

Vanadium in ancient sedimentary rocks of marine origin

PAVLE I. PREMOVIĆ and MIRJANA S. PAVLOVIĆ

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

and

NEBOJŠA Z. PAVLOVIĆ

Research and Development Center, The Djuro Salaj Non-Ferrous Industry, 18000 Niš, Yugoslavia

(Received February 18, 1985; accepted in revised form May 26, 1986)

Abstract—The distribution of vanadium and vanadyl porphyrins in fractions (extractable organic, inorganic and kerogen) of the Serpiano marl and the La Luna shaly limestone has been determined by employing a variety of geochemical and spectroscopic techniques including atomic absorption, atomic emission, electronic absorption and electron spin resonance spectroscopies.

High levels of vanadium and vanadyl porphyrins were found with the major part of the total vanadium located in the kerogen fractions of both rocks. In contrast, while the kerogen of the La Luna rock also contained the major fraction of total vanadyl porphyrins (70%), the corresponding value for the Serpiano marl is only 30%. No vanadyl species were present in the inorganic fraction of either rock.

It is suggested that the source of vanadium in these rocks is volcanoclastic materials and that the vanadyl porphyrin entities were incorporated into the kerogen structure through abiotic, geochemical modifications of biosynthetic pigment-chlorophyll.

INTRODUCTION

TRANSITION METALS are concentrated in marine carbonaceous shales. Vanadium (V) ranges in concentration from 1 to 100 ppm (WEDEPOHL, 1971). Many chemical forms of V are found in marine carbonaceous shales (RILEY and SAXBY, 1982) and, of these, the vanadyl (VO^{2+}) porphyrins are thought to be derived from pigment-chlorophylls (BAKER and PALMER, 1978). The presence of VO^{2+} porphyrins in these rocks was discovered over 50 years ago by TREIBS (1934) and, since this finding, there has been extensive study of the nature and occurrence of porphyrins in shaly-type marine sediments as they are prime geochemical tracers (BAKER and PALMER, 1978).

Two possibilities have been advanced to explain the origin of VO^{2+} porphyrins in carbonaceous sedimentary rocks. The first considers that porphyrin structure originates from naturally occurring pigments (*e.g.* chlorophyll *a*) and that the incorporation of V into the porphyrin occurred in extreme reducing conditions after the rock was laid down (TREIBS, 1936). The fact that V forms more stable porphyrin complexes than most other metals, and even tends to displace them, strongly supports this view. The alternative view (GLEBOVSKAYA and VOLKENSHEIN, 1948) is that the VO^{2+} porphyrins common to petroleum and other bituminous geological material come directly from respiratory pigments of certain types of marine life, particularly ascidians. HODGSON *et al.* (1963) were in agreement with this second view and suggested that the VO^{2+} geoporphyrins may have originated directly from compounds in plants other than chlorophyll. In essence, the question is: does the presence of VO^{2+} porphyrins in these rocks reveal that V-porphyrins were employed in life processes at the time of deposition or are they a consequence of a transformation of other metallo-

porphyrins (such as those contained in pigments known today) subsequent to deposition?

One of the most remarkable characteristics of the Serpiano marl and the La Luna shaly limestone is the high levels of VO^{2+} porphyrins found; as much as 0.45% (BLUMER, 1950) and 3% (GRANSCH and EISMA, 1966) has been reported. Although there have been numerous articles describing the porphyrins in these rocks, little if any consideration has been given to the nature and origin of V in these two marine shaly-type sediments. We address this question here with our studies of the V and VO^{2+} porphyrins in different fractions of the Serpiano and La Luna rocks. It occurred to us that such studies might yield information on the origin of VO^{2+} porphyrins in marine shaly-type sediments in general.

GEOLOGY, PALEOBIOLOGY AND GEOCHEMISTRY

The Serpiano marl. Carbonate sedimentation of the Swiss Alpine complex started mainly at the end of the Lower Triassic period and continued during the Middle Triassic. It reached its maximum thickness in the Swiss part of the Southern Alpine region. In this region, carbonate bank facies (Esino limestone, Salvatore dolomites) surround an euxinic basin characterized by thin-bedded limestones, dolomites, bituminous marls and shales rich in the Middle Triassic fauna fossils (PEYER, 1944). It is in this region, essentially in the "Grenzbitumenzone" of Serpiano, on Monte San Giorgio (Middle Triassic of the Limestone Alps of Ticino, Switzerland), that the pigment-rich bituminous marl (Anis/Ladin stage) occurs on which TREIBS (1934) based much of his earlier work.

The Grenzbitumenzone was deposited in a tranquil basin surrounded by reefs and their lagoons. An extremely restricted oxygen budget and poor substrate conditions prevailed on the sea-bed (RIEBER, 1973). A paleobiological study of the Grenzbitumenzone by RIEBER (1973) showed few fossil remains of terrestrial and marine plants and no other evidence of land-derived and marine plant materials was found.

The isolation and identification of VO^{2+} deoxyphylloerythroetioporphyrin (DPEP) in the Serpiano marl probably marks the first modern study of the geochemistry of organic molecules (TREIBS, 1934). Much later, BLUMER (1950) confirmed Treibs' discovery. The major component of VO^{2+} porphyrins is VO^{2+} -DPEP (up to 4000 ppm, DPEP/etio¹ ≥ 3) (BLUMER, 1950), although BLUMER and SNYDER (1967) presented evidence for the incorporation of VO^{2+} porphyrins into heterogeneous polymers with molecular weights above 1000. However, the amount of these pigments was estimated to be less than 1%. They suggested that these porphyrins are the products of heterogeneous co-polymerization of porphyrins derived from biological sources with the bulk organic matter of rock.

The Serpiano marls contain relatively high levels of transition metals such as molybdenum (up to 57 ppm) (BLUMER and ERLNMEYER, 1950), manganese (up to 40 ppm), nickel (up to 10 ppm) and zirconium (up to 15 ppm) (PAVLOVIĆ, 1983). They also contain high levels of pyrite (RIEBER, 1973) and organic matter (up to 50%) (BLUMER and ERLNMEYER, 1950).

The La Luna shaly limestone. The Maracaibo basin (N.W. Venezuela) came into existence as a structural unit towards the end of the Eocene period. The facies of the Cretaceous and Lower and Middle Eocene of this basin were deposited when the whole region was part of great Maracaibo geosyncline. The Cretaceous sedimentary rocks throughout this geosyncline reflect a structural behavior characteristic of geosynclines the world over; a thick series is overlain by limestones and bituminous shaly limestones of Cogollo and La Luna (Coniacian and Turonian stages) formations, laid down in progressively deepening water which reached its maximum depth during the La Luna time. The source beds of these formations are believed to have generated the major part of the Cretaceous oils produced in the Maracaibo area (HEDBERG, 1964).

Paleobiological studies (HEDBERG, 1931; LIDDLE, 1946; SMITH, 1951) show that these black and uniformly petroleumiferous rock contain the remains of planktonic foraminifers with no sign of fossil structures of terrestrial or marine plants.

One of the most notable characteristics of La Luna limestones is the high content of VO^{2+} -DPEP compounds, which may reach 3% or even higher (DPEP/etio ≥ 100) (GRANSCH and EISMA, 1966; DĪDYK *et al.*, 1975). They also contain other transition metals such as molybdenum (up to 12 ppm), copper (up to 10 ppm) and nickel (up to 10 ppm) (PAVLOVIĆ, 1983).

EXPERIMENTAL

Emission spectrography. Semiquantitative spectrochemical analysis was performed using a Schoentag vessel with an atmosphere of 20% oxygen in argon. The method is similar to that described by MARINKOVIĆ (1963). The spectrographic analyses were carried out in the laboratories of The Research and Development Center (RDC), The Djuro Salaj Non-Ferrous Industry, Niš, using a Carl Zeiss (Jena) Model PGS-2 spectrograph. Emission spectra were recorded on ORWO UV 1-photoplates.

Atomic absorption spectrometry (AAS). AAS was carried out in the laboratories of RDC on a Perkin-Elmer Model 360 AA spectrophotometer with digital read-out unit UDR-3. A nitrogen(I) oxide (N_2O)-ethyne (C_2H_2) flame was used. Further details of the analytical procedure and associated controls for precision and accuracy are given in PAVLOVIĆ (1983).

Electron spin resonance (ESR) and electron-nuclear double resonance (ENDOR) spectroscopy. ESR and ENDOR measurements were made using apparatus and procedures described by PREMORIĆ (1984) and by KIRMSE *et al.* (1980), respectively. ENDOR measurements were carried out in the

laboratories of The Department of Physics, Karl-Marx-University, Leipzig, GDR.

Infrared (IR) spectrophotometry. Rock samples were powdered finely and dispersed evenly in potassium bromide pellets. The pellets were then dried for at least one hour at 373 K before spectra were taken using a Perkin-Elmer 457 IR spectrophotometer set to give undeformed spectra.

Ultraviolet (UV)-visible (VIS) spectrophotometry. UV-VIS electronic spectra of sample extracts were recorded at room temperature on a Carl Zeiss (Jena) Specord Model instrument using 1 cm silica cells.

Thin-layer chromatography (TLC) and elemental analysis. Selected rock fractions were chromatographed on silica gel G using benzene/chloroform (1:1 v/v) as eluent. The porphyrin band was located under UV light (a large spot of bright red fluorescence) and the corresponding silica removed with a microspatula. The purified porphyrin was then extracted from the silica using benzene/methanol (3:1 v/v).

The elemental composition of kerogens was determined in the laboratories of The Institute of Chemistry, Faculty of Science, University of Beograd, Yugoslavia.

Analysis and fractionation. The extraction and fractionation procedure was similar to that used by SAXBY (1970, 1976) and PREMORIĆ (1984). The flow chart in Fig. 1 outlines the major steps in preparing the four fractions. These were:

a) Powdered rock (10 g) was extracted with benzene/methanol (3:1 v/v) for 90 hours in a Soxhlet apparatus. The extract constitutes the soluble organic fraction.

b) The residue remaining in the Soxhlet thimble was treated with boiling hydrochloric acid (HCl, 4 M) to remove most of the carbonates. Carbonate removal was checked by IR analysis. The HCl-soluble materials constitute the second fraction.

c) The insoluble residue from (b) above was demineralized further by repeated treatment with boiling hydrofluoric/hydrochloric acids (HF/HCl, 22 M and 0.25 M, respectively). This acid mixture removes silicates (SAXBY, 1970) and the removal was checked by IR analysis.

d) The final residue from (c) above is kerogen. It contained only small traces of inorganic minerals, including pyrite, as confirmed by AAS, electron microscopy and microprobe analysis. It was fused with excess anhydrous sodium carbonate and the fused material was then dissolved in HCl (12 M).

All fractions were examined for V (in all chemical forms) by AAS. Fraction (a) was examined additionally by ESR and UV-VIS spectroscopy for vanadium as VO^{2+} and VO^{3+} porphyrins. Unfractionated (original) rock samples (1 g) were examined by AAS for total vanadium after a fusing procedure similar to that employed for the kerogen fraction.

RESULTS

The distribution of V in the various fractions of shaly rocks is shown in Table 1. This table reveals that the levels of total V in the rock samples as determined by emission spectrography (superscript *b*), by AAS (superscript *c*) and the sum of V in the various rock fractions (superscript *a*) are in good agreement with another within experimental error.

V in sedimentary rocks occurs in a variety of chemical forms including oxides, hydrous oxides and carbonates. It also occurs as part of the structure of clays and silicates and as organo-V compounds (SAXBY, 1976). For this reason, the distribution of V between the extractable organic, HCl-soluble, HF-soluble and kerogen fractions showed marked differences in concentration of V, as expected (Table 1). The kerogen fraction of the Serpiano and La Luna rock contains

¹ Etioporphyrin III, BAKER and PALMER (1978).

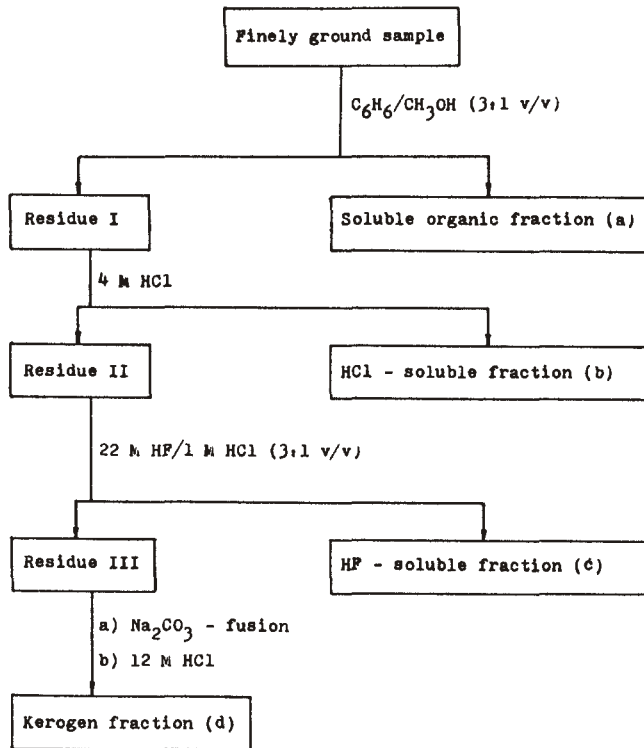


FIG. 1. Flow chart of extraction and fractionation procedure.

51% and 50% of the total V, respectively. These insoluble organic components have extremely high concentrations of V: 4400 ppm (the Serpiano marl) and 5200 ppm (the La Luna shaly limestone). The extract-

able organic matter also contains high concentrations of V: 6800 ppm (the Serpiano marl) and >2300 ppm (the La Luna shaly limestone). In these rocks kerogen V dominates over clay/silicate V (HF-soluble fraction)

Tabela 1. Concentration and distribution of V and VO^{2+} -P in rocks and rock fractions1. Serpiano marls: 2620 ppm^a, 3000 ppm^b.

| Fraction | Marl (wt.%) | V (ppm) | V (wt.%) | VO^{2+} d (ppm) | VO^{2+} -P ^e (ppm) | VO^{2+} -P (wt.%) |
|---------------------|-------------|-------------------|----------|-------------------|---------------------------------|---------------------|
| Marl | 100 | 2700 ^c | 100 | 500 | 4100 | 100 |
| Extractable organic | 4 | 6800 | 13 | 8900 | 70500 | 70 |
| HCl-soluble | 42 | 1215 | 19 | n.d. | n.d. | n.d. |
| HF-soluble | 22 | 2000 | 16 | n.d. | n.d. | n.d. |
| Kerogen | 32 | 4400 | 51 | 300 | 2500 | 30 |

2. La Luna Mara limestone: 1120 ppm^a, 1000 ppm^b.

| Fraction | Limestone (wt.%) | V (ppm) | V (wt.%) | VO^{2+} d (ppm) | VO^{2+} -P ^e (ppm) | VO^{2+} -P (wt.%) |
|---------------------|------------------|-------------------|----------|-------------------|---------------------------------|---------------------|
| Limestone | 100 | 1150 ^c | 100 | 100 | 750 | 100 |
| Extractable organic | <1 | >2300 | <5 | >3000 | >24000 | 30 |
| HCl-soluble | 76 | 550 | 36 | n.d. | n.d. | n.d. |
| HF-soluble | 12 | 900 | 10 | n.d. | n.d. | n.d. |
| Kerogen | 11 | 5200 | 50 | 600 | 4700 | 70 |

^aThe V content obtained by summation of fraction V concentrations, determined by AAS,

^bThe V content obtained by semiquantitative emission spectrography,

^cThe V content obtained by AAS,

^dThe VO^{2+} content determined by ESR, and

^eThe VO^{2+} -P content calculated from the VO^{2+} concentration given in d using 465 as the average porphyrin molecular weight (Baker and Palmer, 1978),

n.d. - not detected

and oxo-V (HCl-soluble fraction). Similar results were reported for the Toolebuc black shale (RILEY and SAXBY, 1982).

The ESR and UV-VIS spectra of extractable organic fractions indicate that VO^{2+} porphyrins are present in the Serpiano and the La Luna rocks but in widely varying concentrations (Table 1). The UV-VIS spectra of these porphyrins (after TLC purification) were similar to the spectrum of extractable and purified VO^{2+} compounds in the Serpiano marl shown in Fig. 2a. In general, these spectra with maxima occurring at about 409 (Soret), 534 (β) and 573 nm (α) are typical of VO^{2+} -DPEP compounds (HODGSON and BAKER, 1967). Concentrations of extractable VO^{2+} porphyrins were calculated from the UV-VIS spectra, using both the α -peak (573 nm, $\epsilon = 2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) and Soret peak (409 nm, $\epsilon = 3.3 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$) (HODGSON *et al.*, 1968). The presence of VO^{2+} -DPEP compounds was further confirmed by the observation of diagnostic shifts in the Soret band on complexation with piperidine (BAKER *et al.*, 1964). The piperidinate complex for the Serpiano marl (as well as for the La Luna shaly

limestone), with the branched Soret band characteristic of VO^{2+} -DPEP compounds clearly evident, is shown in Fig. 2b.

Undoubtedly, the most intriguing result is the relative abundance of VO^{2+} porphyrins incorporated into the kerogen of the Serpiano marl (30% of total VO^{2+} porphyrins) and the La Luna shaly limestone (70% of total VO^{2+} porphyrins). This is the first direct evidence of the presence of VO^{2+} porphyrins organically bound to the kerogen structure of carbonaceous sedimentary rocks. We suggest that these porphyrin entities are not the highly fused aromatic porphyrin molecules proposed by YEN *et al.* (1962) for petroleum asphaltenes. If they were, a strong π - π association between the large aromatic systems of the asphaltic host and the porphyrin system would result in high delocalization of the unpaired electron density of VO^{2+} over the associated aromatic structures. This delocalization would have a very pronounced effect on the ESR spectral parameters (YEN, 1975) and would result in ESR spectra quite unlike those that we observed. Identical anisotropic ESR spectra were seen VO^{2+} porphyrins in both the extractable organic fractions (solid solutions at 77 K) and in the kerogens of the Serpiano marl (Fig. 3) and La Luna shaly limestone (data not shown) with no difference in the ESR spectral parameters. In general, these parameters are typical of synthetic VO^{2+} porphyrins (ASSOUR, 1965) and VO^{2+} porphyrins in geological materials (O'REILLY, 1958, 1959; HOCKING and PREMOVIĆ, 1978; PREMOVIĆ, 1984). This fact indicates that the kerogen VO^{2+} porphyrin entities are, magnetically speaking, well separated units bound to the kerogen matrix through aliphatic bonds (probably polymethylene chains $(\text{CH}_2)_n$, $n \geq 4$). Such linkages would have no effect on the geometric structure or the covalency of metal-ligand bonds of the VO^{2+} porphyrin molecules incorporated thus into the kerogen structure.

In contrast to other marine carbonaceous shales in which VO^{2+} ions are also associated with the clay/silicate fraction (PREMOVIĆ, 1984), ESR analysis of the Serpiano and La Luna rocks showed only VO^{2+} porphyrins with no evidence of other VO^{2+} species.

The elemental compositions of the kerogens are as follows: Serpiano kerogen: C 55.65%, H 4.46%, N 1.73%; La Luna kerogen: C 49.82%, H 5.24%, N 1.63%. The two kerogens are not particularly rich in hydrogen: the Serpiano marl ($\text{H}/\text{C} = 1.0$) and the La Luna shaly limestone ($\text{H}/\text{C} = 1.3$) are rather low in hydrogen compared with most other carbonaceous shales where the hydrogen-carbon ratio is around 1.5 (ROBINSON and DINNEEN, 1967). Nevertheless, these data imply that the kerogens in question contain significant amounts of aliphatic structures. Moreover, the overall appearance of the IR spectra of these kerogens, and in particular the lack of strong absorbances typical of aromatic groups, support the concept of predominantly aliphatic structures. The high molecular weight VO^{2+} porphyrins in the Serpiano marl were studied in detail by BLUMER and RUDRUM (1970). Their mass spectroscopic, IR and UV-VIS data suggest that the porphyrin-

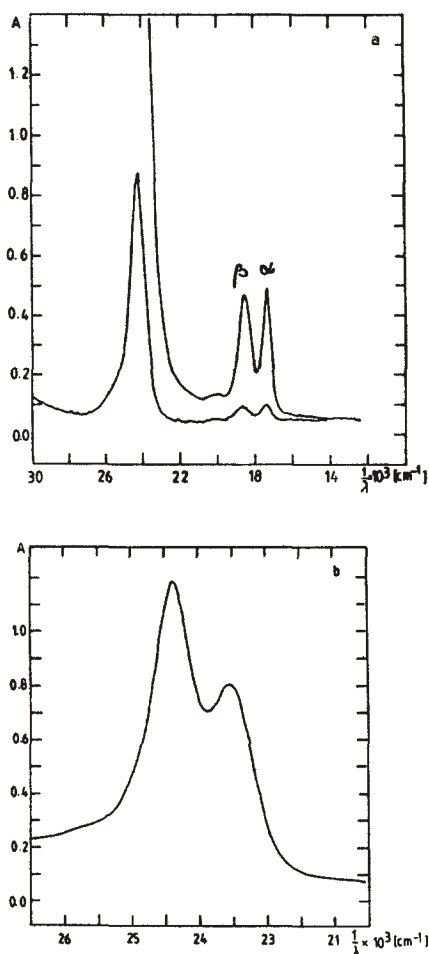


FIG. 2. UV-VIS spectrum of VO^{2+} porphyrins from the Serpiano marl in $\text{C}_6\text{H}_6/\text{CH}_3\text{OH}$ (3:1 v/v) solution: (a) uncomplexed; (b) complexed with piperidine.

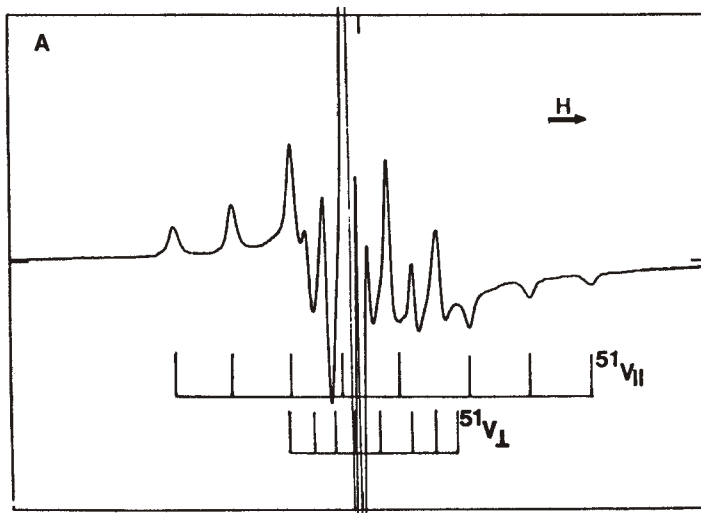


FIG. 3. First derivative, X-band ESR spectrum of Serpiano marl kerogen at 298 K. H is the magnetic field and A is the ESR absorption.

porphyrin linkage is most likely a polymethylene unit (BAKER and PALMER, 1978).

Though MULKS and WILLINGEN (1981) have reported ENDOR spectra for VO^{2+} tetraphenylporphyrin in solid solution at 100 K, we were unable to obtain ENDOR spectra for kerogen VO^{2+} porphyrins, even at 77 K. This absence of signal suggests that there is a strong magnetic interaction between VO^{2+} and other paramagnetic centers associated with the kerogen structure. Such an interaction appears to shorten spin-lattice relaxation time, T_1 , and so make the sample ENDOR-silent (BÖTTCHER and PREMOVIĆ, unpublished).

The data in Table 1 indicate that less than 10% of the total V in the kerogens occurs as VO^{2+} porphyrins: the fraction for the Serpiano marl is 5%, and for the La Luna shaly limestone it is 9%. This finding implies that the remainder of the V is in a valence state which is, at least, ESR inactive at 77 K. In contrast, V in the extractable organic fractions is predominantly in the VO^{2+} porphyrin form: it constitutes around 100% in the Serpiano marl and more than 90% in the La Luna shaly limestone (Table 1). The large excess of total elemental V (Table 1) and nitrogen (the Serpiano marl 1.73% and the La Luna shaly limestone 1.63%) over that accounted for by the VO^{2+} porphyrin contents of these kerogens suggests that other V-nitrogenous substances are present. This, however, is only a postulate and is supported by circumstantial evidence, since V is known to coordinate to ligands with oxygen atoms rather than nitrogen. The nitrogen content of the kerogens in question is higher than that required for VO^{2+} porphyrin entities alone which suggests that the free porphyrins are present also. Free porphyrins have been detected in the Serpiano marl (ca. 1% of the total porphyrins) (BLUMER, 1950) and in the La Luna shaly limestone (<1% of the total porphyrins) (PREMOVIĆ, 1983).

Finally, it can be seen from Table 1 that 70% of the total VO^{2+} porphyrins is in the extractable organic fraction of the Serpiano marl. This is in contrast to the La Luna shaly limestone where the corresponding value is only 30% and this difference suggests that the kerogenization of geoporphyrins of the Serpiano marl was less extensive than in the La Luna shaly limestone. We aim to explore this possibility further in future studies.

DISCUSSION

The source of V

V in ancient marine sedimentary rocks has been studied extensively since its nature and abundance can give valuable information as to the origin, sediment paleoenvironment and diagenesis of these geologic materials. Despite such attention, however, the origin of V in marine carbonaceous shales is still an intriguing geochemical problem, and one that is far from being solved (PREMOVIĆ, 1978).

The source of V in marine shaly-type sediments is a matter of controversy. The most attractive postulate is that V was concentrated in these rocks by the buried remains of V-rich marine organisms (VINOGRADOV, 1936). However, WEDEPOHL (1971) demonstrated by the balance calculation that this route must have been of only minor importance. A plausible mechanism for the enrichment of V in marine carbonaceous shales involves preferential adsorption and reduction of the metal by organic constituents (mainly humic substances) of the sediment. V does often appear to be associated with humic substances which, by forming soluble complexes with V, may play a significant role in its transport and fixation throughout the sedimentary column (SZALAY and SZILAGY, 1967; BLOOMFIELD and KELSO, 1973; CHESHIRE *et al.*, 1977; MCBRIDE, 1978). Certain grey and black carbonaceous shales seem to have incorporated their V in such a manner

with sea-water as the source (PREMOVIĆ, 1978). However, the Serpiano and La Luna shaly rocks have enrichments for V which are approximately 10^6 times greater than the normal sea-water level of around 2 ppb (SILLEN, 1961; WEDEPOHL, 1971). Clearly, we must look elsewhere for the source of these high levels of V of these two rocks.

One of the most intriguing characteristics of the whole Grenzbitumenzone is the occurrence of volcanic ash layers of several millimeters to several centimeters thick (RIEBER, 1973). As might be expected, volcanoclastic materials have a chemical composition similar to that of the igneous rocks of the same family. Basalt and other igneous rock contain relatively high levels of V, up to 0.11% (GMELIN, 1965). These rocks are also rich in other transition metals such as nickel, copper, molybdenum and chromium. Volcanic ash is the most likely primary source of V in the VO^{2+} porphyrin-rich Serpiano marl. Volcanic ash has been suggested as a source for unusual metal enrichment of marine shales by earlier workers (WEDEPOHL, 1971; LEVENTHAL and KEPFERLE, 1982).

When the ash is laid down on the sea-bottom, its chemical alternation is promoted by its loose porous character, fine state of division, large surface area, and the unstable nature of its constituents. The chemical weathering solution becomes rich in V which may occur, under highly reducing conditions, as V(IV) and or V(V) in a variety of chemical forms including: a) hydrous oxides or vanadates that are weakly adsorbed on clays or precipitated in limestone; b) sulfides and; c) V that is strongly bound in porphyrin or humic complexes.

A further source of V and other transition metals was the extensive beds of ash (represented in the Serpiano marl only as thin layers) that lay on the land and were stripped of their V and other transition metals by surface water which then ran into the sea. This V could then be enriched at the sea bottom by the scavenging action of marine organic materials and sulfides.

Although we have no direct evidence for the presence of ash and other volcanic materials in the La Luna shaly limestone we suggest that this deposit in the Maracaibo region is related to volcanic-sedimentary processes for the following reasons:

a) the La Luna deposit is associated with Pre-Cretaceous volcanic rocks (BUCHER, 1952; MENCHER *et al.*, 1953) and sedimentary red beds (La Quinta formation) derived, at least to large extent, from source areas of volcanic rocks (MENCHER *et al.*, 1953). During the Late Cretaceous time of Maracaibo transgression (SUTTON, 1946) an important reworking and bleaching of the Pre-La Luna volcanic and sedimentary rocks occurred (MENCHER *et al.*, 1953);

b) extensive and intense (subaerial and submarine) volcanism is known to have occurred in the Late Cretaceous period near (MENCHER *et al.*, 1953; WOODRING, 1954) and in (the Island of Toas) (LIDDLE, 1946) the Maracaibo region;

c) irregular masses of black chert and silicified beds are common in the basal part of La Luna deposit. It is considered that these deposits are formed as a result of extrusive volcanism and that the source of their silica was submarine weathering of volcanic materials (MENCHER *et al.*, 1953);

d) ashy shales are definitely found in the La Luna deposit and in significant amounts (LIDDLE, 1946).

Source of chlorophyll

Paleobiological studies show that the Serpiano marl (RIEBER, 1973) and La Luna shaly limestone (HEDBERG, 1931; LIDDLE, 1946; SMITH, 1951) contain the remains of planktonic organisms with no sign of fossil structures of calcareous algal or terrestrial plants. Thus, paleobiological evidence suggests that these plants cannot in any way be related to VO^{2+} porphyrin genesis in these rock. As a remaining alternative, the source may be ascribed to some chlorophyll-life forms which have left no identifiable fossil structures such as non-calcareous algae, phytoplanktons and chlorophyll-containing bacteria. On the other hand, geochemical data for the Serpiano (BLUMER, 1950; BLUMER and ERLLENMEYER, 1950) and La Luna (GRANSCH and EISMA, 1966; DIDYK *et al.*, 1978) rocks suggest that these deposits were laid down in a shallow-sea environment under anoxic sedimentation conditions with slow and prolonged, but stable deposition. In such an environment, where stratification of the water column occurs, the chlorobium chlorophylls from organisms growing in the anaerobic section are predominantly precursors of sediment porphyrins (SWAIN *et al.*, 1964; TAKASHI and ICHIMURA, 1968; GOPHEN *et al.*, 1974). This would suggest that pigments from anaerobic photosynthetic bacteria played a significantly more important role as a source material for VO^{2+} porphyrins in the rocks studied than chlorophylls of algal or phytoplanktonic organisms from oxic zone of sea-water column.

VO^{2+} porphyrins in marine shaly-type sediments

The VO^{2+} porphyrins that occur in marine shaly-type sediments can now be arbitrarily divided according to their physicochemical properties into the following three groups: (a) the VO^{2+} porphyrins which show evidence of minimal diagenesis; (b) the VO^{2+} porphyrins with high molecular weight and/or high aromaticity as the products of the polymerization and kerogenization processes (BLUMER and RUDRUM, 1970; BAKER and PALMER, 1978); and (c) the VO^{2+} porphyrin entities incorporated into the kerogen structure.

The incorporation of VO^{2+} porphyrin nuclei into the kerogen matrix is due, almost certainly, to abiotic, geochemical modifications of biosynthetic pigment-chlorophyll. This incorporation is not the final fate of sedimentary VO^{2+} porphyrins. Some extractable low and high molecular weight and/or highly aromatic porphyrins may be expected as products of thermal release from kerogen (EGLINTON *et al.*, 1980; MACKENZIE *et al.*, 1980). It is believed that such a process

is responsible for the production of the wide range of aliphatic petroleum hydrocarbons from kerogen (TISOT and WELTE, 1978). Thus, diagenesis and catagenesis may produce a great number of different VO^{2+} porphyrins from the ubiquitous biogenic pigment-chlorophyll. The VO^{2+} porphyrin concentration of extractable organic fractions is much greater than that of kerogens. This indicates that those VO^{2+} porphyrins formed by thermal degradation of kerogen make only a minor contribution to the VO^{2+} porphyrin content of extractable organic fraction. If this is not true, then a large amount of VO^{2+} porphyrins must have been selectively removed from the kerogen during catagenesis. In the light of modern kerogen studies, there is no reason to believe that such a process, the selective thermal release of VO^{2+} porphyrins from kerogen is likely to have occurred.

As mentioned above, the Serpiano and La Luna rocks are deposited in marine reducing environments and their organic materials are derived mainly from marine organisms (algae, phytoplanktons and bacteria). In general, the kerogen of this rock type is the product of the random condensation and polymerization of biopolymers (such as peptides, carbohydrates), their degradation products, and other monomeric materials such as lipids (WELTE, 1974). This amorphous material is thought to be derived from lipid-enriched humic materials (WELTE, 1974; NISSENBAUM and KAPLAN, 1972; NISSENBAUM, 1974; HUC and DURAND, 1974; HUNT, 1979; ISHIWATARI and MACHIHARA, 1982).

One of the most important characteristics of humic substances, that is, humic and fulvic acids, is their ability to interact with metal ions, metal oxides and metal hydroxides to form associates of widely differing chemical and biological stability. Likewise, humic materials are also characterized by their ability to sequester metal ions, in particular V ions (STEVENSON and ARDAKANI, 1972). According to DUCRET (1951) and SILLEN (1961), V exists only as V(V) in sea-water but humic substances can reduce V(V) to V(IV), in particular as VO^{2+} (VISSER, 1964; SZALAY and SZILAGYI, 1967; BLOOMFIELD and KELSO, 1973; GOODMAN and CHESHIRE, 1975; LAKATOS *et al.*, 1977; WILSON and WEBER, 1979). VO^{2+} and other V ions can then form stable complexes with many biogeochemical substances (e.g. porphyrins, humic acids) through chelation, metal exchange reactions and redox reactions.

CONCLUSIONS

1. The present data indicate extremely high concentrations of V and VO^{2+} porphyrins in the Serpiano marl and the La Luna shaly limestone. It is suggested that the source of V was probably extensive (subaerial and/or submarine) beds of volcanoclastic materials, that were leached of their V.

2. The distribution of V between the extractable organic, HCl-soluble, HF-soluble and kerogen fractions of these rocks showed marked differences in concentrations of V. V in both extractable organic and kerogen fractions dominates over clay/silicate-V and oxo-V.

3. The ESR and UV-VIS spectra indicate that VO^{2+} -porphyrins are present in high concentrations in the extractable organic and kerogen fractions of the Serpiano and La Luna rocks. It appears that VO^{2+} -porphyrin entities were incorporated into the kerogen structure through abiotic, geochemical modifications of biosynthetic pigment-chlorophyll.

Acknowledgements—The authors express their deep thanks to the following scientist who provided specimens for analysis: H. von Rieber (the Serpiano marl) and G. Eglinton (the La Luna shaly limestone). We also wish to thank L. Castle for reviewing the manuscript. The paper has benefited from comments by Robert L. Cullers. Financial support for the project (P-32/83) was provided by the Republic Science Association of Serbia, Region of Niš and Faculty of Science, University of Niš.

Editorial handling: R. G. Burns

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