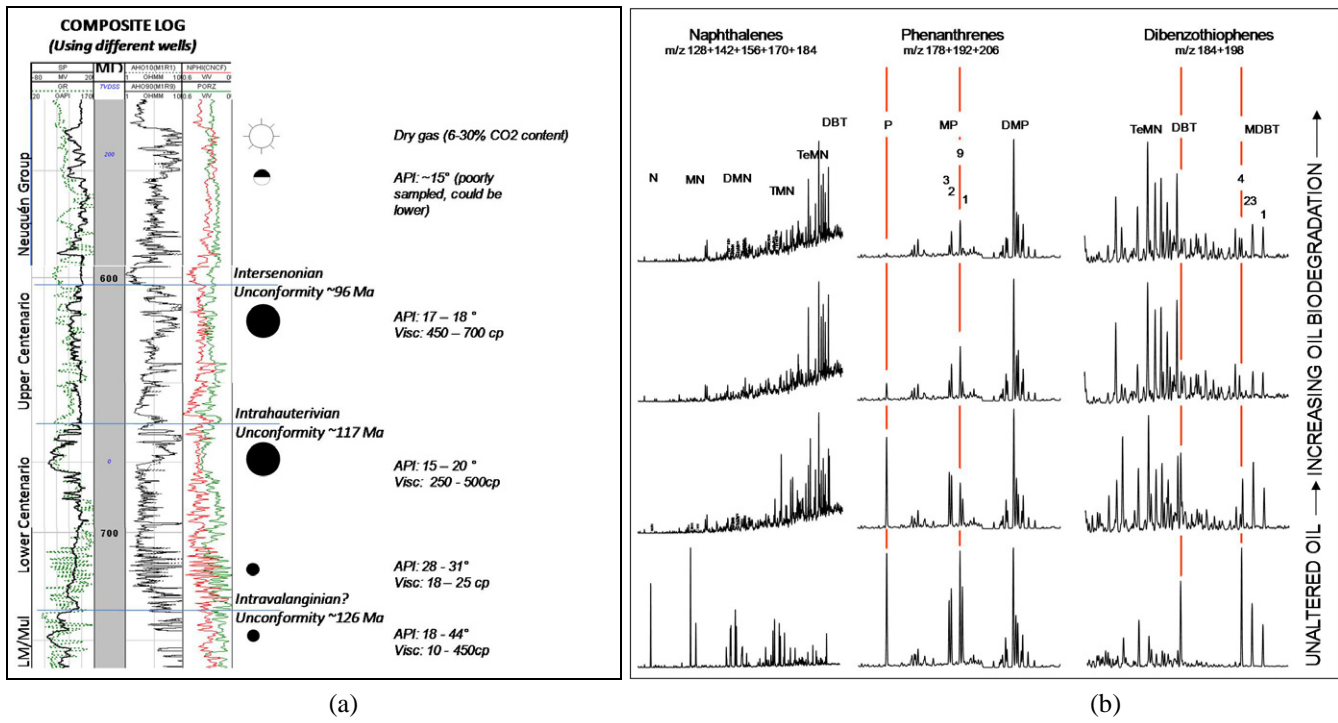


Figure 1: (a) Composite Log with oil quality for each tested reservoirs. Main producing zones are the two Members of Centenario Fm. (b) Mass chromatograms of aromatic hydrocarbon fractions illustrating variations in naphthalenes, phenanthrenes and dibenzothiophenes patterns with increasing oil biodegradation. Red lines allude to selected specific compounds that exhibit the most outstanding changes in their relative concentrations.

N: naphthalenes; MN: methylnaphthalenes; DMN: dimethylnaphthalenes; TMN: trimethylnaphthalenes; TeMN: tetramethylnaphthalenes; P: phenanthrene; MP: methylphenantrenes; DMP: dimethylphenantrenes; DB: dibenzothiophene; MDB: methyl dibenzothiophenes (numbers stand for methylphenantrene and methyl dibenzothiophene isomers).

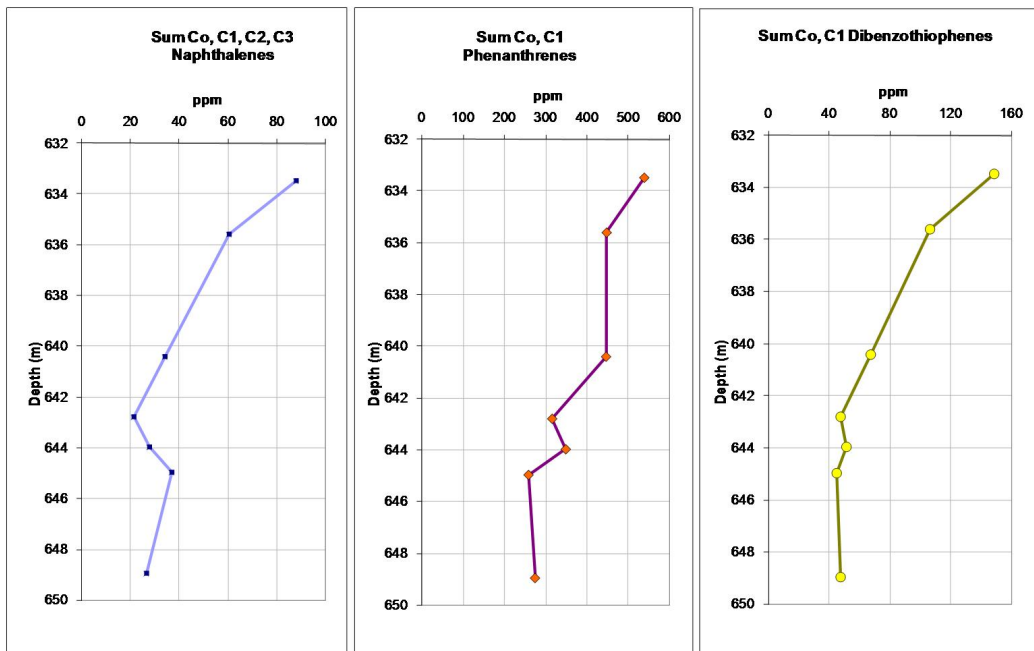


Figure 2: Vertical variation of Naphthalenes, Phenanthrenes and Dibenzothiophenes content in oils extracted from 15 m thick cored interval of the Lower Centenario Main Producing Zone. Increasing biodegradation is interpreted towards the base of the zone where the OWC is developed.