

## ORIGIN OF VANADYL PORPHYRINS IN PETROLEUM:

## LA LUNA SHALY-LIMESTONES AND RELATED PETROLEUMS

Pavle I. Premović

Department of Chemistry, Faculty of Science  
University of Niš, 18000 Niš, Yugoslavia

## ABSTRACT

Geochemical evidence for the La Luna shaly-limestones (the Maracaibo region, N. W. Venezuela) and related petroleums are inconsistent with generally accepted view that vanadyl porphyrins in petroleum are indigenous. The alternative is selective extraction of vanadyl porphyrins by degraded petroleum migrating through a sedimentary stratum containing these pigments.

## INTRODUCTION

During 1933 research effort headed by the German chemist Alfred Treibs at the Technische Hochschule of Munich probably marks the first modern study of molecular geochemistry and it had tremendous impact and far-reaching consequences for geology and earth sciences. In that year Treibs identified the major metalloporphyrins in carbonaceous shales (Treibs, 1934a) and later in petroleums (Treibs, 1934b): vanadyl ( $\text{VO}^{2+}$ ) deoxophylloerythroetioporphyrin (DPEP). Treibs concluded that by this identification "the proof that chlorophyll-bearing plants played a decisive part in the formation of bitumens and petroleums of various origins and of geologic ages is brought with full certainty" (Treibs, 1934b). Following this discovery after working with a very wide sampling of carbonaceous shales and petroleums Treibs also put forward his famous postulate for the transformation of chlorophyll a into DPEP (Treibs, 1936). Since that time, extensive investigations have been made of porphyrin occurrence in the geologic materials because they provide information on the geologic transformation of chlorophyll.

In this paper, the attention is focussed on  $\text{VO}^{2+}$  porphyrins in: the Upper Cretaceous La Luna shaly-limestones and associated petroleums of the Maracaibo region in N. W. Venezuela. Its purpose is to explore the origin of  $\text{VO}^{2+}$  porphyrins in these deposits in such manner that some light may be shed on the question of their origin in petroleum, in general. In essence, the question is: are  $\text{VO}^{2+}$  porphyrins indigenous or introduced constituent of petroleum?

### Stratigraphy and petrology

As well-defined structural unit, the Maracaibo basin (Fig. 1) came into existence toward the end of Eocene. The stratigraphic sequence from the general Maracaibo region is summarized in the stratigraphic column, Fig. 2. The stratigraphy and petrology have been described in many papers (Hedberg, 1931; Liddle, 1946; Smith, 1951).

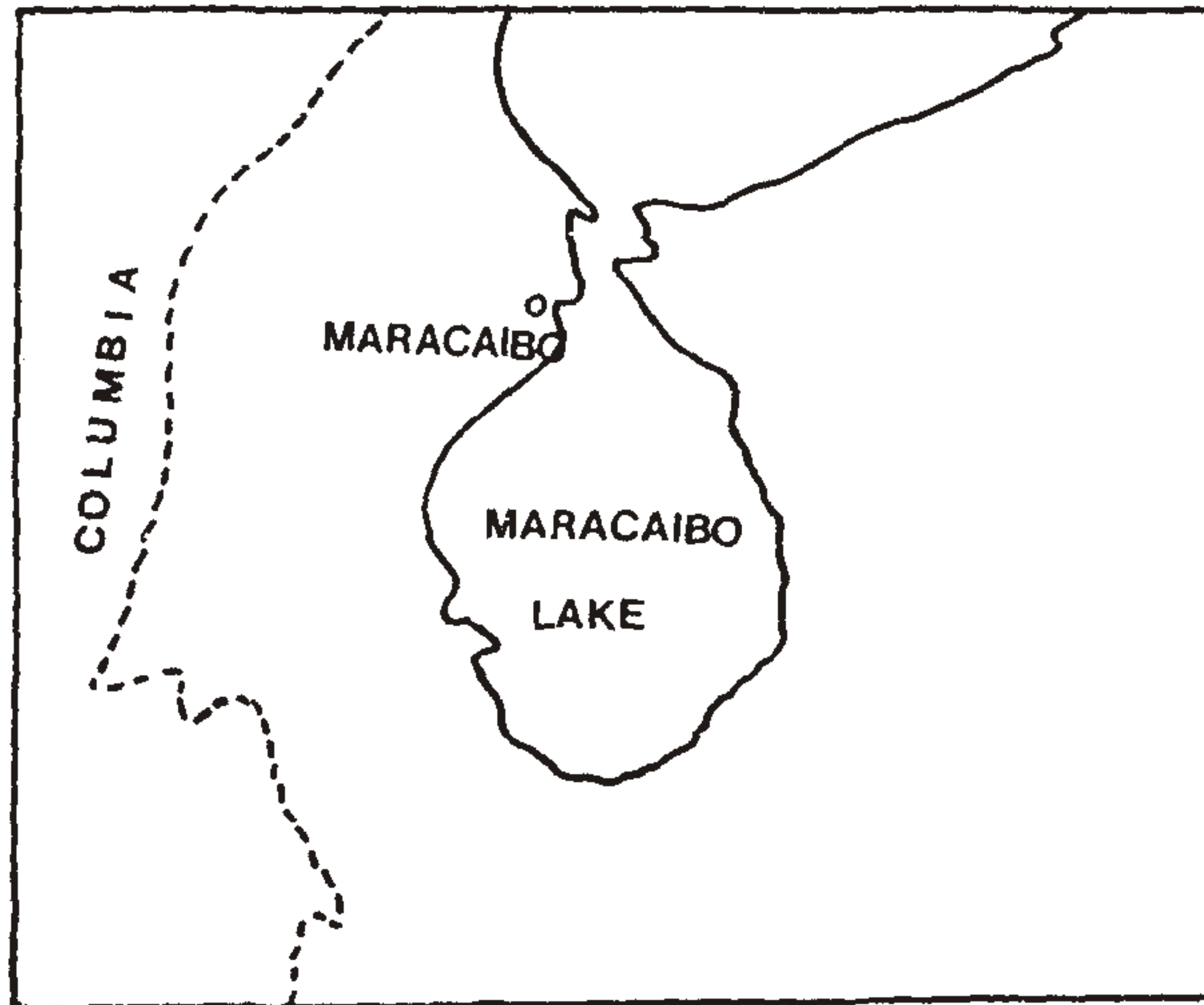


Fig. 1. Sketch of the Maracaibo region, N.W. Venezuela.

THICKNESS ft	FORMATIONS	LITHOLOGY
	LA VILA	CLAYS
	LA ROSA	SANDSTONE
1000	CONCEPCION	SHALES SANDSTONES COALS
2000		
	GUASARE	SANDSTONES
3000	COLON	SHALES
	LUNA	LIMESTONES
	COGOLLO	
4000	BASEMENT	PLUTONIC ROCKS

Fig. 2. Stratigraphic column: the Maracaibo region.

The following discussion considers only the La Luna limestones of the Cretaceous age, and adjacent formations in the Maracaibo area. The general character of this part of the stratigraphic section, may be briefly summarized as follows: the La Luna formation "is typically a thin-bedded to finely laminated, black shaly or cherty, foraminiferal (planktonic) carbonaceous-bituminous limestone" of Cretaceous (Coniacian and Turonian stages) that has been deposited in a deeper marine anoxic environment (Hedberg, 1931). Source beds of this formation are believed to have generated the major part of the Cretaceous petroleum produced in this area: La Concepcion, Sibucara, La Paz, Mara and Boscan (Hedberg, 1964). The La Luna deposit rests conformably on the Cogollo (hard, massive) limestones and in contact with either the Colon (dark gray) shales or Tertiary sandstones above.

Bacterial activity, maturity and  $VO^{2+}$  porphyrins

According to a geochemical study of the La Luna limestone samples (in the well and outcrop sections) of the Maracaibo area by Gransch and Eisma (1966) the organic carbon contents of these samples ranged from approximately 0.1 to 15%. It is generally agreed that the organic matter of the La Luna limestones of Maracaibo is derived mainly from plankton and/or bacteria decomposition products (Premović et al, 1986). The most distinctive feature of these bituminous rocks is their high content of  $VO^{2+}$  porphyrins, as much as 4% or even higher (Gransch and Eisma, 1966).

Paleobiological observations (Hedberg, 1931; Liddle, 1946; Smith, 1951) and geochemical data (Didyk et al., 1978; Premović et al., 1986) suggest that the La Luna limestones of Maracaibo were laid down in shallow-sea environment under anoxic sedimentation conditions with slow (at a rate of ca.  $2.7 \text{ mm a}^{-1}$ ) (Visser, 1982) and prolonged stable deposition. Under such conditions relatively fresh organic materials become available for bacterial sulfate reduction (Westrich, 1983). In such depositional environment with relatively high bacterial activity, porphyrins (derived from phytoplanktons and photosynthetic bacteria) (Premović et al., 1986) and other resistant organic materials (e.g., biolipids) may survive forming the high molecular weight residue. This residue, which is not directly used by microorganisms, becomes then incorporated into new geopolymeric insoluble structure: kerogen. Thus, we suggest that extensive bacterial activity in the La Luna depositional environment of Maracaibo could account for the high  $VO^{2+}$  porphyrin content of the La Luna limestones. As a result of this activity we might expect relatively high  $VO^{2+}$  porphyrin content in both the organic extractable and kerogen fractions of the La Luna limestones with the low state of diagenetic maturity.

The petrographic (Hedberg, 1931; Liddle, 1946; Smith, 1951) and geochemical (Gransch and Eisma, 1966; Didyk et al., 1975) analyses suggest that the La Luna limestones in the outcrop sections have undergone little diagenetic maturation. Hence, the  $VO^{2+}$  distribution is interpreted in terms of the original source material and subsequent diagenetic processes, although minor rearrangements and degradations occurring during the 120 million year history of the sediment may also have occurred.

Premović and coworkers (Premović et al., 1986) have analysed the La Luna limestone outcrop sample using various chemical techniques and methods, which include elemental and infrared analyses, quantitative emission and atomic absorption (AA) spectroscopies, electron spin resonance (ESR), ultraviolet (UV) and visible (VIS) spectrophotometry, electron microscopy and microprobe analysis and solvent extraction. The rock sample used in this study has approximately 6% of organic carbon by dry weight. Kerogen accounts for more than 90% of the total organic matter, Table 1. This kerogen contains 49.8% carbon, 5.3% hydrogen, 1.6% nitrogen and 8.3% sulfur. The kerogen H/C ratio of 1.3 indicates the aliphatic nature of this material and, again, the low state of diagenetic maturity. Although analytical data obtained from outcrop make interpretation somewhat difficult, we consider that the sample analysed contains largely type II kerogen (Tissot and Welte, 1978).

#### Degraded petroleum, asphalt and $\text{VO}^{2+}$ porphyrins

According to recent geochemical study by Bockmeulen et al., (1983) the Maracaibo oils show classical sequence of (bio- and water-) degradation and range from light (non-degraded) oils ( $40^\circ$  API) to heavy (highly degraded) oils (less than  $22^\circ$  API). This is supported by geologic evidence; the widespread occurrence of continental facies, erosional features, and numerous faults exposing structures promoted the oxidative degradation of the Maracaibo oils. The heavy oils of this region are also associated with meteoric waters (Miller et al., 12958). Bockmeulen et al. (1983) and other petroleum scientists (Hedberg, 1931; Liddle, 1946; Smith, 1951; Hedberg, 1964) have provided evidence that these heavy (asphalt-rich) oils developed from lighter (alkane-rich) oils and that the Maracaibo crude oils belong to one major family and have a common origin.

The most striking feature of the Boscan petroleum ( $17.2^\circ$  API) is the high asphalt content: 47.4% (Erdman and Harju, 1963). Erdman and Harju (1963) have found that this heavy (highly degraded) oil contains relatively high concentration of vanadium: 1134 ppm with 70% of the total vanadium incorporated into the asphaltic fraction (asphaltenes and resins). Their UV-VIS analysis indicated the presence of the  $\text{VO}^{2+}$  porphyrins in this petroleum: 3700 ppm with 97% of the total  $\text{VO}^{2+}$  located in the asphaltic fraction.

In contrast to the Boscan crude, the Mara petroleum ( $28.4^\circ$  API), as a moderately degraded oil, has relatively low asphalt content: 13.2%. This oil shows vanadium pattern similar to that observed for the Boscan oil, although the elemental vanadium concentration in the Mara petroleum is lower (2108 ppm) with 74% of the total vanadium located in the asphaltic fraction. The Mara crude yielded only 590 ppm of the  $\text{VO}^{2+}$  porphyrins with 90% of the total  $\text{VO}^{2+}$  porphyrins located in the asphaltic fraction. On the other hand, light (non-degraded) oils, higher than  $35^\circ$  API with less than 2% of asphaltic components, the Concepcion and Sibucara oils yielded less than 1 ppm of  $\text{VO}^{2+}$  porphyrins (Premović, 1983).

In conclusion, it seems evident in the light of geochemical evidence that the origin of both  $\text{VO}^{2+}$  porphyrins and vanadium is related to the origin of asphaltic components of the Maracaibo petroleum. Close relation between: petroleum asphaltic fraction and vanadium was first reported by Hodgson (1954) in his study of the Western Canada oils, and petroleum asphaltic fraction and  $\text{VO}^{2+}$  porphyrins was first reported by Skinner (1952), since then many other examples have been documented by other workers. In the light of the suggested relation of both  $\text{VO}^{2+}$  porphyrins and vanadium to petroleum asphaltic components of the Maracaibo crudes, the following quotation (from the study of trace element constituents of the California oil including  $\text{VO}^{2+}$  porphyrins and vanadium) from Filby (1975) is of particular interest: "the observation that trace elements observed in the California oil occur in oil-soluble form and are predominantly associated with the asphaltic components of the oil (except As) suggests that the origin of the trace elements is related to the origin of the asphaltenes and resins."

#### Asphaltic fraction and $\text{VO}^{2+}$ porphyrins

Sugihara et al. (1970) have separated a number of  $\text{VO}^{2+}$  porphyrins from the Boscan crude oil and concluded that  $\text{VO}^{2+}$  porphyrin molecule are associated with large asphaltic molecules. Other evidence for the association of  $\text{VO}^{2+}$  porphyrins with high molecular asphaltic constituents of the Boscan and other petroleum were reported by Yen et al. (1969). According to these authors, there are two types of  $\text{VO}^{2+}$  porphyrins in petroleum: one free and the other bound. The bound state can undergo transition to the free state upon the addition of free energy (10-14 kcal) either from the polarity of solvent (e.g., tetrahydrofuran) or the temperature system used. These results imply that the bound  $\text{VO}^{2+}$  porphyrin can be visualized as due to association of the (free) porphyrin entity with other relatively extensive molecular system fixed or bound to asphaltic host through the charge transfer (Yen, 1969); Yen et al., 1969; Yen, 1973) and/or the hydrogen bonding (McKay et al., 1978). It is believed that this

porphyrin entity is either predominant monomeric  $VO^{2+}$  porphyrin or much less abundant: the multi-aryl substituted or fused porphyrin (Yen et al., 1969).

Many colloidal characteristics of petroleum (e.g. gel-sol conversion, micelle stability) may be explained on the basis of these association properties of individual systems throughout the asphaltic macrostructure (Yen, 1973). Consequently, it is clear that these (inter- and intra-) associations affect geochemistry and genesis of petroleum and its polar components such as  $VO^{2+}$  porphyrins as well.

Kerogen, asphaltic molecules,  $VO^{2+}$  porphyrins and petroleum

It is now widely accepted that the most petroleum hydrocarbons are generated from kerogen, which generally occurs finely disseminated in fine-grained sedimentary rocks. The transformation process from kerogen to petroleum or thermal maturation, is accelerated by the combined effects of increasing temperature and heating time, which is usually related to increasing depth of burial.

In a first stage, corresponding to diagenesis, the transformation of organic materials continues by means of biological processes as the materials are buried at depths up to 100 m and reaches temperature of 333 K or less. During this stage the most of rather large molecules with heteroatoms (O, S, N) are released, such as asphaltic molecules and  $VO^{2+}$  porphyrins. In the light of geologic evidence the first thousand meters of the overlying Colon sedimentary rocks were laid down on the La Luna deposits of Maracaibo on the end of the Upper Cretaceous period (Senonian stage) (Mencher et al., 1953).

Deeper burial, due to further accumulation of sedimentary overburden, tectonic activity, or both, increases temperature of the sedimentary rock and its included organic matter. The term "catagenesis" is applied to transformation occurring between approximately 333 K and 423 K, depending of the geologic age of the rock (Tissot and Welte, 1978). Very obviously some  $VO^{2+}$  porphyrins produced during diagenesis might be thermally transformed and/or degraded during catagenesis. This temperature range corresponds to the burial depths of ca 2000 m to 5000 m for the La Luna limestones of Maracaibo (Didyk et al, 1975; Visser, 1982). The "principal zone of petroleum formation" (Vasoevich et al., 1966), lies within this temperature range. Mobile (alkane-rich) organic mixture (petroleum) is produced in this zone. Geologic evidence indicate that petroleum was generated in the La Luna deposits of Maracaibo from Eocene time onward (Hedberg, 1964; Zambrano et al., 1972; Bockmeulen et al., 1983; Blaser and White, 1984). Moreover, according to Visser (1982) the La Luna kerogen of Maracaibo started to expel the first hydrocarbon liquid- petroleum about 4 Ma. If the above kerogen-petroleum concept is correct then it is difficult to escape the conclusion that  $VO^{2+}$  porphyrins (and other vanadium compounds) are more likely an introduced rather than indigenous constituent of the Maracaibo petroleum.

Petroleum degradation and  $VO^{2+}$  porphyrins

McKay et al. (1978) have made a special study of deasphalting phenomenon of petroleum and concluded that "petroleum is a delicately balanced mixture of compounds that depends upon each other solubility." According to these authors, two factors primarily responsible for maintaining the mutual solubility of the petroleum components in the petroleum mixture are: the ratio of polar to non-polar components and the ratio of high molecular to low molecular components. Thus, the low solubility of highly polar  $VO^{2+}$  porphyrins (and other vanadium compounds) in light (non-polar, alkane-rich) petroleum might be responsible for their low concentrations in the Concepcion and Sibucara oils.

By the degradation petroleum composition is changed as a result of bacterial and water activities. This process by removal of (non-polar, low molecular weight) saturates entails a relative enrichment of both polar and high molecular weight components. Very obviously petroleum would become

progressively enriched in asphaltic components with the passage of time since each cycle of degradation should reduce the saturate content and enrich petroleum asphaltic components. As a consequence an alteration of the crude oil occurs from a non-polar to polar base. Thus we suggest that light petroleum and highly polar  $VO^{2+}$  porphyrins are essentially immiscible as long as a suitable ratio of polar to non-polar components in petroleum is maintained. When the ratio is altered by the degradation, polar molecules (such as  $VO^{2+}$  porphyrins) are then more soluble and more accessible to petroleum.

Like the degradation the  $VO^{2+}$  porphyrins' enrichment might take place during the petroleum migrating phases and/or in reservoir. The Concepcion and Sibucara oils are entrapped within the Cretaceous Cogollo limestones relatively rich in  $VO^{2+}$  porphyrins (Gransch and Eisma, 1966). However, the fact that the Boscan oil is entrapped with the Eocene reservoir which contains no  $VO^{2+}$  porphyrins (Gransch and Eisma, 1966) renders the reservoir interpretation less probable.

According to Bockmeulen et al (1983), the degradation of the Maracaibo oils did occur during their migration. Thus we suggest that a migrating mixture of hydrocarbons, primary (light, non-polar and non-degraded) petroleum (such as the Concepcion or Sibucara oils) altered by bacterial and water activities is transformed into the secondary (heavy, polar and degraded) petroleum (such as the Boscan oil). This degraded petroleum is enriched (and affected) by the constituents adsorbed by its asphaltic components (such as vanadium) and the constituents accumulated by its asphaltic components (such as  $VO^{2+}$  porphyrins). Different intensities of degradation, different durations, different migration pathways and reservoirs (with different mineralogical and chemical compositions) leave crudes exhibiting different abundances of both  $VO^{2+}$  porphyrins and vanadium. Obviously, some increase in  $VO^{2+}$  porphyrins (and vanadium) is to be expected, of course, because  $VO^{2+}$  porphyrins (and vanadium) are concentrated by removal of alkanes. However, the amount of alkanes lost should not exceed 25% of the original amount of oil and the actual loss of material from the oil is probably less (Winters and Williams, 1969). Even this amount of concentration is far from sufficient to explain a thousandfold (or even higher) increase in  $VO^{2+}$  porphyrins (and vanadium) (the Boscan vs. the Concepcion or Sibucara oils). A large portion of  $VO^{2+}$  porphyrins (and vanadium) present in highly degraded Boscan oil must be related to its asphaltic components. The close association of both  $VO^{2+}$  porphyrins and vanadium with asphaltic components of the Boscan oil and their relative abundances suggest a cause-and-effect relationship.

Direct evidence supporting our concept is provided by Erdman and Harju (1963). These authors demonstrated that the adsorption of vanadium in the Boscan and Mara asphaltic fractions occurred during asphaltic genesis. Indirect support is given by Gulyaeva and Lositskaya (1967) showing that the vanadium uptake would only occur when the oil contained asphaltic fraction.

#### Petroleum and non-indigenous $VO^{2+}$ porphyrins

Conventional chlorophyll-based mechanism of  $VO^{2+}$  porphyrin genesis in petroleum (Treibs, 1936; Baker and Palmer, 1978) carries with it several assumptions, corollaries and consequences. Among the most important is the implicit assumption that  $VO^{2+}$  porphyrins are indigenous to petroleum although some researchers (Radchenko and Sheshina, 1955; Hodgson et al., 1963; Gransch and Eisma, 1966) have cautioned against such a blanket assumption pointing out that, at least, some of the petroleum  $VO^{2+}$  porphyrins might be secondary components. As a consequence the presence of  $VO^{2+}$  porphyrins in petroleum is taken as an evidence which incontrovertibly supports an origin of common petroleum from the remnants of living organisms and at the same time to oppose an inorganic origin.

While it has been established that the generation of  $VO^{2+}$  porphyrins during the petroleum migration is unlikely (Park and Dunning, 1963), little or not consideration has been given to the effect of  $VO^{2+}$  porphyrin accumulation during the migration (Hodgson et al., 1963). Although the

mechanism and mode of petroleum migration are not well understood (Tissot and Welte, 1978), it is clear that petroleum, as a mobile fluid, may migrate (and be degraded) along bedding planes in sedimentary deposits containing  $\text{VO}^{2+}$  porphyrins dissolved these compounds and, thus, enriched itself. Gransch and Eisma (1970), as a result of a research of  $\text{VO}^{2+}$  porphyrins in the La Luna and Cogollo limestones from Maracaibo, suggested such a possibility by stating: "Porphyrin/vanadium complexes are soluble in crude oil... Migrating oil has to pass several layers before it arrives in reservoir rock..."

Finally, in the discussion of origin of metalloporphyrins in the Athabasca oil sands Hodgson et al., (1963) stated: "For accumulation processes, migration through a sediment rich in vanadyl porphyrins (characteristic of near-shore, highly reducing sediment) would favor a dominance of vanadyl pigments over nickel pigments in the final crude oil." According to Sighihara and Bean (1963)  $\text{VO}^{2+}$  porphyrins do dominate over nickel porphyrins in the Boscan and Mara oils.

At the present it is without doubt that  $\text{VO}^{2+}$  porphyrins of the Maracaibo oils originated in the Cretaceous La Luna and Cogollo limestones enriched with these compounds (Gransch and Eisma, 1966; Premović, 1984; Premović et al., 1986). The question is: how and at what stage  $\text{VO}^{2+}$  porphyrins were introduced in these crudes. These pigments may have originated in petroleum of Maracaibo in two ways: (a) through uptake from the La Luna and Cogollo limestones during petroleum migration; or, (b) from formation waters. It is unlikely that  $\text{VO}^{2+}$  porphyrins will be introduced via formation waters. These waters contain no appreciable amount of  $\text{VO}^{2+}$  porphyrins (Hodgson et al., 1963; Yen, 1975; Filby, 1975). Moreover, formation waters contain oxygen (Bockmeulen et al., 1983), and it is known that  $\text{VO}^{2+}$  porphyrins undergo degradation in the presence of this agent (Costantinides and Batti, 1957; Hodgson et al., 1963; Falk, 1964; Yen, 1973). This fact also indicates that the  $\text{VO}^{2+}$  porphyrin enrichment of the Maracaibo oils did not occur before or during their (bacterial and water) oxidative degradation but after this process had taken place.

Thus it appears reasonable to conclude that geochemical evidence support our view that  $\text{VO}^{2+}$  porphyrins of the Cretaceous oils from Maracaibo are more likely an introduced rather than indigenous constituent of these petroleum. In our opinion, the process responsible for this introduction is selective extraction of  $\text{VO}^{2+}$  porphyrins present in the La Luna and Cogollo limestones by degraded petroleum during their migration.

#### Conclusion

Although no petroleum are exactly alike chemically, each petroleum is a distinct and extremely complex mixture of organic compounds there is a similarity within given homologous series of  $\text{VO}^{2+}$  porphyrins among various crude oils, even though they have been produced from widely different environments and in widely different geologic eras (Baker and Palmer, 1978). For this reason, we believe that some common and universal process much have operated that selectively generated  $\text{VO}^{2+}$  porphyrins in petroleum. We suggest, by analogy with the origin of these compounds in the Cretaceous oils from the Maracaibo region in N.W. Venezuela, that this process is selective extraction of  $\text{VO}^{2+}$  porphyrins by degraded petroleum from any sedimentary rock system containing these compounds through which this petroleum had passed on its way to the trap structures. The fact that  $\text{VO}^{2+}$  porphyrins are, generally, absent or they account for only trace of organic carbon present in non-degraded oils lends support to such a notion.

Thus, in conclusion, it is likely that  $\text{VO}^{2+}$  porphyrins present in most petroleum are non-indigenous in nature. It is clear that in some crudes these compounds might be of primary origin but this is difficult to verify by any direct or indirect method, and as far as we are aware no evidence has been ever presented for any petroleum containing  $\text{VO}^{2+}$  porphyrins to support such a notion. One direct consequence of this fact is that  $\text{VO}^{2+}$  porphyrins are not reliable geochemical tracers for petroleum, and their

presence in petroleums is not an evidence supporting a biological origin of common petroleum.

Acknowledgement. This work is supported by the Republic Science Association of Serbia, region of Niš (P-32/83).

#### REFERENCES

- BAKER E. W. and PALMER S. E. (1978) *Geochemistry of Porphyrins*. In *Porphyrins*. Vol. 1 (ed. D. Dolphin), pp. 458-551, Academic.
- BLASER R. and WHITE C. (1984) Source-rock and carbonization study, Maracaibo Basin, Venezuela. *Am. Assoc. Pet. Geol. Mem.* 35, 229-252.
- BOCKMEULEN H., BARKER C. and DICKEY P. A. *Geology and Geochemistry of Crude Oils, Bolivar Coastal Fields, Venezuela*. *Am. Assoc. Pet. Geol. Bull.* 67, 242-270.
- COSTANTINIDES G. and BATTI P. (1957) Oxidation behaviour of bitumen porphyrins. *Chem. Ind. (Milan)* 39, 96-100.
- DIDYK B. M., ALTURKI Y. I., PILLINGER T. and EGLINTON G. (1975) Porphyrins as indicators of geothermal maturation. *Nature* 256, 563-565.
- DIDYK B. M., SIMONEIT B. R., BRASELL S. C. and EGLINTON G. (1978) Organic geochemical indicators of paleoenvironmental conditions of sedimentation. *Nature* 272, 216-222.
- ERDMAN J. G. and HARJU B. (1963) Capacity of petroleum asphaltenes to complex heavy metals. *J. Chem. Eng. Data* 8, 252-258.
- FALK J. E. (1964) *Porphyrins and Metalloporphyrins*, Elsevier.
- FILBY R. F. (1975) The nature of metals in petroleum. In *The Role of Trace Metals in Petroleum* (ed. T. F. Yen) pp. 31-59, Ann Arbor.
- GRANSCH J. A. and EISMA E. (1966) Geochemical aspects of the occurrence of porphyrins in west Venezuelan mineral oil and rocks. In *Advances in Organic Geochemistry* (eds. G. P. Hobson and G. C. Speers), pp. 69-88. Pergamon.
- GULYAEVA L. A. and LOSITSKAYA I. F. (1967) Reaction of oils with vanadium in aqueous solutions. *Geokhimiya* (7), 850-860.
- HEDBERG H. D. (1931) Cretaceous limestone as petroleum source rock in northwestern Venezuela. *Am. Assoc. Pet. Geol. Bull.* 15, 229-246.
- HEDBERG H. D. (1964) Geological aspects of origin of petroleum. *Am. Assoc. Pet. Geol. Bull.* 45, 1755-1805.
- HODGSON G. W. (1954) Vanadium, nickel and iron trace metals in crude oils of Western Canada. *Am. Assoc. Pet. Geol. Bull.* 38, 2537-2550.
- HODGSON G. W., PEAKE E. and BAKER B. L. (1963) The origin of petroleum porphyrins. In *Athabasca Oil Sands* (ed. M. A. Carrigy), pp. 75-100. Research Council of Alberta.



- LIDDLE R. A. (1946) The Geology of Venezuela and Trinidad. Paleont. Res. Inst. Itaca.
- McKAY J. F., AMENO P. J., GOGSWELL T. E., HANSBERGER P. M., ERICKSON R. B. and LATHAM D. R. (1978) Petroleum asphaltenes: chemistry and composition. In Analytical Chemistry of Liquid Fuel Sources (eds. P. C. Uden and H. B. Jensen) pp. 128-142. A. C. S.
- MENCHER E., FICHTER H. J. and RENZ H. H. (1953) Geology of Venezuela and its oil fields. Am. Assoc. Pet. Geol. Bull. 37, 690-777.
- MILLER J., EDWARDS K. L., WOLCOT P. P., ANISGARD H. W., MARTIN R. and ANDEREGG H. (1958) Habitat of oil in the Maracaibo Basin, Venezuela. In Habitat of oil: Am. Assoc. Pet. Geol. pp. 601-640.
- PARK R. and DUNNING H. N. (1961) Stable carbon isotope studies of crude oils and their porphyrin aggregates. Geochim. Cosmochim. Acta 22, 99-105.
- PREMOVIĆ P. I. (1983) Origin of metalloporphyrin compounds in petroleums and bituminous shales. Chem. Rev. (Serb. Chem. Soc.) 26, 129-139.
- PREMOVIĆ P. I. (1984) Vanadyl ions in ancient marine carbonaceous sediments. Geochim. Cosmochim. Acta 48, 873-877.
- PREMOVIĆ P. I., PAVLOVIĆ M. S. and PAVLOVIĆ N. Z. (1986) Vanadium in ancient sedimentary rocks of marine origin. Geochim. Cosmochim. Acta 50, 1923-1931.
- RADCHENKO O. A. and SHESHINA L. S. (1955) Origin of porphyrin in petroleum. Dokl. Akad. Nauk. S. S. S. R. 105, 1285-1288.
- SMITH J. E. (1951) The Cretaceous limestone producing areas of the Mara-Maracaibo district, Venezuela. Third World. Pet. Congr. 2, 56-70.
- SUGIHARA J. M. and BEAN R. M. (1960) Direct determination of metalloporphyrins in Boscan crude oil. J. Chem. Eng. Data 7, 269-271.
- SUGIHARA J. M., BREANTHAVER J. F., WU G. Y. and WEATHERBEE C. (1970) Research on metal compounds in petroleum- present and future. Preprints Div. Pet. Chem. A. C. S. 15, (2), C5-C12.
- TISSOT B. P. and WELTE D. H. (1978) Petroleum Formation and Occurrence. Springer
- TREIBS A. (1934) Über das vorkommen von chlorophyll derivaten in einem ölschiefer aus der oberen Trias. Ann. Chem. 509, 103-114.
- TREIBS A. (1936) Chlorophyll und hämin derivaten in bituminosen gesteinen, erdölen, erdwachsen und asphalten. Ann. Chem. 510, 42-51.
- TREIBS A. (1936) Chlorophyll und hämin derivaten in organische mineral substantzen. Ann. Chem. 517, 172-196.
- VISSER W. (1982) Maximum diagenetic temperature in a petroleum source-rock from Venezuela by fluid inclusion geothermometry. Chem. Geol. 37, 95-101.
- WESTRICH J. T. (1983) The consequences and controls of bacterial sulfate reduction in marine sediments. Ph.D. Thesis. Yale Univ. p. 530

- WINTERS J. D. and WILLIAMS J. A. (1969) Microbiological alteration of crude oil in the reservoir. Symposium on petroleum transformation in geological environments, New York. Paper PETR. 86: E22-E31 A. C. S. (Div. Pet. Chem.).
- YEN T. F. (1969) Association between large pi-system of petroleum heave residuals. A. C. S. Div. Pet. Chem. 35-42.
- YEN T. F., BOUCHER L. J., DICKIE J. P., TYNAN E. C. and VAUGHAN G. B. (\*1969) Vanadium complexes and porphyrins in asphaltenes. J. Inst. Petrol. 55, 87-99.
- YEN T. F. (1973) The charge-transfer nature of bitumens. Fuel 52 93-97.
- YEN T. F. (1975) Chemical aspects of metals in native petroleum. In Role of Trace Metals in Petroleum (ed. T. F. Yen) pp. 1-31, Ann Arbor.
- ZAMBRANO E., VASQUEZ E., DUVAL B., LATREILLE M. AND COFFINIERES  
( )1972) Paleogeographic and Petroleum Synthesis of Western Venezuela. Editions Technip.