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Are vanadyl porphyrins products of asphaltene/kerogen thermal breakdown?

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The idea was examined that during early stages of thermal maturation of source rocks or petroleums, the release of bound vanadyl (VO^{2+}) porphyrins (P) from the immature asphaltenes or kerogen could contribute to an increase in extractable VO^{2+}-P. To simulate such a change in the laboratory, the Dead Sea 'floating' asphalt and total organic (bitumen + kerogen) fractions of the La Luna and Serpiano carbonaceous sedimentary rocks were heated at controlled temperatures (100, 200, 300 and 400°C) for different periods of time. Residual (and altered) asphaltenes or kerogens were then separated from the heated products and analysed for VO^{2+}-P content by electron spin resonance. Three conclusions were reached: (1) thermal degradation of immature asphaltenes or kerogen generated no or very little (<1 wt%) extractable VO^{2+}-P during simulated maturation of petroleums or source rocks and thus by inference during natural maturation; (2) petroleum VO^{2+}-P by far are those that were saved from incorporation into asphaltenes or kerogen precursors (or young asphaltenes or kerogen) during diagenesis; and (3) a high VO^{2+}-P content of a petroleum is not an indication of its immaturity. © *1997 Elsevier Science Ltd. All rights reserved.*

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It is possible, by subjecting a sample of thermally immature source rock to static heating for a set time but at various temperatures, to simulate the way in which petroleums are generated at various maturity levels. After heating, the petroleum (and its asphaltenes) and associated organic compounds (e.g. biomarkers) can be examined for changes resulting from increased maturation. It is now widely accepted that petroleum formation from source rocks takes place at temperatures in the range 50–200°C. This process is extremely slow and needs millions of years to complete. For this reason, to observe simulated petroleum formation by kerogen decomposition on a laboratory time scale, temperatures >250–300°C are required[1].

Vanadyl porphyrins (VO^{2+}-P) were the first biomarkers identified in petroleum or source rocks. Several different structural types occur; the most common are the DPEP and ETIO types. Many authors have used the DPEP/ETIO porphyrin ratio as an indicator of thermal maturity, assuming that DPEP compounds are the predominant VO^{2+}-P type in carbonaceous sedimentary rocks of low thermal maturity. The transformations of VO^{2+}-P in the products from controlled static heating can be used to test similar changes deduced from natural systems, and new relations may be formulated that are difficult to observe in the natural system[2–9].

It is generally accepted that most petroleum VO^{2+}-P are released during early thermal degradation of kerogen within a petroleum source rock[1]. This conclusion is derived from the observation that VO^{2+}-P appear only when the oil window is approached and attain carbon numbers not explicable in terms of direct production of the components from any biotic precursors[10]. According to this concept, petroleum VO^{2+}-P release from kerogen is probably a two-step process. At low temperature the weaker bonds in the kerogen are broken, producing asphaltenes, and with increasing temperature these decompose further, releasing VO^{2+}-P. Some researchers disagree with this concept. Premović *et al.*[6], in their study of vanadium in the immature La Luna and Serpiano source rocks, reasoned that VO^{2+}-P formed by thermal decomposition of kerogen make only a minor contribution to the bitumen VO^{2+}-P content. This can be readily tested by means of laboratory heating experiments. In an attempt to determine the validity of this view, in this work an analysis by e.s.r. has been made of residual or altered asphaltenes or kerogens, as a function of time and temperature, after heating of asphalt and total organic fractions of source rocks.

The Dead Sea (DS) floating asphalt, the La Luna limestone and the Serpiano marl may serve as immature model sources for petroleum VO^{2+}-P and therefore useful in the study of early petroleum VO^{2+}-P genesis. In addition, these geological materials were chosen because of their high VO^{2+}-P contents (mostly DPEP type, i.e. DPEP/ETIO porphyrin ratio >100)[6,11].

Table 1 Composition of organic fractions (wt%) and VO^{2+}-P distribution (%) in various organic fractions of DS asphalt and La Luna and Serpiano sediments

		Whole organic fraction	Bitumen			Kerogen
			Methanol soluble	Resins	Asphaltenes	
DS asphalt	Organic matter	100	18	21	61	–
	VO^{2+}-P	100	1	17	82	–
La Luna	Organic matter	100	27	8	14	51
	VO^{2+}-P	100	10	1	27	62
Serpiano	Organic matter	100	11	–	3	86
	VO^{2+}-P	100	>1	–	5	>90

EXPERIMENTAL

Samples

Asphalt occurrences in the DS basin are recorded from the surface to a depth of 3600 m. Occasionally, large asphalt blocks have been found floating in the DS[12]. Early geochemical investigations of the asphalts and petroleums from the DS Basin suggest for these hydrocarbon accumulations a common origin from a calcareous source rock[11–18]. Detailed studies of saturated or aromatic biological marker hydrocarbons[19] and of VO^{2+}-P isolated from asphalt and petroleums from the DS region by high-performance liquid chromatography (h.p.l.c.) show that the asphalts are products of early generation from an immature source rock. The unheated DS asphaltenes contain 77.5 wt% C, 8.5 wt% H and 1.5 wt% N and have an H/C atomic ratio of 1.3. The DS floating asphalt contains 1000 ppm by wt of VO^{2+}-P[11].

Both the Triassic Serpiano carbonaceous marl and the Cretaceous La Luna petroliferous limestone samples used were from the outcrop sites. The elemental analyses and H/C atomic ratios of their kerogens are characteristic of their immature nature with respect to petroleum generation. The unheated kerogens contain: 61.0 wt% C, 5.5 wt% H (H/C = 1.1) and 4.0 wt% N (Serpiano), and 71.5 wt% C, 6.5 wt% H (H/C = 1.1) and 5.0 wt% N (La Luna). Bitumen fractions of these rocks are characterized by a high concentration of VO^{2+}-P (Serpiano marl[6] and La Luna limestone[20]).

Isolation of asphaltenes/kerogen and e.s.r. analysis

The procedures for isolation of various organic fractions of asphalt or source rocks (heated or unheated samples) and e.s.r. analysis of VO^{2+}-P have been presented in previous publications[6,21,22].

Gel permeation chromatography (g.p.c.)

G.p.c. of the DS asphaltenes was carried out on Sephadex LH-20 with an exclusion limit of molecular weight (MW) ~2000 and Styragel 1000 with an exclusion limit of MW ~30 000. The Sephadex column was calibrated using a meso-P dimethyl ester–phaeophytin mixture[23]. Polystyrene standards were used for MW calibration of the Styragel column. The eluates from the Sephadex and Styragel experiments were combined to give three arbitrary MW fractions: L (<4000), M (<8000) and H (<30 000).

Heating

The isothermal heating experiments were carried out at 100, 200, 300 and 400°C. Quartz tubes (15 cm long, 0.4 cm i.d.) containing known amounts of asphalt (200 mg) were evacuated and sealed. These tubes were placed in an electric oven at a desired temperature. Tubes were withdrawn from the oven at different times, allowed to cool (in air) to room temperature and then cracked open. A similar isothermal heating procedure was used for pure DS asphaltenes and their g.p.c. (L, M and H) fractions as well as for kerogens of the bituminous rocks. The asphaltenes and rock kerogen were isolated and analysed for VO^{2+}-P by e.s.r. During the course of heating DS asphaltenes and rock kerogens to 300°C, no or very little (<1 wt%) bitumen fractions were generated. In addition, these fractions contained no or only traces of VO^{2+}-P (examined by e.s.r.).

Elemental analysis

The samples were subjected to microanalysis with elemental analyser.

RESULTS AND DISCUSSION

Table 1 shows the VO^{2+}-P distribution among the asphalt (methanol-soluble, resins, asphaltenes) and source rock (methanol-soluble, resins, asphaltenes, kerogen) organic fractions. The results indicate that the asphalt asphaltenes (>80 wt%) and kerogens (La Luna 62 wt%; Serpiano >90 wt%) account for the major part of the VO^{2+}-P.

A typical e.s.r. spectrum of VO^{2+}-P incorporated into the DS asphaltenes framework is illustrated in *Figure 1*. Similar spectra were obtained for the VO^{2+}-P of the asphalt, its fractions (methanol-soluble and resins) and its g.p.c. (L, M, H) fractions as well as for the rock kerogens. *Figure 2a* shows the change in relative e.s.r. signal intensity (N, normalized to the signal intensity of unheated DS asphaltenes)* of VO^{2+}-P of heated DS asphaltenes as a function of heating temperature and time. As this intensity is directly proportional to the VO^{2+}-P concentration, it can be deduced that up to ~300°C no change in the asphaltene VO^{2+}-P content is

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* Signal intensity (proportional to the VO^{2+}-P content) was calculated by double integration of the first-derivative ^{51}V hyperfine ($m = -3/2$) line using the Korak computer system. The VO^{2+}-P content was normalized since some doubt existed regarding the concentration coefficient that should be used to convert the $m = -3/2$ signal intensities to absolute concentrations

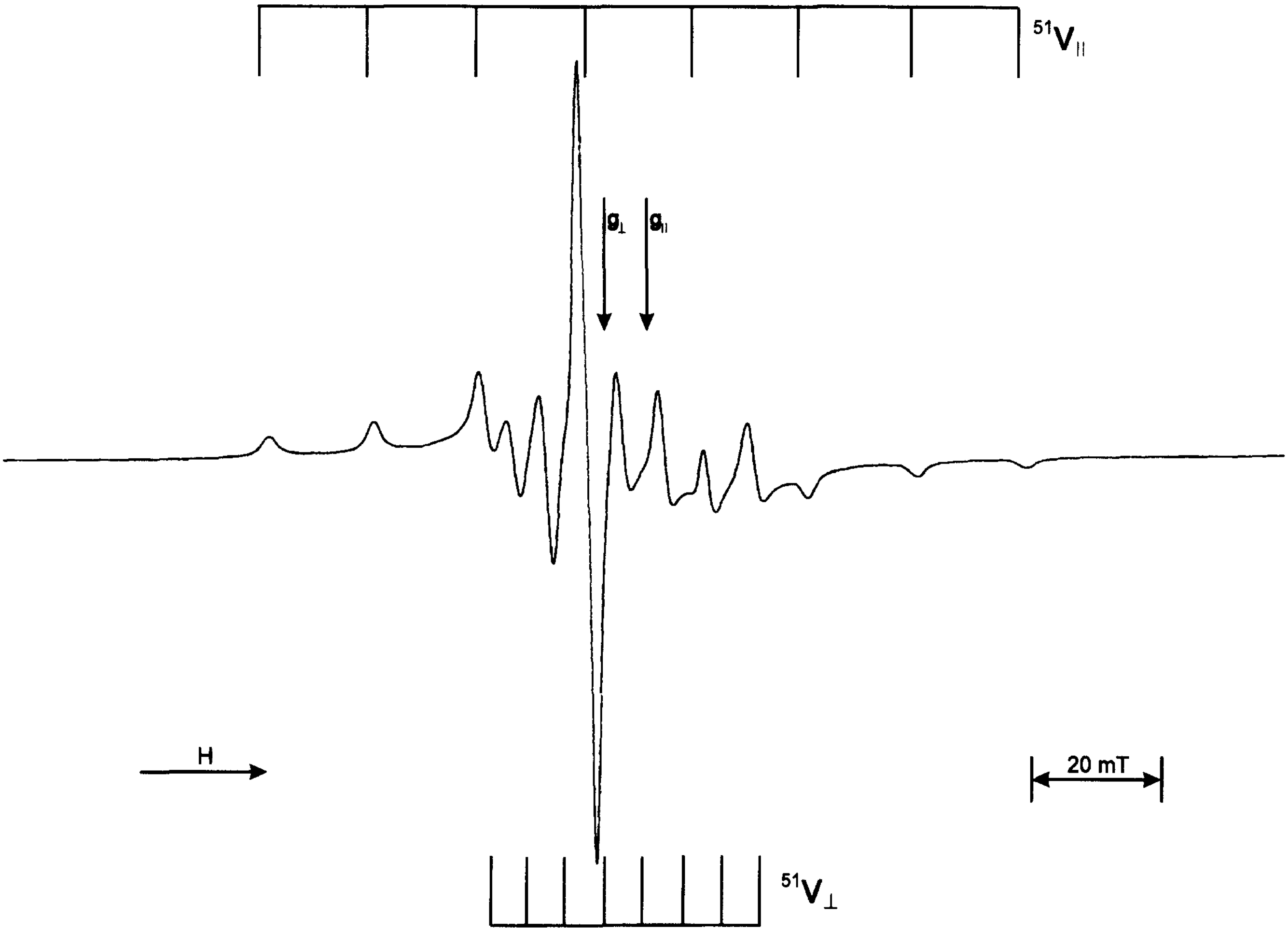

Figure 1 First-derivative room-temperature X-band anisotropic e.s.r. spectrum of VO^{2+}-P of the DS asphaltenes

detected. As reflected by the estimated uncertainties given in *Figure 2a*, very small differences (<1.0 wt%) in the asphaltene VO^{2+}-P concentration would be detected by this method. The VO^{2+}-P content of asphaltenes (within heated DS asphalt) began to decline sharply at 400°C, and reached 48% of the initial VO^{2+}-P content in <1 day. Similar results were obtained for pure asphaltenes (*Figure 2b*) (and its g.p.c. fractions), methanol-soluble fraction (*Figure 2c*), resins (*Figure 2d*) and La Luna isolated kerogen (*Figure 2e*). To assess any catalytic effect of the rock silicate matrix, simulated maturation effects for both the isolated La Luna kerogen and La Luna kerogen within a carbonate-free concentrate are compared in *Figure 2e*. No difference was observed (within experimental error) between the two throughout the entire region. Similar results were found for the Serpiano materials.

The significance of these observations is that at still lower temperatures, that is, geological temperatures (~50–200°C) characteristic of the oil window stage[24], VO^{2+}-P release by immature asphaltenes or kerogens would be expected to be insignificant. Thus, if natural thermal activity were the controlling factor in petroleum generation and maturation, the resulting crude should have virtually no or little secondary VO^{2+}-P, i.e. VO^{2+}-P produced through the decomposition of immature asphaltenes or kerogen. This implies that by far the predominant part of petroleum VO^{2+}-P is that which was saved from incorporation into asphaltenes or kerogen precursors (or young asphaltenes or kerogen) during diagenesis, and the VO^{2+}-P-rich asphaltenes or kerogen would release no or very little VO^{2+}-P in the early crude production stage. This conclusion contradicts the current view that an immature petroleum is characterized by a high VO^{2+}-P content[25]. The present study has also shown that VO^{2+}-P are quite resistant to thermal action, and it seems logical to believe that VO^{2+}-P would perhaps tend to be preserved to a greater extent than other more 'fragile' organic compounds making up the biological residues of protobitumen or protokerogen.

For comparison, a mature kerogen ($H/C = 0.8$) isolated from the La Luna source rock sample taken from between 4400 and 4600 m depth, and containing a relatively high concentration of VO^{2+}-P (DPEP/ETIO porphyrin ratio = 0.56)[26] was heated to ≤ 300°C. However, the VO^{2+}-P decay pattern for this kerogen was similar to that for immature kerogen. This result suggests that natural maturation of the La Luna kerogen had no effect on the release of VO^{2+}-P. It is important to note further that it is not a question of a petroliferous environment not reaching a high enough temperature to bring about the release of VO^{2+}-P within the asphaltene or kerogen structures; rather, it is a matter of the asphaltenes or kerogen not accounting for VO^{2+}-P release at any temperature ≤ 300°C.

In the second part of this study, the effect was examined of burial depth on the bitumen VO^{2+}-P content of the La Luna rock samples exposed to various temperature levels of natural heating during their geological histories. A particular feature of the La

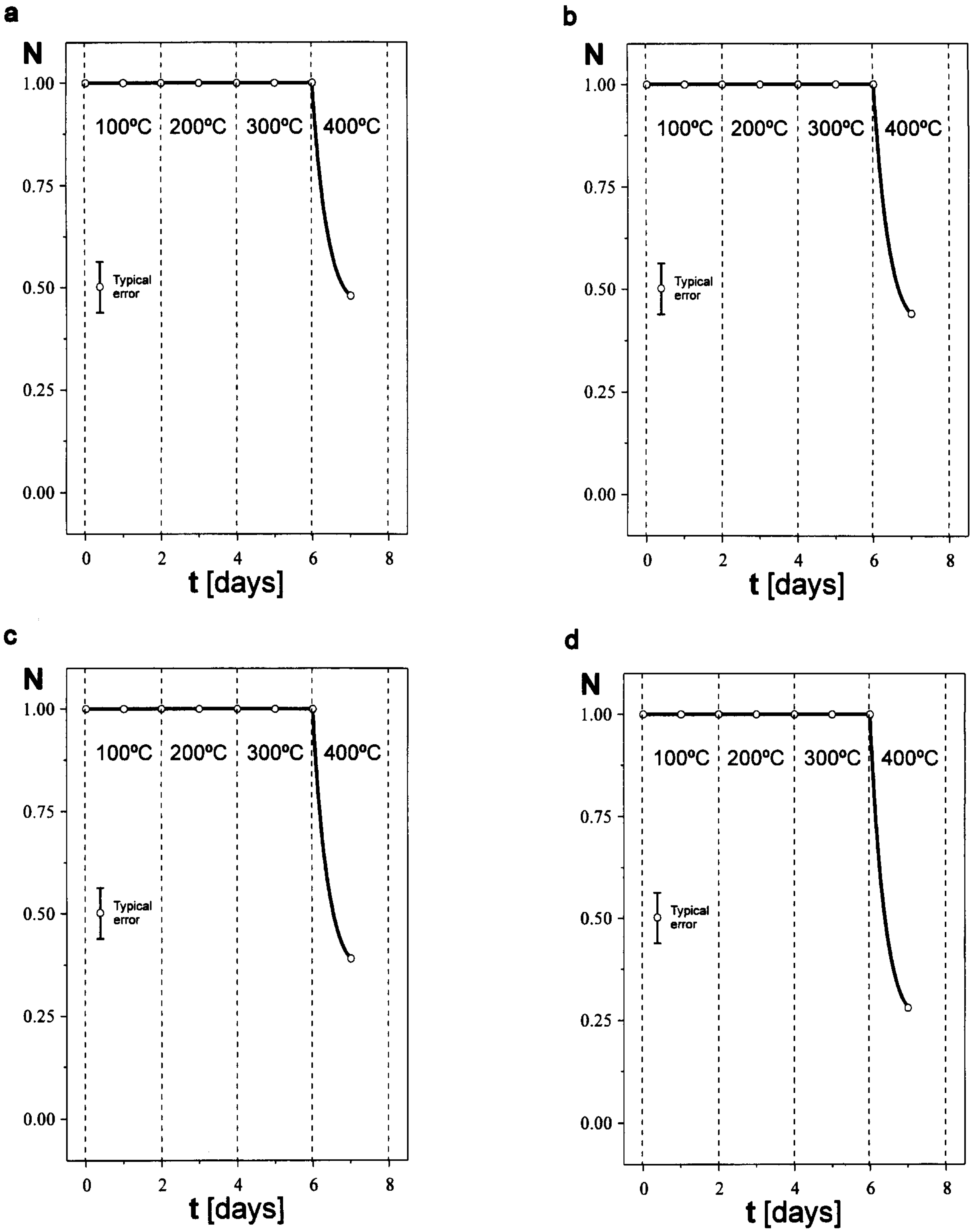

Figure 2 Decrease in normalized e.s.r. signal intensity N of VO^{2+}-P as a function of time, the temperature changes being from 100 to 400°C at 100°C increments during laboratory heating of (a) DS asphalt; (b) DS pure asphaltenes; (c) DS methanol-soluble fraction; (d) DS resins; (e) isolated (pure) La Luna kerogen (O) and kerogen within carbonate-free La Luna sample (Δ)

Luna Formation is the uniformity of composition across the deposit at the same levels of maturation. *Figure 3* shows quantitative data for the average concentrations of bitumen VO^{2+}-P with increasing depth of burial, normalized to the appropriate VO^{2+}-P content of the shallow samples (~30 000 ppm by wt) at the depth range 0–200 m.

Figure 3 shows that, under geological conditions, the concentration of bitumen VO^{2+}-P begins to decrease dramatically between 1000 and 2000 m, and drops to almost zero (<50 wt ppm) at lower depths (>5500 m). A similar decrease in VO^{2+}-P content is observed for the kerogens of the La Luna rock samples studied. According to Talukdar *et al.*[25], the La Luna source rock reached maturity within the oil window at depths between 3600 and 4500 m. It is obvious then that the dramatic decrease in bitumen VO^{2+}-P shown in *Figure 3* does not accord with the current view that substantial quantities of

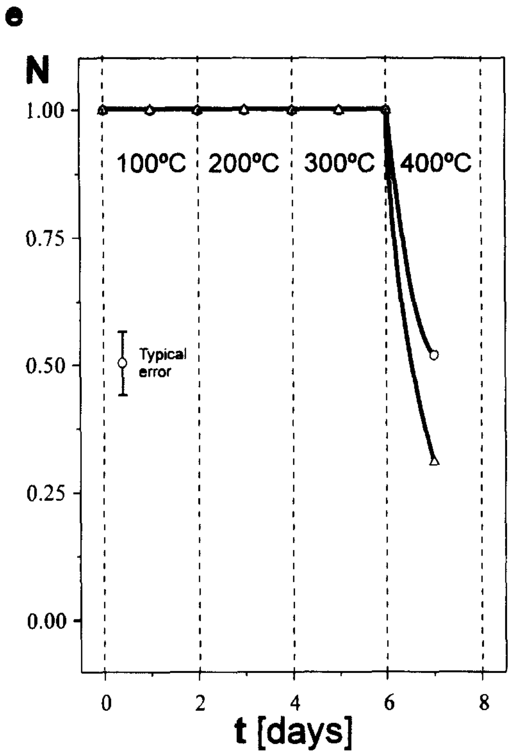

Figure 2e

bitumen VO^{2+}-P are generated from the thermal breakdown of kerogen. That is, if VO^{2+}-P originated through degradation of kerogen, then it would be expected under geological conditions that the bitumen VO^{2+}-P content would start to increase with the onset of petroleum generation (125–130°C)[27], reaching a maximum at higher maturation (145–160°C)[27], i.e. >4000 m.

Gransch and Eisma[28] attributed the rapid decrease in bitumen VO^{2+}-P content to thermal destruction of VO^{2+}-P with increasing burial temperature. However, the present-day temperatures in the La Luna Formation at depths between 1000 and 2000 m do not exceed 70°C[25]. These authors also claimed that the regional heat flow since the deposition of this formation probably did not change significantly. The observed dramatic decrease in bitumen VO^{2+}-P content of the La Luna rock samples cannot be ascribed to thermal action, since the present results have clearly demonstrated that the VO^{2+}-P are thermally stable on heating to 300°C (or even higher). Also, this observation indicates that thermal effect cannot be regarded as being responsible for what appears to have happened in nature. Whether the apparent decrease of the bitumen or kerogen VO^{2+}-P content with burial depth can be attributed to a change in concentration of available VO^{2+}, depositional factors or other effects remains to be determined.

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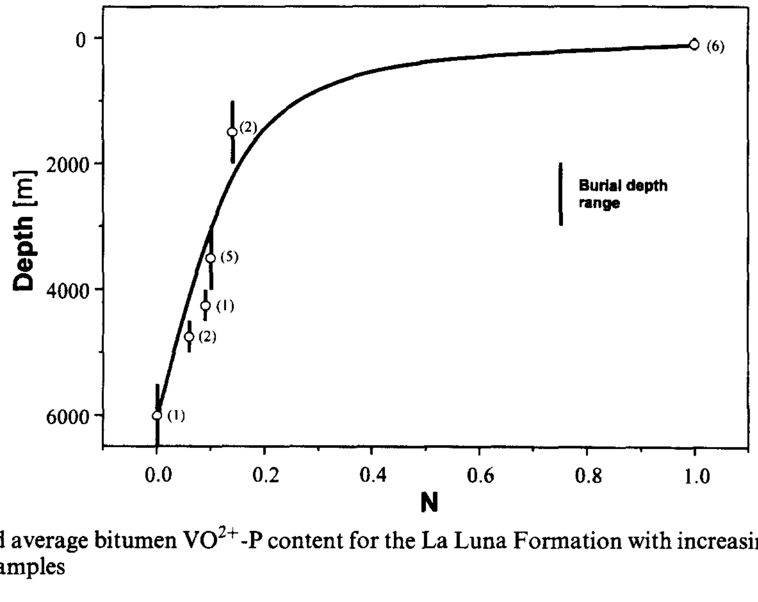

Figure 3 Plot of normalized average bitumen VO^{2+}-P content for the La Luna Formation with increasing depth of burial. Bracketed values indicate number of samples

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