

AN ISOTOPE-BASED OIL-SOURCE ROCK CORRELATION IN THE CAMAMU-ALMADA BASIN, OFFSHORE BRAZIL

J.A. Curiale and S.W. Sperry*

*Unocal Corporation
14141 Southwest Freeway
Sugar Land, Texas 77478 USA

Presented at the 6th Latin American Congress on Organic Geochemistry, Margarita Island,
Venezuela, October 18-21, 1998

Running head: Oil-Source Rock Correlation, Camamu-Almada Basin, Brazil

ABSTRACT - Molecular and isotopic data for oils and source rocks from the Camamu-Almada Basin, offshore Brazil, are examined to establish oil-source rock correlation(s) between the oils and the fresh water, lacustrine source rocks of this basin. Using standard procedures involving random, discrete sampling of the Cretaceous Morro do Barro Formation, it is shown that the molecular distributions of the extractable organic matter (EOM) from discrete samples of this unit correlate well with oils of the basin. In contrast, $\delta^{13}\text{C}$ values of individual *n*-alkanes in the EOM of these same, discrete samples do not correlate with the oils. The intra-formational variability in $\delta^{13}\text{C}$ values is attributed, in part, to the occurrence of CO_2 -limiting conditions during original deposition of the Morro do Barro. When distributed sampling methods are used throughout the organic-rich portion of the stratigraphic section, however, positive correlations are obtained using both molecular and isotopic techniques. Compound-specific $\delta^{13}\text{C}$ distributions for *n*-alkanes in the crude oils match composited distributions from the source section, when the samples used in the section composite are weighted by their hydrogen index values. Our results suggest that in fresh water, lacustrine settings such as this, successful, isotope-based oil-source rock correlations require the use of distributed sampling techniques which properly represent the entire source interval.

RESUMO - Dados isotópicos e moleculares de óleos e rochas geradoras da Bacia de Camamu-Almada, localizada na plataforma continental brasileira, foram analisados para investigar a correlação óleo-rocha entre os óleos da bacia e os folhelhos geradores depositados em ambiente lacustre de água doce. Utilizando-se procedimentos de amostragem aleatória e pontuais para a Formação Morro do Barro (Cretáceo), verificou-se que as distribuições moleculares dos extratos orgânicos das amostras pontuais correlacionam-se bem com os óleos da bacia. Por outro lado, os valores de $\delta^{13}\text{C}$ dos *n*-alcanos individuais dos extratos orgânicos destas mesmas amostras não se correlacionam com os óleos. A variação dos valores de $\delta^{13}\text{C}$ dentro da formação é atribuída, em parte, à ocorrência de condições limitantes de CO_2 durante a deposição da Formação Morro do Barro. Entretanto, a utilização de amostragem composta da seção organicamente rica mostrou correlação positiva, tanto por métodos moleculares quanto por isotópicos. A distribuição de $\delta^{13}\text{C}$ de *n*-alcanos individuais dos óleos correlaciona-se com os extratos das amostras compostas da seção geradora quando estas são balanceadas de acordo com seus índices de hidrogênio. Nossos resultados sugerem que para se obter uma boa correlação isotópica entre óleo e rocha geradora associadas a ambientes lacustres de água doce é necessária a utilização de técnicas de amostragem que representem adequadamente o conjunto do intervalo gerador.

KEY WORDS - Camamu-Almada Basin, Brazil, Oil-source rock correlation, *N*-alkane carbon isotope, atios, Morro do Barro Formation, Offshore Brazil

INTRODUCTION

Successful oil-source rock correlations combine an understanding of geologic history in a basin with various analytical data designed to compare the source-related features of the organic matter in an oil with those in a source rock (Curiale, 1993). Correct correlations are required to identify a definitive petroleum system (Magoon and Dow, 1994), the understanding of which is necessary to explore successfully for oil and gas in a sedimentary basin. This paper concerns the selection of sample material in correlation efforts, specifically in instances of freshwater and hypersaline lacustrine source facies. Our objective is to demonstrate the importance in correlation work of distributed sampling, rather than random, discrete sampling, of thick, lacustrine source sections. We use an offshore Brazilian basin as the study area for this demonstration.

Previous studies have established that stratigraphic changes in characteristics of organic matter occur at different rates, depending on the measurement method being used. For example, high sampling resolution may reveal variations in organic facies, as defined using biomarkers, in situations where bulk stable carbon isotope ratios remain similar (e.g., Curiale, 1994a). Alternatively, $\delta^{13}\text{C}_{\text{om}}$ values throughout an organic-rich interval may change at high temporal frequency, while organic facies character, measured via molecular markers, has changed little (Curiale and Gibling, 1994). In the current paper, we demonstrate the latter situation within the source rock section of the Camamu-Almada Basin, offshore Brazil. Following a brief introduction to correlation philosophy and the geology of the Camamu-Almada Basin, we discuss the oils and source rocks of the basin, and our efforts at oil-source rock correlation on an individual- and distributed-sampling basis. We conclude with a recommendation to consider the entire source interval in cases of source rocks deposited in fresh water, lacustrine settings, because values of $\delta^{13}\text{C}_{\text{om}}$ values can vary rapidly within fairly uniform organic facies.

CORRELATION PHILOSOPHY

Several assumptions are built into approaches to oil-source rock correlation (Curiale, 1993, 1994b). For example, it is generally assumed that oils that have been generated in and migrated away from a source rock retain some genetic signature that is useful in relating them to their source. Although this is true in most cases, exceptions are known (Curiale and Bromley, 1996).

Virtually by definition, differences within a source are assumed to be minor relative to the differences between oils of different families within a sedimentary basin. Indeed, this assumption is required before an oil family can be related to a specific source-rock unit. The application of this assumption without consideration for its proper application can lead to substantial errors in correlations, particularly in instances where one or more genetic parameters fluctuate at high frequency within a source-rock sequence.

High-frequency variations in the genetic signatures of organic-rich sections have been observed for biomarker distributions (Moldowan et al., 1986; Miranda and Walters, 1992; Curiale, 1994c) and carbon isotope ratios (Arthur et al., 1988; Curiale, 1994a, and references therein). In the former case, rapid changes in the distribution of molecular markers have been attributed to rapid changes in depositional setting and organic matter influx (e.g., Miranda and Walters, 1992). In the case of carbon isotope ratios of organic matter, explanations for high-frequency variability have ranged from secular (atmospheric) $\delta^{13}\text{C}_{\text{CO}_2}$ variation (Santos Neto et al., 1998) to photic zone CO_2 limitations (Hollander et al., 1991; Hollander and McKenzie, 1991; Curiale, 1994c). We feel that it is important to recognize the potential for such variability, and for the effect that such variability would have on oil-source rock correlation efforts.

CAMAMU-ALMADA BASIN BACKGROUND

The Camamu-Almada Basin is located principally offshore in southern Bahia State (Figure 1), approximately 100 kilometers south of the city of Salvador. The basin, encompassing almost 3,000 square kilometers, is typical of other Brazilian passive margin basins, and is one of a series of offshore structural basins informally grouped together and called the basins of South Bahia. These basins formed in a N-S orientation extending 600 kilometers between Salvador (the Recôncavo Basin) and the northern boundary of the state of Espírito Santo to the south. By convention, the Camamu-Almada Basin is separated from the Recôncavo Basin to the north by the Boipeba arch and from the Jequitinhonha Basin to the south by the Olivença high. The Camamu-Almada Basin may also be subdivided at the Itacaré high (Figure 1) into the Camamu and Almada sub-basins.

The sediments of the Camamu-Almada Basin record the depositional history of the continental split and drift between South America and Africa. South America and Africa separated during the Early Cretaceous, rotating around a pole in northeastern Brazil (Szatmari, 1998). This separation

resulted from continental rifting, crustal extension and subsequent Atlantic sea floor spreading (Bruhn, 1998). Rifting produced an important bifurcation north of the Camamu-Almada Basin area, resulting in the formation of the Recôncavo Basin and other related basins to the northeast. The Camamu-Almada Basin differs from the Recôncavo Basin (which did not evolve into a marine system) stratigraphically and, more importantly, in tectonic development (Netto and Ragagnin, 1990; Magnavita and da Silva, 1995).

The stratigraphy of the Camamu-Almada Basin is divided into pre-rift continental sediments, syn-rift siliclastic and carbonate rocks, and drift phase marine deposition. Figure 2 illustrates the stratigraphic nomenclature and divisions established for the Camamu-Almada Basin. Pre-rift eastward prograding fluvial-lacustrine sediments of the Upper Jurassic Aliança and Sergi formations unconformably overlie Permian strata of the Afligidos Formation and a Precambrian crystalline basement. The Sergi sandstone is an important basin reservoir unit as well as a major producing unit in the Recôncavo Basin. Pre-rift faulting as a function of younger episodes of deformation is difficult to identify in these units. However, there does appear to be a relationship between a change in prograding direction in pre-rift sedimentation and the onset of rifting between South America and Africa (Bruhn, 1998).

The Lower Cretaceous (Mid-Neocomian) Morro do Barro Formation records the continued development of continental rifting in series of alluvial, fluvial and lacustrine strata. Morro do Barro lacustrine turbidites and shales are important components in the basin petroleum system and are the focus of this paper. Lacustrine Morro do Barro shales can attain a composite thickness of 800 m (Gonçalves *et al.*, 1998). Prior to 1993 the Morro do Barro Formation was called the Candeias Formation in the Camamu-Almada Basin (personal communication, Luciano Magnavita). The rift phase concludes with the deposition of the Aptian Rio de Contas and Taipus Mirim formations. Continued tectonic development of the Camamu-Almada Basin in the early Neocomian is marked by a series of north-south trending, basement involved listric and normal block faults. These asymmetric half-grabens step down eastward into the developing basin and are linked to the initial phases of rifting. The important lacustrine shales that were deposited during this time filled discontinuous to widespread lakes that developed within these structural depressions.

By late Aptian, as the gap between South America and Africa widened, marine conditions representative of the newly opened South Atlantic

Ocean prevailed. Important marine turbidite systems were part of these transgressive marine units. Accumulated eastward basin tilt caused by continued subsidence and gravitational instability led to deformation of Cretaceous age salt. Salt movement eastward and upward may play an important role in present day basin architecture in areas where water depths exceed 2000 meters. Listric normal faults sole out into preferred zones of detachment in the late Aptian carbonate and evaporite units that cut post-rift sediments. These listric faults trend north-south, exhibiting an into-the-basin relative motion. An additional system of E-W faults is suspected of carrying strike-slip displacement, and appears to be related to spreading of the sea-floor during the drift phase.

Aptian to Recent basin tectonic processes are dominated by subsidence, sea-level fluctuation and sediment-supply variability. Regionally, large, deeply-incised submarine canyons occur, controlled by the reactivation of pre-existing faults.

ANALYTICAL METHODS

All experimental methods used in this study are standard, and have been described previously. The oil samples discussed here were in storage at ambient conditions for several years prior to analysis, and this has resulted in the loss of some volatile components. Interpretations discussed here are relevant for the C_{15+} fraction only, both for the oil samples and the cuttings from the 1-BAS-71 well.

Gas chromatographic analytical results presented here were obtained through techniques described in Curiale and Gibling (1994) and Curiale and Bromley (1996), and references contained therein. All peak calculations were based on height measurements (cf. Kipiniak, 1981; Park *et al.*, 1987). GCMS analyses described here were conducted on a VG70 instrument at 5000 mass resolving power. Individual *n*-alkane $\delta^{13}C$ measurements were made by Geolab Nor (Trondheim, Norway); bulk fraction $\delta^{13}C$ values were determined by the methods described in Curiale and Gibling (1994) and references therein.

SOURCE ROCK POTENTIAL AND OIL CHARACTERISTICS OF THE CAMAMU-ALMADA BASIN

Previous studies have established that the fresh water, lacustrine mudstones in the Jiribatuba Member of the Neocomian Morro do Barro Formation are the primary oil-prone source rock unit

of the Camamu-Almada Basin (Mello et al., 1995a, 1995b; Gonçalves et al., 1998). Mello et al. (1995a) records TOC values up to 10% in this unit, and hydrogen indices (HI) up to 700 mg/g. We have examined a typical example of this Neocomian source unit in the southernmost portion of the Camamu-Almada Basin (Almada sub-basin); our data for the 1-BAS-71 well are shown in Figure 3. Concentration of TOC in the source interval approach 5%; values of the HI (not shown) reach 1000 mg/g with an average value of 400-500 mg/g. Levels of thermal maturity, based on vitrinite reflectance, in the Morro do Barro Formation in this well range from 0.5% Ro at the top of the source section to approximately 1.0% at TD, indicating that the original average HI value for this source interval would have been even greater than the present-day measured value of 400-500 mg/g.

The lower Neocomian source unit of the Camamu-Almada Basin produces highly paraffinic oils with a pristane/phytane ratio of approximately 1.5 and a slight odd-carbon *n*-alkane dominance in the C_{23,33} range. Typical gas chromatograms are shown in Figure 4 for two oils tested in the 1-BAS-64 and 3-BAS-73 wells of the basin. Typical sterane-hopane distributions for a Camamu-Almada Basin oil reveal a high hopane/sterane ratio, the presence of minor (but not dominant) amounts of gammacerane, and roughly co-equal amounts of the cholestanes and 24-ethylcholestanes (Figure 5). These analyses suggest that these are genetically identical, and that they are sourced from fresh water to brackish water lacustrine rocks. This conclusion is consistent with previous suggestions for the oils of this basin (e.g., Mello et al., 1995a, 1995b).

Despite the molecular similarities of these two Camamu-Almada Basin oils, minor but reproducible differences are present in the carbon isotope ratios of their *n*-alkanes. As indicated in Table 1, $\delta^{13}\text{C}$ differences in *n*-alkanes of the same carbon number range from 0.3 o/oo to greater than 1.0 o/oo. Although these differences are not sufficiently large to suggest that these oils comprise two distinct oil families, they are substantive and relatively consistent across the carbon number range. In the following section, the analogous values for the Morro do Barro source rocks will be presented, and shown to be much wider ranging. At this point, however, it is interesting to note that the $\delta^{13}\text{C}$ differences in *n*-alkanes for these oils could result from minor differences in contributions from each portion of the source intervals in the Morro do Barro Formation. Minor changes in the composited contribution from the source (see below for a detailed discussion of this concept) could easily result in the isotopic distinctions between

the 1-BAS-64 and 3-BAS-73 oils (Table 1).

OIL-SOURCE ROCK CORRELATION IN THE CAMAMU-ALMADA BASIN

As expected, the distribution of molecular markers in oils from the Camamu-Almada Basin compares favorably with that in the extractable organic matter of the Morro do Barro Formation in this basin (Mello et al., 1995a, 1995b). Our data show that the minor molecular variations that exist between the EOM of different samples are insufficient to conclude that the organic facies fluctuated significantly during lacustrine deposition of this unit (see the ratios listed in Table 2). Therefore, discrete sampling of the organic-rich interval of the Morro do Barro Formation is sufficient to establish a molecular correlation between this source unit and the Camamu-Almada oils.

However, this is not the case with respect to the carbon isotope ratios of the oils and extracts. Using standard procedures of oil-source rock correlations involving the $\delta^{13}\text{C}$ values of *n*-alkanes in both sample types, we attempted to relate the 1-BAS-64 oil to the EOM of discrete samples of the organic-rich Morro do Barro Formation in the 1-BAS-71 well, and were unsuccessful. As the data in Table 1 indicate, no single *n*-alkane $\delta^{13}\text{C}$ distribution for the rock extracts matches exactly with that of the 1-BAS-64 oil, suggesting that the relationship among these samples is not genetic.

The successful molecular correlation between each discrete sample of the 1-BAS-71 source section and the Camamu-Almada oils stands in contrast with the unsuccessful discrete correlation using $\delta^{13}\text{C}$ data, and led us to examine the variability in $\delta^{13}\text{C}$ values within the organic-rich portion of the Morro do Barro Formation. Random sampling of rocks having hydrogen index values greater than 400 mg/g suggest that the $\delta^{13}\text{C}$ variation within the source unit is substantial, ranging (for a single *n*-alkane carbon number) up to 5-6 o/oo. The richness of the source section indicates that multiple intervals may have played a role in sourcing the Camamu-Almada oils, and that the compound-specific $\delta^{13}\text{C}$ values of the *n*-alkanes in the oil may result from mixing of hydrocarbons from numerous discrete source intervals. To test this concept, we computed values for a composite oil by weighting the $\delta^{13}\text{C}$ input of each individual *n*-alkane from *n*-C₂₀ through *n*-C₂₈ according to the hydrogen index of the source rock sample. Results are tabulated in Table 1 and displayed in Figure 6. This approach provided a composite oil whose $\delta^{13}\text{C}_{\text{nc}20-28}$ distribution is almost identical to that of the 1-BAS-64 oil (Table 1, Figure 6). Such an

approach would have little effect on the molecular distributions in the sample set, because the differences among these are substantially less than the isotopic differences.

On the basis of the successful molecular correlation noted above (and alluded to by Mello et al., 1995a, and others), and the successful isotopic correlation achieved by compositing the isotope data, it appears that the 1-BAS-64 oil, and possibly the other oils of Camamu-Almada Basin as well, are sourced from the full organic-rich interval of the Morro do Barro Formation source section. The distributed source rock sampling approach demonstrated here provides a reasonable means for defining an isotopic correlation in situations where discrete sampling for $\delta^{13}\text{C}$ analysis would fail. Such an approach is particularly useful for geological occurrences of thick, thermally mature sections of source-rock, as is the case in the Camamu-Almada Basin.

CONCLUSIONS—ISOTOPE-BASED OIL-SOURCE ROCK CORRELATIONS

The Morro do Barro Formation of the Camamu-Almada Basin provides an unusual case where the organic facies of a thick, organic-rich interval, as measured by molecular geochemistry, remains constant while the carbon isotope ratio of the organic matter changes through time. Although this change may be attributed to secular variation of $\delta^{13}\text{C}_{\text{CO}_2}$ in the atmosphere (cf. Santos Neto et al., 1998), we are not aware of changes of this magnitude (greater than 6 o/oo) in organic matter of the Early Cretaceous, particularly over such a short time period (probably less than 3 Ma). Nevertheless, Scholle and Arthur (1980) observed variations of 2-3 o/oo in mid-Neocomian carbonates (130-140 Ma) of Mexico, and later workers have found values within or below this level of variability. Therefore, we leave open the possibility that $\delta^{13}\text{C}$ variations of organic matter in the Morro do Barro Formation may also be due, in part, to secular variation of $\delta^{13}\text{C}_{\text{CO}_2}$.

An additional mechanism involves variation in the CO_2 concentration of the Morro do Barro lake waters at the time of growth and sedimentation of the phytoplankton. $\delta^{13}\text{C}$ variability within the carbon dioxide of a lake's photic zone has been documented extensively (e.g., Hollander and McKenzie, 1991), and we attribute a substantial portion of the $\delta^{13}\text{C}$ variability within the organic matter of the Morro do Barro Formation to this mechanism. Highly-productive organic rich lakes are often characterized by CO_2 -limiting conditions in the photic zone, a consequence of an increase in

biota mass that occurs faster than the CO_2 in the water column can be replaced by atmospheric CO_2 (Hollander and McKenzie, 1991). The resulting decrease in the partial pressure of CO_2 in the photic zone of the water column limits the extent to which biota may isotopically fractionate the CO_2 during incorporation as biomass. Therefore, during times of unusually high productivity, $\delta^{13}\text{C}_{\text{om}}$ values will be relatively high, whereas during times of normal productivity these values will be low (cf. Gonçalves and Frota, 1998). This phenomenon has been observed in the organic matter accumulating in extant lakes (e.g., Lake Greifen, Switzerland; Hollander and McKenzie, 1991; Hollander et al., 1991, 1992) and in the oil shales accumulated from ancient lakes (Curiale and Gibling, 1994). The variation in $\delta^{13}\text{C}_{\text{om}}$ values that is caused by changes in partial pressure of CO_2 in the lake waters represents an overprinting of the expected variations caused by differing input of primary producers (Hollander and McKenzie, 1991), and proportioning the causes of $\delta^{13}\text{C}_{\text{om}}$ variation between these two mechanisms requires that we control for the $\delta^{13}\text{C}$ value of contributing biomass. In the case of the Mae Sot Basin of Thailand, which contains freshwater, lacustrine, organic-rich shales with $\delta^{13}\text{C}_{\text{om}}$ variations of up to 10 o/oo, Curiale and Gibling (1994) presented organic petrographic evidence arguing for the deposition of a similar type of organic matter over the measured time period.

Others have observed substantial $\delta^{13}\text{C}$ variability in organic matter of lacustrine sediments, and in oils generated from these sediments, and these mechanisms may also have a role to play in these instances. Mello and Maxwell (1990), in an examination of fresh water and hypersaline source beds of offshore Brazil, noted $\delta^{13}\text{C}$ variations of up to 3 o/oo in the extractable organic matter. The $\delta^{13}\text{C}$ values for *n*-alkanes in lacustrine organic matter of the Eocene Green River Formation (Colorado) also show significant variations, which are attributed to differing contributions of at least five different types of biota (Collister et al., 1994). Many other authors have also observed extensive isotopic variability in the organic matter of lacustrine intervals as old as Cretaceous (e.g., Burwood et al., 1992). These variations, and those for the Camamu-Almada Basin oils and source rocks, may be attributed to several causes, including temporal variation of organic matter input and lake water $\delta^{13}\text{C}$ values as discussed above. Changes in organic matter input during Morro do Barro time are expected to be minor, suggesting that variations in $\delta^{13}\text{C}$ of the organic matter may be controlled largely by differences in lake water $\delta^{13}\text{C}$ values caused by CO_2 variations. Nevertheless, this is unlikely to be the sole control, inasmuch as the relationship

between isotopic fractionation and CO₂ concentrations in the water column is also known to be affected by other factors, including cell growth rate and geometry (Popp et al., 1998, and references therein).

We suggest that the cause of isotopic variability of the organic matter in the Morro do Barro Formation is related to the CO₂-limiting conditions interpreted as a mechanism for isotopic variability in the organic matter of the modern sediments of Lake Greifen and the immature Neogene rocks of the Mae Sot Basin, and that the Morro do Barro Formation may be an ancient example of these two analogs. In the Morro do Barro case, and in particular for the correlations between this formation and the oils it has generated and expelled, the success of discrete molecular correlations is insufficient to establish a definitive oil-source rock correlation. Full definition of the petroleum system requires distributed sampling of the source interval and, in the case of carbon isotope ratio values, compositing of individual source intervals weighted by their contribution to the generated petroleum.

ACKNOWLEDGEMENTS

Most of the data discussed here were acquired by APTI Geosciences, Houston, Texas, under contract to Unocal. Expert drafting assistance was provided by John Bockelman and Mike Kirby. Sergio Brandão of Unocal provided managerial support and encouragement. We also thank the Unocal Brazil Team for several of the ideas presented here, and Unocal management for permission to publish. John Hayes, Luiz Trindade and Luciano Magnavita reviewed an earlier version of the manuscript, and we have incorporated their many excellent suggestions for improvement. Finally, we thank the ALAGO organization for organizing the 6th Latin American Congress on Organic Geochemistry on beautiful Margarita Island, Venezuela, where this paper was first presented.

REFERENCES CITED

- Arthur, M.A., Dean W.E. and Pratt, L.M., 1988. Geochemical and climate effects of increased marine organic carbon burial at the Cenomanian-Turonian boundary. *Nature* 335, 714-717.
- Bruhn, C.H.L., 1998. Deep-Water Reservoirs From the Eastern Brazilian Rift and Passive Margin Basin. American Association of Petroleum Geology Course Notes: Petroleum Geology of Rift and Passive Margin Turbidite Systems: Brazilian and Worldwide Examples, Rio de Janeiro.
- Burwood, R., Leplat, P., Mycke, B. and Paulet, J., 1992. Rifted margin source rock deposition: a carbon isotope and biomarker study of a West African Lower Cretaceous "lacustrine" section. *Organic Geochemistry* 19, 41-52.
- Collister, J.W., Lichtfouse, E., Hieshima, G. and Hayes, J.M., 1994. Partial resolution of sources of *n*-alkanes in the saline portion of the Parachute Creek Member, Green River Formation (Piceance Creek Basin, Colorado). *Organic Geochemistry* 21, 645-659.
- Curiale, J.A., 1993. Oil to Source Rock Correlation — Concepts and Case Studies. In: *Organic Geochemistry*, edited by M. Engel and S. Macko, Vol. 11 of Topics in Geobiology, Plenum Press, New York, pp. 473-490.
- Curiale, J.A., 1994a. Geochemical anomalies at the Cenomanian-Turonian boundary, northwest New Mexico. *Organic Geochemistry* 22, 487-500.
- Curiale, J.A., 1994b. Correlation of oils and source rocks — A conceptual and historical perspective. In "The Petroleum System — From Source to Trap," edited by L.B. Magoon and W.G. Dow, *American Association of Petroleum Geologists Memoir* 60, pp 251-260.
- Curiale, J.A., 1994c. High-resolution organic record of Bridge Creek deposition, northwest New Mexico. *Organic Geochemistry* 21, 489-507.
- Curiale, J.A. and Bromley, B.W., 1996. The Migration of petroleum into Vermilion 14 Field, Gulf Coast, USA — molecular evidence. *Organic Geochemistry* 24, 563-579.
- Curiale, J.A. and Gibling, M.R., 1994. Productivity control on oil shale formation — Mae Sot Basin, Thailand. *Organic Geochemistry* 21, 67-89.
- Gonçalves, F.T.T. and Frota, E.S.T., 1998. Early Cretaceous rift source rocks from eastern Brazilian margin: isotope and molecular correlation. American Association of Petroleum Geology International Conference & Exhibition, November 8-11, 1998, Rio de Janeiro, Brazil, pp 182-183 (abstract).
- Gonçalves, F.T.T., Bedregal, R.P., Coutinho, L.F.C. and Mello, M.R., 1998. Petroleum system of the Camamu Almada Basin: A basin modeling approach. American Association of Petroleum Geology International Conference & Exhibition, November 8-11, 1998, Rio de Janeiro, Brazil, pp 676-677 (abstract).
- Hollander, D.J. and McKenzie, J.A., 1991. CO₂ control on carbon-isotope fractionation during aqueous photosynthesis: a paleo-pCO₂ barometer. *Geology* 19, 929-932.
- Hollander, D., Behar, F., Vandenbroucke, M., Bertrand, P. and McKenzie, J.A., 1991. Geochemical alteration of organic matter in eutrophic Lake Greifen: implications for the determination of

- organic facies and origin of lacustrine source rocks. In: *Deposition of Organic Facies* (Edited by Huc, A.Y.). American Association of Petroleum Geologists Studies in Geology 30, 181-193.
- Hollander, D.J., McKenzie, J.A. and ten Haven, H.L., 1992. A 200 year sedimentary record of progressive eutrophication in Lake Greifen (Switzerland): implications for the origin of organic-carbon-rich sediments. *Geology* 20, 825-828.
- Kipiniak W., 1981. A basic problem - the measurement of height and area: *J. Chrom. Sci.* 19, 332-337.
- Magnavita, L. P. and da Silva, H.T.F., 1995. Rift Border System: The Interplay Between Tectonics and Sedimentation in the Recôncavo Basin, Northeastern Brazil. American Association of Petroleum Geologists *Bulletin* 79, 1590-1607.
- Magoon, L.B. and Dow, W.G., 1994. The petroleum system. In: *The Petroleum System – From Source to Trap* (Edited by Magoon, L.B. and Dow, W.G.). American Association of Petroleum Geologists *Memoir* 60, 3-24.
- Mello, M.R. and Maxwell, J.R., 1990. Organic geochemical and biological marker characterization of source rocks and oils derived from lacustrine environments in the Brazilian continental margin. In: American Association of Petroleum Geologists *Memoir* 50 (American Association of Petroleum Geologists) pp 77-95.
- Mello, M.R., Gonçalves, F.T.T., Netto, A.S.T., Amorim, J.L. and Witzke, R.E., 1995a. Application of the petroleum system concept in the assessment of exploration risk: the Camamu Basin example, offshore Brazil. In: 4th International Congress of the Brazilian Geophysical Society (1st Latin American Geophysical Conference), Vol 1, pp. 90-93.
- Mello, M.R., Gonçalves, F.T.T. and Netto, A.S.T., 1995b. A successful application of the petroleum system concept in the Camamu Basin, offshore Brazil. *Bulletin of the American Association of Petroleum Geologists* 79, 486 (abstract).
- Miranda, R.M. and Walters, C.C., 1992. Geochemical variations in sedimentary organic matter within a "homogenous" shale core (Tuscaloosa Formation, Upper Cretaceous, Mississippi, USA). *Organic Geochemistry* 18, 899-911.
- Moldowan, J.M., Sundararaman, P. and Schoell, M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. *Organic Geochemistry* 10, 915-926.
- Netto, A.S. T. and Ragagnin, G., 1990. Compartimentação Exploratória da Bacia de Camamu, Bahia. *Proceedings of the 36th Congresso Brasileiro de Geologia – Natal-Rio Grande do Norte 1990*, pp. 171-180.
- Park J.H., Hussam A., Couasnon P. and Carr P.W., 1987. The precision of area and height measurements with flame ionization detectors in temperature-programmed capillary gas chromatography. *Microchem. J.* 35, 232-239.
- Popp, G.N., Laws, E.A., Bidigare, R.R., Dore, J.E., Hnason, K.L., Wakeham, S.G., 1998. Effect of phytoplankton cell geometry on carbon isotope fractionation. *Geochimica et Cosmochimica Acta* 62, 69-77.
- Santos Neto, E.V., Hayes, J.M. and Takaki, T., 1998. Isotopic biogeochemistry of the Neocomian lacustrine and Upper Aptian marine-evaporitic sediments of the Potiguar Basin, northeastern Brazil. *Organic Geochemistry* 28, 361-381.
- Scholle, P.A., Arthur, M.A., 1980. Carbon isotope fluctuations in Cretaceous pelagic limestones: potential stratigraphic and petroleum exploration tool. *Bulletin of the American Association of Petroleum Geologists* 64, 67-87.
- Szatmari, P., 1998. Tectonic Habitat of Petroleum Along the South Atlantic Margins, 1998 American Association of Petroleum Geology International Conference & Exhibition, November 8-11, 1998, Rio de Janeiro, Brazil, p. 362 (abstract).

Table 1
N-alkane Carbon Isotope Ratios (o/oo) for
Crude Oils, Rock Extracts and Composite Oil

	1-BAS-64 Oil 2370m	3-BAS-73 Oil 2386m	Extract 2050m	Extract 2210m	1-BAS-71 Extract 2400m	Extract 2610m	Composite Oil ^a
<i>n</i> -C ₂₀	-29.8	-30.9	-28.7	-31.2	-28.1	-30.6	-29.7
<i>n</i> -C ₂₁	-30.5	-31.4	-28.2	-31.7	-29.4	-31.5	-30.2
<i>n</i> -C ₂₂	-30.8	-31.4	-29.3	-31.7	-29.1	-31.6	-30.5
<i>n</i> -C ₂₃	-30.9	-31.7	-29.8	-32.0	-28.8	-31.8	-30.6
<i>n</i> -C ₂₄	-30.9	-31.8	-28.6	-31.6	-28.8	-32.7	-30.6
<i>n</i> -C ₂₅	-30.7	-31.5	-29.4	-31.9	-29.1	-33.1	-31.0
<i>n</i> -C ₂₆	-31.2	-31.5	-29.2	-31.9	-29.1	-33.7	-31.2
<i>n</i> -C ₂₇	-31.8	-32.5	-30.2	-32.4	-30.1	-35.0	-32.2
<i>n</i> -C ₂₈	-31.7	-32.9	-30.8	-32.9	-30.6	-35.4	-32.7

^a Composite oil $\delta^{13}\text{C}$ value are calculated by weighting each extract $\delta^{13}\text{C}$ value by its hydrogen index (HI). These HI values, in increasing depth order, are 715 mg/g, 496 mg/g, 661 mg/g and 987 mg/g. See text for further details.

Table 2
Source-Related Molecular Ratios for
Crude Oils and Rock Extracts

Ratio	1-BAS-64 Oil 2370m	3-BAS-73 Oil 2386m	Extract 2050m ⁴	Extract 2210m	1-BAS-71 Extract 2400m	Extract 2610m
A ¹	1.08	1.11	0.68	0.93	1.12	1.13
B ²	0.41	0.40	0.57	0.44	0.46	0.41
C ³	0.17	0.18	0.16	0.17	0.16	0.18

- 1 Ratio A = 5 α (H),14 α (H),17 α (H)-cholestane/5 α (H),14 α (H),17 α (H)-24-ethylcholestane, measured as a height ratio from the m/z 217.20 mass chromatogram
- 2 Ratio B = 30-norhopane/hopane, measured as a height ratio from the m/z 191.18 mass chromatogram
- 3 Ratio C = (22S+22R)-homohopane/2*hopane, measured as a height ratio from the m/z 191.18 mass chromatogram
- 4 Analytically significant differences between this rock extract and the crude oils may result from its thermal immaturity [vitrinite reflectance (R_v) = 0.51%].

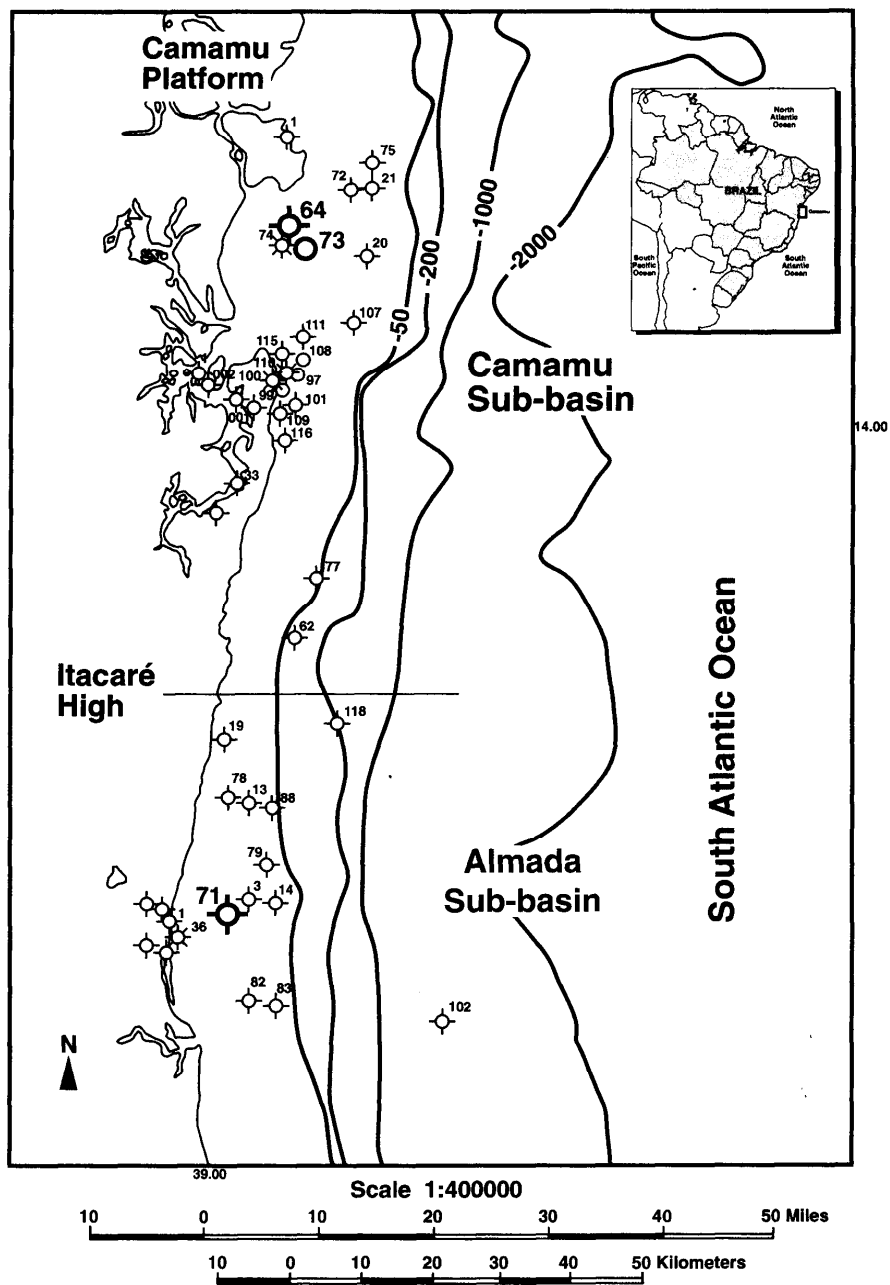


Figure 1. Location map for the Camamu-Almada region of offshore Brazil. Curves trending north-south are bathymetric lines measured in meters. The numbers adjacent to the well symbols are well numbers using the "BAS" well designation. This paper discusses samples from wells 1-BAS-64 and 3-BAS-73 (oil samples; northern part of the basin) and 1-BAS-71 (well cuttings; southern part of the basin); these particular well names are shown in bold font

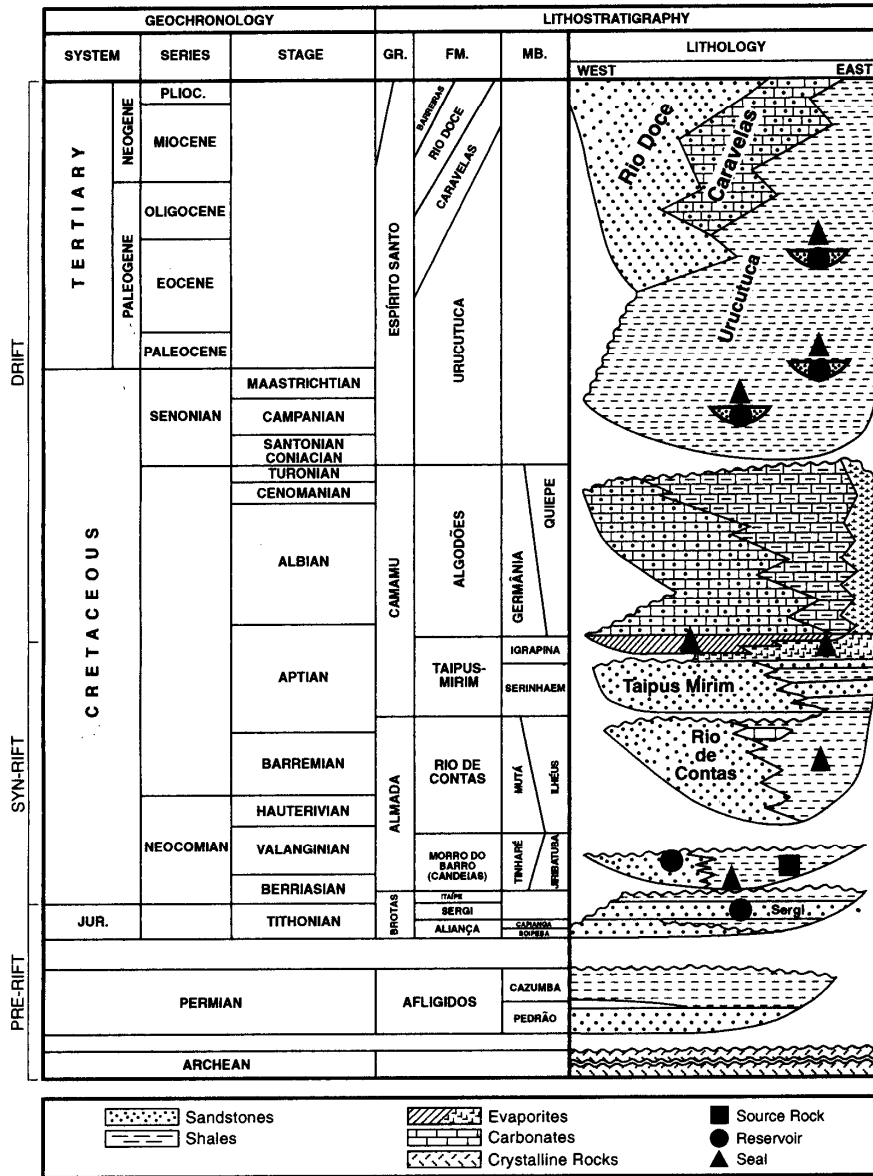


Figure 2. Schematic stratigraphic section for the Camamu-Almada Basin. The primary oil discussed in this study (1-BAS-64 well) is reservoir in the Tithonian Sergi Formation, and is likely to have been sourced from overlying Neocomian lacustrine shales. (Modified after Netto and Ragagnin, 1990)

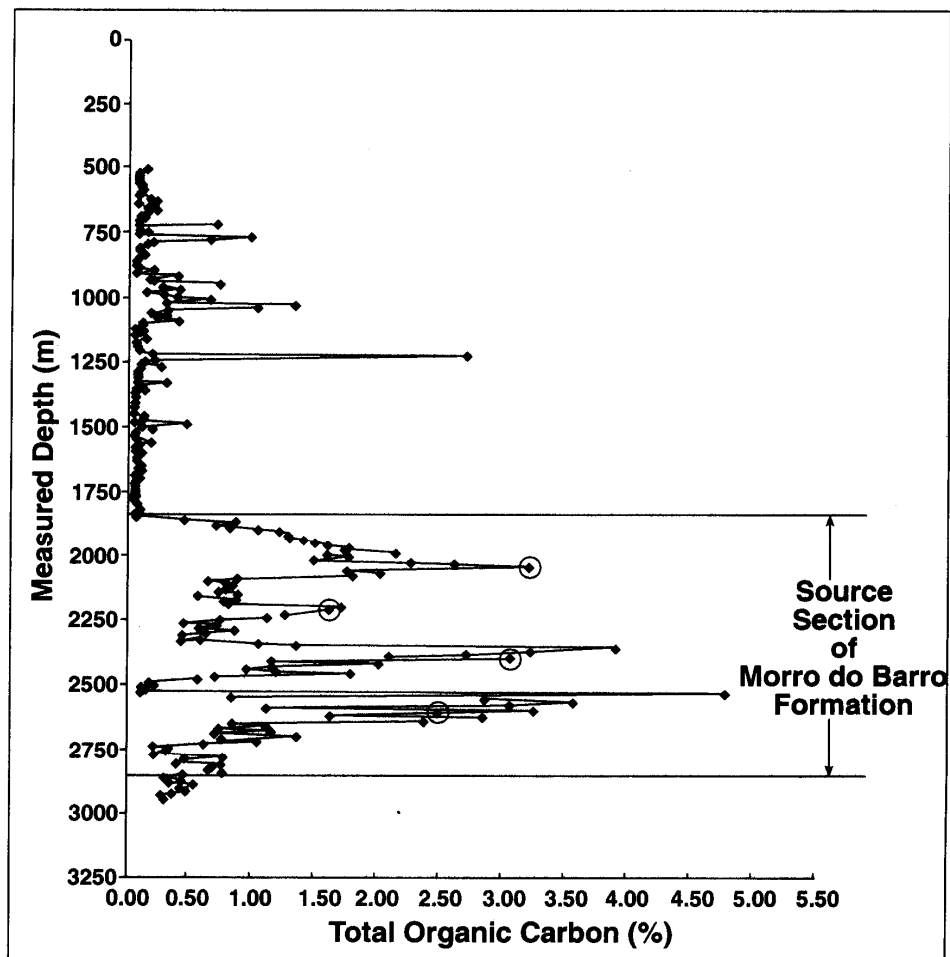


Figure 3. Total organic carbon (TOC) depth log for the 1-BAS-71 well, southern Camamu-Almada Basin (Almada sub-basin). The main source rock section of the Morro do Barro Formation is delineated. The four circled points are the samples chosen as examples of the distributed sampling approach, as displayed in Figure 6. They were chosen for illustrative purposes, as representative of the main source rock interval in the basin

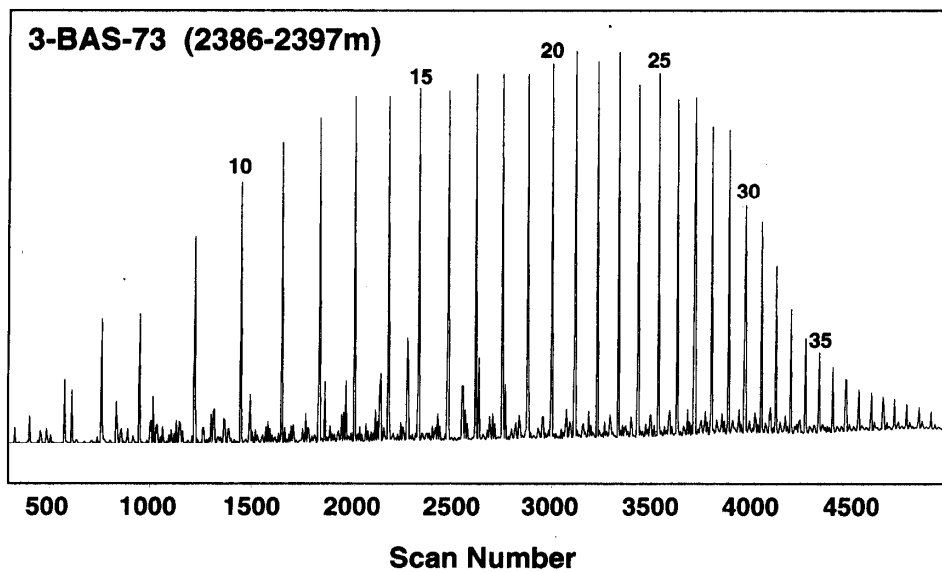
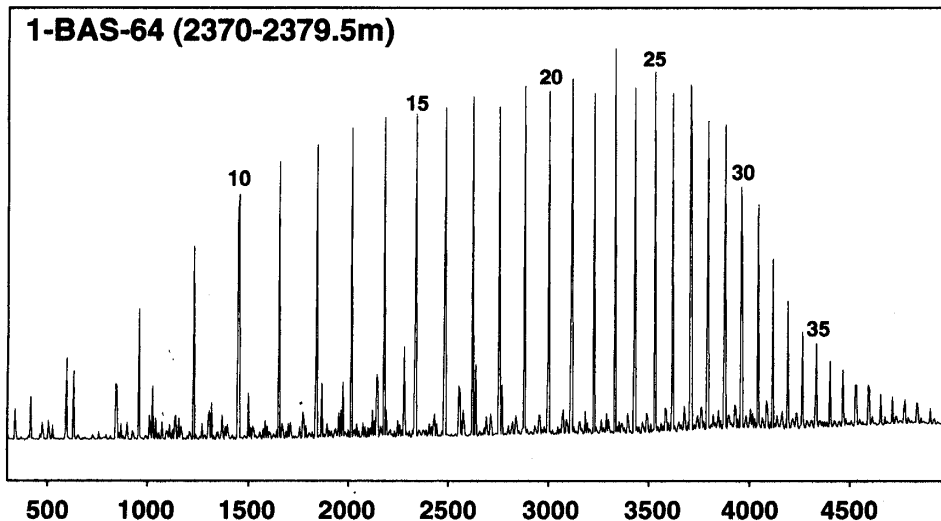


Figure 4. Whole oil (untopped) gas chromatograms for typical oils of the Camamu-Almada Basin. As noted in the text, these oils were in storage at ambient conditions (Unocal library) for several years prior to analysis, leading to some loss of light ends. Drill stem test depths are listed in parentheses after the well name. The number over some peaks is the carbon number of the respective n-alkane

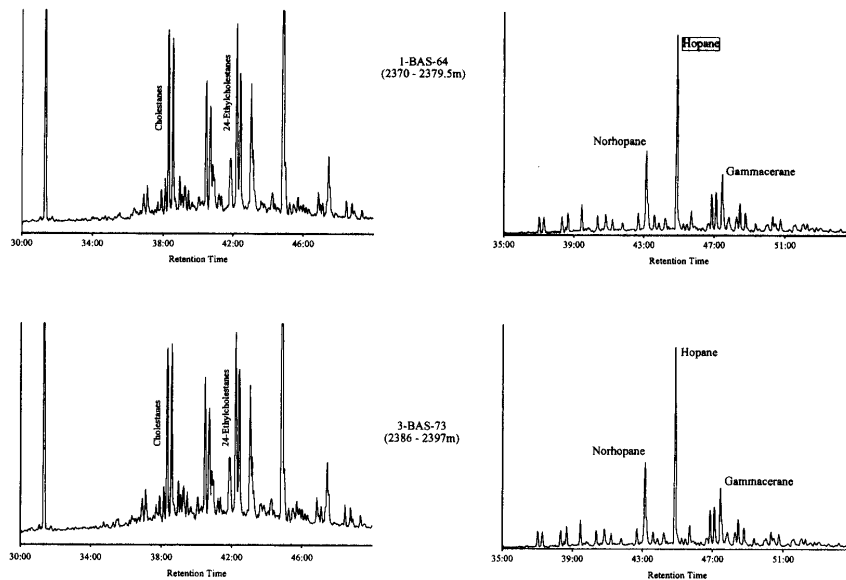


Figure 5. m/z 218.20 (left) and m/z 191.18 (right) mass chromatograms for the 1-BAS-64 (top) and 3-BAS-73 (bottom) oils of the Camamu-Almada Basin. Drill stem test depths are listed in parentheses under the well name. The identities of 30-norhopane, hopane and gammacerane are indicated in the m/z 191.18 traces, and the cholestanes and 24-ethylcholestanes series are identified in the m/z 217.20 traces. The high hopane/sterane ratios in these oils is reflected in the appearance of the 30-norhopane and hopane compounds in the m/z 218.20 trace (hopane is the off-scale peak at about 45 minutes). The off-scale peak at about 31 minutes in the m/z 218.20 trace is an internal standard

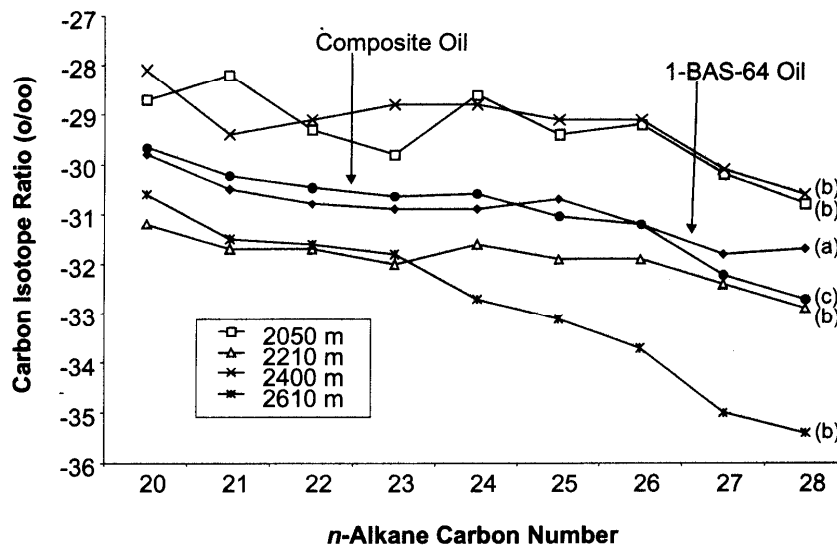


Figure 6. N-alkane carbon isotope ratio distributions for (a) the Sergi Formation oil of the 1-BAS-64 well, (b) the extractable organic matter (EOM) from four cuttings intervals in the 1-BAS-71 well, and (c) a composite extract, defined by weighting the EOM results according to the hydrogen index of each sample (see text, and footnote to Table 1). The inset box lists the measured depths of the samples from the 1-BAS-71 well; the chosen samples are also identified in the TOC-depth plot of Figure 3. Note that the $\delta^{13}C$ distribution of the composite oil is almost identical (analytically) to the distribution for the 1-BAS-64 oil