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Orbital Forcing of Organic-Rich Deposits Formation: Record of the Coniacian-Santonian OAE3 (La Luna Formation, San Miguel River Section, Venezuela)

Introduction

The Coniacian-Santonian oceanic anoxic event (OAE3) is thought to be the last of the Cretaceous OAEs (Arthur ***et al.***, 1990). Compared to extensive research on the Early Cretaceous (OAE1) and middle Cretaceous (OAE2), little is known of the evolution of the Coniacian-Santonian OAE3 (Wagner, 2002; Hofmann ***et al.***, 2003). This event was geographically restricted to shallow settings in paleo-upwelling zones and epicontinental seas (Arthur ***et al.***, 1990). The relationship between Cretaceous oceanic events and rapid climatic changes is widely acknowledge, several authors had reported high-frequency cyclic variations, which correspond to the main frequencies of orbital forcing (De Boer, 1982; 1991; R.O.C.C. Group, 1986; Oglesby and Park, 1992; Van Buchem ***et al.***, 1995; Dean and Arthur, 1998; Sageman ***et al.***, 1998; Hofmann ***et al.***, 2001; Wagner, 2002; Wilson and Norris, 2001; Hofmann ***et al.***, 2003; among others).

The La Luna Formation (Upper Cretaceous) represents an excellent source-rock interval deposited in a tropical epicontinental setting on the northwest South America margin. The calculated original TOC ranges from 2.5 to 10.8 wt %, averaging 5.6 wt % (Talukdar and Marcano, 1994). High TOC intervals occur across the Cenomanian-Turonian boundary, in the Coniacian and early Santonian, and decrease rapidly through the late Santonian (Erlich ***et al.***, 1999). This paper focuses on factors that controlled the accumulation of carbon organic-rich deposits in the La Luna Formation during Santonian time. The studied section is located in the Mérida Andes Mountains near Mesa Bolívar town, along the San Miguel River in Mérida State (Venezuela). This section was sampled every 25 cm for wt% $CaCO_3$ and wt% TOC analysis, a set of 88 samples were collected. Major and minor element analyses (Si, Al, Ti, Na, K, Ba, Mn, Fe, V, Zn, Ni) were performed on 65 samples. Spectral analysis was used to test for the presence of sedimentary cyclicity as a function of calcium carbonate and total organic carbon content. The spectral method applied was the Fast Fourier Transform (FFT) using the algorithms of Pardo-Igúsquiza ***et al.***(1994).

La Luna Formation

The San Miguel La Luna Formation section is 22 m thick and occurs in the nucleus of one symmetrical anticline. The lower contact is not exposed and the upper contact is sharp with Colón Formation and is characterized by the presence of a 1 m thick, phosphate- and glauconite-rich unit (Tres Esquinas Member). The La Luna Formation in this locality is characterized by black marlstones interbedded with black marly limestones, and black limestones. Two informal units have been recognized: a lower one dominated by very compacted marlstones and marly limestones with concretions of variable size (from 0.03 to 1.50 m long), and very thin (3 to 20 cm) siliceous beds; and an upper one characterized by marly limestones and limestones; decrease marlstones, concretions and siliceous beds. The siliceous beds frequency increases toward the top of the lower unit. The stratigraphic succession is laminated throughout although some intervals are not; the upper stratigraphic unit is specially burrowed. Bioturbated levels are mainly associated with marly limestones and limestones. Burrows are characterized by almost circular sections (few millimeter to 1 cm in diameter) and are generally filled with benthic foraminifers.

The benthic foraminiferal assemblage indicates sedimentation in the upper neritic to upper bathyal area. The La Luna

	Limestones			Marly Limestones			Marlstones		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
		n = 14			n = 20			n = 31	
Al	8617	1078	33041	13658	4986	32398	10855	1366	29307
Fe	3257	806	12899	5778.3	1560	11856	4833.9	1133	12421
Na	693.2	67.7	1425.1	895.61	383	1924.4	799.62	1.22	2120.3
K	2572	440	6521.1	5383.5	1071	10482	4550.2	568	8942.6
Ti	365.9	83.03	1304.3	544.27	115.1	1088.5	395.73	50.81	890.74
Si	75193	11744	222641	112330	1266	282783	207896	54108	418740
P	17868	170.5	91020	16853	912.7	189007	10948	346.1	214662
Ba	214.3	34.6	541.42	307.23	72.25	1051.5	239.5	63.08	993.68
Mn	31.06	13.19	55.28	37.93	23.57	82.01	27.29	4.35	77.12
V	105.6	22.19	274.67	443.4	44.98	1256.1	473.87	41.89	1350.6
Zn	131.3	28.12	319.81	506.95	73.88	1859.8	520.04	105.4	1917.6
Ni	96.88	15.18	238.21	261.01	35.52	988.5	158.81	31	652.75
V/(V+Ni)	0.53	0.085	0.8	0.6	0.05	0.88	0.68	0.16	0.89
Ba*/Al*	3.93	1.07	7.64	4.01	0.6	23.63	4.78	0.44	42.14
Si*/Al*	13.1	3.16	46.8	10.16	0.1	30.03	51.43	4.3	300.27

Table 1. Composition range with respective mean value of major and trace elements and element ratios for different facies in selected samples. Element values are in ppm. Ba*/Al* y Si*/Al* are shale-normalized, shale stands for the shale average composition of Turekian and Wedepohl (1961).

Formation in this locality is dated as Santonian to early Campanian (?)(Rey *et al.*, 2002).

Geochemical results

Total organic carbon percentages (%TOC) are between 0.3 to 5.54%. The general TOC content decreases upward, with the highest average (~4%) at the base and the lowest average values (~2%) at the top of the succession. Superimposed to this general trend are variations in organic carbon weight percent. Inorganic geochemical data for different facies are listed in Table 1. Pearson's correlation coefficients between elements analyzed, calcium carbonate and total organic carbon were calculated.

The total organic carbon shows a negative correlation with calcium carbonate (r = -0.43), and increases in the laminated levels.

Aluminium has an excellent correlation with Ti (r = 0.95), Fe (r = 0.80) and K (r = 0.83), a moderate to good correlation with V (r = 0.42) and Zn (r = 0.57), and a moderate correlation with Na (r = 0.36). Although Al, Ti, Fe, K, and Na are abundant in marly limestones and marlstones (Table 1), they do not correlate with calcium carbonate, high values were observed in laminated limestones. A good correlation was obtained between TOC and Al, Ti, Fe and K (r = 0.54, 0.48, 0.55, 0.63, respectively).

Barium, silica and phosphorus do not show internal correlation, as well as they do not show a correlation with calcium carbonate and total organic carbon. Only silica has a good negative correlation with calcium carbonate (r = -0.68), and it reflects silicification processes. Considering the role of detrital aluminosilicates as barium carriers, Ba content was shale-normalized (Ba*/Al*) to give an estimation of their relative enrichment or impoverishment following equation (Ba content/Al content)$_{sample}$ / (Ba content/Al content)$_{shale}$, shale stands for the shale average composition of Turekian and Wedepohl, (1961). High shale-normalized Ba values were observed in marlstones and marly limestones facies (Table 1). This occurs mainly in the middle of the section, around the siliceous levels; and in the upper unit associated to high phosphorus values. The same method was followed with silica; shale-normalized Si

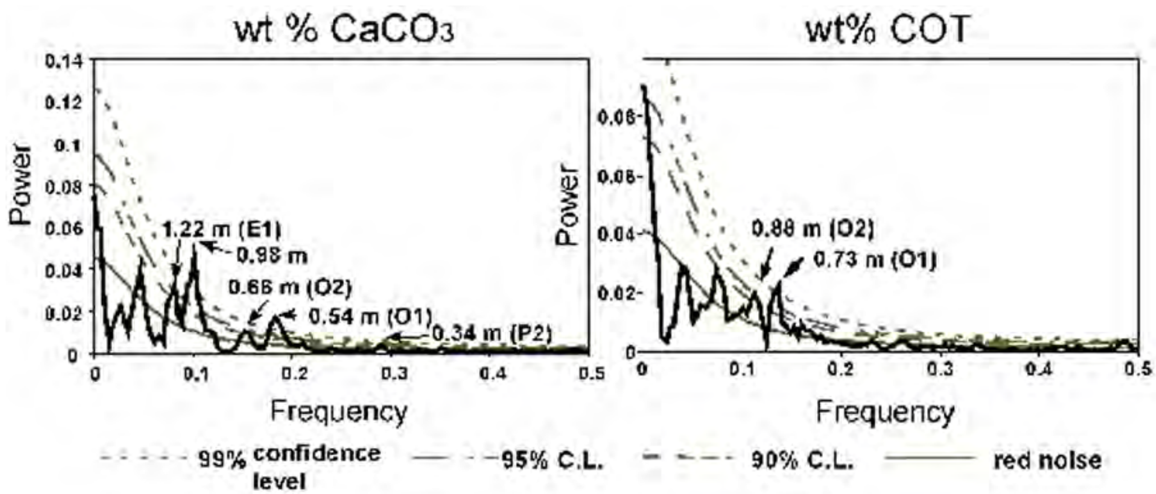

Fig. 1 Power spectra of the calcium carbonate (% CaCO3) and total organic carbon (%TOC) time series. The examination of power spectra with wavelength allows comparing the cyclicity in the La Luna Formation in terms of cyclic orbital variation. It was not found a wavelength ration of peak 0.98 with the rations of present-day periods of the orbital elements.

content (Si*/Al*) increases in marlstones and in lesser degree in limestones facies (Table 1). This is especially observed toward the top of the lower unit. Phosphorus content increases in the upper stratigraphic unit, higher values are associated to marlstones and marly limestones (Table 1).

Vanadium concentrations increase in marly limestones and marlstones (Table 1). The vanadium-nickel ratio, expressed as V/(V+Ni), shows an average value greater than 0.5; toward the base varies between 0.63 and 0.89 and upward ranges between 0.46 and 0.77. Vanadium has a good correlation with TOC (r = 0.60). Manganese content is low in the studied section (average 31.37 ppm).

Cyclicity

Variations in $CaCO_3$ and TOC content show cyclic patterns at the scale of tens of centimeters expressed as repeated alternation of carbonate-poor and organic matter-rich bases, and carbonate-rich tops. Spectral analyses (FFT) were used and peridiograms were obtained for calcium carbonate and total organic carbon. The 95% confidence level was used to inspect the validity of the frequency peaks. For the carbonate data, the spectrum reveals different cycles with wavelengths of 1.22, 0.98, 0.66, 0.54, and 0.34 m; and for the organic carbon data the spectrum reveals two cycles with wavelengths of 0.88 and 0.73 m.

To test the hypothesis that the cyclic sediments resulted from processes with Milankovitch frequencies, the wavelength ratios were examined and compared with the ratios of present-day periods of the orbital elements. Differences were calculated and errors estimated. The periods of orbital elements in the Late Cretaceous were only slightly shorter than those of the present day (2000 years shorter at most for the obliquity and precession, Berger and Loutre, 1989; Berger *et al*., 1992); the use of rations for interpretation is independent of absolute time and can avoid some errors brought in by sedimentation rate estimation (Boyd *et al*., 1994). The examination of power spectra with wavelength ration allows comparing the cyclicity in the La Luna Formation in terms of cyclic orbital variations. For variations in calcium carbonate content, the eccentricity (E1), obliquity (O1 and O2) and precession (P2) signals are all found in the sequence studied, though the last is less clear. Variations in total organic carbon apparently responded to an obliquity signal (O1 and O2)(Fig. 1).

Discussion and Conclusions

The accumulation of organic carbon in the La Luna Formation during Santonian time was periodic than a constant phase, and consistently reveals high amplitude cyclic variations, which apparently correspond to the main frequencies of orbital forcing.

Element assemblages analyzed can be interpreted in terms of aluminosilicate phase fluxes, redox conditions and paleoproductivity. Because Al concentration is a good measure of detrital flux, the excellent correlation between Al, Ti, Fe and K indicate that these elements are associated entirely with detrital phases. Vanadium and zinc have a moderate to good correlation with Al suggesting that the affiliation with the aluminosilicate phases is not a dominant control in this section. These elements are considered geochemical indicators of redox conditions (Davis *et al.*, 1999). Barium, silica and phosphorus are considered geochemical proxies of productivity.

Pearson's correlation coefficients did not show a correlation between calcium carbonate and elements analyzed, however, the detrital fraction (Al, Fe, Ti, K), sensitive redox elements (V, Zn) and productivity elements (Ba, Si, P) showed higher values in marlstones and marly limestones (Table 1). A good correlation was observed between total organic carbon, detrital fraction and sensitive redox elements (Table 2). These results suggest that the cyclicity observed in the La Luna Formation was a response to orbitally-controlled fluctuations in continental runoff. Variations in the intensity of upwelling can be observed in the studied section, but they did not control the cyclicity observed in the La Luna Formation. The carbonate-poor hemicycles are interpreted to represent wetter climatic conditions and the carbonate-rich hemicycles represent dryer conditions. In this scenario the rainy climate favors the increase of the terrestrial input to the ocean and the biogenic dilution. The rainy climate and high runoff produce a surface water of lower salinity and modulate the degree of the stratification in water column, and favor the preservation of organic carbon on the sea floor.

Similar results had been reported in Africa (Deep Ivorian Basin) during Coniacian-Santonian, atmospheric circulation apparently triggered marine black shale sedimentation as a response to climate-controlled fluctuations in continental runoff (Hofmann *et al.*, 2003). Our observations corroborate Cretaceous OAEs finding by others workers who have consistently proposed short-term climate change during greenhouse periods.

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