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Primary Migration within the Querecual Formation, Venezuela: Geological and Geochemical Evidences

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Abstract

The Querecual Formation is an over-mature 700-m-thick stratigraphic section made up of limestones of Cretaceous age. This formation is thought to be the source rock for most crudes of the Eastern Venezuela basin, including the Orinoco heavy-crude belt. The Querecual Formation has been studied in detail through 36 rock samples taken from its type section (Querecual river, Anzoátegui state, Venezuela). The distribution of organic matter was studied in hand specimens, thin sections, and polished sections. Samples were analyzed for total organic carbon, bitumen, bitumen fractions (saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes), and n-alkane distribution in the bitumen.

Primary migration within the Querecual Formation is thought to occur through macro and micro fractures. It is interpreted that primary bitumen migration in the upper two thirds of the formation occurred upward, and in the lower third, downward. Bitumen moved as the consequence of the resultant of two forces, one derived from flotation or gravity segregation, and the other one derived from over-pressure. The observed compositional bitumen's fractionation is thought to be controlled by molecular weight, polarity and structure of its constituents.
Key words: Primary migration, bitumen, saturated hydrocarbon, gas chromatography, expulsion.

Resumen

La Formación Querecual corresponde en su sección tipo a una secuencia sobremadura de 700 m de espesor, de calizas del Cretácico. Esta formación corresponde a la roca fuente de muchos de los crudos de la Cuenca Oriental de Venezuela, incluyendo la Faja Bituminosa del Orinoco. La Formación Querecual se estudió en detalle a través de 36 muestras tomadas en su sección tipo (río Querecual, estado Anzoátegui, Venezuela). La distribución de la materia orgánica fue estudiada en muestras de mano, secciones finas y secciones pulidas. En las muestras se analizó el carbono orgánico, bitumen y sus fracciones (hidrocarburos saturados, hidrocarburos aromáticos, resinas y asfaltenos) y la distribución de los n-alcanos del bitumen.

La migración primaria en la Formación Querecual ocurrió a través de macro y micro fracturas. Se ha interpretado que la migración primaria del bitumen en los dos tercios superiores de la formación ocurrió hacia arriba y en el tercio inferior hacia abajo. El bitumen migró como consecuencia de dos fuerzas, una derivada de la flotación o segregación gravitacional, y la otra consecuencia de la sobrepresión. El fraccionamiento composicional del bitumen fue controlado por el peso molecular, la polaridad y la estructura de los constituyentes del bitumen.
Palabras clave: Migración primaria, bitumen, hidrocarburos saturados, cromatografía de gases, expulsión.

Introduction

The primary migration process, by which bitumen is expelled from the source rock, is the least understood step in the sequence of processes leading to the subsurface accumulation of petroleum. The movement of bitumen within and through the source-rock with low porosity and low permeability is what has been termed primary migration. The process by which bitumen, crude oil, or gas move after expulsion from the source rock is termed secondary migration (Tissot and Welte 1984).

Studies on primary migration in petroleum source rocks are of key importance due to the information they provide about the bitumen produced and expelled, and the way this process occurs. All of this makes it possible to know about the process that initiates the formation of petroleum reservoirs and the filling up of these reservoirs within a petroleum system.

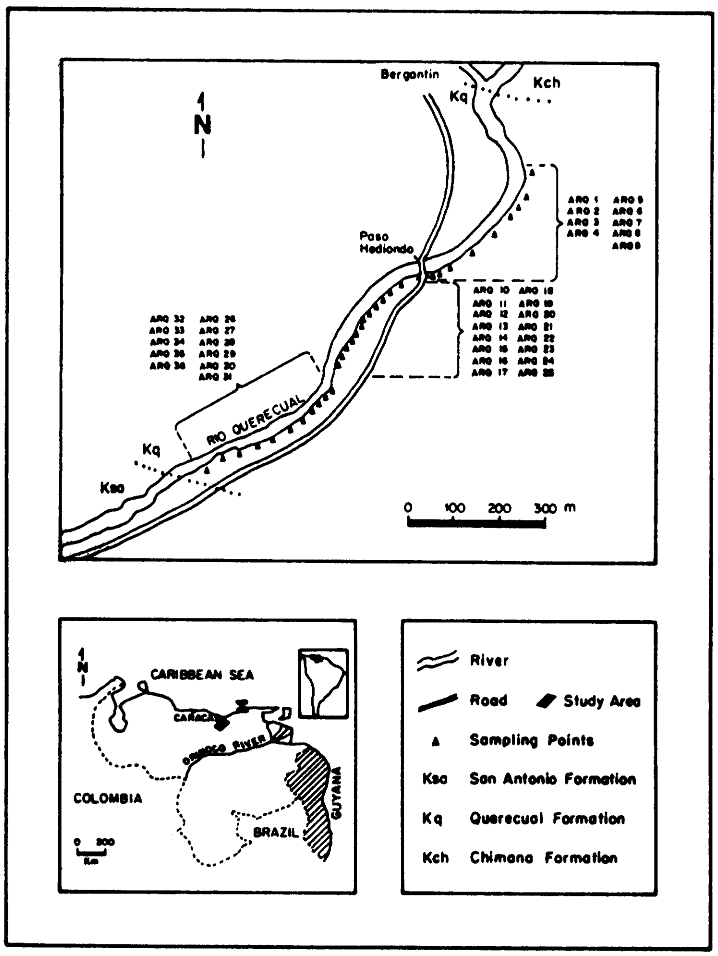

Figure 1.
Location of samples.

Different approaches have been taken in primary migration research, such as: 1. The establishment of primary migration mechanisms (Price 1976; Mc Auliffe 1978; Bray and Foster 1980; Leythaeuser et al. 1982; 1983a; Thomas and Clause 1990abc); 2. The experimental simulation of natural situations, in an effort to find reasons for the compositional differences found between crudes in the reservoir and bitumen in the source rock (Chakmakhchev et al. 1983ab; Philp and Engel 1987; Bonilla and Engel 1988; Brothers et al. 1991); 3. The recognition of primary migration evidences based upon organic constituents (bitumen and kerogen), inorganic constituents (mineralogy), and rock properties (texture, porosity, permeability) (Brukner and Veto 1983 Sajgo et al. 1983; Leythaeuser et al. 1983b; Comer and Hinch 1987; Leythaeuser et al. 1987; Leythaeuser et al. 1988ab; Leythaeuser et al. 1995; di Primio and Leythaeuser 1995;) and 4. The experimental simulation of bitumen expulsion from a source-rock (Lafargue et al. 1990).

This work studies the primary migration process in the Querecual Formation, based on the third approach mentioned above, with the purpose of determining the ways in which bitumen migrates and the changes in the composition of bitumen along the section under study. Regardless of the high degree of maturity of the Querecual Formation, the study presented on primary migration, based on geochemical and geological evidences, indicates the bitumen generation, migration and expulsion process in high-maturity phase of the source rock. Previous studies in rocks with wide maturity ranges (Littke et al. 1987; Leythaeuser et al. 1984) show that regardless of maturity there are evidences of fractionating effects due to the expulsion process of the source rock.

The Eastern Venezuela basin holds one of the largest oil accumulations of the world, which includes the oil fields of Oficina, and the Orinoco heavy-crude belt (Galarraga 1986) with reserves of the order of $3x10^{12}$ bbl (Meyer and Dietzman 1981). It is thought that most of these crudes have the Querecual Formation as their source-rock. Although this formation may have been of enormous importance as a source rock, it has not been studied in detail. The purpose of this study is to establish the geological and geochemical characteristics of the primary migration that has occurred within it.

Geology and Geochemistry

The Querecual Formation is characterized by interbedded black laminated and massive limestones, and black laminated shales, rich in planktonic foraminifera (González de Juana et al. 1980; López 1992). This formation, of Cenomanian-Coniacian age, has been described as deposited in a predominantly anoxic environment (Hedberg 1937; Vivas et al. 1988). It outcrops in the Serranía del Interior, a mountain range in the states of Anzoátegui and Monagas. The type section, located along the Querecual river, Anzoátegui state (Fig. 1), is made up of black massive and laminated limestones, that contain large discoidal carbonate concretions (González de Juana et al. 1980; López 1992). The upper part of this section includes siliceous limestones and dolostones. The thickness of the type section is 700 m (Hedberg 1937). This section is easily studied in detail along the Querecual river since it outcrops almost continuously with a dip of 80°.

The Serranía del Interior, where the Querecual Formation outcrops, is a large anticlinorium striking N70°E that is located in the northern part of the states of Anzoátegui and Sucre, that covers an area of 5600 km^2. Structurally it is formed by a folded and faulted sedimentary sequence. At the end of the Cretaceous, the rise of the igneous and metamorphic complex of northern Venezuela took place, causing a north to south compression of the existing sediments. During the late Eocene orogeny the rise of the Serranía del Interior took place, when large overthrusts developed in a north to south direction, peaking in late Miocene, and continuing into the beginning of the Pliocene. The Querecual Formation outcrops on the southern flank of the Bergantín anticline which is separated by the Urica fault from a less-disturbed southern block (Rosales 1967; González de Juana et al. 1980).

The Querecual Formation contains predominantly type II kerogen, while it is considered to be overly mature based on a vitrinite reflectance of about 2 %, its total organic carbon concentration varies from 0.2% to 5.6% (average of 1.9 %). The predominance of phytane over pristane indicates the deposition of organic matter in a reducing environment, while the predominance of C_{27} sterane over C_{29} sterane is usually associated with marine organic matter (Ailloud et al. 1980; Janezic et al. 1982; Talukdar et al. 1987; López 1992).

Experimental Methods

Sample Collection: Thirty-six rock samples were collected along the Querecual Formation type section (Fig. 1). Samples were taken approximately every 20 m of stratigraphic thickness, taking into account visible weathering, presence of organic matter accumulations, and lithological characteristics. Portions of samples for bitumen extraction were selected from fragments that showed no signs of weathering. The presence of pyrite ensures a high Fe^{++}/Fe^{+++} ratio which is indicative of no weathering or incipient weathering that has no measurable effect on the bitumen fraction (D' Aversa 1982; Garagorry 1982; Pinto de Brito 1982; Perdomo 1982).

Sample Analysis: Hand specimens and thin sections were examined in order to detect and describe all organic matter accumulations within the rock. Thin sections were also analyzed with reflected and fluorescent light. The mineralogical composition of the rocks was established by X-ray diffraction using a diffractometer Philips model 1390, with CoKα radiation at 40 Kv and 20 mA. The porosity and permeability of the rocks were determined with the Litton porosimeter-permeameter, model CMS-200. The total carbon concentration was determined by using a carbon analyzer (LECO, model E-C12). The inorganic carbon was analyzed using a Bernard Calcimeter and the organic carbon was calculated as difference between total and inorganic carbon.

Bitumen Extraction and Separation: The extraction of bitumen from the pulverized rock (130 g) was performed with dichloromethane, using a Soxhlet extraction equipment for 40 hours. The bitumen extracted was divided into fractions, asphaltenes were precipitated with n-heptane (1:40). The soluble fraction was separated using liquid chromatography on alumina (100-120 mesh, activated at 200 °C and 25 mm Hg for 12 hours). The saturated hydrocarbons were eluted with n-hexane, the aromatic hydrocarbons with toluene and a mixture of toluene:methanol (70:30) was used for the elution of polar compounds.

The saturated hydrocarbons fraction was analyzed with a Perkin-Elmer chromatograph model 8500, equipped with a 30-m silica column, a flame ionization detector, an initial temperature of 100 °C (1 minute), a heating rate of 4 °C/min., and a final temperature of 300 °C (40 minutes).

Isolation and analysis of kerogen: The separation of kerogen from the inorganic constituents was done using a HCl-HF attack. Pyrite was separated by decantation with bromoform. Rock-Eval pyrolysis was done in a

Rock-Eval II (50 mg), under the following conditions: Initial temperature of 300 °C (3 minutes), a heating rate of 25 °C/min., and a final temperature of 600 °C. The reflectance of vitrinite was determined using a Zeiss microscope.

Results and Discussion

Geological Evidences

The main evidence that bitumen moved through the Querecual Formation is the presence of organic matter accumulations observed along stylolites, in fractures parallel and oblique to stratification, and filled fossil shells. The dimension of these accumulations varies from decimeters to microns. The different styles of bitumen accumulations observed in this study are illustrated in figures 2 to 4.

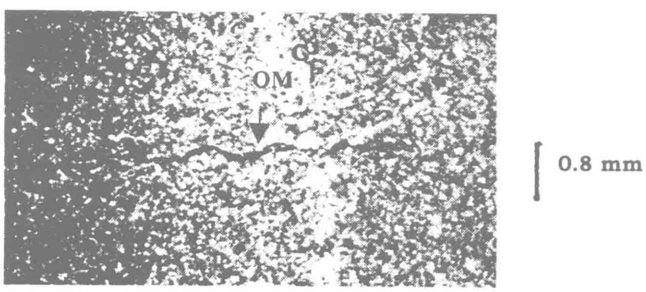

Figure 2.
Stylolite of sample ARQ4, close to the base of the Querecual Formation, filled with organic matter. C is calcite, and OM is organic matter.

In the laminated and massive limestones, organic matter was observed in stylolites parallel and oblique to lamination (Fig. 2). The accumulations in stylolites must be the consequence of organic matter movement during maturation, or the concentration of the original disseminated organic matter of the rock. The stylolites probably contained organic matter as observed in other carbonate source rock by Leythaeuser et al. (1995); these authors suggested that the carbonate redistribution by pressure solution resulted in the accumulation of organic matter in stylolites. In the massive limestones organic matter was observed mostly in fractures that are less continuous and less abundant than those found in laminated limestones. The smaller number of fractures in the massive limestone compared to the laminated limestone must be a consequence of rock texture and its influence on the fracturing process, since essentially the same organic matter moves across both laminated and massive limestone during the primary migration.

As regards the origin of the fractures filled up with organic matter, Ungerer et al. (1983) propose that the expansion of the organic matter does not play an important role in the expulsion of bitumen, since it doesn't exceed 15% of the initial volume during the catagenesis, but it may become important during metagenesis if the generation of dry gas produces a considerable expansion. This could only be possible in specific cases of hydrocarbons being actually transformed into dry gas and no bitumen expelling takes place in previous generation stages. Taking into consideration the reasons proposed by Du Rouchet (1981) and Ungerer et al. (1983) for the generation of fractures, it may be proposed, for the Querecual Formation, that the migration of bitumen was consequence of the compacting processes in the source rock. Since the kerogen has a high proportion of fluids a plastic behavior is assumed (as evidence in figure 4), which may undergo deformation under geostatic stresses. These stresses are transmitted to the fluids and the resulting pressure cause the expelling of the bitumen through the rock's pores or through the fractures. Due to the low porosity and permeability observed in the analyzed samples from the Querecual Formation, where porosity varies from 0.46% to 5.58%, and since it was not possible to detect permeability through the method used, it can be concluded that primary migration in the Querecual Formation mainly occurred through stylolites and fractures of the rock.

After fractures occur primary migration towards the top of the section occurs by flotation. The movement of bitumen by flotation towards the top of the Querecual Formation is similar to the migration mechanism in the form of drops or globules proposed by Tissot and Welte (1984), who consider the movement of bitumen in the form of drops or globules may contribute to primary migration only when there are fractures in the source rock, which is the case of the Querecual Formation.

An interesting feature is the relationship of organic matter in fractures with secondary calcite in the same fractures. Some fractures such as the one shown in Fig. 3, are lined with organic matter while the remaining space is filled with secondary calcite. Other fractures, such as the one shown in Fig. 4, are lined with calcite while the interior space is filled with organic matter. This is taken to indicate that calcite precipitated at a time when aqueous solutions were the dominant fluid phase, which was previous to significant organic matter maturation, while organic matter used the same pathways later on.

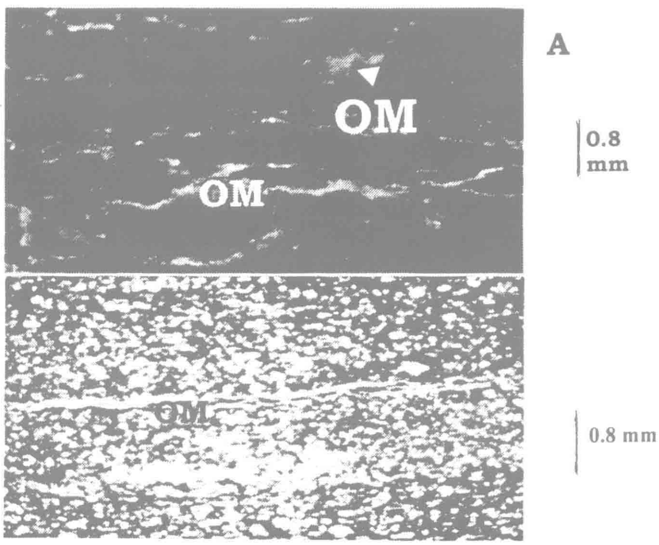

Figure 3.
A. Fluorescent organic matter in fractures parallel to the lamination of sample ARQ21 in the central part of the Querecual Formation. OM is organic matter.
B. Fracture parallel to the lamination in sample ARQ26, close to the top of the Querecual Formation. The fracture has organic matter associated with secondary calcite. OM is organic matter, and C is calcite.

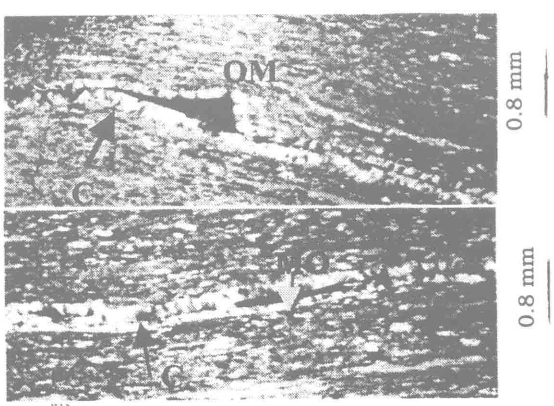

Figure 4.
Thin section of the laminated limestone MRG24 with fractures lined with calcite and filled by organic matter (A). Notice the effect of pressurized organic matter (B). C is calcite, and OM is organic matter.

Geochemical Evidences

The values of vitrinite reflectance for the kerogen samples from the Querecual Formation range from 1.7% to 2.0% (Table 1). Although vitrinite reflectance vary with kerogen type (Price and Barker 1984), since the kerogen of the Querecual Formation is only of Type II, the values of reflectance obtained establish a fairly uniform maturity for the organic matter in this formation. Pyrolysis data show little variation: Tmax, 569 °C to 580 °C; hydrogen index, 2 to 18; and oxygen index, 7 to 53 (Table 1). These data give additional support for a thermally mature kerogen along this type section. Since this stratigraphic section shows only small variations in maturity, any changes in composition of the bitumen, or its fractions, must be due to primary migration or the nature of its organic matter, but not due to differences in maturity. On the other hand, based on the study of biological markers (steranes and terpanes) in samples of the type section of the Querecual Formation, common to those analyzed in this study (Sequera 1994) a similar distribution was observed in the fragmentograms of steranes and terpanes along the section, which makes it possible, on the other hand, to establish the homogeneity in the type of organic matter along the type section of the Querecual Formation, based on the distribution of biological markers, and, on the other, consider that changes observed in bitumen and its fractions may be considered a consequence of primary migration instead of changes in organic facies.

The principal characteristics of fragmentograms indicate that organic matter in the Querecual Formation is of the mixed type (marine and terrestrial), with higher contents of sterane C27 with respect to C29, showing a predominance a marine organic matter. As to fragmentograms of tricyclic and pentacyclic terpanes ($m/z = 191$) the signal corresponding to terpane C23 was observed, which supports the contribution of marine organic matter. On the other hand, the presence of 18α-Oleanane, indicates the contribution of terrestrial organic matter (Sequera 1994)

Distribution of bitumen and its fractions. Bitumen concentration at the type section of the Querecual Formation presents a minimum in the middle part of the section (between 200 m to 600 m from the base), while at the base and top of the section concentrations are higher (Fig. 5). Similar results are obtained for the concentrations of saturated hydrocarbons, while the asphaltene fraction decreases toward the base and the top (Fig. 6). These changes are accompanied by changes in the ratio HC/NSO (saturated plus aromatic hydrocarbons/resins plus asphaltenes). The higher values of the HC/NSO ratio are observed toward the base and top, while they decrease along the middle part of the section (Fig. 7).

Figure 8 shows the concentration of organic carbon (Corg) and bitumen along the stratigraphic section of the

Querecual Formation. The Corg shows great variations that are indicative of the important differences in the organic matter accumulation-preservation characteristics of the strata that make up the Querecual Formation. The variations in the bitumen concentration are much more subdued than those that correspond to Corg, indicating that the bitumen concentration is dominated by migration effects and is not determined by the concentration of total organic matter. Bitumen is less concentrated in the middle part of the section, indicating that bitumen has migrated out of the section towards the bottom and top where the ratio Bit/Corg is highest (Fig. 9). The considerable decrease in the bitumen concentration close to the top and bottom of the section indicates that it is escaping (or has escaped) toward either end, giving rise to the start of secondary migration within adjacent formations. The asphaltenes concentration increases dramatically very close to top and bottom of the formation indicating an efficient separation of the constituents of bitumen whereby expulsed bitumen becomes more petroleum-like.

The variations observed in the bitumen and bitumen fractions along the type section of the Querecual Formation may be considered a consequence of primary migration. This migration consists of the movement of bitumen in the upper part of the formation toward the top, and the bitumen of the lower part toward the base. This movement produced higher concentrations and overall enrichment of the light fractions (saturated and aromatic hydrocarbons) along the respective migration paths. The heavy fractions (resins and asphaltenes), are preferentially retained in the middle part of the section as a consequence of their greater polarity and high molecular weight.

Other compositional parameters that are used as indexes of primary migration are the ratio of the bitumen concentration or of its fractions to organic carbon (Corg) expressed by Bit/Corg, HC/Corg, etc. (Leythaeuser et al. 1984; Escobar et al. 1989). The plot of Corg vs. Bit/Corg, presented in Fig. 9, indicates that those samples with higher Bit/Corg values are located toward the base and top of the Querecual Formation; this is considered evidence for a more effective bitumen migration in those directions. It would otherwise be difficult to explain an anomalously high concentration of bitumen at the base of the formation if downward migration is not invoked.

Saturated Hydrocarbon Distributions. The saturated hydrocarbon distributions obtained by gas chromatography group into three patterns (Fig. 10): In samples located at the top of the section the saturated hydrocarbons distributions are unimodal centered at light n-alkanes (n-C_{17} to n-C_{20}, sample ARQ34; Fig. 10). These distributions are characteristic of marine organic matter, and represent the relative increase of light n-alkanes migrated from other parts of the stratigraphic section. The distribution belonging to samples located in the middle

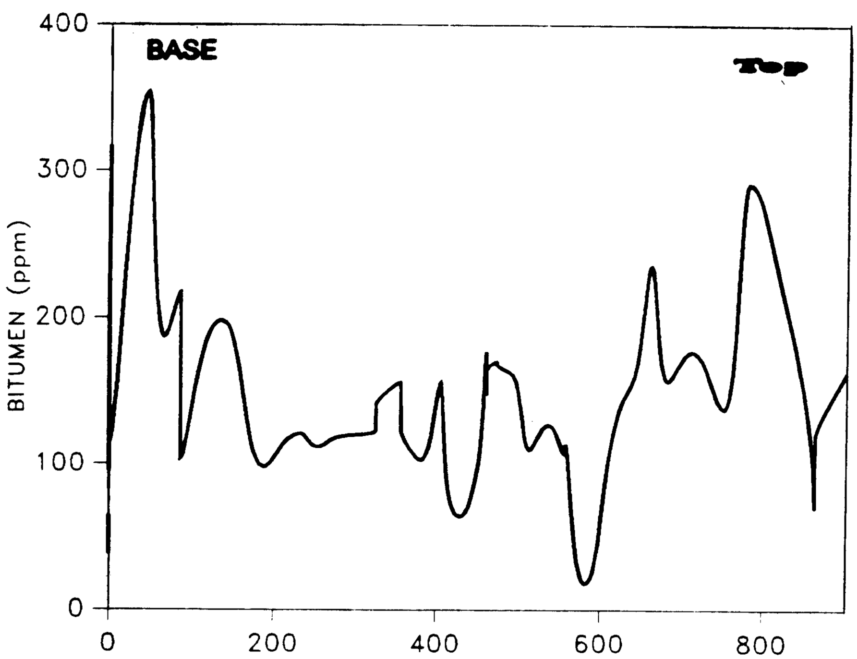

Figure 5.
Bitumen concentration along the type section of the Querecual Formation.

and base of the section are also unimodal but toward n-alkanes > n-C20 (samples ARQ3 and ARQ8, Fig. 10). These distributions are not characteristic of marine organic matter typical of the Querecual Formation, or overmature source rock; these distributions have been associated to the preferential expulsion of n-alkanes < n-C_{20} during primary migration. Some bimodal distributions of saturated hydrocarbons belong to samples located in the middle of the section (samples ARQ1, ARQ27 and ARQ28, Fig. 10). These bimodal distributions may be the result of complex mixtures of bitumen that has migrated (enriched in light hydrocarbons), bitumen that has been preferentially left behind by light fractions that moved further (enriched in heavy hydrocarbons), and bitumens that have been derived locally and have not migrated much.

The ratio pristane/n-C_{17}, decreases along the section toward the top in a form that is not similar to the Bit/Corg and HC/NSO distributions. This ratio has been used as an expulsion index (Leythaeuser and Schwarzkopf 1986); in this case it could be interpreted to indicate that there is preferential expulsion of n-C_{17} with respect to pristane toward the top of the section.

The results obtained by gas chromatography on the saturated hydrocarbon fraction, with those obtained for the concentration of bitumen and its four fractions, are concordant with the interpretation of an upward migration in the upper two thirds of the section and a downward migration in the lower third. Bitumen from any one point is the result of complex mixtures of indigenous bitumen, migrated bitumen enriched in the light fractions, and bitumen left behind by light fractions, according to a complex repeating sequence of organic matter maturation, development of overpressure, fracturing, migration and depressurization, etc. The existence of these complex mixtures of bitumens has clear implications for the established methodology of oil/source-rock correlation. This point will be considered in detail elsewhere.

SAMPLE	Ro	HI	OI	Tmax °C
TOP 0 METERS				
ARQ35	1.7 (16)	5	9	490
ARQ32	---	9	7	579
ARQ28	1.9 (8)	18	7	569
ARQ25	---	5	11	580
ARQ21	---	1	9	422
ARQ16C	---	6	14	575
ARQ15B	---	5	10	567
ARQ5	2.1 (9)	5	10	579
ARQ1	2.0 (9)	2	53	574
BOTTOM 700 METERS				

Tabla 1.
Values of vitrinite reflectance (Ro) and Rock-Eval data: Hydrogen Index (HI), Oxygen Index (OI) and Tmax for kerogen of some samples of the type section of Querecual Formation.

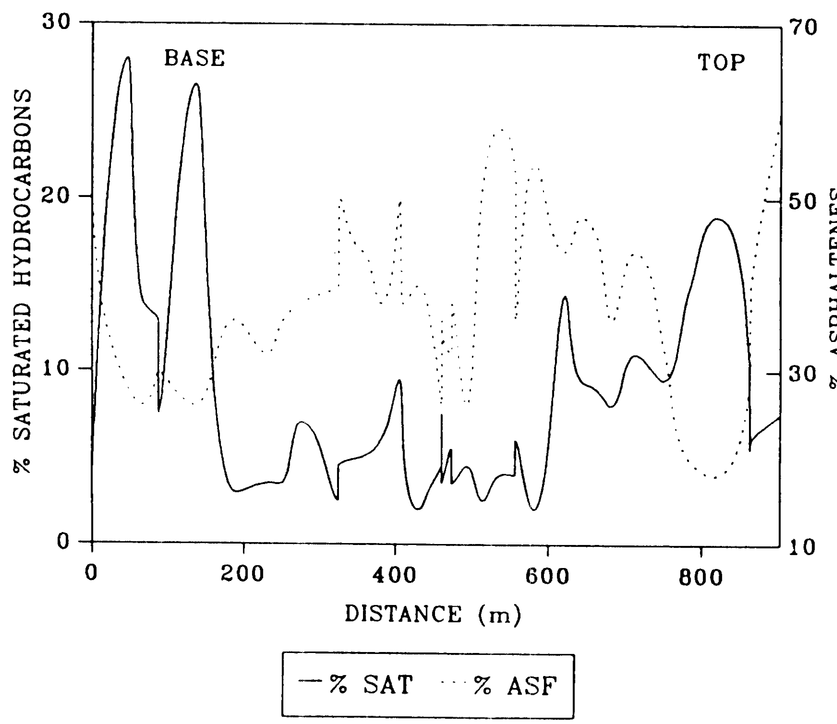

Figure 6.
Saturated hydrocarbons and asphaltenes concentration in bitumen along the type section of Querecual Formation.

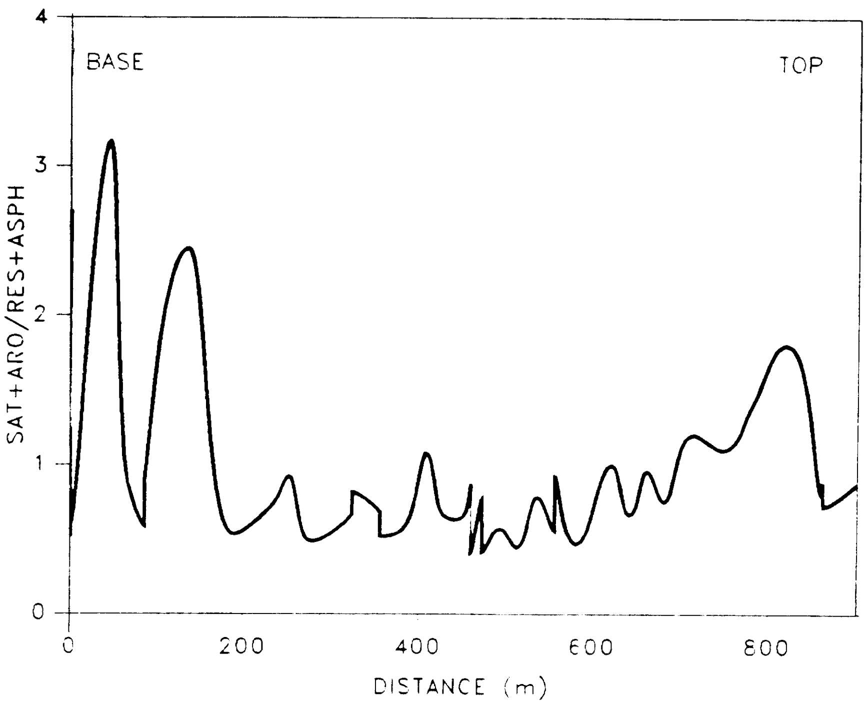

Figure 7.
Ratio of hydrocarbons to NSO compounds along the type section of the Querecual Formation.

Conclusions

The analysis of the geological and geochemical data obtained from the rocks of the Querecual Formation at its type section has led us to conclude that:

1. Organic matter has migrated within the Querecual Formation through fractures.
2. Organic matter migration has, in some cases, been preceded and, in some others, been followed by aqueous solutions that precipitated calcite along fractures.
3. Organic matter has moved from the upper 2/3 of the Querecual Formation toward the top, and from the lower 1/3 toward the bottom, probably in response to the resultant of two effects, over-pressure, which acts in any direction, and buoyancy, which only acts upward.
4. Migrated bitumen seems to suffer differentiation related to molecular weight, structure and polarity of its constituents.
5. Bitumen extracted from the rock at any position along the stratigraphic section is a mixture of indigenous bitumen and migrated bitumen. The migrated bitumen can be enriched in the high hydrocarbons or enriched in the heavy ends, if it has been "left behind". The existence of complex mixtures of bitumen at any one point has to be taken into account when correlating source-rocks with oils.

Acknowledgments

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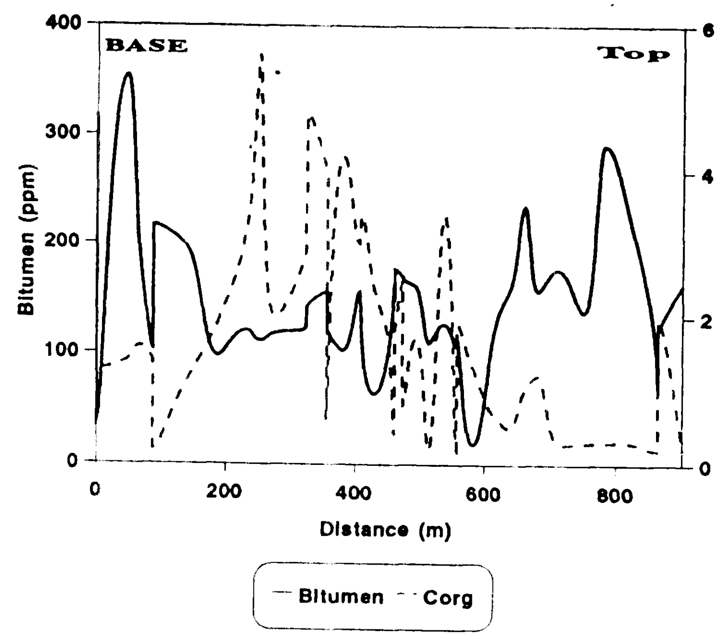

Figure 8.
Bitumen and organic carbon concentration along the type section of the Querecual Formation

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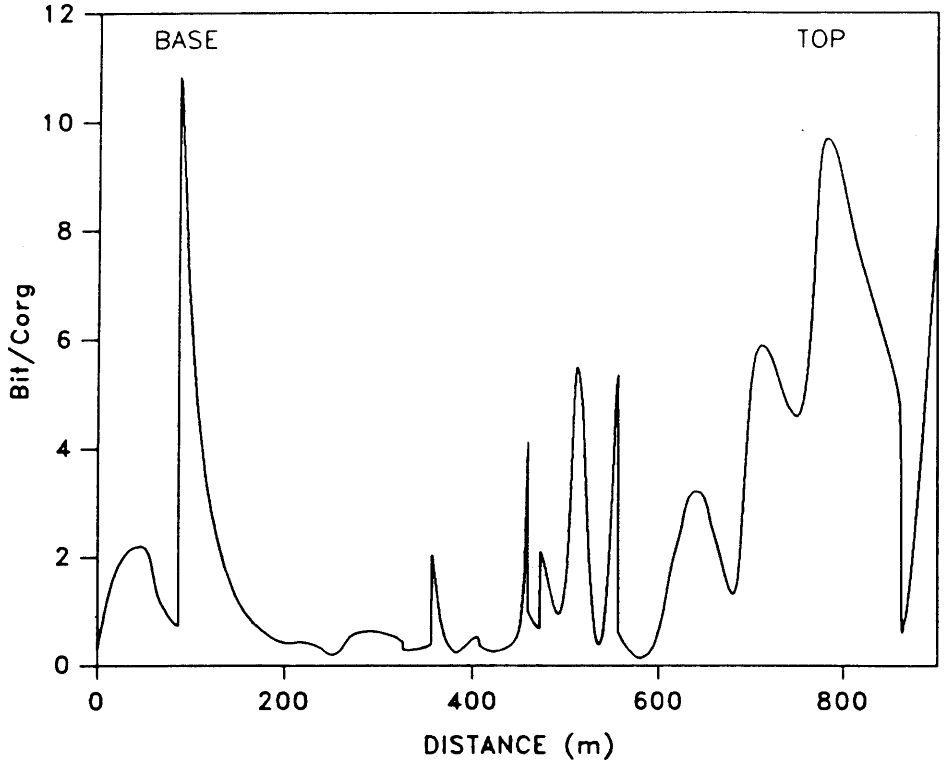

Figure 9.
Ratio of Bit/Corg along the type section of the Querecual Formation. Note that bitumen concentration are expressed in ppm and Corg in percent, so that bitumen constitutes a very minute fraction of the total organic matter.

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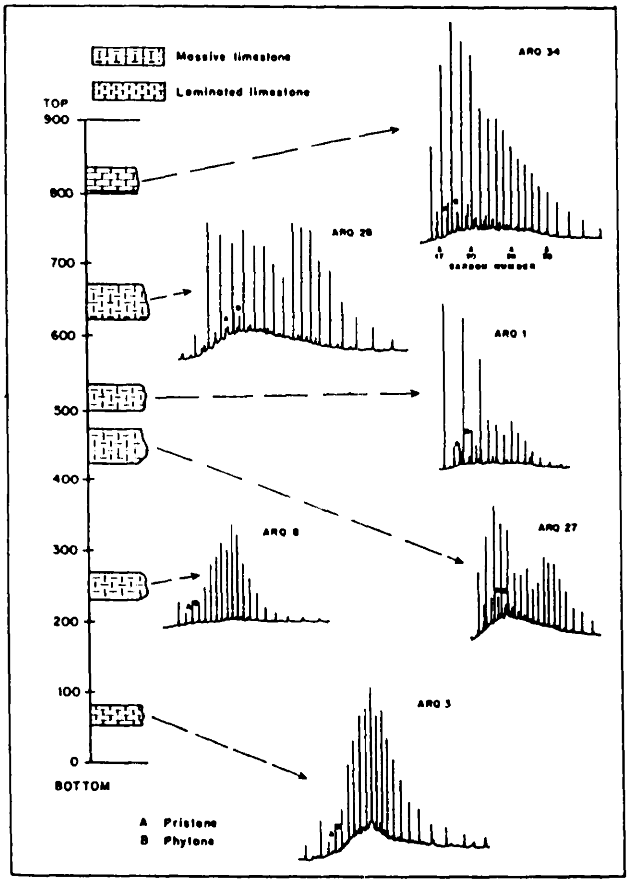

Figure 10.
Gas chromatographs of saturated hydrocarbons of bitumens of the Querecual Formation.

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