GEOCHEMICAL COMPOSITION OF BEACH TAR FROM THE SE COAST OF THE PARIA PENINSULA, NE VENEZUELA: DERIVATION FROM NATURAL SEEPAGES

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ABSTRACT

Tar residues ("tarballs") occur frequently on the SE coastline of the Paria Peninsula, NE Venezuela. This paper reports on tarballs recovered from approximately 14 km of shoreline during monthly sampling over a two-year period up to April, 2011. The tarballs were analysed geochemically and results show that more than 70% of them could be included within a single compositional group on the basis of their physical and organoleptic properties. The tarballs were fingerprinted using biomarkers (hopanes, steranes, alkanes, aromatic steroids, phenanthrenes and dibenzothiophenes) by gas chromatography and gas chromatography--mass spectrometry. Sulphur and trace element contents were also determined. These analyses indicate that the tarballs do not have an anthropogenic origin but that they probably originated from petroleum generated by argillaceous limestones in the Turonian-Campanian Naparima Hill Formation. This formation includes marls and organic-rich shales and limestones, and is an important source rock at oilfields in Trinidad and the southern Gulf of Paria. In the southern part of the Gulf, petroleum escapes from Neogene reservoirs to the seafloor via natural seepages associated with the Los Bajos and other fault systems. It is inferred that the petroleum is then transported by wind and tidal currents to the

shoreline of the SE Paria Peninsula where it strands as tarballs. We discuss the geochemistry of the tarballs collected to investigate the source of this material.

Key words: marine seepages, seepage oils, tarballs, Trinidad, Venezuela, Gulf of Paria, Naparima Hill Formation, Los Bajos fault, organic geochemistry.

INTRODUCTION

Tar residues and beached oils in the form of pellets of varying sizes ("tarballs") have been reported from oceanic and coastal locations near tanker routes (e.g. Romero et al., 1981; Asuquo, 1991; Plummer, 1996; Gabche et al., 1998; Owens et al., 2001). Tarballs are derived from floating petroleum products which may become stranded on coastlines and beaches (Corbin et al., 1993). Many tarballs are of anthropogenic origin due for example to operational losses of hydrocarbons from offshore rigs, terminal-derived oil spills, and accidental oil spillages from commercial maritime traffic. However, coastal residues can also result from natural submarine seepages (Kvenvolden et al., 2000; Hostettler et al., 2004). Detailed geochemical analysis of these residues can help to determine their origin and degree of biodegradation (Gallego et al., 2006).

The Gulf of Paria is located in the SE Caribbean, on the eastern flank of the Eastern Venezuelan Basin between Trinidad and NE Venezuela (Fig. 1a). Petroleum exploration to the SW of Trinidad began in the 1950s and has resulted in major hydrocarbon discoveries including the Soldado, Posa and Soldado North fields (Michelson, 1976; Flinch et al., 1999). Geochemical studies (Rodrigues, 1988; Requejo et al., 1994) have reported a predominantly marine organic matter source for most Trinidadian oils which can be correlated with source rock intervals in the organic-rich argillaceous limestones and shales in the Late Cretaceous Naparima Hill Formation and, to a lesser extent, in the underlying Gautier Formation.

Figure 1

Beaches along the SE coast of the Paria Peninsula are close to offshore oil-production facilities and also to prolific natural marine oil seeps characterized by flow rates of around 0.1 brl/day·mile (Johnson, 1971). This paper reports on beach tar recovered from the Gulf of Paria (long. 61º 56' W to 62° 9' W, lat. 10° 38' N). The climate is

predictable in terms of precipitation and there are two seasons: wet from June to November and dry from January to April (Fuglister, 1951). In the dry season, easterly or NE winds predominate 70% of the time and minor tar strands on the SE coast of the Paria Peninsula. In the wet season, easterly winds predominate; but when currents are more northerly and SE winds prevail, more tar strands are found on the coastline studied (Georges and Oostdam, 1983).

GEOLOGICAL SETTING

Regional background

Tectonically, the Gulf of Paria is located within a region of diffuse and complex interaction between the Caribbean and South America plates (Figs. 1b and 1c) (Erlich and Barret, 1992). The plate boundary is expressed in eastern Venezuela and Trinidad by the El Pilar fault zone (PF: Figs. 1b and 1c) (Bowen, 1976). Oblique collision of the Caribbean arc with the South American passive margin during Neogene times was followed by regional transpression. This tectonic history resulted in the formation of strike-slip fault systems which accommodated plate movements and the opening of the Gulf of Paria (Duerto and McClay, 2010). Right-lateral strike-slip faulting across Trinidad (Babb and Mann, 1999) continues at the present day (Weber et al., 2001).

A regional N-S cross-section through the Gulf of Paria (Fig. 1c) shows that it can be divided into a southern compressional zone and a northern transtensional area. The compressional domain is characterized by north-vergent Miocene-Pliocene thrusts (Flinch et al., 1999). Late Miocene to Pliocene thrust-related structures extend from those in the Central and Southern Ranges of Trinidad (Fig. 1b). Thrusts and folds generally verge southward on Trinidad but north-vergent back-thrusts also occur. By contrast, the transtensional domain to the north (Fig. 1c) is characterized by down-to-the-basin normal faults and WNW-ESE-trending half-grabens and structural highs (Flinch et al., 1999).

The boundary between the compressional and transtensional zones is defined by a set of north-dipping normal faults known as the Warm Spring fault system (Russo et al., 1993) (WSF: Fig. 1b). The occurrence of north-south trending lateral and oblique ramps joining this fault system has also been observed (Escalona and Mann, 2010).

In the southern Gulf of Paria (Fig. 1b), major hydrocarbon accumulations have been discovered in Tertiary-Quaternary reservoir rocks (Robertson and Burke, 1989). The structures at Posa field comprise south-vergent and E-W trending thrusts; at Pedernales field, structures are approximately NE-SW trending thrust-related features (Flinch et al., 1999. NW-SE striking right-lateral wrench faults of Neogene age (e.g. the Soldado and Los Bajos fault systems) have generated structural traps at fields in the Gulf of Paria and southern Trinidad including Soldado and Forest Reserve (Wilson, 1968). The Los Bajos fault may have acted as a conduit for the vertical migration of hydrocarbons between Late Cretaceous source rocks and Miocene reservoir rocks (Wilson, 1968).

The Los Bajos fault is a continuation of the western part of the Warm Spring fault, and both are oblique to the trend of the El Pilar fault system. In regards to the structural relationship among these three faults, El Pilar and Warm Spring are the main structures that accommodate large strains induced by the South American-Caribbean plate convergence. Los Bajos play a secondary role in tectonism in the Gulf of Paria, allowing the deformation front displacement caused by the Warm Spring fault motion (Flinch et al., 1999). The Los Bajos fault has about 10 km of lateral offset, extending parallel to the Trinidadian coastline and cutting the western part of the Southern Range (Fig. 1b) (Soto et al., 2010). Offshore, the fault may be more important as a sealing feature than a migration pathway. By contrast, the Soldado fault and other strike-parallel structures are sensitive to fault breakthrough and necessarily require structural closure to retain their charge.

Stratigraphic framework

The stratigraphy of the southern portion of the Gulf of Paria is similar to that of the Eastern Venezuelan Basin (Fig. 2) (Flinch et al., 1999).

Figure 2

In the compressional domain, the oldest sedimentary rocks are Early Cretaceous shales, silty claystones, marls and quartz arenites (Carr-Brown and Frampton, 1979). During the Late Cretaceous, the Gulf of Paria formed the northern passive margin of the South American continent and underwent post-rift thermal subsidence (Erikson

and Pindell, 1998). Hemipelagic sediments were deposited at this time including mudstones, black-grey shales and sandstones (Cuche Formation), as well as shales, organic-rich mudstones, argillaceous limestones, turbidites, and submarine fan sediments (Gautier, Naparima Hill and Guayaguayare Formations) (Di Crocce et al., 1999). Upwelling of nutrient-rich waters, together with phases of global anoxia (Schlanger et al., 1987), resulted in the accumulation and preservation of extensive petroleum source rocks (Algar, 1998).

During the Late Cretaceous and Paleogene, the depositional environment varied from deep water to turbiditic and continental sedimentary processes. The Miocene strata consist of a thick wedge of delta associated silts, sands and shales (Diaz de Gamero, 1996). The Early-Middle Miocene transition was characterized by the Cipero and Herrera units, which are explained by turbiditic fan deposits from the Orinoco River. In the Late Miocene-Pliocene, three prominent cycles of deltaic sedimentation have been determined and reported as the Cruse, Forest, and Manzanilla deltaic units (Garciacaro et al., 2011). Finally, the Pleistocene formations (the lignitic and pyritic Morne L'Enfer and Cedros) comprise massive sandstones interbedded with clayey shales and siltstones (Rodrigues, 1988).

PETROLEUM SYSTEM OF SW TRINIDAD

Source and reservoir rocks

Organic geochemical studies of potential source rocks in the southern Gulf of Paria and Trinidad suggest that oil-prone facies of the Late Cretaceous Naparima Hill and Gautier Formations have the best source potential (Rodrigues, 1988). The Turonian-Late Campanian Naparima Hill Formation has total organic carbon (TOC) concentrations of between 2 and 8% and hydrogen indices (HI) from 234 to 640 mg HC/g TOC, and includes Type II kerogen probably of algal or bacterial origin. The Late Albian -- Early Cenomanian Gautier Formation has TOC concentrations below 7.5% and HI values between 101 and 527 mg HC/g TOC, and is dominated by kerogen Types II and III (Rodrigues, 1988). Other Cretaceous units such as the Guayaguayare and Cuche Formations have limited liquid hydrocarbon potential and contain gas-prone woody and coaly type III kerogens Rodrigues (1988). The Maastrichtian Guayaguayare Formation is immature to mature and has low to

moderate TOC (2.5-2.9%) and HI (402-412 mg HC/g TOC). Rodrigues (ibid.) reported TOC values up to 30% for samples from the overmature Barremian--Early Albian Cuche Formation. Some Tertiary shales contain terrigenous kerogen (Leonard, 1983; Rodrigues, 1988).

The main reservoirs are of Neogene age and were formed during Late Miocene transpression. The most probable migration pathway involves the Los Bajos fault system which connects Cretaceous source rocks and Neogene turbiditic/deltaic sandstone reservoir rocks in the upper Miocene-Pliocene Cruse and Forest Formations, and turbidite sandstones in the Miocene Herrera and Retrench Formtions. Hydrocarbon traps usually have both stratigraphic and structural components (Rodrigues, 1988).

Source rock facies

Four genetic types of oil-prone source rock facies, sourced from predominantly marine organic matter, have been reported in the southern Gulf of Paria and Trinidad. These correspond to calcareous, clastic and siliceous lithofacies of argillaceous limestones, clayey shales and diatomitaceous mudstones, respectively (Requejo et al., 1994). The carbonate facies can be divided into “A” and “B” sub-facies which differ subtly in their source rock characteristics.

The highest petroleum potential is associated with siliceous and calcareous lithofacies, which comprise hemi-pelagic sediments deposited under anoxic or near-anoxic conditions. The clastic lithofacies include nearshore sediments transported to the continental slope along canyons either through submarine debris flows, slumping or turbidity currents (Rodrigues, 1988). Most samples from each genetic type can be defined as thermally immature to early mature, and highest vitrinite reflectance (Ro) values are approximately 0.6% (Requejo et al., 1994). In general, source rock extracts considered in the present work have sulphur contents of 0.3-1.2 % (Rodrigues, 1988).

The two carbonate source-rock sub-facies occurs widely throughout the southern Gulf of Paria and Trinidad and have the following geochemical characteristics: unusual high *n*-alkane to isoprenoid ratios at low stages of thermal maturity; pristane/phytane ratios lower than unity; significant presence of gammacerane; abundance of C_{13+}

paraffins, dibenzothiophenes and αββ steranes; and depletion of diasteranes. Sub-facies "B" can be distinguished from "A" by higher proportions of cheilanthanes or lower contents of both 28,30-bisnorhopane and gammacerane (Requejo et al., 1994).

Both carbonate sub-facies exhibit a similar *n*-alkane distribution patterns to the siliceous organic facies. The latter can be defined by: a prevalence of isoprenoids over *n*-alkanes and pristane/phytane ratios above one; a regular sterane distribution dominated by the ααα (20R) isomers; abundance of 28,30-bisnorhopane; low phenanthrene/dibenzothiophene (Phe/DBT) values; and a slight enrichment in naphthalenes relative to phenanthrenes (Requejo et al., 1994). An enrichment in 28,30-bisnorhopane is typical of thermal immaturity, although this biomarker has also been related to anoxic depositional conditions (Mello et al., 1988).

The clastic facies has the following geochemical characteristics: an abundance of *n*-alkanes in the C_{25}-C_{31} range with an odd-carbon predominance, and pristane/phytane ratios much greater than unity; high hopane to sterane ratios and enrichment in 18α(H)-22,29,30-trisnorneohopane (Ts), 18α(H)-oleanane, moretane, and diasteranes (mainly C_{29} isomers); absence of 28,30-bisnorhopane and 25,28,30-trisnorhopane; low abundance of dibenzothiophenes and tricyclopolyprenanes; and predominance of phenanthrenes relative to naphthalenes (Requejo et al., 1994). These characteristics support the catalytic role of clays in diasterane formation and a terrigenous origin for the organic matter originating from higher plants (Peters et al., 2005).

MATERIALS AND METHODS

Tarballs were collected every month from nine beaches between the villages of Macuro and Mapire (Fig. 1a) between June 2009 and April 2011. At each location along the 15 km long beach, several randomly located 1 m wide transects running from the waterline to the supratidal zone were selected for tar collection. All stranded tarballs in the transect were collected at or near the time of low tide and were described in detail (physical and organoleptic properties: size, colour, shape, odour, viscosity).

Shoreline oiling conditions can be represented on a histogram of normalized tarball concentration, estimated by calculating the weight of tar per unit beach length (g/m). This format has been commonly used for reporting tarball concentrations on beaches (e.g. Corbin et al., 1993) and has been shown to give an accurate assessment of the amount of tar, regardless of the state of the tide or the width of the intertidal zone (Anderlini and Al-Harni, 1980).

The tarballs (including sand and rock fragments) were pre-cleaned with a knife and placed on aluminium foil for transport to the laboratory for analysis. Samples were then weighed on a digital scale and dissolved in dichloromethane. They were then filtered through glass wool to remove sand grains or other debris, and air-dried under a hood to remove the dichloromethane. The sand and surficial debris were placed back on the original aluminium foil, weighed, and subtracted from the initial mass measurement.

A first portion of the extract was redissolved in dichloromethane and filtered through activated copper to remove elemental sulphur. An aliquot (approx. 0.05 g) of this portion was then separated into its constituent fractions (SARA method; Jewell et al., 1974). Asphaltenes were precipitated with *n*-heptane in a 1:40 v/v ratio following the ASTM D3279 standard procedure (ASTM, 2007); each sample was passed through a batch-type reactor in constant agitation for 1 hour at 60 ºC, followed by a 12-hour inactive period (Speight, 2007). The dichloromethane was replaced by hexane and loaded onto a silica gel liquid chromatography column for the separation of maltene compounds (Zakaria et al., 2000). Saturates (hexane eluent), aromatics (toluene), and resins (30% methanol in dichloromethane) were collected separately. The geochemical fingerprinting involved comparison of tarball data to those of crude oil types from the Gulf of Paria reservoirs. This evaluation included the use of biomarker distributions determined by gas chromatography/mass spectrometry (GC/MS) and gas chromatography/flame ionization detection (GC/FID) data. These approaches followed the modified EPA 8015 and EPA 8270 methods described in Douglas et al. (1994) and Page et al. (1995).

The GC analysis was carried out using a J&W Agilent PONA GC column (50 m x 0.2 mm i.d.; film thickness 0.25 µm) in a Delta Chrom Series 9980 instrument with a

flame ionization detector. The analyses were performed using GC ChemStation software (Agilent Technologies 1990-2000). The saturated and aromatic hydrocarbons were subsequently analyzed using GC/MS (an Agilent Technologies 6890 GC coupled to an Agilent 5973 Mass Detector). A capillary column (30 m length x 0.25 mm i.d., film thickness 0.25 µm) HP-5MS model was used. The samples were analyzed by selected ion monitoring (SIM) mode. Oven temperature was programmed to run from an initial temperature of 80 °C to 290 °C at 4 °C/min, then to 290 °C for 20 min. The gas chromatograph was equipped with a splitless injector at 270 °C. m/z 99, 178, 184, 191, 198, 217, 231 and 412 ions were scanned with a dwell time of 0.1 seconds. The overall precision of the integrated peak areas from reconstructed ion chromatograms was from 1 to 3 %.

A final portion of the extract was analyzed by inductively-coupled plasma atomic emission spectroscopy (ICP-AES) for the quantitative analyses of vanadium and nickel concentrations (using the ASTM D-5708 standard; ASTM, 2005) through a Perkin-Elmer Optima 3000 spectrometer. Sulphur contents were determined (following the standard method; ASTM, 2010) by means of an energy-dispersive X-ray panalytical spectrometer (Axios model).

RESULTS AND INTERPRETATIONS

Characteristics and monthly concentrations of tarballs sampled

Most of the tarballs collected (more than 70%) could be classified within a single group on the basis of their physical characteristics. These were odour tarballs ranging from 1 to 9 cm in diameter, and consisting of viscoplastic semi-solid material. The black colour of these tarballs was an initial indication that the tar was relatively fresh. The remaining tarballs do not occur constantly and could not be classified into significant groups. These latter tars appear to be very likely of anthropogenic origin.

The pattern of mean monthly tar concentrations (Fig. 3) reflected seasonal variations in currents and wind/wave regimes. In the wet season when northerly oceanic currents and SE winds dominate, more tarballs were collected on the beaches. The average monthly concentrations of tar residues collected was “moderate” (10-100 g/m), following the classification of Corbin et al. (1993). These data show that beaches

along SE coast of the Paria Peninsula show a consistent minimum level of background oiling, independent of spill incidents at the Soldado or other oilfields and of tanker traffic through the Gulf of Paria. We therefore infer a continuous input of tarballs, possibly originating from seepage oils reaching the seafloor via active offshore seeps.

Figure 3

Bulk geochemical data

The average organic extract of the tarballs was 14 wt. %. An average 22 wt. % were aliphatic hydrocarbons, 28 wt. % aromatic compounds, 5 wt. % resins and 45 % wt. asphaltenes (uncertainties equal to ± 2 %). These distributions are generally characteristic of tar residues subjected to weathering and microbial degradation (Barakat et al., 1999).

Mean sulphur, vanadium, and nickel concentrations for the tarball group were 0.3 % (± 0.05 %), 287 ppm (± 2 ppm), and 52 ppm (± 2 ppm), respectively. Although these concentrations can be influenced by several processes, the proportions of vanadium to nickel are similar as a result of the structural similarities between organo-metallic compounds that contain these elements (Lewan, 1984).

Organic matter source and depositional environment

The unimodal distribution of the *n*-alkanes and a pristane/phytane (Pr/Ph) ratio of 0.8 (Fig. 4) suggest that the petroleum in the tarballs was generated from organic matter deposited in a marine environment under reducing conditions (Tissot and Welte, 1984). Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios (0.91 and 0.85, respectively) suggest that the petroleum was generated from mature Type II kerogen. However, these ratios are known to be affected by processes such as maturation (Koopmans et al., 1999) and biodegradation (Peters et al., 2005). Consequently, these measures must be interpreted with care.

Figure 4

Fig. 5a shows a representative mass chromatogram of triterpanes from tarball samples (numbers in Figs 7, 8, 9 and 13 refer to the terpanes, hopanes, steranes and triaromatic steroids listed in the Appendix, pp. 000). The most abundant terpanes were the marker compounds αβ-norhopane and C_{30} αβ-hopane, suggesting a marine source (Simoneit, 1977). The m/z 191 fragmentogram presented a distribution of tricyclopolyprenanes

in the C_{20}-C_{30} range and low relative abundances of these compounds compared to pentacyclic terpanes. The predominance of the C_{23} homologue over the other members of the tricyclopolyprenane series ($C_{24\text{-}3}$ relative to $C_{23\text{-}3}$ about 0.8) confirmed that the tarball petroleum was generated from a marine carbonate source rock deposited under anoxic conditions (Waples and Machihara, 1991). In addition, the homohopane index (0.65), together with a C_{23}-tricyclic terpane to 18β(H)-20,21,22,28,29,30-hexakisnorhopane ($C_{24\text{-}4}$) ratio above 3.0, and the abundance of isosteranes, imply sedimentation in a highly saline environment (Ourisson et al., 1982; Peakman et al., 1989). However, only some compounds of the 25-norhopane series were detected in a representative m/z 177 fragmentogram (see Fig. 5b). The presence of these 25-norhopanes appeared to be related to moderately hypersaline and anoxic marine environmental conditions (Blanc and Connan, 1998). Within the extended hopanes, the dominance of the 22S over 22R epimers may indicate a low level of biodegradation (Peters et al., 2005).

Figure 5

Fig. 6 shows a typical m/z 412 fragmentogram for one tar sample. The near-absence of 18α(H)-oleanane is apparent and the samples displayed a gammacerane index of 0.16. An oleanane index of approximately zero suggests a high contribution of marine-derived organic matter (Zakaria et al., 2001), while Sinninghe Damste et al. (1995) proposed that the presence of gammacerane indicates hypersaline and oxygen-depleted marine environments.

Figure 6

Regarding steranes (see m/z 217 fragmentogram of the saturated fraction, Fig. 7), an abundance of C_{27} and C_{29} isosteranes and regular steranes compared to the C_{28} homologue was observed, indicating marine carbonate source rocks (Seifert and Moldowan, 1978; Mello et al., 1988). The high proportion of C_{29} regular steranes may be characteristic of lipids associated with algal material, since C_{29} sterol -- the C_{29} homologue precursor -- is found in Phaeophytae and brown algae (Permanyer et al., 1994; Volkman et al., 1999). Also, a terrestrial (land plats) source of C_{29} steranes has been suggested by many researchers (i.e., Peters et al., 2005). In addition, relatively low concentrations of diasteranes (0.13) also suggest that the tarball petroleum was generated by organic matter deposited in a carbonate-dominated marine environment (Petersen et al., 2012). The average sulphur content, V/Ni ratio (5.5 ± 0.1) and Ni concentration likewise indicate that the corresponding source rocks were deposited in

a marine carbonate environment under anoxic conditions (Galarraga et al., 2008). During deposition of carbonatic facies, bacterial sulphide is not completely sequestered by iron and Ni ions will therefore precipitate in metal sulphides, in contrast to stable vanadyl ions which form organo-metallic compounds thus leading to high V/Ni ratios (Lo Monaco et al., 2007).

Figure 7

Within the aromatic fraction, the relative abundance of the methyldibenzothiophene isomers (MDBT) varied in the following order: 4 > 2+3 < 1 (Fig. 8a). Therefore, all samples showed the usual distribution pattern for methyldibenzothiophene homologues corresponding to a carbonate source rock (Hughes, 1984; Wang and Fingas, 1995). Furthermore, the distribution pattern for the methylphenanthrenes (3 < 2 < 9 > 1; Fig. 8b) and the predominance of 9-methylphenanthrene (9-MPhe) over its isomers likewise indicate that the tarball petroleum was generated from a marine source rock (Budzinski et al., 1995). However, water washing and biodegradation may have affectted phenanthrene and dibenzothiophene homologues and their patterns must be interpreted with care (Galarraga et al., 2010). The average methylphenanthrene/chrysene ratio was 3.6 (± 0.2).

Figure 8

Thermal maturity

An m/z 99 mass fragmentogram (Fig. 9) showed no dominance of odd over even C_{15+} *n*-alkanes in the tarball petroleum. Therefore the carbon preference index (CPI) and odd-even predominance (OEP) values (0.99 and 1.01, respectively) may indicate thermal maturity levels in the oil window (Marteau et al., 2002). However, *n*-alkanes are the first compounds to be removed during biodegradation (Wenger et al., 2002), and consequently the CPI and OEP indexes may not be completely consistent.

Figure 9

Thermal maturitation can also be evaluated using the %20S ratio, which increases from 0 to 0.55 with increasing thermal maturity (Seifert and Moldowan, 1978). The tarball petroleum showed a maturation level of 0.45, indicating thermal maturity (equivalent to the onset of the peak oil generation, eq.Ro close to 0.6 %). The hopane isomerization ratio (%22S) for the group showed similar values (58 % on average), and this parameter appears to be restricted to maturation levels from the immature to early oil window (Mackenzie and Maxwell, 1981) and indicates the minimum maturity (eq. Ro ≥0.6 %) of the source rock. Also, the tar samples had a ratio of

tricyclopolyprenanes to hopanes of ca. 0.6, which is consistent with an eq.Ro value below 0.75 % (van Graas, 1990). In addition, the significant predominance of 17α(H)-22,29,30-trisnorhopane over 18α(H)-22,29,30-trisnorneohopane (Ts/Tm around 0.5) may indicate that the carbonate source rocks were in the early stages of maturation (Seifert and Moldowan, 1981; McKirdy et al., 1983).

Finally, m/z 253 fragmentograms did not exhibit clear signals for monoaromatic steroid hydrocarbons. By contrast, as shown in the m/z 231 fragmentograms of the aromatic fraction (see Fig. 10), the TA(I)/TA(I+II) ratio can be used to determine the level of maturity reached by organic matter (Mackenzie et al., 1981); TA(I) and TA(II) are defined as the whole contents of C_{20} plus C_{21} triaromatic-steroids and the sum of all C_{26} to C_{28} ones, respectively (Peters et al., 2005). The mean value measured (≈ 13 %), also indicating materials generated from kerogen within a maturity range in the early stages of the oil window (Tissot and Welte, 1984).

Figure 10

DISCUSSION

Tar weathering

The studied tarballs displayed a characteristic gas chromatogram of saturates with unresolved humps caused by naphthenic components (Killops and Al-Juboori, 1990). Characteristic peaks of C_{15}-C_{35} *n*-alkanes (with a maximum at C_{22}) alternated with peaks corresponding to acyclic isoprenoids (Fig. 4). This pattern is typical of non-severely altered tar residues (Hostettler and Kvenvolden, 1994) corresponding to "level 2" of the biodegradation scale proposed by Peters and Moldowan (Peters et al., 2005). The partial depletion of short-chain *n*-alkanes in the gas chromatogram of saturated hydrocarbons (Fig. 4) is consistent with the removal of C_1-C_{15} *n*-alkanes by volatilization and also by biodegradation (Cassani and Eglington, 1991).

According to several authors (e.g. Hegazi et al., 2004), in comparison with heavy polycyclic aromatic hydrocarbons (PAHs), low molecular weight PAHs are significantly susceptible to biodegradation, solubilization and possibly to photo-oxidation. Therefore, light PAH ratios, such as methylphenanthrene/chrysene, can be used as weathering indicators of beach tarballs (Chandru et al., 2008). In this case,

this ratio shows values of approximately 3.5, which is consistent with the observation that the samples had not undergone a high degree of weathering.

Contrary to expectation, values of DBT/Phe and Pr/Ph ratios lower than unity may indicate that none of the samples lie within the marine carbonate/marl/sulphate-rich lacustrine fields on a plot of Pr/Ph versus DBT/P (after Hughes et al., 1995). Nevertheless, these observations could be explained firstly by the modification of the Pr/Ph ratio as a result of biodegradation, but mainly by the influence of biodesulphurization and/or water washing on the low contents of dibenzothiophene and other organic sulphur compounds present in crude oils and hydrocarbon seeps (Lee et al., 1995; Galarraga et al., 2010). In this context, focussing on aromatics, an anomalous methylphenanthrene index value of 0.98 (MPI-1; Radke and Welte, 1983) was recorded, possibly a result of water washing (Galarraga et al., 2010) and/or the fact that MPI-1 is not a reliable maturity indicator in organic matter derived from carbonate source rocks (Cassani et al., 1988).

Oil-source rock correlation

The major aim of this study was to determine probable source rocks for the tarball petroleum. In this regard, the analytical results suggest that most of the tarball petroleum originated from natural seepages, probably located in the Gulf of Paria along the Los Bajos fault zone where many active seeps are known to occur (Wilson, 1968; Rodrigues, 1988). It is inferred that the seepage oil was transported by ocean currents to the Paria Peninsula, where it was stranded in the form of tarballs after moderate weathering. Bermudez (1989) indicated that the sources may be large-scale seepages that have been active for a period of at least several decades.

The Naparima Hill Formation is the most likely source rock for the tarball petroleum analysed in this study. A comparison between the terpane and sterane distributions of the carbonate sub-facies “B” in this formation (see Figs 10 and 13 in Requejo et al., 1994) and a representative tarball sample (see Figs. 5a and 7) showed their nearly identical characteristics, including:

(i) the presence and relative enrichment in gammacerane (rarely found in Venezuelan oils; De Freitas, 2009);

(ii) significant proportions of tricyclic terpanes and 28,30-bisnorhopane;

(iii) considerable content of isosteranes; and

(iv) very low diasterane content.

Other evidence also supports a link between the carbonate sub-facies “B” and the tarball group studied here include the moderate sulphur content, similar maturation levels (early oil window), and the Pr/Ph and Ts/Tm ratios below. The tarball petroleum also displayed a slightly lower abundance of C_{13+} paraffins, a lower DBT/Phe, and higher Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios than the carbonate sub-facies “B”; however, these conflicting data may result from the combined weathering effects of biodegradation, water washing and evaporation (Peters et al., 2005).

The tarball petroleum samples appear to have been derived from a source rock deposited in an anoxic carbonate-dominated environment under reducing conditions. This observation is consistent with previous analysis of extracts from the Naparima Hill Formation and possibly also the Gautier Formation (Requejo et al., 1994). The sampled tarballs from the SE coast of the Paria Peninsula presented only minor variations in molecular ratios which may indicate that they were all expelled from the same source rock section during a single pulse of petroleum generation and migration.

CONCLUSIONS

The results of this research allow the following principal conclusions to be drawn:

1. About 70% of the stranded tarballs from sampling sites along the SE coastline of the Paria Peninsula can be classified as belonging to a single group on the basis of their physical characteristics.

2. All the tarballs in this group have been affected by moderate levels of biodegradation and weathering, and their similar organic geochemical characteristics indicate their derivation from a single marine carbonate source rock.

3. Petroleum in the tarballs is very likely derived from seafloor oil seepages associated with the El Bajo fault zone off the SW coast of Trinidad; this petroleum leeked from subsurface Neogene sandstone reservoirs.

4. Geochemical correlations indicate that the tarball petroleum was generated by the carbonate-dominated “sub-facies B” of the Late Cretaceous Naparima Hill Formation, a known regional source rock, with possibly some secondary input from the underlying Gautier Formation.

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FIGURE CAPTIONS

Fig. 1. (a) Location of the Paria Peninsula in eastern Venezuela and of the Gulf of Paria showing locations A and A' used to construct a N-S cross-section; (b) structural map of the Gulf of Paria, and (c) schematic N-S cross-section A-A' across the Gulf of Paria. Note: Los Bajos fault zone inside the square box in Fig. 1b.

Fig. 2. Stratigraphic units in the southern Gulf of Paria and correlation with those in the Eastern Venezuela Basin.

Fig. 3. Variations in mean monthly tarball levels recorded between 2009 and 2011 for the SE coast of the Paria Peninsula.

Fig. 4. Typical saturate gas chromatogram of the tarball group.

Fig. 5. (a) and (b), respectively, m/z 191 and m/z 177 mass fragmentograms for the tarballs analysed.

Fig. 6. Representative m/z 217 ion fragmentogram for the tarballs analysed.

Fig. 7. Example of m/z 412 ion fragmentogram for the tarballs analysed.

Fig. 8. (a) m/z 178+192 ion fragmentogram for a representative sample; (b) combined m/z 184 and m/z 198 mass fragmentograms for the same sample.

Fig. 9. Typical m/z 99 mass fragmentogram for the tarballs analysed.

Fig. 10. Characteristic m/z 231 ion fragmentogram showing triaromatic steroids for the tarballs analysed.