SEPM Research Conference
Paleogeography and Hydrocarbon Potential of the La Luna Formation and Related Cretaceous Anoxic Systems

Latinoamericana

Chemostratigraphic Correlation of the Source Rock in the La Luna-K/T(!) Petroleum System In Southwestern Venezuela

Henry Briceño *   y Angel Callejón *
* UCV and E.I.G. Litos C.A. litos@eldish.net
** PDVSA E & P. acallejon@hotmail.com

INTRODUCTION

Stratigraphic sections of La Luna Formation and its lateral equivalent, Navay Formation, were described and sampled at Las Delicias, La Ortiza, La Vueltosa and Río Cuite, in the Venezuelan Andes (Figure 1). Whole rock samples were analyzed for, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Y, Zr, Nb, Mo, Ag, Cd, La, Ce, Hf. Ta, Th y U by ICP; and major oxides, Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, Cr_2O_3, MnO, Fe_2O_3 by XRF. Additionally, TOC, kerogen and rock-eval analyses were performed on selected samples. Studies were aimed to establish environmental conditions and changes during sedimentation. Elemental ratios and multivariate statistics were preferred for variable grouping and association.

DISCUSSION OF RESULTS

Among the diagnostic elemental ratios, the quotient Th/V seems to be a good environmental index. Th is preferentially fixed on clays and indicates continental sources, and V is associated to organic facies, which in marine environments tend to be more abundant in distal and/or deep realms. Combining biostratigraphic data with Th/V ratios, we have found that for samples accumulated in oceanic environments, Th/V ratios are smaller than 0.045. Hence La Luna (pelagic facies and Tachira Ftanite) was apparently deposited in deeper waters than Navay (La Morita and Quevedo members) (Figure 2). In Delicias and La Ortiza, some isolated samples, with relatively high Th/V, usually phosphatic, with flow structures and erosional basal contacts are found in otherwise homogeneous low Th/V sequences. They have been interpreted as turbidity flows from higher positions.

Persistent cycles of high Th/V values, specially in Navay, seem to imply extended periods of sedimentation and some regularity in sediment preservation rates, and perhaps a relationship with glacioeustatic variations. To test the hypothesis, we used Fourier transforms for Th/V data and Haq curve data for the period from 116 My BP to 66 My BP, and found that harmonic cycles of 3.14 My correspond very well with these high Th/V cycles. From these, we calculated sediment preservation rates of 15.32 and 15.14 m/Ma, for La Luna in La Ortiza and Delicias respectively, and 18.86 and 16.24 m/Ma for Navay in La Vueltosa and Río Cuité, respectively.

Ratios Nb/V and Zr/Ni were compared with the pyrolisis-derived HI and TOC and used for establishing variations in source-rock potential in the studied area. These results were significantly useful for modeling purposes.

MULTIVARIATE ANALYSIS

We used Factor Analysis for handling the large geochemical database, and were able to separate groups of chemical species in Factor weights plots, whose association is controlled by specific physical-chemical processes. Hence, the individual behavior of an element or compound is, in general, very similar to the behavior of the rest of the species in its group, although not necessarily the same. Factor scores plots are useful for separation and identification of samples belonging to specific formations and even members within formations, bringing valuable help to the process of correlation. The following associations of species were taken from factor weight plots: **Clastic association:** Includes those species usually present in the siliciclastic fraction as primary constituents of the particles or as coatings on their surfaces. Includes species such as

SEPM Research Conference
Paleogeography and Hydrocarbon Potential of the La Luna Formation and Related Cretaceous Anoxic Systems

Latinoamericana

Al_2O_3, SiO_2, Th, Nb, La, Ce, Fe_2O_3 and TiO_2. Sometimes it is possible to discriminate between a clay association (controlled by Al_2O_3) and a siliceous association (controlled by SiO_2), within the siliciclastic group. In such cases a sediment size segregation, due to energy differences may be claimed. **Organic Association:** Includes TOC and metals usually fixed in the organic fraction such as Ni, V, Mo, Cd, Zn and Cu. High concentrations of these species occur in rocks deposited in high productivity environments, sites of high TOC preservation rates or low clastic input. **Carbonate association:** Constituted by those species present in carbonate rocks, such as CaO and less prominently Sr and P_2O_5, and LOI.

ACCUMULATION RATES

Determination of accumulation rates was approached by using cumulative curves of species, from bottom to top of stratigraphic sections, as suggested by Briceño et al. (1996a, 1996b) and Galea et al. (1996). To obviate the distortion introduced by uneven sampling intervals along columns, the graphs are constructed with even spacing between samples along the y-axis (sample number), instead of using stratigraphic elevation. Constant slope portions of the curve represent, in the column, homogeneous intervals with constant accumulation rates of the considered component. On the other hand, breaks and inflexions of the curve highlight changes in accumulation rates indicating geochemical discontinuities. These diagrams have a considerable advantage over chemical variograms to define chemofacies. Once the geochemical data has been normalized we combined in one curve, several components or associations of components to generate consolidated accumulation rates curves, where all relevant geochemical discontinuities in the rock column will be obtained. Furthermore, there is the possibility of assigning numerical hierarchy to each discontinuity as a function of number of species experimenting changes. The immediate product of this analysis is the precise delineation of chemofacies.

CHEMICAL ACCUMULATION RATE DIFFERENCES.

Accumulation rate differences are calculated by subtracting pairs in the % cumulative data and plotting the results against sample number from base to top in the column (Chemical Accumulation Rate Differences plots or **CARD** plots). This treatment opens a new perspective to the detection and interpretation of geochemical changes along stratigraphic sections. In **CARD** plots, constant slope portions of the curve indicate a constant relationship between the accumulation rates of the species considered. Slope breaks indicate changes in the relationship. From our results, homogeneous intervals transcend lithological types and seem to be related to geological events of higher hierarchy, such as major cycles or the development of sequential units. Combining biostratigraphic, petrographic, sedimentological and geochemical data, we corroborated that some rate differences are associated to specific environmental physico-chemical factors, such as redox conditions in marine environments, energy level, sediment source, etc.

%La cum - %Ce cum or **%La cum - %Sm cum.**
Geochemical behavior of Rare Earth Elements (REE) in the secondary environment is very similar, so their ratios remain rather constant from source rocks to soils to the derived sediments. Even diagenetic processes do not change the ratios significantly and fractionation due to oxidation states, seem to be neglectable as compared to variations caused by source changes. Hence, any significant change in the REE proportions in the sediment or sedimentary rock sequence, readily observed in **CARD** plots, would indicate a supply from another sediment source. La Luna shows long and persistent cycles, with eventual variations (Figure 3). For Navay, there are more interruptions of larger cycles, perhaps related to the more dynamic and shallower environment of sedimentation. The diachronic occurrence of source changes for the major cycles is evident for these sections.

%Ni cum - %V cum
Porphirins are the most important organometallic complexing agents in carbonaceous rocks and fossil fuels, and among the more thermodynamically stable are those porphirins of V and Ni. In marine environments, they are preferentially fractionated to the organic phases in the sediments as porphirins, asphaltenes and other components of high molecular weight in the kerogen. Ni and V content in porphirins will depend on type of

SEPM Research Conference
Paleogeography and Hydrocarbon Potential of the La Luna Formation and Related Cretaceous Anoxic Systems

Latinoamericana

organic matter and will be higher in sediments whose organic compounds were derived from algae and photosynthetic bacteria. Changes in distribution of Ni and V may reflect the preferential partitioning of Ni towards ethioporphirins, which may be caused by differences in chlorophyll type as porphirin precursor. Ni and V proportions, will be a function of redox potential during sedimentation and early diagenesis. Hence, very reducing conditions will favor preferential fixation of V over Ni, and more oxic conditions will reverse this relationship. This fact implies that accumulation rate differences between Ni and V reflect redox conditions during sedimentation. We combined biostratigraphic, petrographic and sedimentological data and corroborated the redox implications for these curves (Figure 4). For La Luna, sedimentation began under dysaerobic conditions which persisted up to the Santonian-Coniacian boundary, when a second major cycle of less dysaerobic to oxic conditions began, suggesting an important link with the global oceanic redox change of Late Cretaceous.

%Al_2O_3 cum - %SiO_2 cum.
These differences in accumulation rates allow the determination of changes within the siliciclastic fraction, related to changes in the clay:quartz proportions, in turn dependent on energy changes in the depositing media. These variations, which are rather similar for Delicias and Ortiza with two major cycles, display complex variations for Cuite and Vueltosa.

%(Al_2O_3+SiO_2) cum - %CaO cum
These differences in accumulation rate indicate changes between siliciclastic and calcareous sedimentation, highlighting those variations in sedimentation patterns and improving the sedimentological, stratigraphic and tectonic interpretation. There are significant differences among Delicias and Ortiza and rather similar patterns for Cuite and Vueltosa. These evidences indicate the need of careful extrapolation from restricted data to modeling procedures in hydrocarbon exploration.

CONCLUSIONS

Conclusions from this study encompass both, methodological procedures for data treatment and display, as well as chemostratigraphic statements on La Luna and Navay formations. First, multivariate statistical analysis is at the present, a necessary tool for understanding the complex interplay of environmental conditions during sedimentation. Second, chemofacies are best defined by using multivariate analysis combined with accumulation rate curves instead of conventional variograms. Third, La Luna, as well as Navay were deposited diachronically and major geochemical cycles may be correlated between sections, but individual chemofacies are difficult to connect. Fourth, the major oceanic redox change in Cretaceous time seems to have occurred diachronically around the Coniacian - Santonian boundary in the studied region. And fifth, Sedimentation of La Luna was in deeper (or more distal) waters, less affected by glacioeustatic changes, more dysaerobic environments, and prevailing calcareous sediments as compared to the Navay Formation.
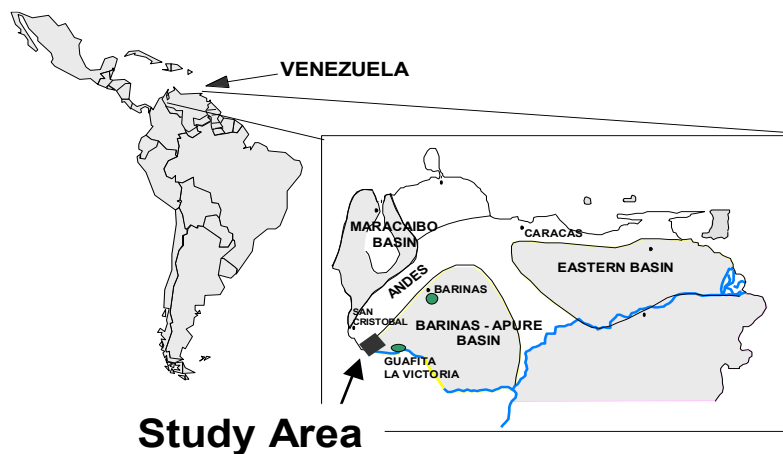

Figure 1. Location of Study area in southwestern Venezuela.
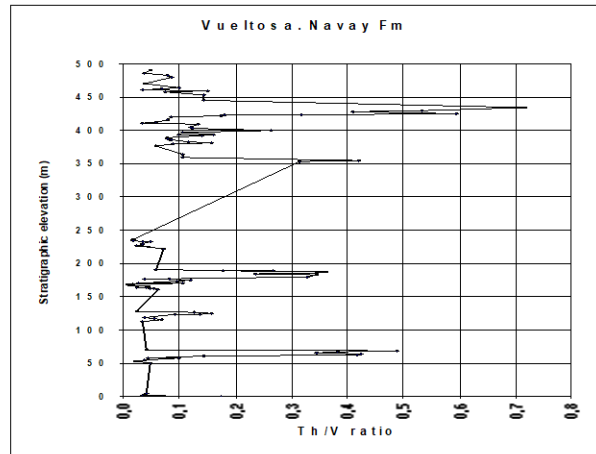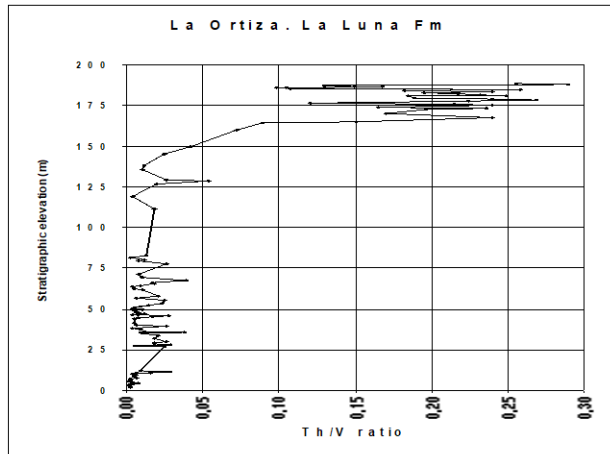
Figure 2. Th/V ratios for La Luna and Navay formations. Samples from oceanic environments have Th/V smaller than 0,045. Higher values of the ratio indicate platform environments.
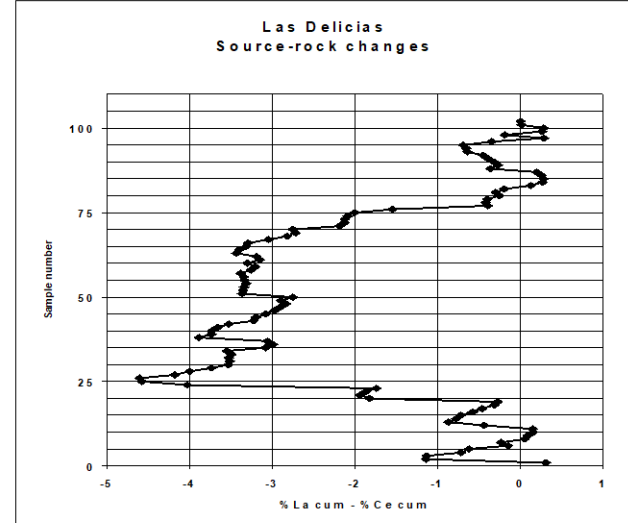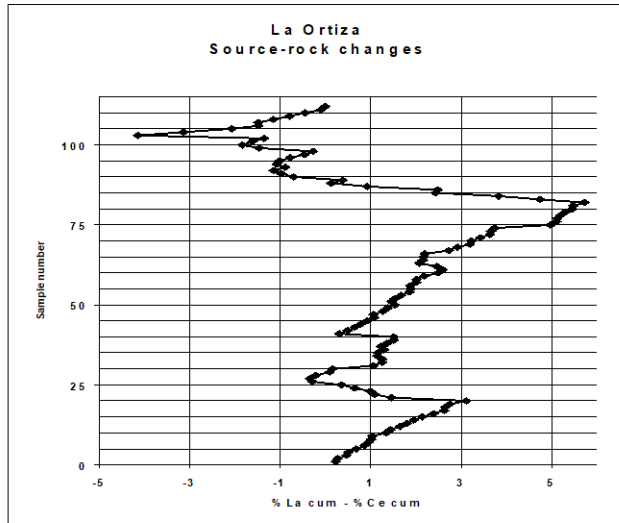

Figure 3. CARD plot for sediment source changes from %La cum – %Ce cum.
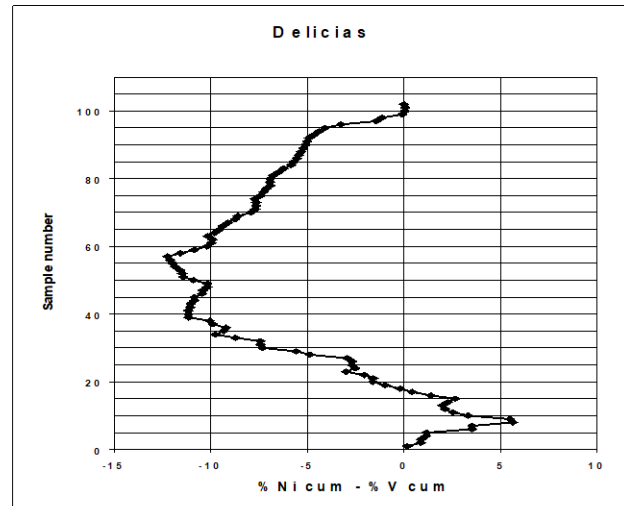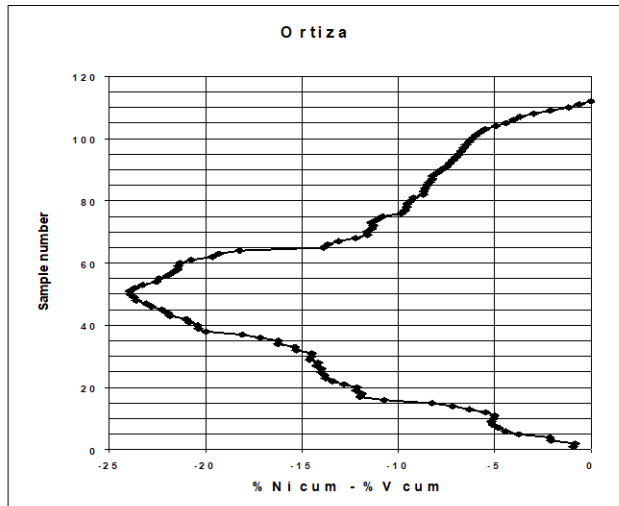

Figura 4. CARD plot for redox conditions changes for La Luna and Navay formations.