

CARBON ISOTOPIC COMPOSITION OF MIXED OILS FROM THE POTIGUAR BASIN, BRAZIL*

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ABSTRACT—In the Potiguar Basin, Brazil, mixed oils with varying contributions from lacustrine freshwater and marine hypersaline source rocks have been identified. A combination of gross, fractional and compound-specific isotopic analyses was undertaken to investigate variations associated with the extent of oil mixing. $\delta^{13}\text{C}$ values of whole oils and oil fractions show trends that apparently are divergent, but which can be related to facies variations and pronounced biodegradation, processes which affect the relative concentration of compounds with different isotopic ratios. Compound-specific isotopic ratio analyses confirmed some previous results obtained for oil shales, contributing new data on petroleum samples: *n*-alkanes show small variations in their isotopic ratios; pristane, phytane, the C_{21} acyclic isoprenoid and gammacerane are generally more positive than *n*-alkanes, and $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopane is the most ^{13}C depleted, reflecting its partial origin from chemoautotrophs and methanotrophs. Isotopic ratios of $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopane show progressively more positive ratios for oils with increasing contribution of lacustrine freshwater character. Integration of biomarker quantification and compound-specific isotopic analyses helps elucidate anomalies in the isotopic composition of whole oils and oil fractions.

RESUMO—Na Bacia Potiguar, Brasil, óleos mistos com contribuições variáveis a partir de rochas geradoras depositadas em ambientes lacustres de água doce e marinho hipersalinos foram identificadas. Uma análise isotópica integrada, incluindo óleos totais, frações e isótopos de compostos individuais foi realizada visando investigar variações associadas com a quantidade de mistura. Os valores de $\delta^{13}\text{C}$ dos óleos totais e frações mostram tendências que são aparentemente divergentes, mas que podem estar relacionadas a variações de facies e biodegradação pronunciada, processos que afetam a concentração relativa de compostos com diferentes razões isotópicas. As análises isotópicas de compostos específicos confirmaram alguns resultados anteriores obtidos para folhelhos betuminosos, contribuindo com novos dados em amostras de petróleo: *n*-alcanos mostram pequenas variações em suas razões isotópicas; pristano, fitano, isoprenóide acíclico em C_{21} e gamacerano são geralmente mais positivos que *n*-alcanos e $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopano é o composto mais depletado em ^{13}C , refletindo sua origem parcial a partir de organismos quimioautotróficos e metanotróficos. As análises isotópicas de $17\alpha(\text{H})$, $21\beta(\text{H})$ -hopano mostra razões isotópicas progressivamente mais positivas em óleos com maior contribuição de rochas lacustres de água doce. A integração da quantificação de biomarcadores e análise isotópica de compostos individuais auxilia a elucidação de anomalias na composição isotópica de óleos totais e frações.

INTRODUCTION

The carbon isotopic compositions of source rock bitumens, crude oils and oil fractions (saturates, aromatics and NSO compounds) have been used for correlation purposes and to characterize prevailing depositional conditions. Petroleums are normally lighter than source-rock bitumens and saturate hydrocarbon fractions are depleted in ^{13}C , whereas NSO fractions are enriched in ^{13}C , aromatic hydrocarbons are usually of intermediate isotopic composition (Fuex, 1977; Stahl, 1978; Schoell, 1984). In most cases, lacustrine source rocks and petroleums are depleted in ^{13}C by comparison to those of marine origin, but their carbon isotope values are not, by themselves, diagnostic (Sofer, 1984; Peters et al.,

1986; Mello et al., 1988a, b). There is always some overlap between the isotopic composition of samples from the two environments, and the reverse relationship, where marine source rocks and petroleums are more depleted in ^{13}C than nonmarine samples, has also been reported (Magoon and Anders, 1992).

In the context of petroleum migration, carbon isotopes have also been used to distinguish migrated hydrocarbons from indigenous bitumen within an interbedded shale/sandstone sequence (Engel et al., 1991). Additionally, the effects of petroleum migration on isotopic composition have been explored in field settings (Silverman, 1965) and by laboratory simulations (Philp and

Engel, 1987; Bonilla and Engel, 1986). Both approaches suggested isotopic shifts associated with enrichment of isotopically lighter, lower molecular weight compounds. However, detailed investigation of marine source rock cores in contact with a reservoir has shown that major variations in the bulk isotope compositions are associated with stratigraphic heterogeneities (up to 4‰) and that little or no isotopic change could be firmly attributed to the effects of primary migration (Macko and Quick, 1986).

Recent developments in analytical instrumentation have made possible on-line measurement of the carbon isotopic composition on individual compounds (Freeman et al., 1990; Hayes et al., 1990), enhancing understanding of the precursor organisms for many compounds and facilitating elucidation of carbon pathways. Several factors can influence the isotopic composition of individual components including the source of carbon, the biosynthetic pathway, and a balance between organic productivity and water stratification. Compounds depleted in ¹³C (as low as -65‰; Freeman, 1991) derive from organisms which utilize isotopically depleted carbon sources such as methane and respired CO₂. Enrichments of ¹³C result from assimilation of HCO₃⁻ under CO₂-limited photosynthesis and oxidative heterotrophy, whereas water stratification can promote a more noticeable depletion of ¹³C (Freeman, 1991; Hollander et al., 1992).

Comparison of lacustrine and marine shales shows a broader range for the isotopic composition of individual compounds in the former. For example, compounds from the Tertiary lacustrine Condor Oil Shale range from more than 15‰ enriched to nearly 35‰ depleted in ¹³C relative to primary producers, whereas most hydrocarbons from the Cretaceous marine Julia Creek oil shale fall within 7‰ (Freeman, 1991). It was suggested that the relative intensity of the processes that enrich and deplete organic matter is greater in lacustrine basins, because they are more enclosed systems where variations occur on a smaller scale, associated with greater isotopic fractionation due to limited supply of carbon. Furthermore, the presence of sulfate in marine settings inhibits methanogenesis. Stratigraphically oriented sampling of the lacustrine Green River Formation, where distinct sulfur cycles have been characterized, revealed values as low as -60‰ for the branched/cyclic fraction (Collister et al., 1991; Collister, 1992). Hopanes produced by hydrous pyrolysis of the

Green River kerogen also have a large variation, but this tends to homogenize with increasing temperatures (Bjørøy et al., 1991b), possibly because ¹³C-depleted compounds are released earlier.

The isotopic compositions of *n*-alkanes and isoprenoids in crude oils vary within a narrow range. Reported δ¹³C values of *n*-alkanes in oils fall between -32‰ and -28‰, whereas isoprenoids are usually enriched in ¹³C by 2‰ relative to *n*-alkanes (Bjørøy et al., 1991a; Sofer et al., 1991). Variations are more pronounced for lacustrine oils (-34‰ to -26‰), where higher molecular weight compounds tend to be isotopically lighter (Sofer et al., 1991). This difference apparently reflects higher variability in the lacustrine system, but it is not completely understood and is of limited significance because *n*-alkanes can be derived from cracking of other compounds.

Variations in the carbon isotopic ratios of migrated mixed oils, fractions and individual compounds have not been investigated nor integrated with their distribution within the basin. Therefore, the well constrained samples of the Potiguar Basin, with well characterized pathways of mixing and migration (Trindade et al., 1992) are ideal for such a study. In addition, compound-specific isotopic analyses in petroleum systems have been focused more on *n*-alkanes and isoprenoids, with those of biomarkers restricted to 28,30-bisnorhopane other hopanes and steranes (Schoell et al., 1992). Also, integration of biomarker quantification and compound-specific carbon isotopic analyses is attempted as a potential approach to distinguish oils from different sources and maturities.

ANALYTICAL METHODOLOGY

Samples—Carbon isotopic analyses were focused on two trends of migrated mixed oils of the Potiguar Basin described by Trindade et al. (1992). These trends were selected because of the clear variations, associated with the extent of oil mixing, in the relative and absolute concentration of biomarker ratios and concentrations. Examples of marine-hypersaline and lacustrine-freshwater source rocks, as well as unmixed end-member oils, were also investigated to provide compositional information and end-member values for the carbon isotope ratios.

Carbon isotopic analyses of whole oils and fractions

Carbon isotope ratios were determined for whole oils and oil fractions (saturates, aromatics and NSO compounds) isolated by thin-layer

chromatography (TLC). Measurements used CO₂ generated by combustion of the samples at 520°C for 24h on a combustion line with O₂ as carrier gas. The CO₂ was purified cryogenically and the ratio measured using a Varian MAT-230 mass spectrometer. The data are presented in terms of delta-notation ($\delta^{13}\text{C}$, ‰), as proposed by Craig (1953), relative to the Pee Dee Belemnite standard (PDB), a carbonate from South Carolina.

Gas Chromatography - Isotopic Ratio Mass Spectrometry (GC-IRMS)

Carbon isotopic compositions of individual compounds were determined using a gas chromatograph linked to an isotope-ratio mass spectrometer (Finnigan Delta-S) at Indiana University, following procedures described by Hayes et al. (1990), Freeman (1991), Ricci et al. (1994). Measurements were made for the total saturate fraction and the branched/cyclic fraction after molecular sieve occlusion.

The gas chromatograph was equipped with a Hewlett-Packard Ultra-1 column (fused silica, 50mx0.32mm i.d., 0.52-mm film thickness). On-column injection was used, and 0.4ml of a solution of fully deuterated standards ($n\text{-C}_{16}\text{D}_{34}$, $n\text{-C}_{21}\text{D}_{42}$, $n\text{-C}_{24}\text{D}_{50}$ and $n\text{-C}_{30}\text{D}_{74}$), with known isotopic values (-28.60, -33.98, -26.77 and -27.09‰, respectively) dissolved in hexane were coinjected with the sample (typically 0.5ml, 1mg/30ml). Pulses of CO₂ gas were also used as standards ($\delta^{13}\text{C} = -44.39‰$). The GC column conditions for these

analyses were 60°C to 150°C at 10°C/min, 150°C to 320°C at 3°C/min and isothermal at 320°C for 40min. He was used as carrier gas.

The separated compounds eluting from the GC were quantitatively converted to CO₂ and H₂O in a combustion furnace (20ml volume) filled with CuO and held at 850°C. The results are registered as a trace that depicts the ratio of the ion currents of masses 44 and 45. Carbon isotope ratios are determined by integration of the ion currents, which, after correction for background signals, are compared to values for the internal standards. The minimum peak voltage considered adequate for a reliable measurement was 0.1v, excluding, therefore, several less abundant components. Coelution of compounds is another limiting factor that can affect the values.

ISOTOPIC COMPOSITIONS OF WHOLE OILS AND FRACTIONS

Mixed oils with contributions from both Neocomian lacustrine freshwater and Aptian marine hypersaline source rocks were identified in the Potiguar Basin (Trindade et al., 1992). Determination and integration of biomarker ratios and concentrations reveal discernible landward trends in which the most migrated oils in trends A-A' and C-C' (Figure 1) are less mature and contain higher lacustrine freshwater contributions and the least migrated oils are composed of dominantly hypersaline contributions and are more mature. Thus, carbon

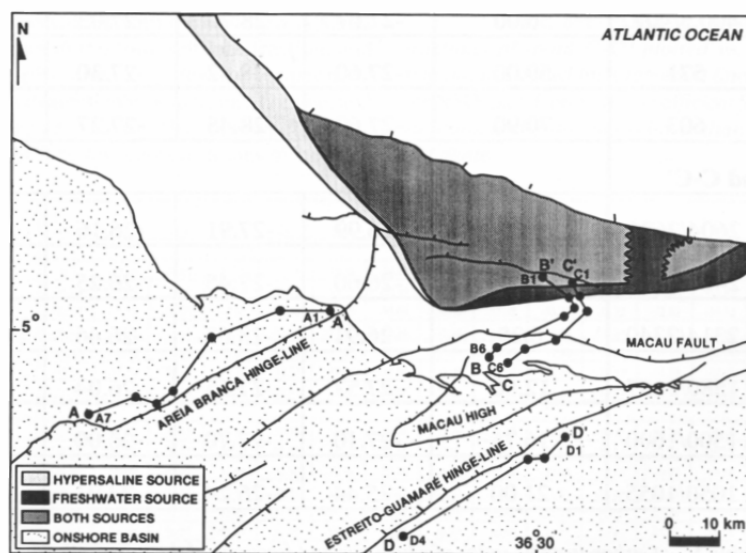


Figure 1. Location of source rocks and mixed oil trends in the Potiguar Basin, Brazil

isotopic ratios of oils and fractions are evaluated herein in order to investigate whether changes exist and are reflected in individual compounds, and to assess potential causes.

In the Brazilian marginal basins, including the Potiguar Basin, it has been consistently reported that source rocks deposited under lacustrine freshwater conditions and derived petroleum are generally isotopically lighter ($\delta^{13}\text{C}$ PDB $< -28\text{‰}$) than marine hypersaline sediments and oils ($\delta^{13}\text{C}$ ranging from -25‰ to -27‰ ; Mello et al., 1984; 1988a, b; Cerqueira, 1985). However, these numbers should not be considered rigid limits, and short-term stratigraphic variations can affect the isotopic compositions in parallel with biomarker ratios and concentrations (Trindade and Brassell, 1992). Also, the effects of increasing productivity and

water stratification, which promote enrichment and depletion of ^{13}C , respectively, need to be considered. In agreement with a tendency of lighter ratios for lacustrine freshwater source rocks, the total extractable organic matter of a sample representative of this sequence has an isotopic ratio of -27.40‰ , whereas a marine hypersaline sample is relatively ^{13}C enriched (-26.40‰).

Mixed oils, with contributions from both sources, have intermediate δ values and an attempt was made to describe the variations in their isotopic compositions in relation to their extent of oil mixing and approximate distance of migration.

Comparison of isotopic ratios in A-A' and C-C' trends, as expected, show that saturated hydrocarbon fractions are the most depleted in

Sample	Depth(m)	Distance from source (km)	$\delta^{13}\text{C}$ (‰) whole oil	$\delta^{13}\text{C}$ (‰) saturates	$\delta^{13}\text{C}$ (‰) aromatics	$\delta^{13}\text{C}$ (‰) NSO
Trend A-A'						
A1	840/842.5	18.20	-26.22	-27.11	-26.10	-25.33
A2	727.5/743	25.45	-26.10	-27.00	-26.04	-25.45
A3	971.8/974.3	40.00	-26.56	-27.28	-25.70	-25.70
A4	701/702.5	52.00	-27.40	-28.34	-26.70	-26.43
A5	400.5/407	56.00	-27.67	-28.76	-27.03	-25.96
A6	571	59.00	-27.60	-28.42	-27.30	-26.24
A7	603	70.90	-27.60	-28.45	-27.27	-26.05
Trend C-C'						
C1	2604/2621	0.00	-26.99	-27.91	-26.16	-25.82
C2	2421/2428	3.50	-26.60	-27.45	-26.25	-25.93
C3	2314/2340	6.25	-26.91	-28.63	-26.46	-25.82
C4	1580/1607	12.50	-27.57	-27.65	-26.04	-25.01
C5	1500/1600	16.75	-27.10	-27.70	-26.00	-25.00
C6	1050/1055	21.00	-25.44	-26.24	-24.91	-24.61

Table 1. Carbon isotopic ratios of whole oils and fractions of the mixed oils from the Potiguar Basin

^{13}C , whereas NSO fractions are the most enriched in ^{13}C (Table 1 and Figure 2a and b). There is however, a noteworthy difference between the two trends: samples from the A-A' trend are progressively depleted in ^{13}C with increasing distance of migration (Figure 2a), whereas the most migrated oil samples of C-C' trend are enriched in ^{13}C (Figure 2b). The results for the trend A-A' are consistent with a higher contribution from lacustrine freshwater samples for the most migrated oils. For C-C' trend, however, apart from the NSO fraction, there is comparatively little systematic variation among the five samples closer to the source, and the isotopic enrichment appears mainly in the most migrated sample (C6). Its unusual isotopic composition may be partly attributable to advanced biodegradation and preferential removal of *n*-alkanes, which are more ^{13}C -depleted than the saturate fraction. Facies changes might also be involved, since the two trends are approximately 30km apart and lacustrine systems are prone to subtle lateral changes. Hence, significant variability in the isotopic ratios of the mixed oil trends can be expected, in a matter comparable to biomarker ratios and concentrations (Trindade et al., 1992).

ISOTOPIC COMPOSITION OF INDIVIDUAL COMPOUNDS

The isotopic compositions of individual compounds within the total saturate and branched/cyclic fractions were measured to assess variations associated with oil mixing. *n*-Alkanes were targeted in the total saturate fraction, and pristane, phytane, C_{21} acyclic isoprenoid (2,6,10,14-tetramethylheptadecane), hopane, and gammacerane among the branched/cyclic components. The low concentrations of steranes

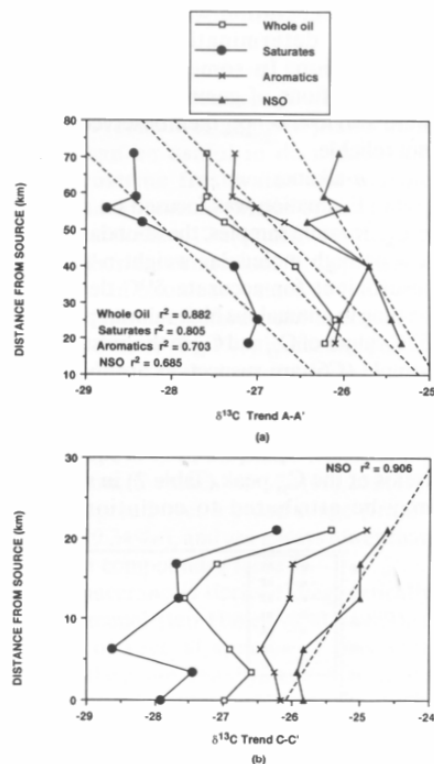


Figure 2. (a) $\delta^{13}\text{C}$ PDB (‰) of whole oils and fractions of trend A-A' plotted vs. distance of migration. Dashed lines represent linear regressions for the data of different fractions.

(b) $\delta^{13}\text{C}$ PDB (‰) of whole oils and fractions of trend C-C' plotted vs. distance of migration. Dashed lines represent linear regression for NSO data. Correlation coefficient for whole oils, saturates and aromatics is lower than 0.5 and was not plotted.

Sample	Distance from source (km)	$\delta^{13}\text{C}$ (‰)														
		C ₁₇	C ₁₈	C ₁₉	C ₂₀	C ₂₁	C ₂₂	C ₂₃	C ₂₄	C ₂₅	C ₂₆	C ₂₇	C ₂₈	C ₂₉	C ₃₀	C ₃₁
Trend A-A'																
A1	18.20	-30.87	-32.16	-33.07	-32.25	-32.86	-32.25	-34.87	-34.00	-32.79	-32.76	-32.81	-32.03	-31.30	-29.76	-31.35
A2	25.45	-31.89	-31.89	-34.60	-32.89	-33.73	-33.23	-33.55	-33.58	-32.14	-33.26	-32.97	-32.84	-31.85	-28.66	-29.91
A3	40.00	-32.40	-32.71	-32.97	-35.61	-34.40	-34.88	-35.04	-34.58	-33.62	-33.21	-33.22	-32.82	-33.32	-32.15	-31.14
A4	52.00	-31.06	-32.32	-32.56	-33.12	-33.29	-32.88	-33.36	-32.94	-32.07	-32.44	-32.24	-31.83	-31.66	-31.07	-28.84
A5	56.00	-30.99	-32.22	-33.90	-33.09	-33.60	-33.25	-33.49	-33.06	-32.40	-31.98	-32.02	-31.99	-32.38	-31.48	-32.36
A6	59.00	-30.71	-31.39	-30.30	-31.28	-32.57	-32.64	-32.80	-33.08	-32.05	-32.48	-32.52	-31.59	-32.03	-29.94	-27.30
A7	70.90	-31.32	-31.51	-32.94	-32.25	-32.61	-33.18	-34.26	-34.28	-33.53	-33.35	-33.87	-32.46	-29.05	-31.35	-27.40
Trend C-C'																
C1	0.00	-29.80	-29.92	-30.77	-29.83	-30.55	-31.05	-32.08	-32.79	-31.15	-31.07	-30.70	-30.30	-30.10	-29.63	-29.91
C2	3.50	-29.21	-29.82	-30.47	-30.40	-32.16	-33.62	-32.66	-33.00	-32.09	-31.84	-31.54	-31.21	-30.72	-30.65	-28.47
C3	6.25	-29.87	-30.09	-32.21	-31.93	-32.34	-32.59	-32.40	-32.74	-32.15	-32.06	-31.97	-30.92	-29.38	-29.07	-27.38
C4	12.50	-30.03	-30.22	-32.82	-32.54	-32.78	-32.86	-32.91	-33.03	-32.20	-31.81	-31.99	-31.15	-30.47	-30.71	-36.28
C5	16.75	-29.90	-30.96	-31.58	-31.22	-31.31	-31.61	-31.56	-31.35	-30.62	-31.03	-31.60	-31.44	-31.44	-31.35	-29.25
C6	21.00	-23.94	-26.94	-30.27	-29.67	-31.89	-32.32	-32.63	-30.89	-30.60	-31.53	-30.83	-33.35	-31.28	-32.49	-33.56

Table 2. Carbon isotopic composition of the *n*-alkanes of the mixed oils from the Potiguar Basin

and their coelution with other components hindered determination of their isotopic composition. In some of the samples, the concentrations of gammacerane and hopanes were also low, hence, their observed values were not reliable.

n-alkanes

Evaluation was focused on *n*-C₁₇ through *n*-C₃₀. In some samples, the abundances of either low or high molecular weight *n*-alkanes were insufficient for accurate $\delta^{13}\text{C}$ determination, leading to anomalous high values, specifically, the $\delta^{13}\text{C}$ values of C₁₇ and C₁₈ in the most biodegraded sample (C6) are suspect, as are those of higher homologues (C₂₉, C₃₀) in the more mature samples (e.g. A1, A2; Fig. 3b). C₃₁ coelutes with 17 β (H),21 α (H)-hopane, hence the low isotopic ratios of the C₃₁ peak (Table 2) in some samples may be attributed to coelution given that

particularly low $\delta^{13}\text{C}$ values (-44‰ to -64‰) have been reported for 17 β (H),21 α (H)-hopane in the Green River Formation (Collister, 1992).

The isotopic compositions of *n*-alkanes on trends A-A¹ and C-C¹ vary little. They fall dominantly between -29‰ and -31‰ (Table 2 and Figure 2a and b); values that are comparable to previous reports (Bjørøy et al., 1991a; Sofer et al., 1991). However, there is no systematic variation in the isotopic composition among the mixed oils, indicating that lacustrine freshwater and marine hypersaline contributions to the petroleum cannot be distinguished by the isotopic signals of *n*-alkanes.

$\delta^{13}\text{C}$ values for *n*-alkanes from the lacustrine Parachute Creek Member of the Green River Formation suggest mixing of five populations, derived from multiple biological sources (Collister, 1992; Collister et al., 1994). However, the main source for long-chain *n*-alkanes in immature samples is higher plants, which are not influenced by depositional environment, and secondarily algae (Tissot and Welte, 1984). Thus, the non-diagnostic character of *n*-alkanes combined with their further generation by cracking of higher molecular weight compounds due to increasing maturity, can help explain the lack of correlation between their isotopic compositions and their predominant sources in mixed oils.

Isoprenoids

Pristane, phytane, and a homologous C₂₁ acyclic isoprenoid (2,6,10,14-tetramethylheptadecane) are abundant after molecular sieving, and well resolved by GC-IRMS, providing accurate isotopic ratios. Pristane and phytane were originally thought to derive from phytol, a substituent of many chlorophylls (Didyk et al., 1978). In addition, phytane can be derived from archaeobacteria (Holzer et al., 1979), and tocopherol is another source of pristane (Brassell et al., 1981; Goossens et al., 1984; ten Haven et al., 1987). Phytol and tocopherol are derived from primary producers, which are, in general, enriched in ¹³C relative to chemoautotrophic bacteria and other organisms living at or below the chemocline in stratified lakes (Freeman, 1991; Collister et al., 1994).

There is a good correlation between the isotopic ratios of pristane and phytane (Figure 4), but pristane is on average 1.5‰ depleted in ¹³C relative to phytane, which precludes an origin from common precursors. This observation contrasts with the isotopic equality found by Collister (1992) and Collister et al. (1994) in the

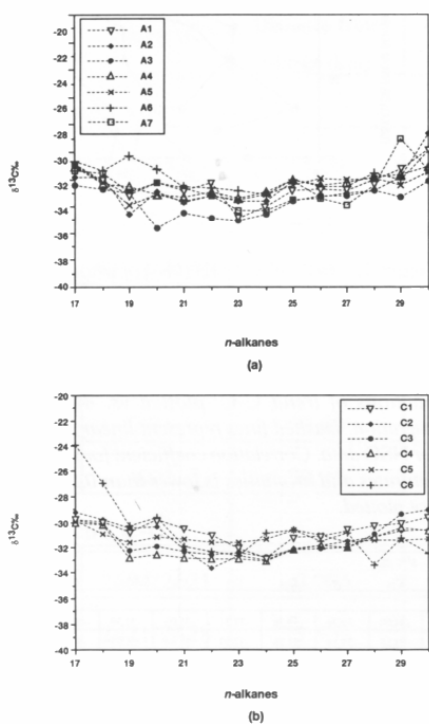


Figure 3. (a) $\delta^{13}\text{C}$ PDB (‰) of individual *n*-alkanes of mixed oils from trend A-A¹. Values obtained from single runs of each sample.

(b) $\delta^{13}\text{C}$ PDB (‰) of individual *n*-alkanes of mixed oils from trend C-C¹. Values represent the average of a minimum 2 runs for each sample.

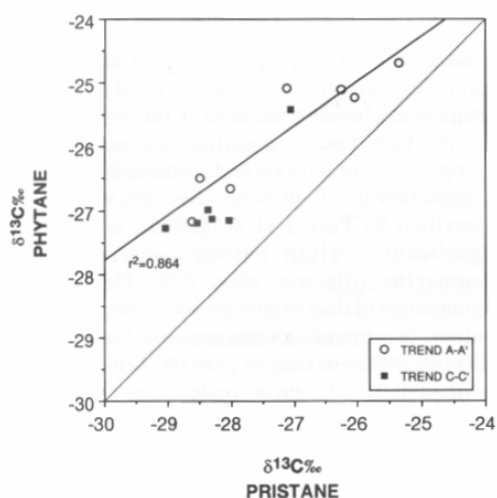


Figure 4. $\delta^{13}\text{C}$ PDB (‰) pristane vs. $\delta^{13}\text{C}$ PDB (‰) phytane of mixed oils. Pristane is more depleted in ^{13}C than phytane in all samples.

Green River Formation, which suggested derivation from similar sources.

Polycyclic alkanes

Attention was focused on $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane and gammacerane because steranes and other hopanes were not present in sufficient

abundance for their isotopic ratios to be reliably determined.

Hopanes are derived from diverse prokaryotic bacterial precursors (Ourisson et al., 1979; 1982; Freeman et al., 1990), and their abundance can be useful in discrimination between lacustrine freshwater and marine hypersaline environments (Mello et al., 1988a; 1988b). In particular, $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane occurs in higher concentrations in hypersaline environments. In bitumens, values of δ for this compound in bitumens have been reported to range from -65‰ to -26.4‰, indicating partial origin from chemoautotrophic and methanotrophic sources (Freeman et al., 1990; Hayes et al., 1990; Freeman, 1991; Collister, 1992; Collister et al., 1994). In the mixed oils from the Potiguar Basin, δ values of $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane also spread over a broad range (from -41.95‰ to -29.34‰), and are always lower than those of other compounds (Table 3).

Gammacerane is derived diagenetically from tetrahymenol (ten Haven et al., 1989), a constituent of several species of protozoa belonging to the genus Tetrahymena, that can be found in recent sediments (ten Haven et al., 1989; Venkatesan, 1989). Gammacerane is a common

Sample	Type	Depositional Environment	$\delta^{13}\text{C}$ (‰)						
			Pristane	Phytane	<i>i</i> -C ₂₁	Hopane	Gammacerane	C ₂₇ sterane	β -carotane
E3	Source Rock	Hypersaline	-25.04 ± 0.02	-25.79 ± 0.01	-24.27 ± 0.01	-	-	-	-
E4	Source Rock	Freshwater	-26.94 ± 0.14	-24.75 ± 0.25	-24.84 ± 0.53	-	-	-	-
E1	Oil	Hypersaline	-27.64 ± 0.05	-28.26 ± 0.01	-27.18 ± 0.04	-38.84 ± 0.28	-29.31 ± 0.12	-23.91 ± 0.06	-29.07 ± 0.09
E2	Oil	Freshwater	-29.84	-28.01	-29.09	-	-	-	-
Trend A-A'									
A1	Oil	Mixed	-26.05 ± 0.36	-25.22 ± 0.07	-27.31 ± 0.51	-37.33 ± 0.27	-	-	-
A2	Oil	Mixed	-26.25 ± 0.03	-25.10 ± 0.08	-28.72 ± 0.10	-38.81 ± 0.27	-26.95 ± 0.42	-	-
A3	Oil	Mixed	-25.36 ± 0.38	-24.67 ± 0.32	-27.18 ± 0.34	-35.35 ± 0.26	-	-	-
A4	Oil	Mixed	-28.02	-26.65	-	-	-	-	-
A5	Oil	Mixed	-28.61	-27.17	-	-	-	-	-
A6	Oil	Mixed	-28.50 ± 0.52	-26.49 ± 0.32	-29.91 ± 0.34	-38.94 ± 0.06	-	-	-
A7	Oil	Mixed	-27.11 ± 0.10	-25.07 ± 0.12	-29.01 ± 0.01	-35.33 ± 0.26	-	-	-
Trend C-C'									
C1	Oil	Mixed	-28.30 ± 0.16	-27.14 ± 0.17	-28.66 ± 0.01	-41.95 ± 0.05	-26.21 ± 0.02	-	-
C2	Oil	Mixed	-28.02 ± 0.23	-27.15 ± 0.34	-26.80 ± 0.01	-36.52 ± 0.93	-28.69 ± 0.01	-	-
C3	Oil	Mixed	-29.03 ± 0.56	-27.27 ± 1.42	-27.26 ± 0.49	-38.02 ± 0.01	-22.09 ± 0.01	-	-
C4	Oil	Mixed	-28.36 ± 0.01	-26.98 ± 0.03	-26.99 ± 0.06	-36.57 ± 0.55	-24.46 ± 0.37	-	-
C5	Oil	Mixed	-27.06 ± 0.01	-25.41 ± 0.01	-26.45 ± 0.35	-37.14 ± 0.42	-	-	-
C6	Oil	Mixed	-28.53 ± 0.01	-27.20 ± 0.01	-25.74 ± 0.01	-29.34 ± 0.17	-24.57 ± 0.01	-	-

Table 3. Carbon isotopic composition of the branched/cyclic fraction of source rocks, end member oils and mixed oils of the Potiguar Basin. $i\text{-C}_{21} = \text{C}_{21}$ acyclic isoprenoid; Hopane = $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane; C₂₇ sterane = $14\alpha(\text{H}), 17\alpha(\text{H})$ -cholestane. \pm = standard deviation.

constituent of sediments and petroleums, but its abundance relative to other triterpanes is noticeably enhanced in hypersaline settings (ten Haven et al., 1985; 1988; Brassell et al., 1988; Mello et al., 1988a, b; de Leeuw and Sinninghe Damsté, 1990). Gammacerane is enriched in ^{13}C compared to *n*-alkanes and hopane in the mixed oils from the Potiguar Basin (Tables 2 and 3). This enrichment is consistent with derivation of gammacerane from a grazing heterotroph, possibly a protozoan. Collister et al. (1994) reported similar enrichment in some samples, but coelution with ^{13}C -depleted 3β -methylhopane in other samples gave rise to significant overall variation (-47.7‰ to -28.8‰) in $\delta^{13}\text{C}$ of the gammacerane peak.

DISCUSSION

The carbon isotopic composition of organic compounds in recent sediments is governed by carbon source (dissolved CO_2 , respired CO_2 and HCO_3^-) and by the trophic character of precursor organisms (e.g. primary producers vs. heterotrophs). These, in turn, are controlled by the interplay between productivity and water stratification. For petroleums, carbon isotopic compositions are also influenced by maturity and modified by biodegradation. The isotopic compositions of the mixed oils of the Potiguar Basin, their fractions and individual compounds, are a function of these factors.

Source constraints

In the Brazilian marginal basins, oils with $\delta^{13}\text{C} < -28\text{‰}$ have been attributed to lacustrine freshwater origins, whereas marine hypersaline oils are less depleted in ^{13}C (Cerqueira, 1984; Mello et al., 1988a, b). This difference has been related to the uptake of HCO_3^- as an additional carbon source by biota in saline and hypersaline environments, although its use is more dependent on pH than salinity. In spite of more pronounced depletion of ^{13}C for most of the lacustrine freshwater samples, this trend is not always the case, because facies variations, the balance between productivity and preservation, and the predominance of primary photosynthetic or heterotrophic contributions can influence the results. Another major factor in lakes is the presence of light CO_2 below any chemocline that happens to form.

Previous studies argued that marine and nonmarine oils cannot be distinguished from the carbon isotopic compositions of their whole oils. Sofer (1984) reported a distinction between oils of marine and terrestrial origin that could be expressed statistically in terms of the isotopic

relationship between saturate and aromatic fractions. However, this method is not unequivocal, because the controls on the isotopic composition described earlier also affect the isotopic ratios of saturate and aromatic fractions. A depletion of ^{13}C in nonmarine oils was also described by Peters et al. (1986), although significant overlap between marine and nonmarine oils was observed. Thus, the combination of data from biomarker analyses and isotopic determinations was suggested as a more effective means to characterize the depositional environments of source rocks. The need for independent data sets is clearly shown by the fact that the inverse relationship, wherein marine source rocks and petroleums are more depleted in ^{13}C than those attributed to nonmarine origins is seen in Cook Inlet, Alaska (Magoon and Anders, 1992).

For trend C-C¹, enrichment in ^{13}C of whole oils and fractions broadly corresponds with migration distance, whereas the reverse is true for oils from trend A-A¹ (Figure 2a). For both trends, biomarker parameters suggest that the most migrated oils possess greater contributions from freshwater sources. Hence, variations in biomarker distributions and concentrations do not parallel the isotopic ratios of the whole oils and their fractions. Two considerations bear on the interpretation of this observation. First, the isotopic ratios of organic compounds in recent sediments exhibit a broad range in lacustrine systems (e.g. Freeman et al., 1990; Collister et al., 1992) and, second, biomarkers appear to provide a better discrimination of depositional environments than the isotopic compositions of whole oils or oil fractions (Peters et al., 1986). Thus, the differences between the two trends of migrated oils can be attributed to variability in source rock facies.

n-Alkanes, the predominant saturated hydrocarbons, are all more depleted in ^{13}C than the total saturate fraction for both trends. Hopanes, which are in part derived from chemoautotrophs and methanotrophs, are substantially more negative. Acyclic isoprenoid alkanes, which are generally representative of primary producers, and gammacerane, which is derived from protozoa that feed on phytoplankton, are the only compounds with carbon isotopic ratios comparable to, or higher than, the total saturate fraction (c.f. samples C1 and A2; Figures 5a, b). Mixed oils from the Potiguar Basin and pyrolysates from the Messel Shale (Eglinton et al., 1991) both show similar

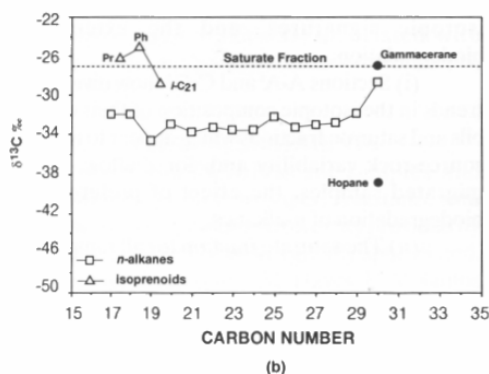
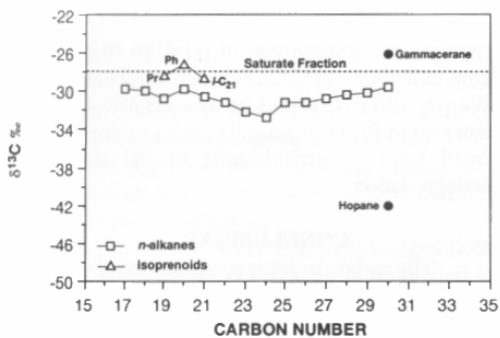


Figure 5. (a) Carbon isotopic composition of saturate fraction (dashed line) and the most abundant saturate compounds for sample C1.

(b) Carbon isotopic composition of saturate fraction (dashed line) and the most abundant saturate compounds for sample A2.

patterns for the carbon isotope ratios of their biomarkers, whereby the extractable organic matter and the total organic carbon, respectively, are more enriched in ^{13}C than n -alkanes. These results indicate that other components among the saturated hydrocarbons, including unresolved compounds that constitute the bulk of this fraction, are significantly enriched in ^{13}C , and might therefore suggest derivation from primary producers.

The only compound that showed any systematic variation in its carbon isotopic composition associated with the extent of oil mixing is $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane. The extreme δ values for hopane are those of the most and least migrated samples, respectively (Figure 6). This pattern may reflect lower contributions of hopane from chemoautotrophs and methanotrophs in the lacustrine freshwater environment, which could have promoted such variation in trend C-C¹ oils.

Maturity constraints

Most published carbon isotopic data for individual biomarkers have been recorded for immature sequences. In addition to the free lipids found in immature samples, petroleums also contain compounds that are released from kerogen by thermal processes. These latter components can overprint the isotopic signatures of the free lipids as maturity increases.

The results from carbon isotopic analyses of whole oils and the various fractions of oils along trend A-A¹ show that the more migrated samples, which are less mature on the basis of biomarker parameters, are more depleted in ^{13}C (Figure 2a). For light hydrocarbons, it is believed that compounds released early from kerogen breakdown are more ^{13}C depleted because of the preferential cleavage of the weaker ^{12}C - ^{12}C and ^{12}C - ^{13}C bonds relative to their ^{13}C - ^{13}C counterparts (Stahl, 1979). Thus, in the case where petroleum is generated from a single, homogenous source rock, the compounds generated during the initial phase of maturation are more depleted in ^{13}C than the more mature components, formed later during the cracking process (Schoell, 1984). However, these arguments concerning selective bond cleavage are valid only for light hydrocarbons, not for biomarkers. In addition, the overall changes in carbon isotopes attributable to maturation processes can be masked in petroleums, because source constraints affect the isotopic ratios in broader intervals.

Source and maturity constraints

The lack of a common relationship between the isotopic composition of whole oils, saturate fractions and individual biomarkers for trends A-A¹ and C-C¹ can be attributed to a combination of source characteristics and maturity of the oils. The concentration of

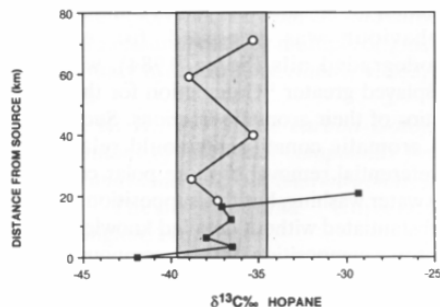


Figure 6 $\delta^{13}\text{C}$ PDB (‰) of $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane vs. distance from source (km).

17 α (H),21 β (H)-hopane in source rocks deposited under marine hypersaline conditions is greater than in source rocks deposited in lacustrine freshwater environments, but its relative abundance decreases with increasing maturity irrespective of environmental factors. For C-C¹ trend, the concentration of 17 α (H),21 β (H)-hopane initially increases, apparently due to greater contributions from hypersaline sources, maximizes, and then decreases with maturity (Figure 7a). In mixed oils from the Potiguar Basin, 17 α (H),21 β (H)-hopane is the most depleted ¹³C component (Table 3) and the strong ¹³C depletion of hopanes probably reflects contributions from methanotrophs and chemoautotrophs (Freeman et al., 1990). In part, the fact that the isotopic ratios for the whole oil and saturate fractions of the most migrated petroleum in trend C-C¹ are less ¹³C depleted can be linked to the lower concentrations of 17 α (H),21 β (H)-hopane and other hopanes. The major variation in hopane concentration (360-2520 ppm, Trindade et al., 1992) observed in Trend C-C¹, could account for an isotopic variation in the whole oils of approximately 2‰, assuming that other compounds do not vary a lot.

No significant change in the isotopic composition of 17 α (H),21 β (H)-hopane is, however, apparent for samples from the A-A¹ trend, which may be attributed to the generally more advanced maturity conditions (Trindade et al., 1992). The concentration of 17 α (H),21 β (H)-hopane in trend A-A¹ decreases in the progressive more mature and less migrated samples. A plot of hopane concentration vs. $\delta^{13}\text{C}$ of whole oil shows a clearer correlation for trend C-C¹, where higher concentrations of hopane are associated with ¹³C-depleted samples (Figure 7b).

Biodegradation modifications

$\delta^{13}\text{C}$ values of *n*-alkanes are significantly more negative than those of the total saturate fraction for all samples (Tables 1 and 2). Similar behaviour was reported for extremely biodegraded oils (Sofer, 1984), which also displayed greater ¹³C depletion for the isotopic ratios of their aromatic fractions. Such changes to aromatic constituents could relate to the preferential removal of more polar compounds by water washing, but this supposition cannot be substantiated without detailed knowledge of the isotopic composition of these compounds.

The variation of $\delta^{13}\text{C}$ is greatest for sample C6 (Figure 1b) which is the most biodegraded sample among those analyzed. Also, its whole-oil isotopic ratios and its saturate and aromatic

fractions are anomalous in relation to other samples from trend C-C¹. Selective removal of *n*-alkanes, with $\delta^{13}\text{C}$ values on average 3‰ lower than that of the corresponding saturate fraction, could lead to enrichment in ¹³C during biodegradation.

CONCLUSIONS

The carbon isotopic compositions of whole oils, fractions and individual compounds of mixed oils from the Potiguar Basin span a range of values that can be variably related to factors such as the prevailing depositional conditions, the relative proportion of specific compounds with distinct isotopic signatures, and the extent of biodegradation:

(i) Sections A-A¹ and C-C¹ show divergent trends in the isotopic composition of their whole oils and saturate fractions which appear to reflect source-rock variability and, for shallow, most migrated samples, the effect of preferential biodegradation of *n*-alkanes.

(ii) The saturate fraction for all samples is

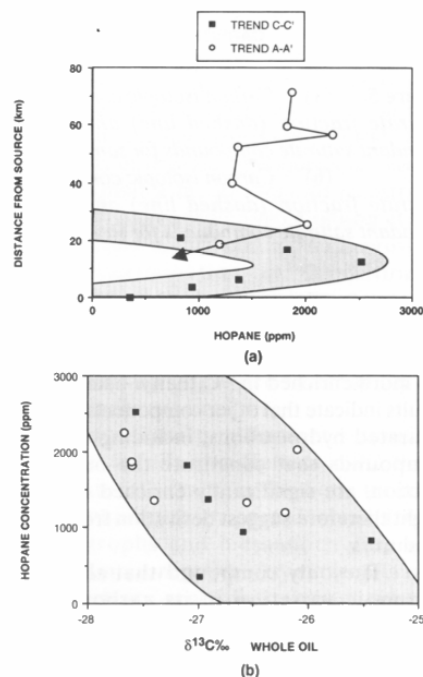


Figure 7. (a) Concentration of 17 α (H), 21 β (H) - hopane (ppm) vs. distance from source (Km).

(b) Concentration of 17 α (H), 21 β (H) - hopane (ppm) vs. $\delta^{13}\text{C}$ PDB (‰) of whole oil.

less ^{13}C -depleted than the *n*-alkanes, which are the dominant components. Thus, it can be inferred that the majority of the unrecognized saturated hydrocarbons must be markedly enriched in ^{13}C , akin to pristane and phytane, which are components known to represent contributions from primary producers.

(iii) Variations in the isotopic compositions of individual components that can be related to the extent of oil mixing as revealed by biomarker ratios and concentrations appear evident only for $17\alpha(\text{H}), 21\beta(\text{H})$ -hopane in trend C-C'. These changes can be related to a balance of prominent contributions from primary producers and secondary microorganisms, associated with lacustrine and marine hypersaline environments, respectively.

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