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TRABAJO 53

STERANE ISOMERIZATION RATIOS OF OILS AS MATURITY INDICATORS AND THEIR USE AS AN EXPLORATION TOOL, NEUQUEN BASIN, ARGENTINA

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ABSTRACT. The relationship between vitrinite reflectance and C29 sterane isomerization ratios (ααα20S/ααα20R) is documented in this paper. Vitrinite reflectance maturities derived from sterane isomerization ratios of oils in the Neuquen Basin provided a critical key to the understanding of the oil generation kinetics and the specifics of generation timing from the Vaca Muerta formation in the Confluencia area, central Neuquen Basin, Argentina.

INTRODUCTION

In the past few years the study of biomarkers ("molecular fossils" derived from once living organisms), has made a significant contribution to oil exploration. Initially, biomarkers were used for oil-oil and oil-source rock correlations by simply looking for similarities in the biomarker patterns as determined by a gas chromatograph-mass spectrometer (GC/MS). As our understanding of biomarkers has increased, it became evident that certain biomarker patterns can be tied to depositional environments and in some cases to age. It was also recognized that the abundance ratio of certain biomarkers (or biomarker ratios) change systematically with increasing maturity. This was a very significant development, especially in oil provinces where the source rocks are not known, because it enabled us to obtain information about the source rocks from the GC/MS (biomarker) analysis of crude oils.

Understanding the maturity levels of oils can also help estimate "kitchen" depths and areal extent when combined with thermal basin modeling as well as give clues to oil generation kinetics. Often the experimental determination of such parameters is impractical because appropriate, low maturity source rock samples are rare and the process could be lengthy and costly.

In the Neuquen Basin, Argentina (Figure 1), the U. Jurassic - L. Cretaceous Vaca Muerta shales are considered to be a major source for oils in the basin. Examination of present-day temperatures and observed conventional maturity indications (RockEval TMAX and limited vitrinite reflectance) suggest that the timing of oil generation and the volume of generated oil in the Confluencia area (Figure 2) may be sensitive to the kinetic assumptions for the source strata. However, oil generation kinetics are not well established for the lower Vaca Muerta shales. Sterane isomerization ratios of oils in the Neuquen Basin provided a critical key to the understanding of the oil generation kinetics and the specifics of generation timing from the Vaca Muerta.

DISCUSSION

The maturity dependence of the abundance ratio of the ααα 20S and ααα 20R isomers of the C27, C28, and C29 steranes has long been noted (Mackenzie and McKenzie, 1983). Living organisms synthesize only the precursor for the 20R isomer. In low maturity source rocks of various depositional environments, the 20R isomer is always very dominant. With increasing maturity the 20R goes through an isomerization reaction to form the 20S isomer. Hence, the 20S/20R (or S/R) ratio increases with increasing maturity. As a maturity indicator, the S/R ratio is basically insensitive to the depositional environment and the initial ratio is always near zero at low maturity. The development of a method to use the S/R ratios in oils to estimate the thermal maturity of the source rock involved the establishment of an empirical relationship between the maturity (measured as vitrinite reflectance) of the kerogen in a source rock and the S/R ratio of the bitumen extracted from the same sample. Once that relationship has been established, the S/R ratio of an oil can be used to calculate the vitrinite reflectance equivalent (VRE) of the source of that oil. For analytical reasons the C29 sterane isomers are most suitable for the measurement of the S/R ratio.

Figure 3 shows the progression of the C29 S/R sterane isomerization ratio with increasing maturity. The ratio increases until an equilibrium is reached at a ratio of S/=1.3. At higher maturities, the ratio remains the same or decreases slightly while the absolute abundance of the steranes decreases, i.e., the peaks representing these compounds become small until they completely disappear at high maturities.

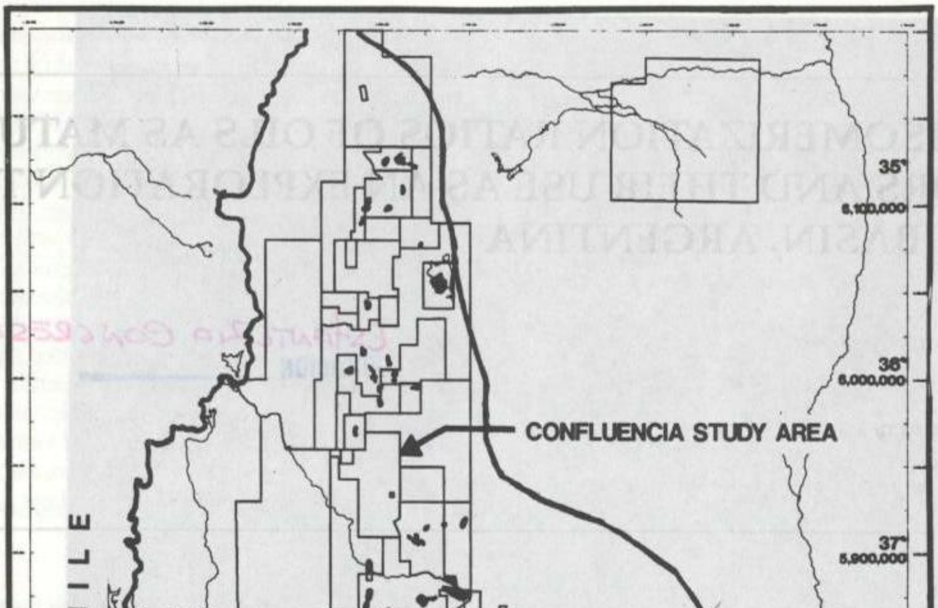


FIGURE 1: NEUQUEN BASIN LOCATION MAP

Figure 4 shows the relationships between the vitrinite reflectance and the C29 S/R sterane isomerization ratio in 76 shale and coal samples from around the world. Data points include in house analyzed samples as well as values reported in the literature (Zumberge, personal communication, Goodarzi *et al*, 1989). Excluding four high maturity samples, the relationship between %Ro (or VRE, for Vitrinite Reflectance Equivalent) and the S/R ratio is given by a best fit line VRE = 0.482(S/R) + 0.375 or for simplicity, VRE = 0.5(S/R) + 0.35. Because the S/R ratios do not exceed a value of 1.3, this relationship is valid up to vitrinite reflectance of approximately 1.0%. It has also been observed that in some organic rich carbonate source rocks this relationship sometimes does not hold.

In the Neuquen Basin, thirteen (13) oil samples generated by the Vaca Muerta formation were evaluated for sterane isomerization ratios.

Based on the S/R ratios, the oils were generated at VRE values ranging from 0.7 to 0.85 % (Figure 5). The data suggested that the Vaca Muerta Formation has normal to slightly below normal oil generation kinetics (normal oil generation kinetics corresponds to Ro of 0.8 - 0.9 %). These kinetic assumptions were incorporated into the basin modeling program.

A compactional heat flow model was used for modeling in the Neuquen Basin. Compaction calculations were selected after Falvey and Middleton (1981) and Falvey and Deighton (1982).

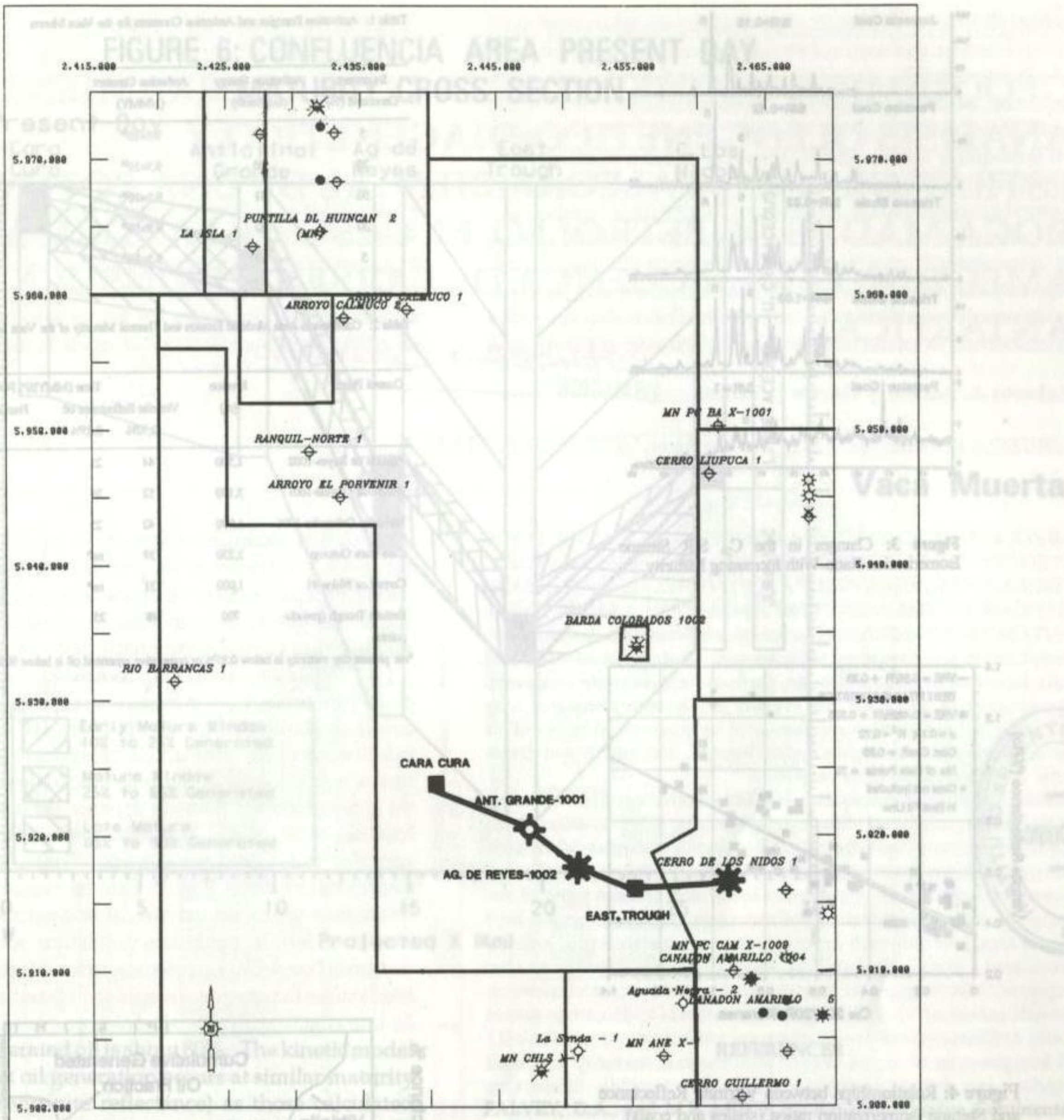


FIGURE 2: CONFLUENCIA AREA CONTROL POINTS

Geothermal gradients were computed using the differential equation for transient diffusion heat flow.

Heat transfer in this model is assumed to be by vertical conduction. The kinetics of oil generation for the Vaca Muerta marine shales and marls in the Confluencia area were modeled using a first order Arrhenius equation with a range of activation energies (Table 1).

A relatively simple burial history was modeled for the six control points (wells and outcrops) in the study area (Figure 2, 6). Thrusting and erosion supplanted continuous deposition approximately 25 Ma.

The magnitude of erosion varied from 700 meters to a maximum of 3230 meters (Table 2). Tectonic subsidence was relatively constant throughout the modeled history. A simple constant heat flow model with a heat flow of 1.1 HFU (46 mw/m2) was used. This value was selected based on calibration of present day bore-hole temperatures and vitrinite reflectance measurements. The Sweeney and Burnham (1990) "Easy Ro" technique was utilized to calculate vitrinite reflectance.

The Vaca Muerta in the various wells and outcrops examined in the Confluencia area have attained a thermal maturity equivalent to vitrinite reflectance of 0.7 to 0.85% from 52 to 23 Ma (prior to thrusting) based on these assumptions (Table 2). This time interval and maturity range corresponds with peak oil generation as calculated from the kinetic assumptions (Table 1). In five of the control points, post Miocene erosion caused quenching of the maturation process and, therefore,

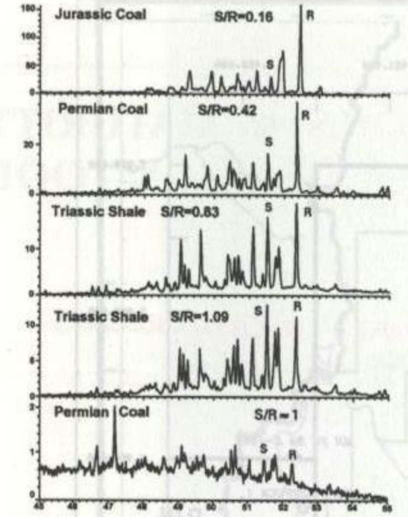


Figure 3: Changes in the C_{29} S/R Sterane Isomerization Ratio With Increasing Maturity.

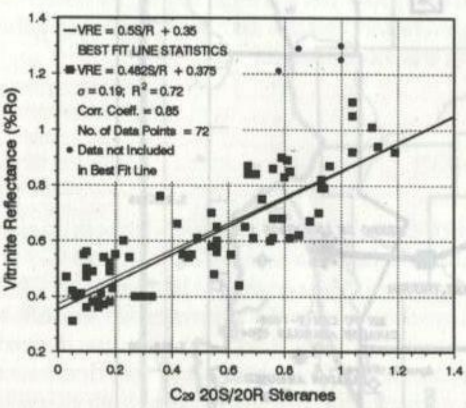


Figure 4: Relationships between Vitrinite Reflectance and Sterane Isomerization ratios (shales and coals)

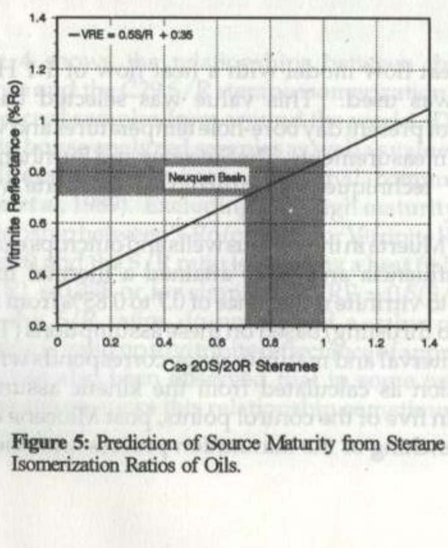


Figure 5: Prediction of Source Maturity from Sterane Isomerization Ratios of Oils.

Table 1: Activation Energies and Arrhenius Constants for the Vaca Muerta

Increment Generated (%)	Activation Energy (kcal/mole)	Arrhenius Constant (1/MMY)
5	49	9.5×10^{26}
20	50	9.5×10^{26}
50	51	9.5×10^{26}
20	52	9.5×10^{26}
5	53	9.5×10^{26}

Table 2: Confluencia Area Modeled Erosion and Thermal Maturity of the Vaca Muerta

Control Points	Erosion (m)	Time (MMYBP) Formation Reached			
		Vitrinite Reflectance of:		Fraction of Cumulative Generated Oil:	
		0.70%	0.85%	10%	80%
Aguada de Reyes-1002	1,500	44	23	47	23*
Anticlinal Grande-1001	3,100	52	24	52	24*
Barreales Colorados-1001	1,900	42	25	45	25
Cara Cura Outcrop	3,230	39	na*	42	na*
Cerro Los Nidos #1	1,000	31	na*	35	na*
Eastern Trough (pseudo-points)	700	48	25	48	25*

*na: present day maturity is below 0.85% or cumulative generated oil is below 90%

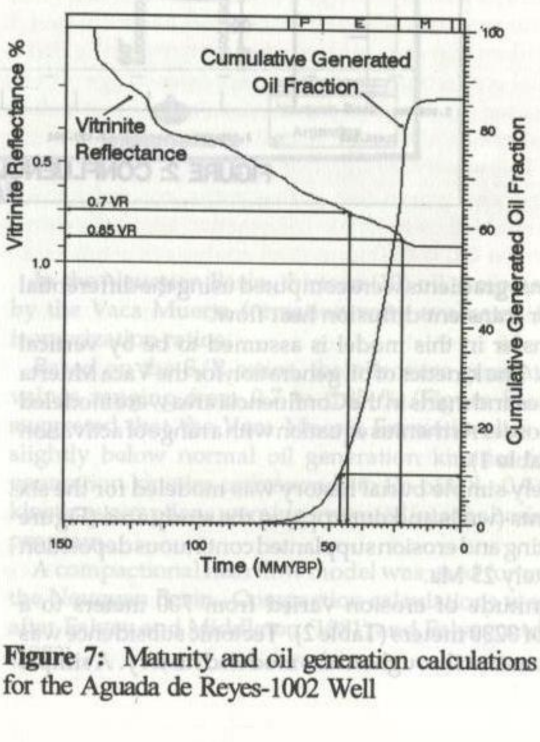
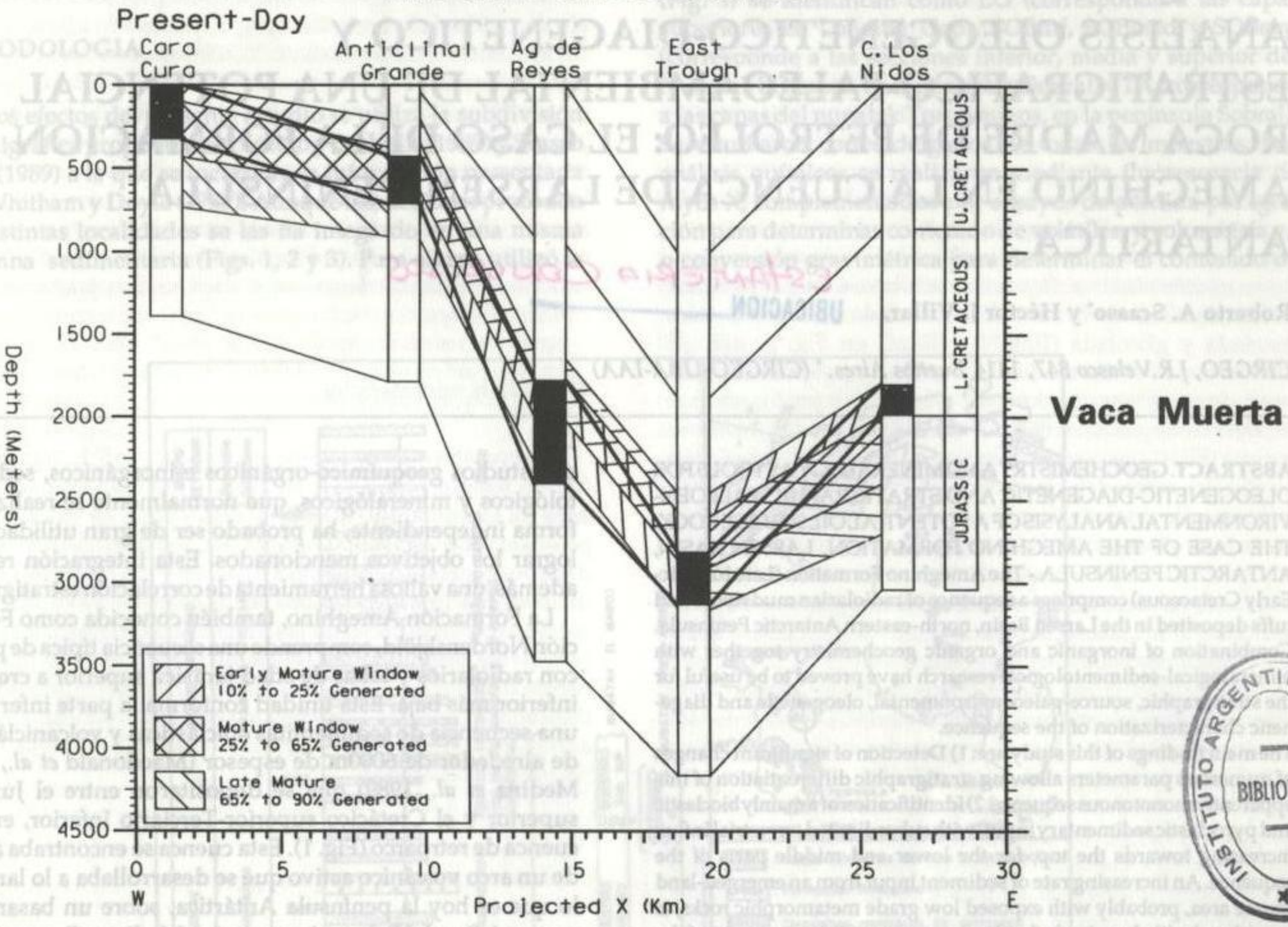


Figure 7: Maturity and oil generation calculations for the Aguada de Reyes-1002 Well

FIGURE 6: CONFLUENCIA AREA PRESENT DAY MATURITY CROSS SECTION



the cumulative generated oil is about 80%. The kinetic model calculates that peak oil generation occurs at similar maturity levels (in units of vitrinite reflectance) as those calculated from the sterane isomerization ratios (Table 2, Figure 5). Figure 7 is an illustration of these calculations for the Aguada de Reyes-1002 well. The timing of oil generation in relation to trap formation, as calculated by the model, was an important factor in evaluating the Confluencia area.

CONCLUSIONS

Vitrinite reflectance maturities derived from sterane isomerization ratios of oils were critical to understanding oil generation kinetics in the Neuquen Basin. Generation timing from the Vaca Muerta formation in relation to trap formation was an important factor in evaluating the Confluencia area.

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