Revista Brasileira de Geociências 18(3):273-282, setembro de 1988

GEOCHEMICAL RECONNAISSANCE OF THE MID-CRETACEOUS ANOXIC EVENT IN THE SANTOS BASIN, BRAZIL

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ABSTRACT The reconnaissance of the Mid-Cretaceous anoxic event in the offshore Santos Basin (Brazil) is the result of several biostratigraphical and organic geochemical investigations carried out by Petrobrás. The geochemical evidence of anoxia was identified at wildcats located in the central-southwestern part of the Santos Basin, where, differently from the remaining of the basin, the Cenomanian/Lower Turonian sequence was not affected by the regional erosional event that occurred in the Late Turonian. The sequence contains organic carbon-rich strata, with enrichment of sapropelic and humic organic matter deposited during the second global anoxic event of the Cretaceous, the environment varying from middle neritic to upper bathyal. The average geochemical characteristics of this sequence are the best in the basin: 1.2 to 1.8% weight total organic carbon (TOC), 2 to 4 kg HC/t.rock (hydrocarbon source potential) and 200 to 300 mg.HC/g.TOC (hydrogen index). However, these data suggest that it should be regarded as a moderate hydrocarbon source rock, even in places where the sequence is encountered within the "oil generation window".

RESUMO RECONHECIMENTO GEOQUÍMICO DO EVENTO ANÓXICO MESOCRETÁCICO NA BACIA DE SANTOS, BRASIL. O reconhecimento da anoxia oceânica do "Mesocretáceo" na Bacia de Santos é conseqüência da realização de numerosos estudos geoquímicos e bioestratigráficos pela Petrobrás nos últimos anos. As evidências geoquímicas da anoxia foram constatadas nos poços exploratórios situados na parte centro-sudoeste do sítio sedimentar, onde, ao contrário de grande parte do restante da bacia, a seqüência do Cenomaniano-Eoturoniano se encontra preservada do evento erosivo regional que ocorreu no Neoturoniano. Esta seqüência contém siliciclásticos finos, ricos em matérias orgânicas sapropélica e húmica, depositados em ambiente nerítico médio a batial superior durante o segundo evento anóxico oceânico do Cretáceo (EAO-2). As características geoquímicas médias da seqüência – carbono orgânico total (COT) de 1,2 ~1,8% peso, potencial gerador de 2 ~ 4 kg HC/t.rocha e índice de hidrogênio de 200 ~300 mg HC/g.COT – são suficientes para situá-la, apenas, como um gerador modesto de hidrocarbonetos junto a áreas onde a seqüência se encontra dentro da zona catagenética (matura).

INTRODUCTION The identification of layers of black shale deposited in basins along the Brazilian continental margin during the Mid-Cretaceous anoxic event has been made possible chiefly by two major undertakings, both initiated at end of the 1960's: intensified hydrocarbon exploration on the Brazilian continental shelf and the Deep Sea Drilling Project (DSDP). DSDP data have revealed widespread distribution of black shales synchronically deposited in almost all oceans during the Middle Cretaceous (Mobertly & Larson 1975, Schlanger *et al.* 1976). Schlanger & Jenkyns (1976) postulate that this was induced by a global oceanic anoxic event (OAE). Occurring in the Cenomanian/Turonian, the Mid-Cretaceous OAE (OAE-2) was the most notable of all Cretaceous anoxic events, more intense than both the preceding (the OAE-1 in the Aptian/Albian) and the subsequent (the OAE-3 in the Coniacian/Santonian), according to Arthur & Schlanger (1979) and Jenkyns (1980) (Fig. 1).

Along the Brazilian continental margin, especially in the basins north of parallel 30°S, there is practically no record of the Aptian/Albian OAE (OAE-1) since marine conditions would only extend to this region later in the Albian. On the other hand, the Cenomanian/Turonian OAE (OAE-2) has been reported in several of Brazil's coastal basins.

The present paper deals with the Santos Basin, where strata correlated with the anoxic event were first recognized through paleoecological interpretation of foraminifera (Koutsoukos 1982). These strata revealed geochemical characteristics indicative of a cyclical alternation of anoxic and oxigen-rich conditions (Gibbons *et al.* 1983). The authors did not link their observations to the global anoxic event, but Viviers (1985) identified foraminifer fauna suggestive of anoxia in the organic carbon-rich intervals mentioned by the authors, correlating this with the second Cretaceous global anoxic event (OAE-2). Viviers (1986) reaffirmed previous observations and located the aforementioned intervals in the Cenomanian/Mid-Turonian Sequence.

This study presents succint organic geochemical data on the Santos Basin as surveyed by Petrobrás in recent years. It intends to offer an important contribution to the general study of the OAE-2, given that data concerning the western part of the northern South Atlantic must at present rely solely on DSDP findings, which are limited to Site 356, the only Brazilian coastal hole to reach the Middle Cretaceous. Evidence for Mid-Cretaceous anoxia in the Santos Basin is also an important indication that the OAE-2 did indeed occur in the far southwestern part of the Mid-Cretaceous Angola-Brazil Basin (Fig. 2).

THE SANTOS BASIN The Santos Basin is located on the continental shelf off southeastern Brazil, between latitudes 23° and 28°S. Totally submersed, it is bordered on the west and northwest by the Santos Hinge Line, on the north by the Cabo Frio High, on the east by the São Paulo Plateau, and on the south by the Florianópolis Platform.

The basin was first identified during seismic refraction studies undertaken by Columbia University's Lamont Geological Observatory in 1960, but it was only one decade later that it was formally designated the Santos Basin, upon the 1970 publication of Miranda's interpretation of the latest geophysical data reported by Petrobrás.

Evolution of the Santos Basin closely resembles that of other basins along Atlantic continental margin. It includes the Lake, Gulf, and Sea megasequences, which represent respectively the rift, proto-oceanic, and oceanic phases of the model proposed by Asmus & Porto (1980). Its stratigraphic

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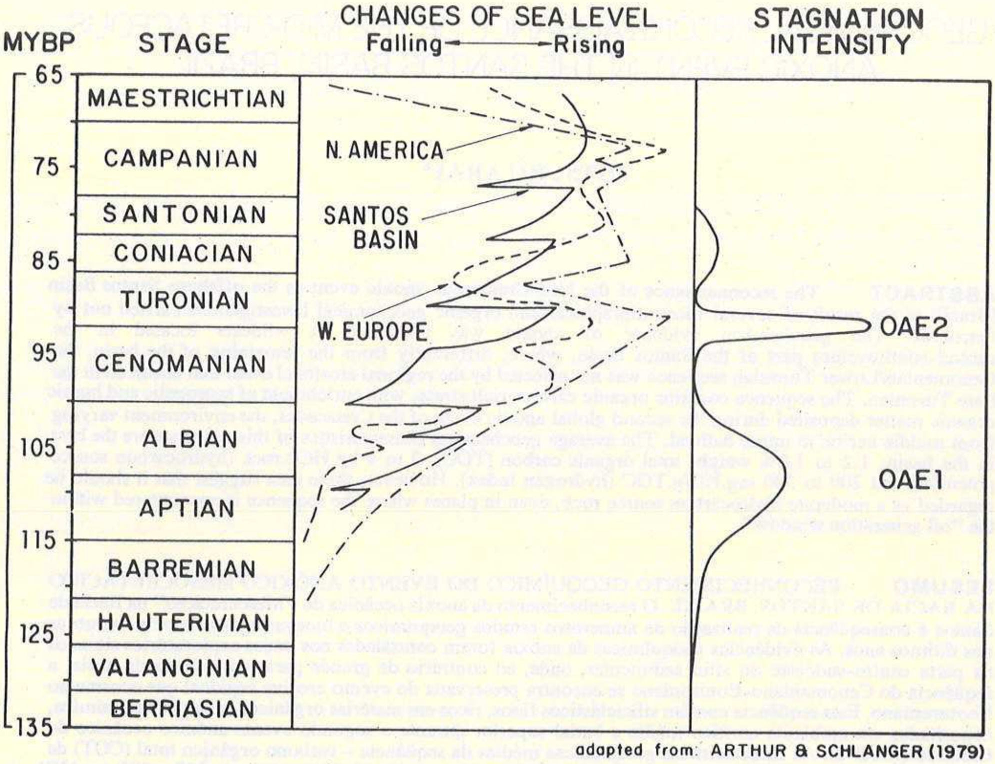


Figure 1 – Relative sea-level stands and intensity of anoxic events in the Cretaceous period (adapted from Arthur & Schlanger 1979)

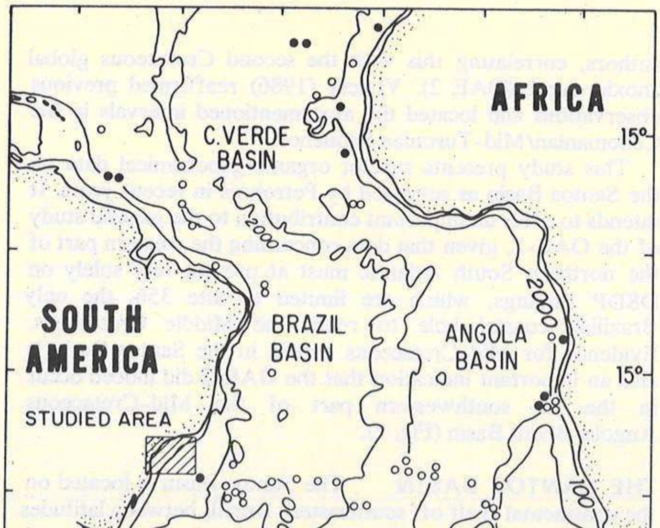


Figure 2 – Location of Deep Sea Drilling Project sites in the present South Atlantic Ocean. Isobaths in meters. Sites with drilled mid-Cretaceous and/or older sequences are shown by black circles. Sites with mid-Cretaceous not reached or absent are shown by open circles

column is made up of units wich are synchronically represented in other Brazilian coastal basins.

The geological column shown in figure 3 presents latest available geological data (Pereira *et al.* 1986).

The operational basement (base of the known sedimentary sequence) in the Santos basin consists of basic volcanic rocks 120 Ma old, overlain with Lake megasequence sediments (Guaratiba Formation or Pre-Salt Sectión). Unlike its neighboring Campos Basin, this megasequence has not been studied in depth, drilling so far having been limited to three wells which have only indicated lithologic types characteristic of proximal facies (alluvial fan and fan-delta).

Evaporites of the gulf megasequence were deposited over sediments of the rift stage, constituting the Proto-oceanic Phase.

These evaporites (São Vicente Formation) stretch to the outermost portion of the São Paulo Plateau, reaching thicknesses of 2,000 to 2,500 m at their depocenter (Pereira *et al. op.cit.*). Initiated in the Albian, the compactional displacement of this immense salt layer contributed substantially to structuralization of the basin.

Representing the last major phase in tectonic and depositional evolution, *i.e.*, the Oceanic Phase, deposition of the Sea Megasequence (Post-Salt Section) began during the Albian.

In the Early/Middle Albian an extensive carbonate platform covered the evaporites (Guarujá Formation). It was impeded only at the borders adjacent to emergent lands, where coarse fan-delta deposits were dominant. Owing to the low sea-level stand and to the degree of oxigenation of the environment, the Lower to Middle Albian sequence is devoid of organic-rich rocks.

The Late Albian was characterized by a marked sea-level rise, inducing the progressive submergence of the carbonate platform from then until the Middle Turonian. As a result, the

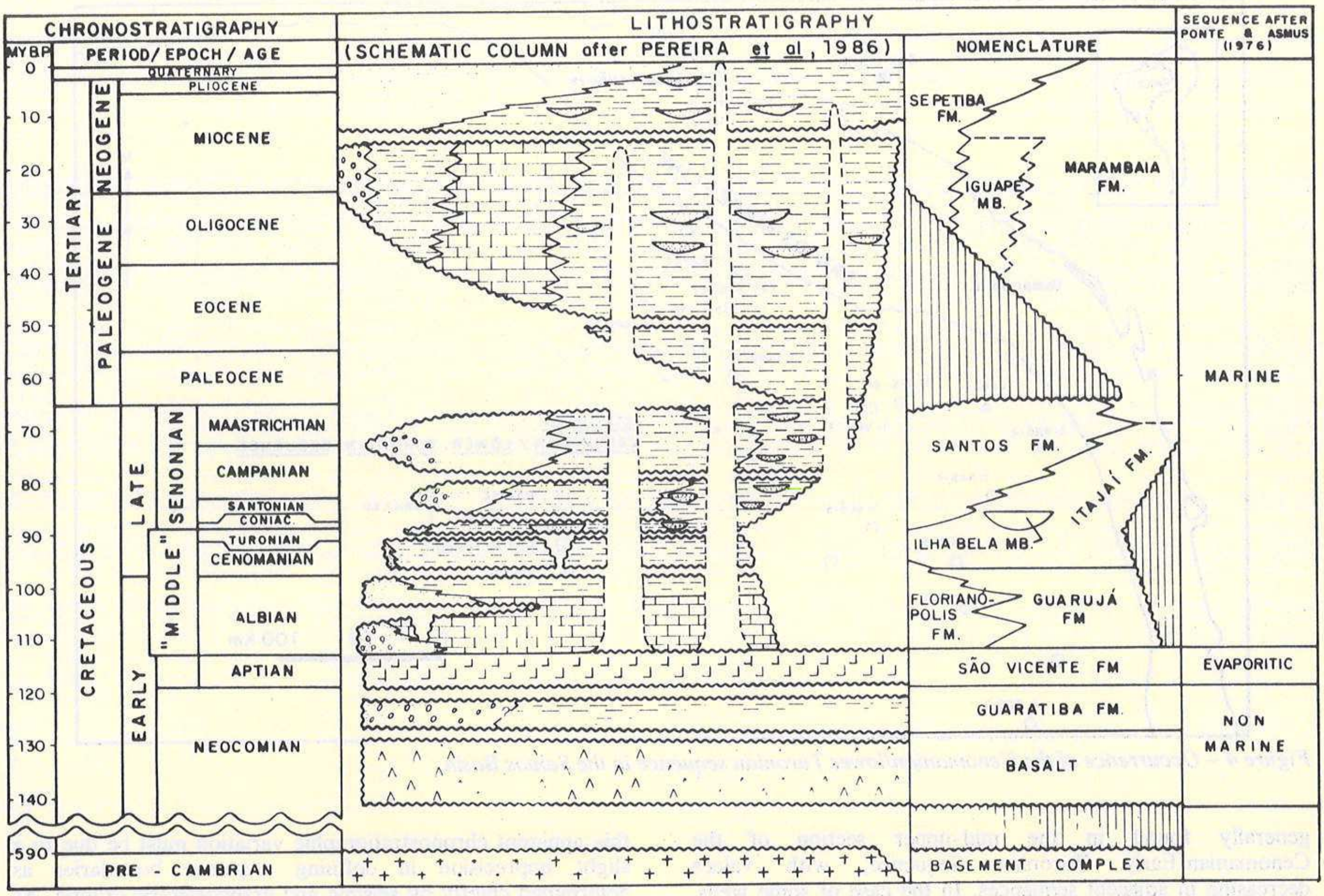


Figure 3 – Schematic geologic column of the Santos Basin

formerly typical carbonate platform became increasingly terrigenous.

The transgressive phase reached its climax during the Cenomanian/Middle Turonian, when prevailing sedimentation was characterized by outer shelf and upper slope pelites. Deposition of this sequence coincided with the OAE-2, prompting the incorporation and preservation of substantial amounts of organic matter and giving rise to the informally so-called Anoxic Itajaí black shales, which enjoy a relatively high organic carbon content.

A prograding depositional process began during the Late Turonian, lasting until the end of the Cretaceous. Representing the first prograding cycle, the Upper Turonian/Coniacian sequence constitutes most of the upper Itajaí Formation, which was probably deposited under wave-dominated deltaic conditions. Subsequent cycles (Santonian/Lower Campanian and Campanian/Maestrichtian sequences) were markedly prograding and suffered accentuated continental influence; these sequences constitute most of the Santos Formation.

During the Tertiary, a transgressive sea again covered the basin, causing pelites (clastic facies of the Marambaia Formation) to be deposited on the slope and carbonates (Iguape Member) on the shelf.

During the Neogene, a prograding environment prevailed, and coarse to fine clastics of the Sepetiba Formation were deposited.

METHODOLOGY This study has relied on geochemical data concerning **1.** total organic carbon; **2.** pyrolysis; and **3.** vitrinite reflectance, obtained respectively with the use of **1.** a Leco apparatus; **2.** Rock-Eval apparatus; and **3.** a Zeiss photomicroscope. All analyses were carried out at the Laboratório do Setor de Geoquímica, Divisão de Exploração, Centro de Pesquisas Leopoldo A. Miguez de Mello (Cenpes), Petrobrás, Rio de Janeiro. Recovered from Santos Basin exploratory wells, most samples consisted of cuttings with some core samples and sidewall core samples.

Pyrolysis permitted measurement of the geochemical parameters defined by Espitalié *et al.* (1977): free hydrocarbons (S1); hydrocarbon source potential (hydrocarbons produced under pyrolysis) (S2); carbon dioxide produced under pyrolysis (S3); hydrogen index (HI); and oxygen index (OI).

RECONNAISSANCE OF THE ANOXIC ITAJAÍ SHALE Geochemical data from the Santos Basin reveal greater levels of total organic carbon, hydrocarbon source potential, and HI in the central-southwestern area of the basin. Data were obtained from the lower part of the Itajaí Formation or, more precisely, from the Anoxic Itajaí, consisting mainly of dark gray shales (color 5Y 5/1). This unit is generally equivalent to the Cenomanian/Early Turonian sequence, bounded by seismostratigraphic horizon H4 and H5 (Pereira *et al. op. cit.*) at the base and top respectively. The Late Turonian regional erosive event eliminated a large part of the sequence, limiting its present-day occurrence to the central-southwestern part of the basin. This tendency is clearly evidenced in the distribution of wells reporting Cenomanian/Early Turonian occurrences (Fig. 4).

The plotting on geochemical profiles of organic carbon and potential yield data from the most representative wells reveals a close relationship between the peak of geochemical parameters and the Cenomanian/Early Turonian Sequence. For each well analyzed, maximum geochemical values are

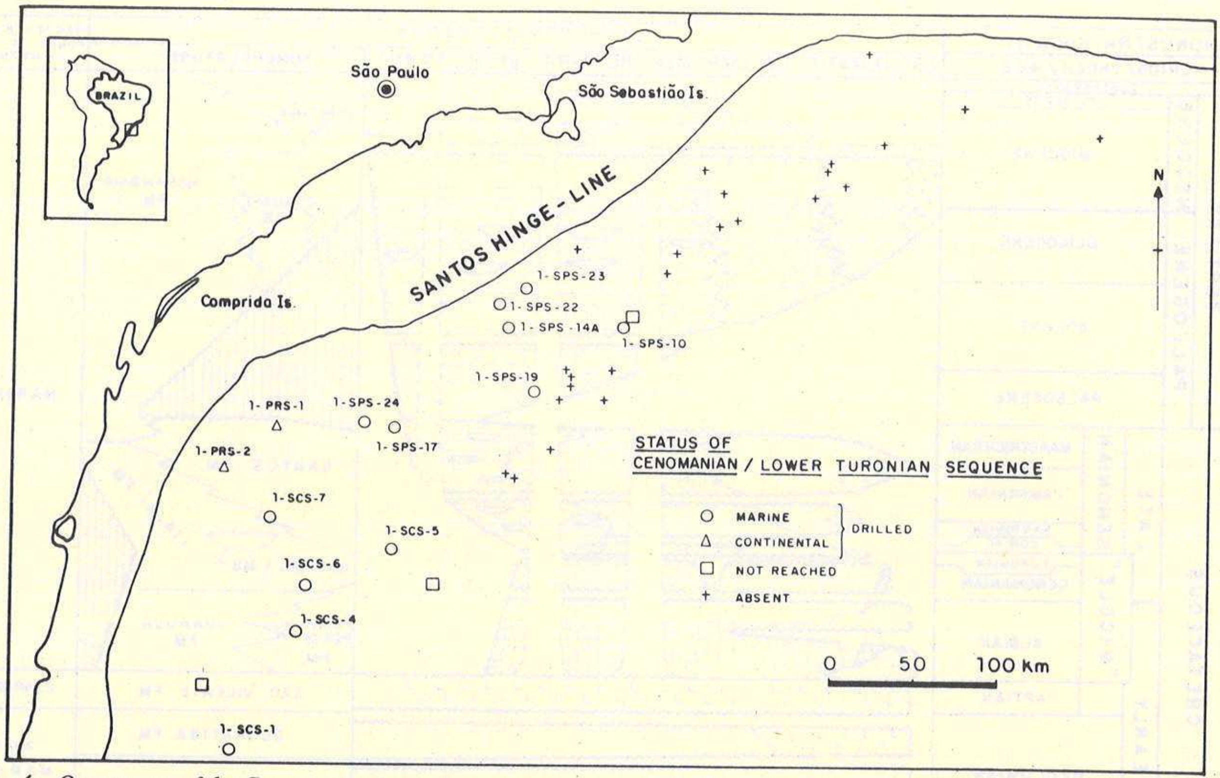


Figure 4 – Occurrence of the Cenomanian/lower Turonian sequence in the Santos Basin

generally found in the mid-upper section of the Cenomanian/Early Turonian Sequence, with values decreasing in adjacent sequences. In the case of some wells, such as 1-SPS-17 and 1-SCS-1, maximum values occur at the boundary between the Cenomanian/Early Turonian Sequence and the overlying Late Turonian/Coniacian Sequence. Rather than indicating diachronism of the anoxic event in these wells, this apparent chronostratigraphic variation must be due to a slight imprecision in defining sequence boundaries as determined chiefly by seismic and graphoelectric criteria. As possible evidence for this, the zone of maximum values of geochemical parameters clearly mirrors the biostratigraphic datum based on the extinction of the pollen *Classopollis major* (top of Interval γ, Uesugui 1976) (Fig. 5).

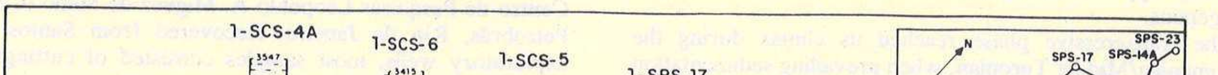


Figure 5 – Geochemical section through the studied wells

INTERPRETATION OF GEOCHEMICAL DATA Geochemical data have been plotted on maps and diagrams to facilitate interpretation. Maps of organic carbon and parameters derived from pyrolysis show averages for the Anoxic Itajaí section of each well. The maturation map (vitrinite reflectance) shows measured and interpolated values at the level of seismographic horizon H5.

Total organic carbon The average content of organic carbon in the Cenomanian/Early Turonian Sequence varied from 0.2% to 1.9% in weight. Lowest values refer to wells in the far southwest of the basin, where the sequence was deposited in subaerial environment (Viviers 1986). When data from these wells is omitted from calculations, average content increases to over 0.8%. Highest values refer to the central-southwest of the basin, where averages of 1.2% to 1.8% were obtained (Fig. 6).

According to Arthur *et al.* (1984), sediments presenting organic carbon content over 1% suggest greater probability of deposition under anoxic conditions.

Hydrocarbon source potential (S2) Average hydrocarbon source potential for the Cenomanian/Early Turonian Sequence ranges from near zero to 4.0 kg HC/t of rock. When data from the far southwestern area are discarded, the variance is limited to 1.0 to 4.0 kg HC/t of rock. Optimum values were once again recorded in the central-southwestern part of the basin, where all averages exceed 2.0 kg HC/t of rock. When data from the far southwestern area are discarded, anomaly for this basin, they are nonetheless modest compared to values reported at DSDP holes (*e.g.*, Herbin *et al.* 1986, 1987, Tissot *et al.* 1980).

Hydrogen index (HI) HI values for the Cenomanian/Early Turonian Sequence averaged 30 to 295 mg HC/g of organic carbon (OC). Omitting data from the far southwestern area, all averages surpass 100 mg HC/g OC. In the central southwest, HI values average greater than or equal to 200 mg HC/g OC, approaching 300 mg HC/g OC at well 1-SCS-4 (Fig. 8).

HI *versus* OI diagram The HI *versus* OI Diagram (Espitalié *et al.* 1977), an adaptation of the Van Krevelen Diagram, is most useful in classifying types I, II, and III of sedimentary organic matter by using Durand & Monin's (1980) and Tissot & Welte's (1978) criteria.

Data plotted on the diagram indicate type II and III organic matter in the great majority of samples extracted from the Cenomanian/Early Turonian Sequence (Fig. 9). Studies of kerogen on the strew-slides reveal this to be the result of a mixture of amorphous and humic organic matter, derived primarily from terrestrial sources (Arai 1987). Some samples from core no. 3 of well 1-SCS-1 present a high HI typical of type I organic matter, but these samples represent rather insignificant interlayers a few decimeters thick.

Vitrinite reflectance Vitrinite reflectance is one of the most efficient tools used to determine maturation of organic matter. According to Tissot & Welte (1978), the transition from the diagenetic or immature phase to the catagenetic or mature phase occurs at about 0.5% Ro. For the purposes of this study however, a transition point of 0.6% Ro (Arai 1984) was considered the most adequate indicator of the initiation of the main phase of hydrocarbon generation in Brazilian marginal basins.

Average vitrinite reflectance values indicate that despite substantial burial, most of the Anoxic Itajaí samples are from the initial catagenesis zone, barely reaching the phase of maximum hydrocarbon generation, *i.e.*, reflectance values of around 1% Ro (Fig. 10). Some data, such as those derived from the upper part of the Turonian section in well 1-SPS-14A, are still indicative of the diagenetic (immature) phase.

The degree of maturation recorded at the top of the Cenomanian/Early Turonian Sequence (seismostratigraphic horizon H5) ranges from 0.5% Ro to a little over 0.8% Ro, but the vast majority of data from the area under study present values of up to 0.7% Ro, indicating only moderate catagenesis (Fig. 11).

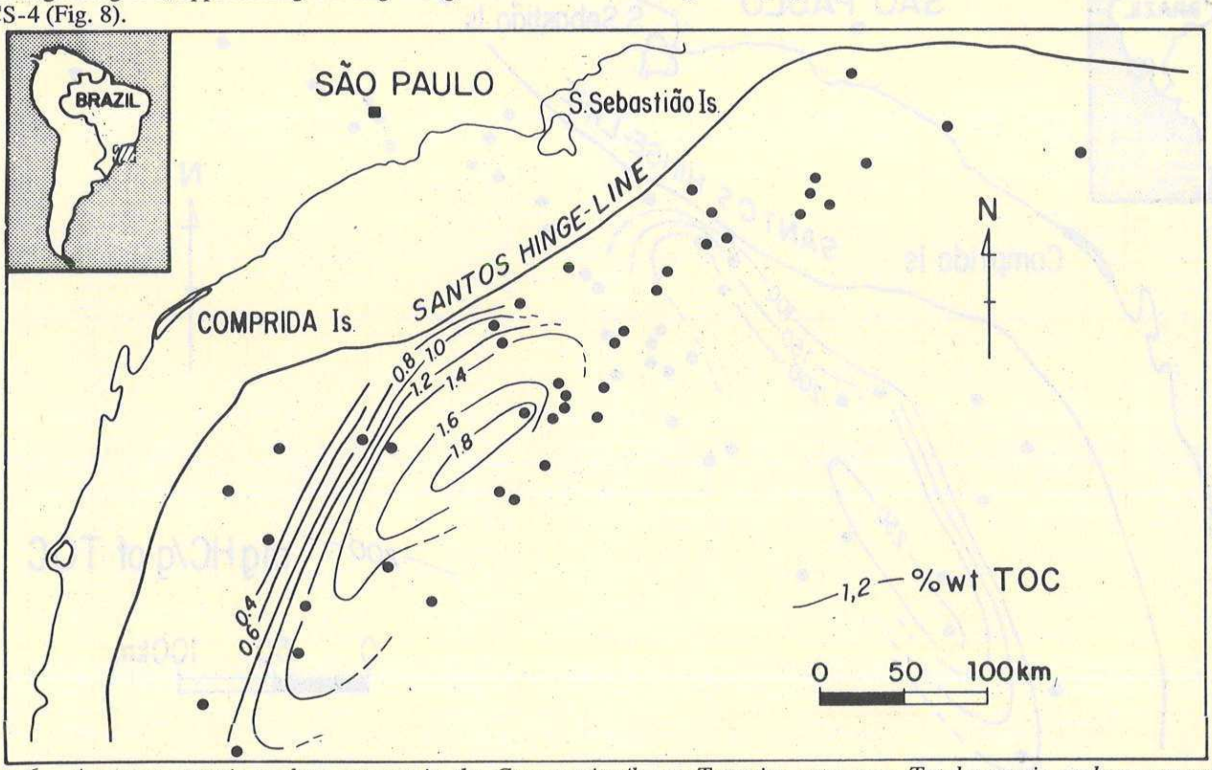


Figure 6 – Average organic carbon content in the Cenomanian/lower Turonian sequence. Total organic carbon concentration contoured in % weight

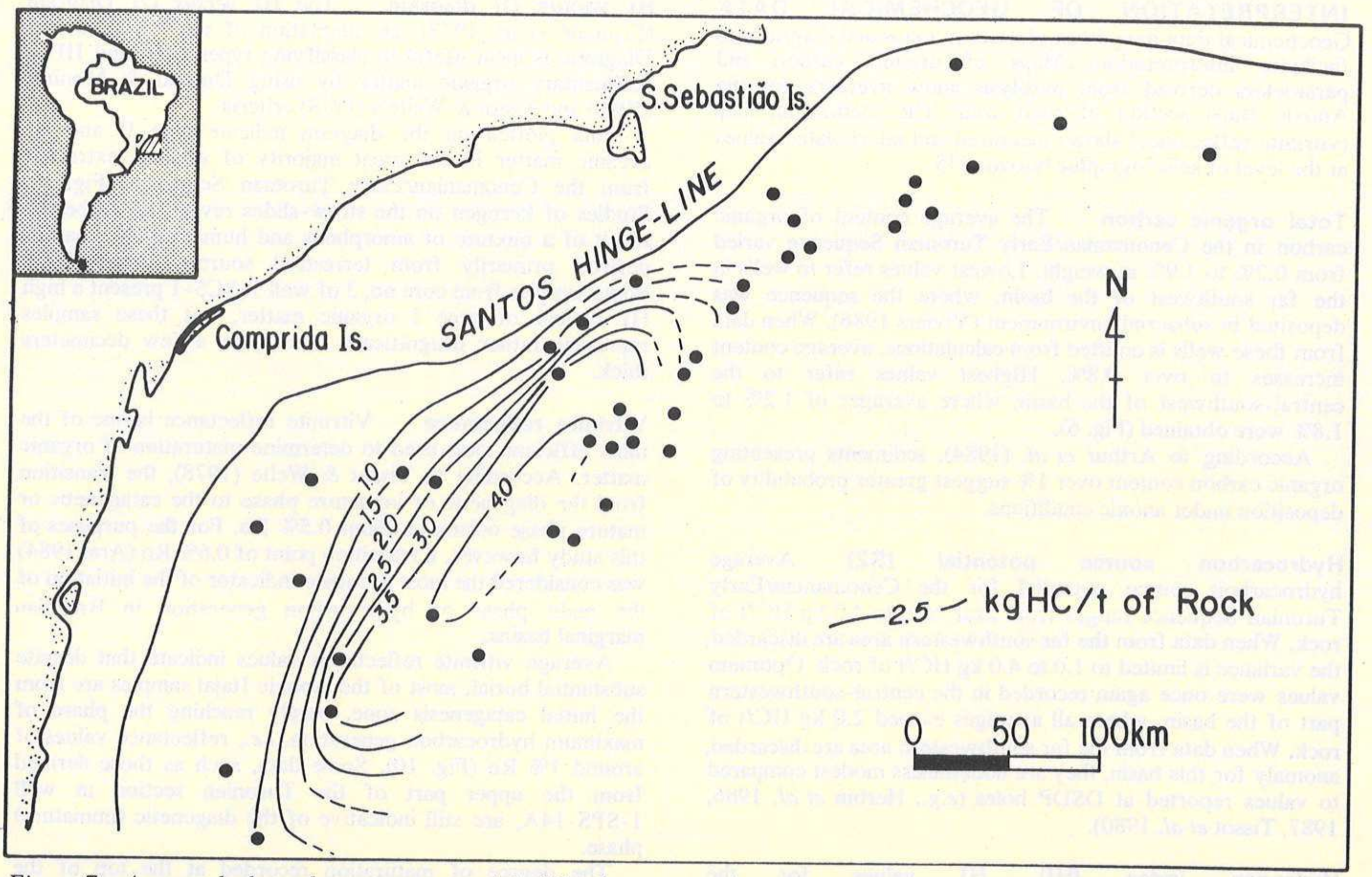


Figure 7 – Average hydrocarbon source potential of the Cenomanian/lower Turonian sequence. Source potential values contoured in kilogram of hydrocarbon per ton of rock

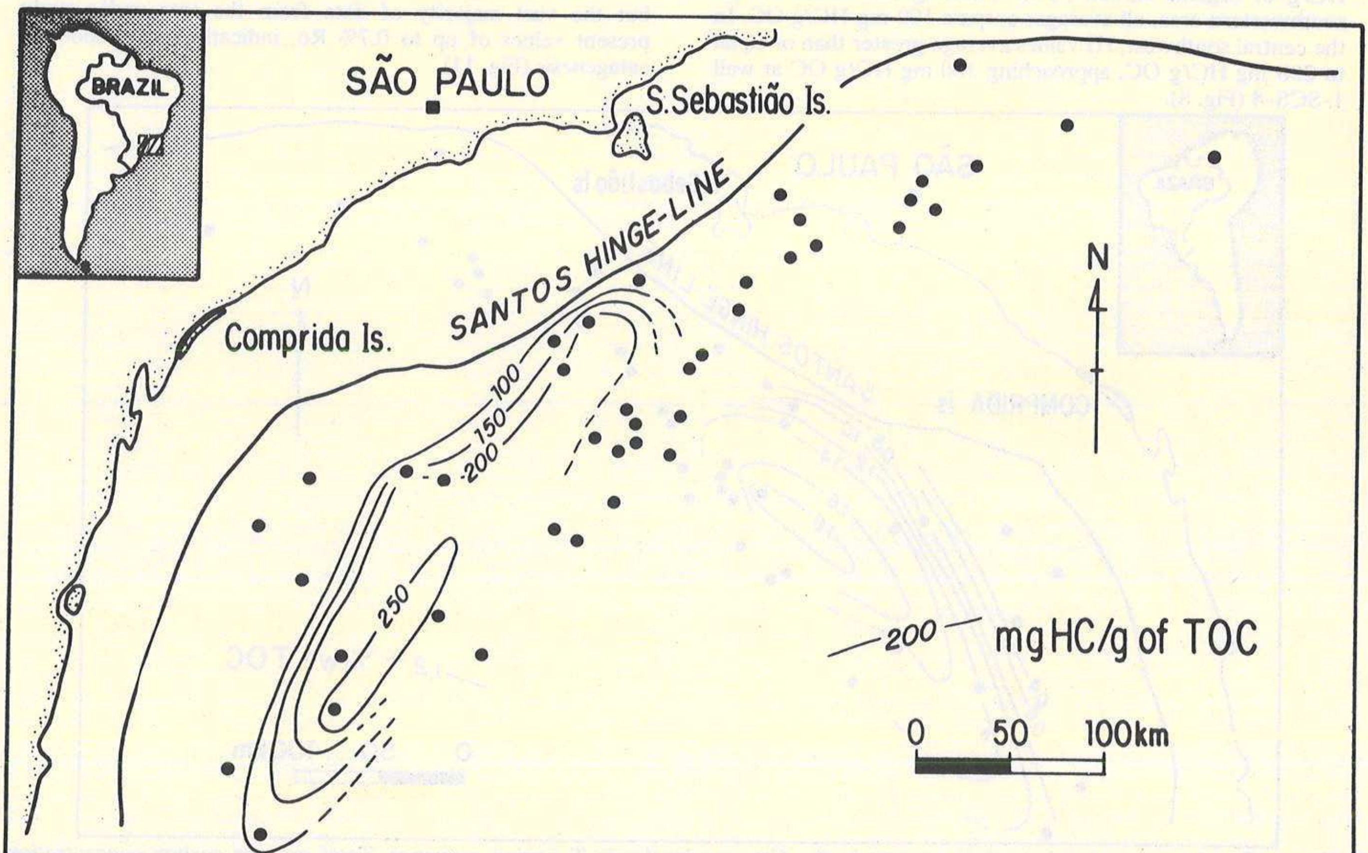


Figure 8 – Average hydrogen index of the Cenomanian/lower Turonian sequence. Hydrogen index values contoured in milligram of hydrocarbon per gram of organic carbon.

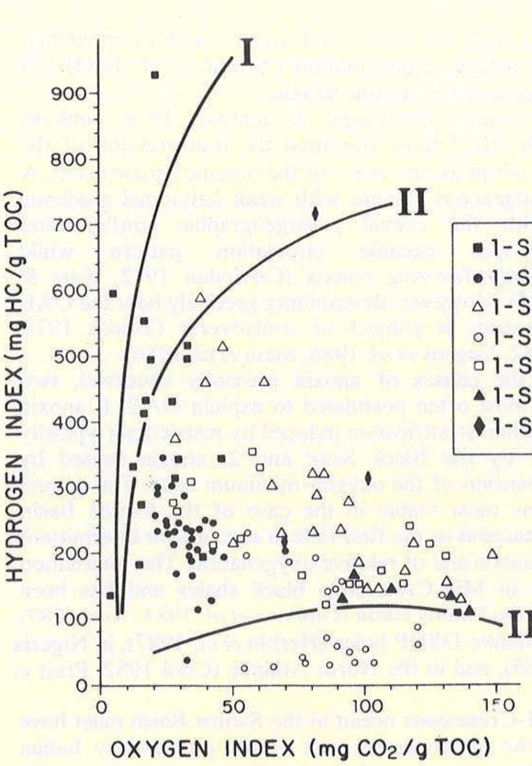


Figure 9 – IH vs. IO Diagram (Van Krevelen's Diagram adapted by Espitalié et al. *1977).*

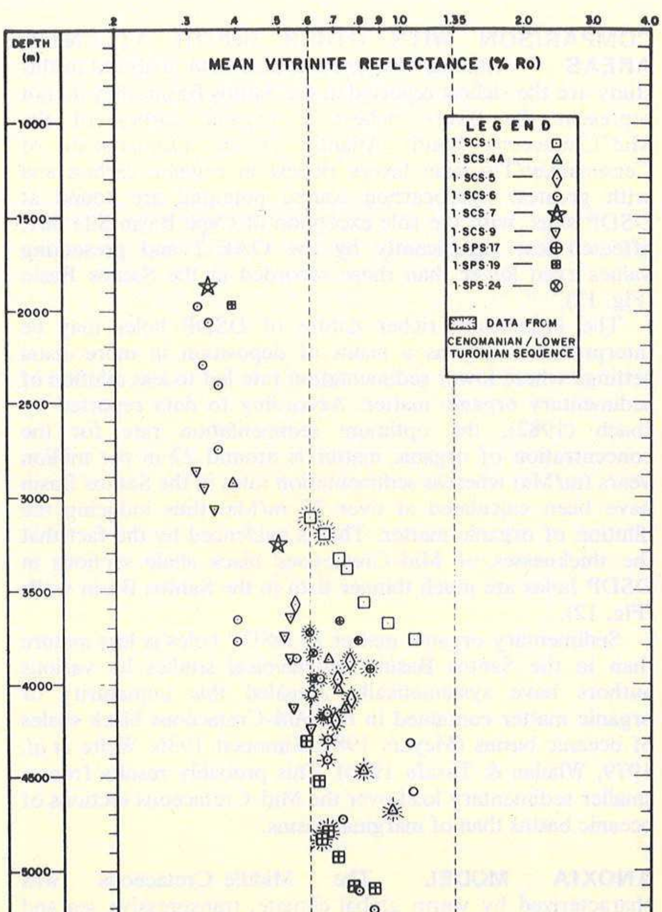


Figure 10 – Mean vitrinite reflectance profiles

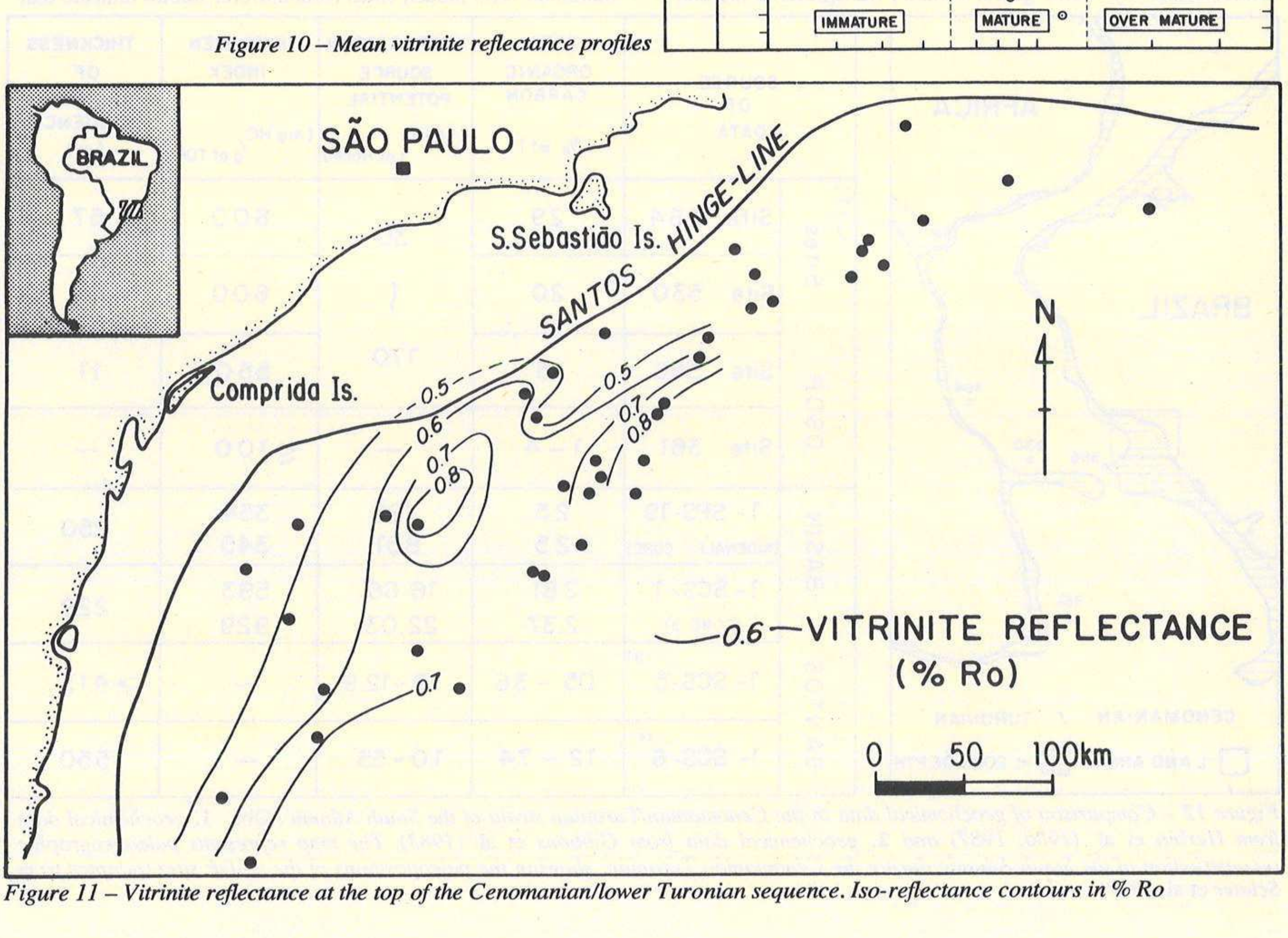


Figure 11 – Vitrinite reflectance at the top of the Cenomanian/lower Turonian sequence. Iso-reflectance contours in % Ro

COMPARISON WITH OTHER SOUTH ATLANTIC AREAS Although the geochemical data analyzed in this study are the richest reported in the Santos Basin, they do not represent the layers richest in organic carbon of the Mid-Cretaceous South Atlantic Ocean. Occurrences of Cenomanian/Turonian layers richest in organic carbon and with greatest hydrocarbon source potential are found at DSDP sites, with the sole exception of Cape Basin Site 361, affected less significantly by the OAE-2 and presenting values even lower than those recorded in the Santos Basin (Fig. 12).

The organically richer nature of DSDP holes may be interpreted mainly as a result of deposition in more distal settings where lower sedimentation rate led to less dilution of sedimentary organic matter. According to data reported by Ibach (1982), the optimum sedimentation rate for the concentration of organic matter is around 22 m per million years (m/Ma) whereas sedimentation rates in the Santos Basin have been calculated at over 32 m/Ma, thus inducing the dilution of organic matter. This is evidenced by the fact that the thicknesses of Mid-Cretaceous black shale sections in DSDP holes are much thinner than in the Santos Basin wells (Fig. 12).

Sedimentary organic matter in DSDP holes is less mature than in the Santos Basin. Geochemical studies by various authors have systematically revealed this immaturity of organic matter contained in the Mid-Cretaceous black shales of oceanic basins (Meyers 1984, Simoneit 1986, Welte *et al.* 1979, Whelan & Tarafa 1986). This probably results from a smaller sedimentary load over the Mid-Cretaceous sections of oceanic basins than of marginal basins.

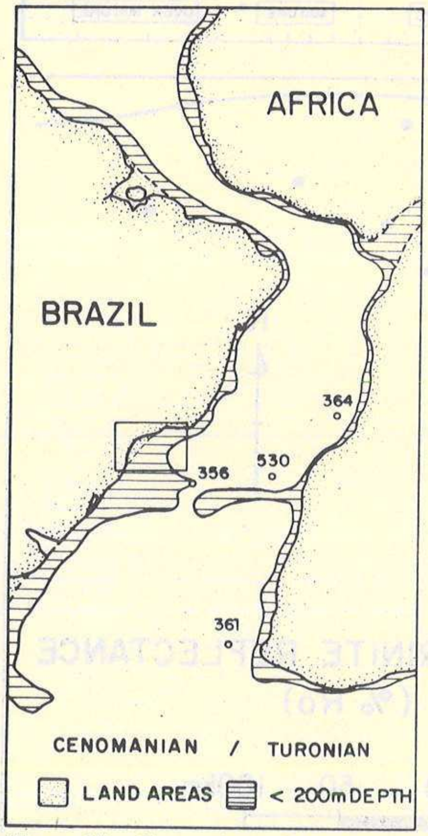
ANOXIA MODEL The Middle-Cretaceous was characterized by warm global climate, transgressive sea and consequently high sea-level stand, rapid sea-floor spreading, and intense pelagic sedimentation (Arthur *et al.* 1984) – a propitious scenery for oceanic anoxia.

Several authors (Schlanger & Jenkyns 1976, Jenkyns 1980, Habib 1982) have identified the transgression of the Cretaceous ocean as one cause of the oceanic anoxic event. A warm, homogeneous climate with weak latitudinal gradients coupled with the coeval paleogeographic configuration prevented free oceanic circulation pattern while concommitantly favoring anoxia (Govindan 1982, Katz & Pheifer 1986). However, determining precisely how the OAE operated ramains te subject of controversy (Thiede 1978, Kennett 1982, Degens *et al.* 1986, Stein *et al.* 1986).

Among the causes of anoxia presently observed, two models are most often postulated to explain OAE: **1.** anoxia caused by saline stratification induced by restriction (typically exemplified by the Black Sea); and **2.** anoxia caused by vertical expansion of the oxygen-minimum zone. The second model seems most viable in the case of the Santos Basin Middle Cretaceous as the first fails to account for intermittent periods of anoxia and of relative oxygenation. This alternation is common in Mid-Cretaceous black shales and has been reported in the Santos Basin (Gibbons *et al.* 1983, Arai 1987), in South Atlantic DSDP holes (Herbin *et al.* 1987), in Nigeria (Akpan 1985), and in the North Atlantic (Cool 1982, Pratt *et al.* 1986).

The Mid-Cretaceous ocean in the Santos Basin must have resembled the northwestern part of the present-day Indian Ocean, where oxygen is virtually absent from the oxygen-minimum layer in depths ranging from – 150 to – 800 m (Kennett 1982).

Paleobathymetric and paleoenvironmental reconstructions accepted for this basin are also compatible with an oxygen-minimum zone model, since foraminiferal studies indicate that



	SOURCE OF DATA	TOTAL ORGANIC CARBON (% wt)	HYDROCARBON SOURCE POTENTIAL (Kg HC/t of Rock)	HYDROGEN INDEX (mg HC/g of TOC)	THICKNESS OF BLACK - SHALE SEQUENCE (m)
DSDP Sites (1)	Site 364	29	30 ~ 170	600	57
	Site 530	20		600	50
	Site 356	15		550	11
	Site 361	1 ~ 4	—	≤100	—
SANTOS BASIN	1-SPS-19 (SIDEWALL CORE)	2.5 2.5	7.98 8.51	354 345	250
	1-SCS-1 (CORE 3)	2.81 2.37	16.66 22.03	593 929	229
	1-SCS-5 (2)	0.5 ~ 3.6	1.9 ~ 12.9	—	>413
	1-SCS-6 (2)	1.2 ~ 7.4	1.0 ~ 5.3	—	550

Figure 12 – Comparison of geochemical data in the Cenomanian/Turonian strata of the South Atlantic. Obs.: **1.** *geochemical data from Herbin* et al. *(1986, 1987) and* **2.** *geochemical data from Gibbons* et al. *(1983). The map represents paleogeographic reconstruction of the South Atlantic during the Cenomanian/Turonian, showing the paleopositions of the DSDP sites (adapted from Sclater* et al. *1977)*

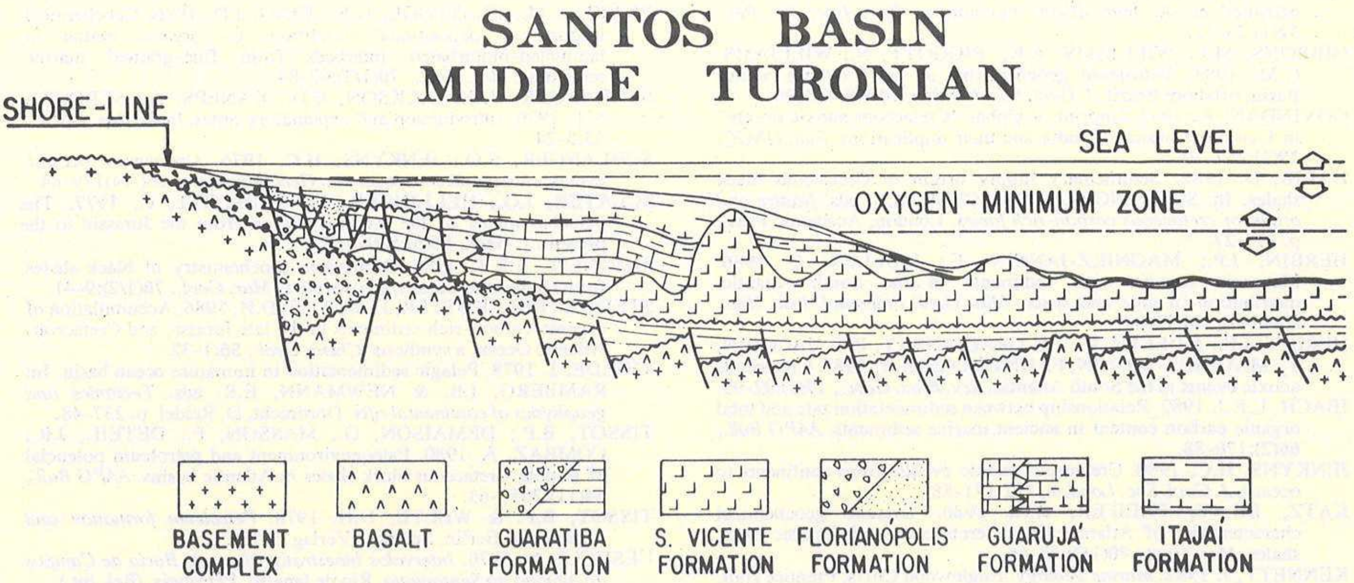


Figure 13 – Schematic representation of geological and oceanographic situation along dip section of the Santos Basin by latest OAE-2 time (adapted from Pereira et al. *1986).*

middle/deep neritic through upper bathyal environments prevailed during deposition of the Anoxic Itajaí shales (Viviers 1986).

The scenery suggested for the Middle Cretaceous Santos Basin is that a transgressive sea possessing an anoxic intermediate layer, which produced an anoxic bottom extending from deep neritic down through upper bathyal environments (Fig. 13). This model should be tested once wells have been drilled through the Middle Cretaceous in locations of greater paleodepths (lower bathyal to abyssal) within the primitive Atlantic.

CONCLUSIONS Organo-geochemical studies together with geological and paleontological data indicate that the lower unit of the Itajaí Formation (informally designated Anoxic Itajaí) represents the global anoxic event of the Middle Cretaceous, known as OAE-2, which occurred, more precisely during Cenomanian through Turonian times.

The Anoxic Itajaí stands out geochemically from other Santos Basin stratigraphic units due to its relatively high carbon content and hydrocarbon source potential. These findings gain special importance since the Anoxic Itajaí is located on the Brazilian coast, where insufficient DSDP Mid-Cretaceous data are available; moreover, the findings can be construed as evidence that the OAE-2 occurred in the far southwestern part of the Mid-Cretaceous Angola-Brazil Basin.

Despite its relative organic richness, the Anoxic Itajaí unit is not as rich as Mid-Cretaceous black shales recovered at most DSDP sites. This geochemical inferiority is probably the result of dilution induced by a too high sedimentation rate.

Most of the Anoxic Itajaí is in the initial phase of catagenesis, barely reaching the degree of maturation which corresponds to maximum hydrocarbon generation.

An oxygen-minimum zone model of anoxia is most appropriate for the Santos Basin Middle Cretaceous. A Black Sea-type restricted basin model, with saline stratification, would be inadequate due to the frequent intercalation of relatively oxygenated levels among black shales.

Acknowledgements I am grateful to Petrobrás management for marking the publication of this paper possible; and to the geologist Dimas Dias-Brito for his kind encouragement and support.

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MANUSCRITO 516
Recebido em 8 de janeiro de 1988
Revisão aceita em 26 de abril de 1988

A eventual vivência do método científico, ao invés de treinar pequenos cientistas, deverá estar voltada para colaborar no longo e complicado processo de formação do pensamento lógico e crítico do estudante.

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