Geochemical characterization of oceanographic and climatic changes recorded in upper Albian to lower Maastrichtian strata, western Venezuela

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Organic and inorganic geochemical data (Rock-Eval, TOC, biomarker GC/MS, and mineral, major and trace element analyses) were used to characterize the paleoceanographic and paleoclimatic conditions that influenced the deposition of upper Albian to Maastrichtian rocks of western Venezuela. These data show that the late Albian to early Santonian was characterized by the accumulation and preservation of hydrogen-rich marine algal and foraminiferal organic matter, and was modulated, in part, by siliciclastic dilution (via eolian and fluvial/turbidite processes). The contemporaneous development of paleobathymetric barriers surrounding the Maracaibo and Barinas/Apure Basins resulted in stagnation and poor circulation, and along with high evaporation rates, produced salinity stratification and entrapment of anoxic bottom waters. Bottom water oxygen levels increased from the late Santonian through the end of the Cretaceous as seasonal upwelling intensified, and stratified and entrapped anoxic bottom waters underwent frequent overturn and ventilation. These major changes in depositional patterns can now be identified and linked to regional or global oceanographic and climatic events. The depositional events that best demonstrate this link include: (1) late Albian to early Cenomanian drowning of the Maraca Formation carbonate platform (linked to the global mid-Cretaceous platform drowning event); (2) Cenomanian-Turonian drowning of the Guayacan Member (Capacho Formation) carbonate platform (southern Maracaibo Basin) and deposition of organic carbon-rich sediments (linked to the global Cenomanian-Turonian oceanic anoxic event); (3) deposition of Tres Esquinas Member (La Luna Formation) phosphates and glauconites in the Santonian to Campanian (linked to a regional increase in fluvially-derived sediments); and (4) onset of delta progradation from Colombia into western Venezuela during the Campanian through Maastrichtian (linked to regional tectonic activity and cooling global climate).

INTRODUCTION

Organic carbon-rich Cretaceous marine strata of northern South America have long been recognized as the main source for the region's vast hydrocarbon resources. Characterizing the paleoceanographic and paleoclimatic conditions under which these units were deposited is key to understanding their formation. In this study, we integrate organic and inorganic geochemical data (x-ray diffraction, x-ray fluorescence, Rock-Eval, and total organic carbon) from 199 samples from 14 key outcrops in the Sierra Perijá and Mérida Andes Mountains of western Venezuela. These data allow us to link local depositional events to regional and global paleoceanographic and paleoclimatic events.

ORGANIC GEOCHEMISTRY

Biomarker analyses

Biomarker analyses were done on one uncontaminated representative sample of the La Luna Formation from the type section in the northwestern part of the Maracaibo Basin (Figure 1). Other samples analyzed from the type section were slightly oil stained, and thus were not used for biomarker determinations. The TOC content for the unstained sample is 5.5%, HI (Hydrogen Index) is 460, the atomic H/C (Hydrogen/Carbon) ratio is 1.05, and the atomic O/C (Oxygen/Carbon) ratio is 0.11. The sample contains 6.1% (by weight) organic sulfur (in the kerogen), and the atomic S/C (Sulfur/Carbon) ratio is 0.33. The HI and atomic H/C ratio for unstained La Luna samples are characteristic of Type II marine organic matter and range from 400-460 and 1.03-1.05, respectively. The relatively high atomic O/C ratio (0.11) suggests that unstained outcrop samples may be slightly weathered. Since weathering may have lowered the HI and H/C ratios, the apparent hydrocarbon source quality of the section may also appear to be lower. The maturity of the sample is regarded as low based on a Rock-Eval Production Index of 0.01 and T_{max} value of 424 ^{o}C, and is in a pre-oil stage of petroleum generation. Values for two biomarker maturity parameters are consistent with a low level of maturity; the C_{29} sterane 20S/20R ratio is 0.54, and the T_S/T_m ratio is 0.09.

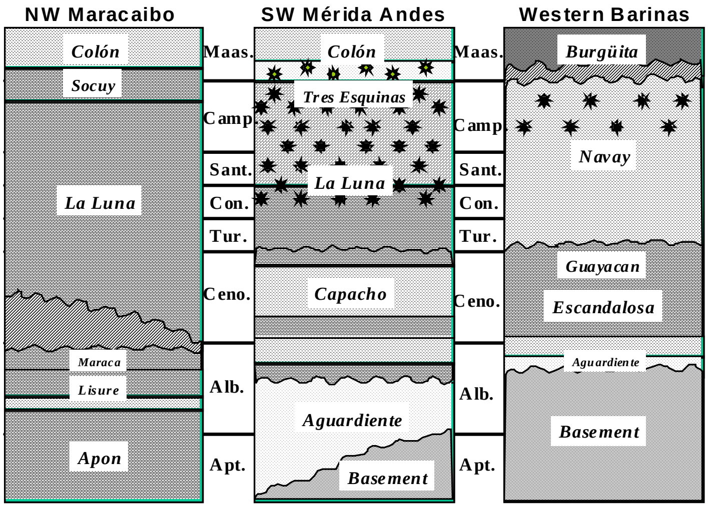

Fig. 1. Generalized stratigraphic columns for the Cretaceous of western Venezuela.

Bitumen indicators of depositional environment

The low pristane/phytane ratio (0.45) of the sample is commonly attributed to input of algal organic matter. The tricyclic terpane pattern is dominated by the C_{23} component, and the C_{22} tricyclic terpane is relatively abundant. In the pentacyclic terpane (or hopane) trace, the T_S/T_m ratio is low, C_{35} hopane is greater than C_{34}, and 28, 30-bisnorhopane and gammacerane are present. The 30-norhopane series, generally characterized by a high C_{29}/C_{30} ratio, is present in moderate amounts. All of these terpane-related characteristics are attributed to a carbonate (i.e. non-clastic) depositional setting containing preserved marine organic matter, e.g., algae, bacterially reworked remains of planktic organisms, and bacteria. The occurrence of bisnorhopane has been related to an anaerobic bacterial source and/or anoxic bottom water conditions; high C_{31}/C_{30} and C_{35}/C_{34} hopane ratios are indicative of bacterial organic matter input.

Gammacerane has also been linked to a bacterial precursor, and is considered indicative of reducing, stratified, and high salinity conditions. The presence of 28, 30-bisnorhopane and gammacerane may therefore reflect the nature of bottom waters in the Maracaibo Basin during deposition of organic carbon-rich parts of the La Luna Formation. The hopane/sterane ratio is rather low (0.93) in comparison to samples from other carbonate environments. Low hopane/sterane ratios may suggest that the algal organic matter is more abundant during certain periods than bacterial organic matter.

Temporal variations in TOC and phosphorus content

Original (pre-burial) TOC content of the data set was determined in order to understand the interplay between organic matter deposition and phosphate accumulation. Temporal plots of corrected TOC (TOC_{corr}) and phosphorus (expressed as fluorapatite) were the constructed from mean values for all upper Albian through lower Maastrichtian samples from all locations in the database, and are shown in Figure 2.

The high TOC rocks deposited just across the Cenomanian-Turonian boundary probably correspond to a high TOC and ^{13}C excursion noted in the western Maracaibo Basin and in southwestern Colombia. This event has been described by many workers for Cenomanian-Turonian boundary sections worldwide. High

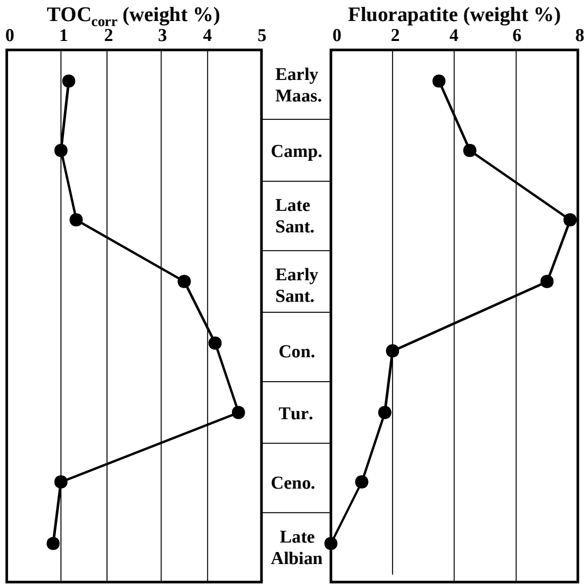

Fig. 2. Temporal plots of mean TOC_{corr} and phosphate (as measured in fluorapatite). The sum of all mean values = 199 total analyses; all temporal plots reflect 199 analyses.

TOC intervals also occur within the Turonian, continue across the Turonian-Coniacian boundary into the Coniacian, occur across the Coniacian-Santonian boundary, and into the lower Santonian (Figure 2). The three high TOC intervals observed in this study (Cenomanian-Turonian, Turonian-Coniacian, and Coniacian-Santonian) appear to have regional significance. At least two of these high TOC intervals (Cenomanian-Turonian and Turonian-Coniacian) have been observed by other workers from the western Maracaibo Basin, and all three high TOC intervals have been recorded (along with positive ^{13}C excursions) from Upper Cretaceous rocks of England and Italy. TOC_{corr} content decreases rapidly through the upper Santonian to lower Maastrichtian.

Fluorapatite content shows a very different pattern, with low values from the upper Albian through Coniacian, followed by a rapid increase in the lower and upper Santonian (Figure 2). In general, Turonian through Coniacian rocks have low phosphate content (mainly disseminated authigenic phosphate nodules), though rare *allochthonous* phosphates (re-deposited in deeper-water, organic carbon-rich sediments) occur in the northeastern Mérida Andes. High phosphate intervals that followed the Coniacian do not appear to be directly associated with high TOC intervals (Figure 2); rather, the high phosphate intervals appear to have been preceded by high TOC intervals, and may have been caused by episodes of mass fish mortality, due to explosive marine algal productivity. Reworking of pre-existing phosphatic deposits and their subsequent re-deposition, as well as the process described above may account for the presence of phosphates in post-Santonian rocks.

INORGANIC GEOCHEMISRTY

Cross-plots of Al/Total Clay (R^2 = 0.89) and Ti/Total Clay (R^2 = 0.86) data suggest a more complicated relationship between clays and heavy minerals than exists in other areas. However, the lack of a perfect correlation (R^2 = 1) shows that some Al has probably been sequestered in small amounts of feldspar, glauconite, or Fe oxides. Fairly good R^2 values also exist between Rb and Ti, and K and Ti (0.78 and 0.76), suggesting that a link is present between all these elements. The most likely host minerals for this association are clays, specifically illite and I/S, with subordinate kaolinite and chlorite. This association is clearly demonstrated by the high R^2 (0.94) between Al and Ti, and the good R^2 values of K versus Al and Rb versus Al (0.77 and 0.8, respectively).

Temporal variations in key minerals and major and trace elements

Temporal variations in the clay content of western Venezuelan Cretaceous rocks are shown in Figure 3. High clay content (mean greater than 20% by weight) occurs in Albian through middle Cenomanian rocks, but generally decreases across the Albian-Cenomanian boundary. Clay content continues to decrease into the Turonian and lower Coniacian before there is an increase into the lower Santonian (Figure 3). Very low clay content occurs in the upper Santonian, with an abrupt increase at the Santonian-Campanian boundary. Average clay content remains constant into the Maastrichtian, however, local variations are common.

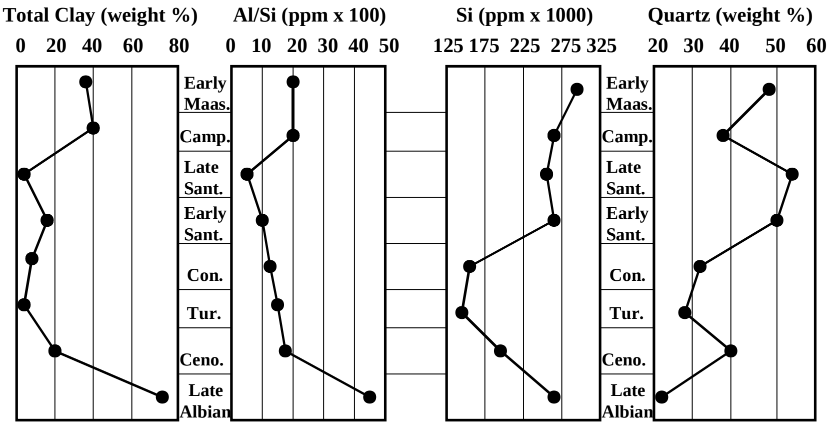

Fig. 3. Temporal plots of mean Total Clay, Al/Si, Si and quartz.

Intervals of 'excess' Al (mean Al/Si ratio of 0.2 ppm and greater) generally coincide with intervals of high clay content, although the trends diverge in the Coniacian and lower Santonian. Samples in these intervals are frequently depleted in Al, which tends to cause low Al/Si values. Contemporaneous increases in quartz and Si content may reflect the contribution of detrital and/or biogenic Si to the depositional system. The temporal distribution of Si therefore reflects a combination of detrital (clays, feldspars, and quartz) and authigenic (biogenic and diagenetic) sources (Figure 3). The upper Albian to Coniacian distribution of Si, when compared to the temporal plot for total clay reflects a dominantly detrital source; Si distribution in the lower and upper Santonian may reflect a combination of detrital (quartz) and biogenic (due to upwelling) sources. Increasing Si content in the Campanian and Maastrichtian appear to coincide with a similar increase in detrital clay content. The temporal plot for quartz (Figure 3) shows a general inverse correlation with total clay (and Al/Si). This is not unexpected, and may be a function of grain size sorting (fluvial vs eolian) as well as changing sediment source areas. An inverse correlation also exists between quartz and clays and high TOC rocks (Figures 2, 3), which may be due to a combination of dilution by siliciclastics and poor preservation of organic matter. Low productivity has also been proposed to explain low TOC intervals in similar geological settings. Intervals of 'excess' Zr (mean Zr/Al ratio greater than 0.004 ppm) were present in the system within the Cenomanian, upper Santonian, Campanian, and lower Maastrichtian. However, the covariance of total clay and 'excess' Zr from the Cenomanian to Turonian, and Campanian to

Maastrichtian suggests that Zr and clays are decoupled during periods of covariance, and argues for two processes (turbidites and eolian) controlling siliciclastic/heavy mineral deposition.

The temporal distribution of Ti strongly resembles that of total clay, which is reflected in the high R^2 value (0.86). However, the Ti/Al distribution shows that Ti enrichment (mean Ti/Al ratio greater than 0.04 ppm) occurs within the Cenomanian, late Santonian, and Campanian. Values do not reach 0.04 ppm above the Campanian, which suggests that Ti is in relative equilibrium with clay. One possible interpretation of this trend is that Ti is mainly derived from clay minerals in the Campanian to lower Maastrichtian, but is linked to both clays and the RAS (rutile/anatase/sphene) triad prior to the Campanian.

DEPOSITIONAL, OCEANOGRAPHIC, AND CLIMATIC EVENTS INFERRED FROM GEOCHEMICAL DATA

The relative abundance and temporal variation of specific major and trace elements and minerals, and organic carbon in western Venezuelan Upper Cretaceous rocks may be linked to key local or global depositional and oceanographic events. The most important depositional events recorded in the study area are (1) Drowning of the Maraca Formation carbonate platform at the end of the Albian to early Cenomanian (associated with the global late Albian platform drowning event); (2) Drowning of the Guayacan Member carbonate platform at the Cenomanian-Turonian boundary (associated with the global organic carbon burial event); (3) Onset of deposition of Tres Esquinas Member phosphates and glauconites in the Santonian to Campanian (associated with a regional increase in fluvially-derived sediments); (4) Rapid progradation of the Colón/Molino/Burgüita Formation delta system in the late Campanian through Maastrichtian (associated with regional structural activity, Antarctic cooling, and progressive oxygenation of the central North Atlantic) (Figure 4).

Albian-Cenomanian drowning of the Maraca Formation carbonate platform

The nearly globally synchronous drowning of carbonate platforms near the end of the Albian has been extensively documented, and may be linked to several major oceanographic and climatic events. Drowning of the Maraca Formation platform has been attributed to flooding of shelf areas with anoxic bottom waters. Although no direct confirmation of this model exists, direct evidence of relative sea level rise and the resultant consequences is abundant (Figure 4).

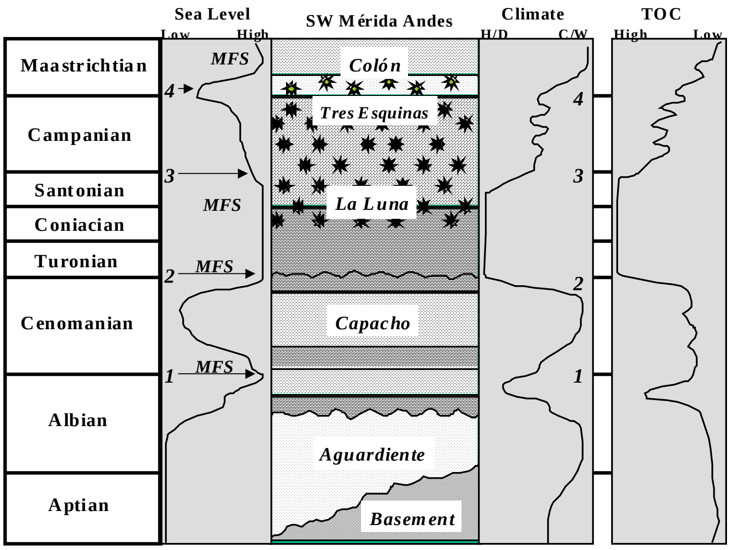

Fig. 4. Temporal variations in relative sea level, climate and TOC for southwestern Venezuela. See text for an explanation of event numbers (1-4). MFS, maximum flooding surface. Note that TOC lags the climate and sea level curves and records higher cyclicity (due to greater data resolution). H/D, hot/dry; C/W, cool/wet.

Rapid flooding of the shallow Albian shelf in western Venezuela is reflected in a major southeastward retreat of the Albian to Cenomanian Capacho Formation (Seboruco Member) delta system (Figure 1), and the preservation of a condensed interval at the top of the Maraca Formation. Flooding of the shelf at the end of the Albian, and the rapid release of nutrients contained within the Capacho Formation delta system may have been sufficient to enhance termination of shallow water carbonate productivity. This event was recorded as an abrupt decrease in total clay (Figure 3) and Ti. This initial marine transgression was diminished in the southeastern Maracaibo Basin by renewed delta progradation during the middle Cenomanian. In this case, high quartz concentrations, as well as high Zr, Zr/Al are closely linked to turbidite events (confirmed through thin section petrography).

Terrigenous clastic contributions to the marine environment nearly ceased during the Cenomanian (Figures 3, 4). However, areas along the ancestral Mérida Andes show a very abrupt increase in total clay, Zr/Al, and quartz near the Cenomanian-Turonian boundary. This event may be associated with an episode of delta progradation and drowning of the Guayacan Member platform.

Drowning of the Guayacan Member carbonate platform and organic carbon burial at the Cenomanian-Turonian boundary

The second major sea level rise to affect western Venezuela occurred at the Cenomanian-Turonian boundary, and caused nearly total cessation of deltaic sedimentation in the study area (sharp decrease in total clay, Zr, and Ti). The cessation of deltaic sedimentation is also accompanied by a sharp increase in TOC content (Figures 2, 4), which corresponds to the worldwide organic carbon burial event. This transgression also led to drowning of the Guayacan Member platform at the Cenomanian-Turonian boundary (Figure 4). A hiatus has been inferred at the boundary based on outcrop evidence, and the presence of high Zr/Al ratios. High Zr/Al ratios may be the result of concentration of Zr during intervals of very slow sediment accumulation.

In western Venezuela, this high TOC interval represents the onset of semi-permanent stagnant bottom water conditions, enhanced by the presence of paleobathymetric barriers in the northwest, south, and east. These conditions were exacerbated by high evaporation and low precipitation rates as demonstrated by palynofloral and lithologic data and paleoclimate models. The concept of episodic regional aridity during the Turonian through early Santonian has also been suggested for Colombia based on the observation of large amounts of eolian quartz in La Luna Formation equivalent units.

Additional support for this concept can be found in biomarker data from the La Luna Formation and Colombian equivalents. Specifically, the presence of 28, 30-bisnorhopane (anoxic conditions) and gammacerane (reducing, stratified, high salinity conditions) in biomarker extracts from Venezuelan and Colombian La Luna samples supports the model. Density stratification and the development of anoxic bottom waters also occurred in marginal Tethyan basins during the same time interval. Arid climatic and restricted oceanographic conditions therefore resulted in the production of a high salinity, low oxygen water mass in the shallow shelf areas of western Venezuela which then acted as a local source of ‘bottom’ waters for the Maracaibo and Barinas/Apure Basins.

The third major marine transgression to affect western Venezuela occurred during the Coniacian to early Santonian (Figure 4). Variations in TOC content from outcrops along the southwestern Mérida Andes show that intervals of initially high TOC content were followed by an abrupt decrease in TOC (Figure 2). The lower TOC intervals are coincident with sharp increases in Si, quartz, and total clay (Figure 3), and a slight increase in Ti. Since no evidence for a fluvio-deltaic source exists in the study area at this time, low TOC content was probably caused by dilution by eolian-derived siliciclastics. Thin section petrography of samples from Turonian, Coniacian, and lower Santonian intervals also shows that quartz silt and rare heavy minerals are finely disseminated throughout the rock matrix, indicating deposition from suspension. However, low TOC intervals in the Coniacian and early Santonian could also have been produced through a brief return to more ‘normal’ marine bottom water conditions (dissolved O_2 greater than 2.0 ml/l).

Early Santonian to early Campanian onset of Tres Esquinas Member deposition

During the early Santonian, depositional patterns appear to have mirrored that of the Turonian and Coniacian. Late Santonian depositional patterns, however, were very different from those of the Turonian through early Santonian. Paleoclimate models and palynofloral data suggest that high fluvial outflow was more common during the late Santonian through Maastrichtian. Prior to the late Santonian, little or no siliciclastic sediment was contributed to the Maracaibo and Barinas/Apure Basins from fluvial sources. This is demonstrated by increases in total clay (Figure 3) and 'excess' Zr and Ti from the upper Santonian to the Campanian, which also coincides with high phosphate intervals (Figure 2). Eolian siliciclastic input appears to have been variable at this time. Intervals of 'excess' Zr and Ti (high Zr/Al and Ti/Al ratios relative to total clay) and abundant quartz silt indicate that fluvially-sourced turbidites were the primary mechanism for siliciclastic transport to the marine environment in the northern Mérida Andes. Alternatively, some high Zr/Al ratios could be due to concentration of Zr within locally important condensed intervals, or at intraformational unconformities.

A major change in the pattern of organic carbon accumulation also occurred in the upper Santonian to Campanian (Figures 2, 4). This is demonstrated by an abrupt decrease in TOC content in the upper Santonian and Campanian. One explanation for this decrease can be attributed to dilution by fluvially derived siliciclastics, while decreasing stratification of the water column (due to seasonal upwelling) may be another explanation. Additionally, the decrease in TOC content is coincident with the maximum geographic extent of Tres Esquinas Member phosphate and glauconite deposition in the eastern Maracaibo Basin.

Recent geochemical data show that high latitude sea surface temperatures reflect a cooling trend for the latest Santonian through Maastrichtian (Figure 4). Cooler sea surface temperatures, accompanied by a greater land-ocean thermal gradient may have increased Trade Wind intensity, thereby enhancing seasonal upwelling of the previously stratified Maracaibo and Barinas/Apure Basins. De-stabilization of salinity-stratified, anoxic waters would have caused catastrophic overturn of the water column, and provided increased opportunities for ventilation and renewed infaunal activity. Indirect evidence of the consequences of such a process is abundant. The widespread occurrence of phosphatic fish bone beds in western Venezuela and eastern Colombia has been attributed to the affects of rapid bursts of marine algal productivity (*red tides*). These events were most likely the result of the surge of nutrients derived from increased fluvial runoff and upwelling of anoxic bottom waters. Evidence of this process (which was also observed in central and eastern Colombia) is reflected in the occurrence of multiple high phosphate intervals (Figure 2) during the late Santonian and Campanian, which can sometimes occur immediately following high Zr/Al intervals.

Late Campanian through Maastrichtian progradation of the Colón/Molino/Burgüita Formation delta system

Uplift of the Central Cordillera of Colombia in the Campanian to Maastrichtian also impacted western Venezuela in three important ways. First, thrust loading in Colombia caused foreland subsidence of the Maracaibo Basin, which contributed to the fourth major sea level rise of the middle to Late Cretaceous. This rapid subsidence is reflected in a southward shift of deep-water (outer shelf to bathyal) Colón Formation shale facies. The transgression has also been interpreted from marine strata in Colombia. Second, the new accommodation space was rapidly filled by sediments derived from the erosion of uplifted older strata in Colombia (Colón/Molino/Burgüita Formation delta system). Third, changes in local climate patterns due to uplift of the Central Cordillera may have magnified the impact of changing (wetter and cooler) global climate (Figures 4, 5).

Regional lithostratigraphy shows that siliciclastic sediments were initially supplied to western Venezuela from the west and south (Figure 5). Sharp increases in total clay (Figure 3), Zr, and Ti in the upper Campanian indicate that siliciclastics were contributed to the basin via a combination of eolian as well as fluvial (turbidite) processes. There appears to be a good general agreement between high total clay intervals and intervals of low quartz and Zr/Al ratios in the early Maastrichtian. The relative lack of heavy minerals in lower Maastrichtian turbidites may coincide with the aforementioned southward shift of Colón

Formation deep-water shale facies, and increased foreland subsidence of the Maracaibo Basin. An increase in total clay and a decrease in quartz at the end of the early Maastrichtian may represent a change in sediment source areas for the deltas. Siliciclastic deposition appears to have occurred through a combination of eolian and fluvial processes.

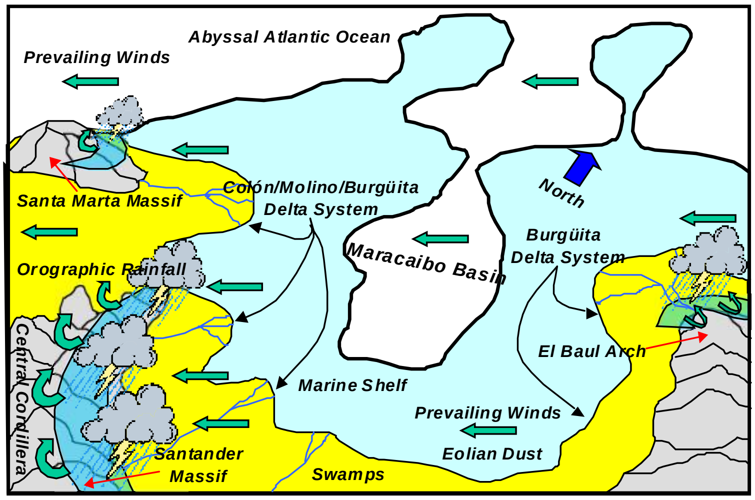

Fig. 5. Early Maastrichtian paleogeography and paleoclimate, western Venezuela.

Visual kerogen analyses and Rock-Eval data indicate that abrupt increases in TOC content in the Campanian and early Maastrichtian (Figure 2) are due to the addition of terrestrial organic matter, probably during turbidite events. Otherwise, TOC content of the section is generally low (mean less than 1.5%; Figure 3), which is typical of better-oxygenated central North Atlantic Maastrichtian sediments. Foreland basin subsidence, and subsidence of the Paraguana Block probably allowed highly saline Maracaibo Basin bottom waters to escape north into the Atlantic Ocean, and be replaced with better-oxygenated waters. Isolated upper Campanian to lower Maastrichtian high phosphate intervals (Figure 2) are the products of continued *red tide* events; some phosphatic gravels were apparently sequestered and bioeroded first within inner to middle shelf environments, prior to transport and redeposition.

CONCLUSIONS

A well-defined connection exists between the abundance of key major and trace elements and minerals, the occurrence of high TOC rocks, and the depositional processes of siliciclastic sediments. This study shows that four important regional depositional events can be distinguished by their geochemical characteristics, and linked to regional or global oceanographic and climatic changes. These include (1) Drowning of the Maraca Formation carbonate platform at the end of the Albian to early Cenomanian (associated with the global late Albian platform drowning event); (2) Drowning of the Guayacan Member carbonate platform at the Cenomanian-Turonian boundary (associated with the global organic carbon burial event); (3) Onset of deposition of the Tres Esquinas Member phosphatic and glauconitic sediments in the Santonian to Campanian (associated with a regional increase in fluvially-derived sediments); and, (4) Rapid progradation of the Colón/Molino/Burgüita Formation delta system in the late Campanian through Maastrichtian (associated with regional structural activity, Antarctic cooling, and progressive oxygenation of the central North Atlantic).