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Vanadium of petroleum asphaltenes and source kerogens (La Luna Formation, Venezuela): isotopic study and origin ☆

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Abstract

High-resolution mass spectrometry indicates that the isotopic abundance of ^{50}vanadium (V) of the Late Cretaceous La Luna petroleum asphaltenes and related source kerogens of marine origin (both highly enriched with V > 2000 ppm) is higher by about 3.5% than that of inorganic source ($VOSO_4 \cdot 5H_2O$, Merck). Similar results are obtained with the isotopic analysis of the asphaltenes (containing high V) extracted from the floating asphalts (Dead Sea, Israel). We propose that the difference in the $^{50}V/^{51}V$ values between the La Luna petroleum asphaltenes/source kerogens and inorganic source can be best ascribed to the biological processing of the seawater V. The fact that the isotopic composition of V of the vary over a very narrow range (2.46–2.52) suggests an essentially same (or similar) and fixed (micro)-biological source of V. Isotopic analysis was also extended to the methanol-soluble fractions of the La Luna asphaltic petroleums (DM-119/-120/-124) highly enriched with extractable (alkyl) vanadyl-porphyrins (VO^{2+}-P). This analysis shows that the isotopic abundance of ^{50}V for the methanol-soluble fractions agrees (within the limits of experimental error) with those of the asphaltenes/kerogens.

Keywords: Vanadium; Isotopes; Petroleum; Asphaltenes; Kerogen

1. Introduction

The origin of high ^{50}vanadium (V) associated with the asphaltenes in asphaltic petroleums, in general, is one of the intriguing problems of petroleum geochemistry since its origin is undoubtedly closely related to the origin of an immature source kerogen itself and the associated asphaltic petroleum [1]. Although there is no general agreement on the issue, majority opinion seems to incline toward a non-endemic origin of V associated with an immature source kerogen. According to this view, the V incorporation into this kerogen is essentially due to abiotic, diagenetic reactions of initial humic substances with the associated seawater (inorganic) V^{5+}.

It is suggested that the bulk of the La Luna source kerogens (abundant in V) are derived from the organic remains of phytoplanktons giving a rise to humics enriched by non-endemic V during diagenesis [2]. Thus, it is not unreasonable to suggest that the La Luna immature petroleum asphaltenes/source kerogens abundant in V (or, at least, those parts of their macromolecular skeletons which are highly enriched with V) are relics of initial marine humic substances. These humics were also enriched with V though the relative V abundance in the La Luna immature petroleum asphaltenes/source kerogens obviously require an additional source of their V beside common seawater [2]. High vanadyl-porphyrins (VO^{2+}-P) are especially associated with the asphaltenes of La Luna asphaltic petroleums and related source kerogens of marine origin [2–4].

Whilst considerable attention has been paid to the isotopic composition of the various forms of non-metals (e.g. C/S) in petroleum [5], few studies have documented biological fractionation of transition metals because of difficulty of measuring precisely the isotopic ratios of these metals [6]. In contrast to relatively light elements (e.g. C/O/N/S), transition metals such as V may not be fractioned substantially by inorganic processes because the relative mass difference between V isotopes is less than that of C/O/N or S isotopes. However, biological activity may produce measurable V-isotopic fractionation because the metabolic processing of V involves a number of steps, such as transport across membranes and uptake by enzymes, that may fractionate isotopes [6].

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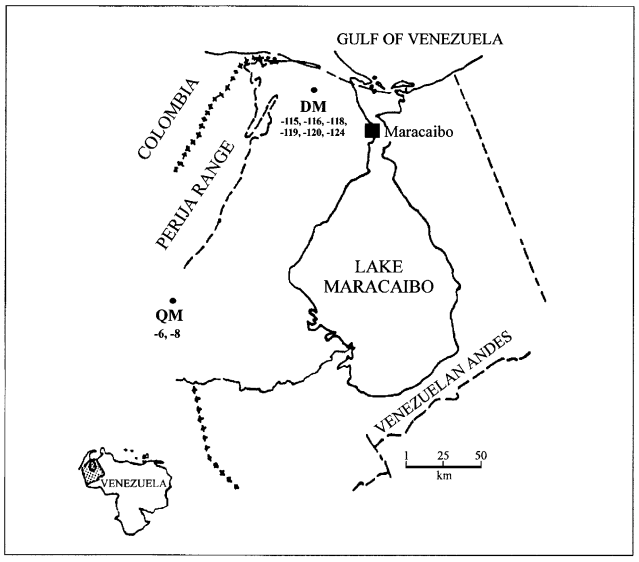

Fig. 1. Geological map indicating the La Luna sample locations: crude oils (West Mara fields) and the source kerogens (Maraca).

Previously, we noted that the V isotopic compositions of the La Luna petroleum asphaltenes differed by as much as 2–5% from inorganic source ($VOSO_4{\cdot}5H_2O$, Merck) [7]. The possibility that such a difference arose from a different preference for the V isotopes of the original living organisms (which buried remnants contributed to formation of the source kerogens) warrants extension of our previous study the asphaltene V isolated from asphaltic petroleums of the La Luna Formation (Venezuela) containing enhanced concentrations of V (≥3000 ppm). Here we amplify our preliminary report with a description of our geochemical techniques/methods and report additional isotopic measurements for La Luna asphaltenes/source kerogens.

2. Experimental

2.1. Samples

Six petroleum samples (DM-115/-116/-118/-119/-120/-124) were obtained from two different West Mara oil fields, Fig. 1. Two source kerogens (QM-6/-8) were obtained from the Maraca location, Fig. 1. The samples of floating asphalts were obtained from large floating blocks that appeared in Dead Sea. Brief geological descriptions and the V analyses are given in Table 1.

2.2. Isolation of the methanol-soluble/asphaltene/kerogen fractions

The isolation procedure and analysis of various organic fractions of heavy petroleums/petroleum-source rocks has been presented in previous publications [2,4].

2.3. Emission spectrometry

A PGS-2 plane grating spectrograph (Carl Zeiss, Jena) was used with a photoelectric detection attachment, an arc plasma excitation source, and a Bausch and Lomb diffraction grating as the monochromator [8].

2.4. Atomic absorption spectrometry (AAS)

A Perkin–Elmer model 4000 atomic absorption spectrometer was used with a Perkin–Elmer platinum hollow-cathode lamp and a nitrous oxide/acetylene burner head.

2.5. Electron spin resonance (ESR) analysis

The electron spin resonance (ESR) measurements were performed on finely-ground powders of the asphaltene/kerogen samples that were transferred to an ESR quartz tube. Spectra were recorded on a Bruker ER-200 series ESR spectrometer with a Bruker ER-044 X-band bridge using standard 100 kHz field modulation. X-band measurements were made at 9.3 GHz utilizing a rectangular TE cavity.

2.6. Vanadium isotopic composition

The mass spectrometer used in this investigation was a 12-inch radius 90° sector, magnetic instrument of home design, equipped with surface ionization/Nier-type ion-sources. The pressures in the analyzer region were maintained below 10^{-8} torr and operating pressures in the source region were below 5×10^{-7} *torr*. The beam of molecules to be investigated was generated by heating the V samples in a renium (Re) canoe in the vicinity of a Re ionizing filament. The Re filament was replaced for each run and the new filament was preheated at elevated temperatures for several hours until no impurities could be detected at the operating temperature for a V analysis. An electron multiplier was used for the detection of the ion currents.

3. Results and discussion

3.1. Experimental V isotope ratios

The measured V isotope ratios of the geological materials/inorganic source investigated are given in Table 1. These values are also graphically shown in Fig. 2. They have not been corrected for the source/multiplier discriminations. The errors given in Table 1 and Fig. 2 for the $^{50}V/^{51}V$ ratios of the individual samples include the standard deviation $\sigma = [\sum_i (\Delta_i)^2/(N-1)]^{1/2}$ and as well as the errors arising from correction of the $^{50}V/^{51}V$ isotope ratio for the inorganic standard ($VOSO_4{\cdot}5H_2O$, Merck). These errors serve to give an indication of the precision of the individual measurements. It is evident from Table 1 and Fig. 2 that none of the asphaltenes investigated have a $^{50}V/^{51}V$ ratio significantly different from the average value: all asphaltene $^{50}V/^{51}V$ ratios agree with the average value to within

Table 1
$^{50}V/^{51}V$ isotope ratios and the $V/VO^{2+}/VO^{2+}$-P contents in the La Luna kerogens/asphaltenes/methanol-soluble fractions, Dead Sea asphaltenes and inorganic sample (the average value: 2.49 (the La Luna asphaltenes), 2.47 (the La Luna kerogens), 2.54 (Dead Sea asphaltenes), 2.52 (the La Luna methanol-soluble fractions))

Sample	Well	Total V (±20 ppm)	VO^{2+}-P (±50 ppm)	V as VO^{2+}-P (ppm)	V as VO^{2+}-P (±5% of total V)	$^{50}V/^{51}V \times 10^{-3}$ (±0.07)
La Luna asphaltenes	DM-115	5300	–	–	–	2.46
	DM-116	4900	–	–	–	2.48
	DM-118	5000	–	–	–	2.52
	DM-119	5500	14,600	1390	25.0	2.49
	DM-120	4800	19,000	1810	40.0	2.50
	DM-124	–	–	–	–	2.50
La Luna kerogens	QM-6	2300	–	–	–	2.48
	QM-8	4000	–	–	–	2.46
Dead Sea asphaltenes	DSAN-2	850	7400	700	82.0	2.53 ± 0.05
	DSA-3	1100	10,000	950	86.0	2.54 ± 0.05
	DM-124	–	–	–	–	2.53
La Luna methanol soluble fractions	DM-120	–	–	–	–	2.52
	DM-119	–	–	–	–	2.51
Inorganic source: $VOSO_4 \cdot 5H_2O$	–	–	–	–	–	2.41

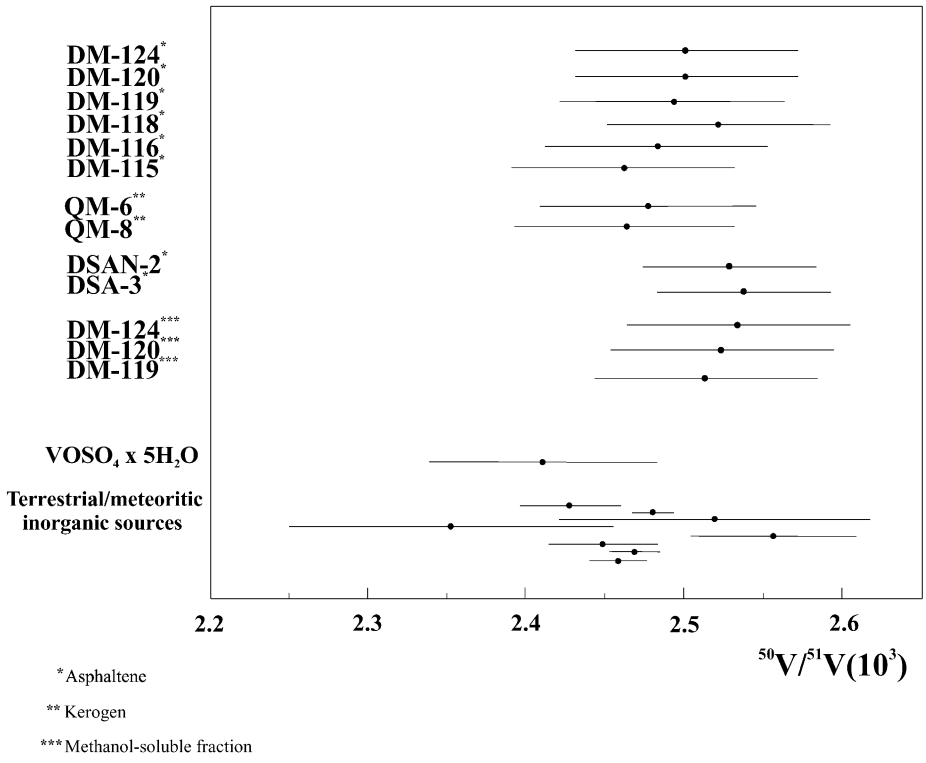

Fig. 2. Vanadium isotope spreads of the La Luna petroleum fractions/source kerogens and terrestrial/meteoritic (inorganic) sources.

<1.5%. In Table 1, the $^{50}V/^{51}V$ abundance ($2.41 \pm 0.07 \times 10^{-3}$) ratio of the inorganic source ($VOSO_4 \times 5H_2O$, Merck) is also given. Our results show that, within the limits of error, the isotopic abundance of ^{50}V of the petroleum asphaltenes studied is higher by about 3.5% than that of the inorganic source. The difference in the isotopic compositions between the asphaltenes and inorganic source are comparable with the analytical errors of the measurements but the results are consistent. Table 1 also shows that the isotopic composition of V in the asphaltenes extracted from the La Luna asphaltic petroleums varies over a very narrow range (2.46–2.52).

A summary of some published $^{50}V/^{51}V$ ratios of terrestrial sources containing V in nature pertinent to this discussion is also shown in Fig. 2, in which the average values for each of these categories are indicated. Although the respective record for inorganic V displays a large scatter, the average seems to be tethered to a mean somewhere between 2.42 and 2.48. Also it is noteworthy that the isotopic anomaly of alleged biologically controlled portion of V in the La Luna asphaltenes is probably somewhat higher, as V in these materials represents a mixture of predominant biologically processed and minor seawater (inorganic) metal.

We also report the V isotopic compositions of two immature La Luna source kerogens: QM-6/-8. Previous work has shown that these kerogens are highly enriched with V (>2000 ppm) [3]. Our results (Table 1 and Fig. 2) show that, within the limits of error, the isotopic abundances of ^{50}V of the La Luna petroleum asphaltenes and source kerogens are similar. Thus, we may conclude that the $^{50}V/^{51}V$ ratios of the La Luna petroleum asphaltenes and the source kerogens are similar if these asphaltenes/source kerogens are genetically related. In other words, the relationship between the V isotope ratios of the source kerogens and the associated petroleum asphaltenes can be used to correlate petroleums with the source rocks.

We regard the V isotopic difference between the La Luna petroleum asphaltenes/source kerogens and the inorganic source as highly significant. The closely similar V isotopic properties of the La Luna petroleum asphaltenes/kerogens indicate that thermal decomposition of a source kerogen during (early) catagenesis and petroleum (primary/secondary) migration cannot seriously obliterate the primary V isotopic signature of original marine humics. Consequently, if the major source of V in these asphaltenes/source kerogens was soluble seawater V (in particular vanadate ions $H_nVO_4^{n-3}$) [9], then, in order to account for the difference in the V isotopic composition between the La Luna petroleum asphaltenes/source kerogens and inorganic V, either (a) the V isotopic composition of these asphaltenes/source kerogens have been uniquely affected by some natural geochemical reaction(s) associated with diagenesis of the source kerogen or (b) that there was isotopic discrimination during biological processing of V (prior to diagenesis) by the original marine life. There is no doubt that isotopic changes of V during diagenesis should be generally very low and these secondary effects can never obscure seriously the isotopic signature of V associated with the original

biological material. Accordingly, the isotopic difference observed cannot be attributed to isotopic effects associated with diagenesis.

3.2. Isotopic composition and microbiological processing

Since V is an essential trace element for even procaryotic organisms [10], the incorporation of V into a petroleum asphaltene (i.e. a source kerogen) might be subject to biological control and not the kinetic/equilibrium processes that organic geochemistry typically consider. From this, it would appear that the difference in the $^{50}V/^{51}V$ values between the La Luna petroleum asphaltenes/source kerogens and the inorganic source could be best ascribed to the biological processing of (inorganic) seawater V by a specific type of marine (micro)organisms. In such a circumstance where the biological processing and accumulation of V are complete, the V isotopic composition of the La Luna petroleum asphaltens/source kerogens would be invariable and similar to the original (micro)biological V. For this interpretation to be invalidated, we would have to postulate a geochemical process that was capable of copying the fractionation typical of biological processing.

Many land plants themselves enhance soil V concentrations several times to the region of 20–1000 ppm [11]. In addition, the V concentrations have been shown to be variable for different types of marine organisms but a review of these data imply that 30 ppm is the maximum concentration for endemic V [12]. The accumulation especially reaches dramatic proportions in the greenish V carrying blood cells (vanadocytes) in certain members of a group of curious marine animals knows as tunicates. In fact, among the three classes that make up the tunicates, V occurs only in *Ascidiacae* (sea squirts). The V content in various forms of ascidia was found to range from 16,500 ppm on dry basis [13]. Noteworthy, that Flesch et al. [14] reported a 4% difference in the $^{50}V/^{51}V$ ratio in V from the tunicate *Ascidia ceratodes*. A biogenic interpretation of the $^{50}V/^{51}V$ ratio of the La Luna petroleum asphaltenes/source kerogens is consistent with the fact that V in some types of marine organisms could be enriched above the levels found in other marine organisms.

Paleobiological studies [15,16] show that the La Luna black and uniformly petroliferous rocks contain the remains of planktonic foraminifers with no sign of fossil structures of terrestrial or marine plants. Our preferred hypothesis is that V of the La Luna asphaltenes/source kerogens originated from a specific microbiological source [2], providing the possibility of V (and VO^{2+}) arising via a more direct biogenic pathway. Indeed, laboratory studies and observations on microbiological mining (for industrial and other purposes) indicate the ability of certain microorganisms (especially bacteria) to extract metals (such as V) from metal-bearing rocks (through direct and/or indirect leaching of metal) or metal-enriched waters through intracellular uptake of metal [17]. For example, Goren [18] has coupled the iron (Fe)oxidizing bacteria such as *Thiobacillus ferrooxidans* and *Ferrobacillus thiooxidans* with the oxidation of V in acidic leaching solution:

$$V^{3+} \xrightarrow{O_2,Fe^{3+}} V^{4+}(\text{or } VO^{2+}) + Fe^{2+} \xrightarrow{O_2,Fe^{3+}} V^{5+} + Fe^{2+}$$

The Fe^{3+} ion acts as an oxidant for V and the Fe^{2+} ion formed is reoxidized by other Fe-oxidizing bacteria. Thus these autotrophs are active in oxidizing V and making it more stable in natural leaching waters for transport to marine water. A detailed discussion of this topic, however, is outside the scope and purpose of this report.

The relatively narrow range of the $^{50}V/^{51}V$ ratio values for the La Luna petroleum asphaltenes/source kerogens (Table 1 and Fig. 2) indicates an essentially same (or similar) and fixed marine (micro)biological source of V. In contrast, the relatively wide range of the $^{50}V/^{51}V$ ratio values for the La Luna petroleum asphaltenes/source kerogens would be expected for various (micro)biological sources of V with variable isotopic compositions. We believe that a single species of marine microorganisms of the Late Cretaceous La Luna sea played a crucial role in the selective V accumulation and that its buried remnants were one of the main sources of V incorporated into the source kerogen macromolecular framework (i.e. those parts of its macromolecular skeleton which are enriched with V). Although the process by which V is added to the La Luna humics during early diagenesis may be ultimately biogenic, an ultimate inorganic source probably controlled quantitatively the V accumulation. Clearly, the identification of a particular marine (micro)organism which sourced V in the La Luna source kerogens would greatly advance our efforts at reconstruction of the La Luna sedimentary paleoenvironment during the Late Cretaceous. However, because V isotope effects associated with microbial/chemical processes have received no attention, our interpretation at this time must be regarded with some caution.

3.3. Isotopic composition and porphyrin/non-porphyrin V

From the earlier considerations, we may conclude that the organically combined V of the La Luna petroleum asphaltenes/source kerogens probably best represents the primary V associated with the original (micro)biological material. Indeed, there are only two major classes of V of primary importance in the petroleum asphaltenes/source kerogens: porphyrin V [3] and non-porphyrin V [19], i.e. V in the La Luna asphaltenes/source kerogens represents a mixture of porphyrin V (essentially as VO^{2+}) and non-porphyrin V. According to Treibs [20] VO^{2+}-P are derived mainly from chlorophylls, which, during diagenesis, have undergone various chemical changes including the overall replacement of Mg^{2+} by inorganic VO^{2+}. The kerogen VO^{2+}-P have been studied extensively in this Laboratory for the last 20 years but non-porphyrin V have not yet been explored. VO^{2+}-P are particularly observed in the La Luna asphaltic petroleum asphaltenes/source kerogens, where they are

Table 2
The source rocks of marine kerogens abundant in VO^{2+}-P

Lithology and rock	Region	Geologic period
Muna River shale	Siberia, Russia	E./M. Cambrian
Impsonite/grahamite	Oklahoma, USA	Silurian/Ordovician
Zvonce shale	Serbia, Yugoslavia	Silurian
New Albany shale	Indiana, USA	E. Carboniferous (Mississipian)
Desmoinesian shale	Western USA	L./M. Carboniferous (Pennsylvanian)
Meade Peak shale	Montana, USA	E. Permian
Kupferschiefer	Germany/Poland	L. Permian
Sichan shale	China	L. Permian
Zavalje marl	Croatia	L. Triassic
Serpiano marl	Switzerland	L. Triassic
Posidonienschiefer	Germany	L. Jurassic
Kimmeridge shale	United Kingdom	L. Jurassic
Akkuyu shale	Turkey	L. Jurassic/E. Cretaceous
Julia Creek shale	Australia	M. Cretaceous
Oulad Abdoun shale	Morocco	L. Cretaceous
Nebi Mussa limestone	Israel	L. Cretaceous
El Lajjun limestone	Jordan	L. Cretaceous
La Luna limestone	Venezuela	L. Cretaceous

protected by incorporation in their polymeric network. According to Premović et al. [2], the incorporation of V into porphyrin structures and the formation of the source kerogen VO^{2+}-P must be a secondary process. Hence, we may reason that (micro)biological (non-porphyrin) V was probably the main source of V within the VO^{2+}-porphyrin skeletons of the La Luna petroleum asphaltenes/source kerogens. However, it should be pointed out that the porphyrin components of widespread VO^{2+}-P in these petroleum asphaltenes/source kerogens are inherited from the chlorophylls of phytoplanktons/photosynthetic bacteria living in the Late

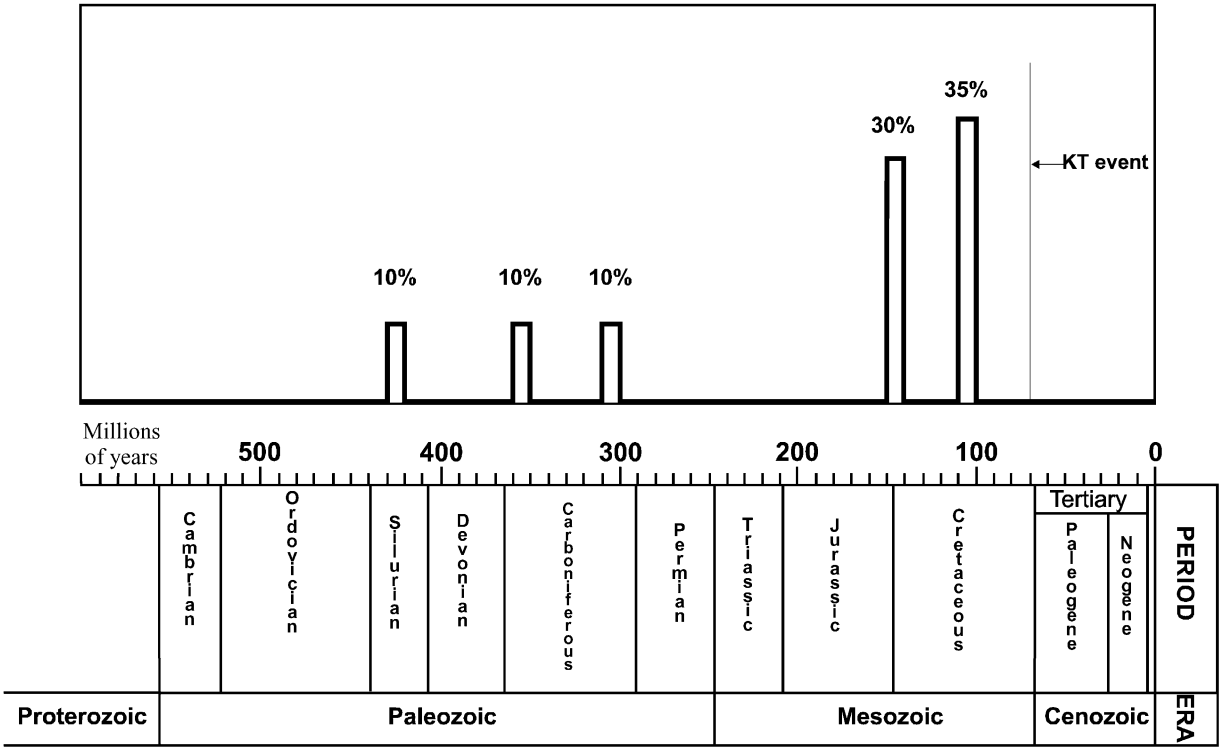

Fig. 3. Stratigraphic distribution of sedimentary kerogens (rich in VO^{2+}-P) of marine origin given as a percentage of total kerogen (enriched with VO^{2+}-P) of the world's the petroleum source rocks. More than 95% of marine kerogen enriched with VO^{2+}-P in the world is stored in the petroleum source rocks of four stratigraphic intervals: Ordovician/Silurian (10%); Early/Late Carboniferous (20%); Early Jurassic (30%) and Middle/Late Cretaceous (35%).

Cretaceous La Luna seawater [2–4 and references therein].

Our data (Table 1) indicate that in two samples (DM-119/-120) of the La Luna petroleum asphaltenes $\leqslant 40\%$ of total V is present in the VO^{2+}-P skeletons. We could expect that the biochemically distinctive components of the (micro)biological organism (supposedly responsible for the V enrichment of the La Luna source kerogens) may display characteristic (though probably minor) differences in their V isotopic compositions. If V of VO^{2+}-P incorporated into the structures of the La Luna petroleum asphaltenes/source kerogens is derived from the same (micro)organism(s) as the bulk of V, then these compounds should have a $^{50}V/^{51}V$ ratio similar to that of V of the petroleum asphaltenes/source kerogens. For this reason, we extracted the methanol-soluble fractions highly enriched with alkyl VO^{2+}-P (containing $>80\%$ of total V) from the La Luna asphaltic petroleums (DM-119/-120/-124). Mass spectrometric analyses show that these fractions have similar V isotopic composition as V of the La Luna petroleum asphaltenes/source kerogens, Table 1.

Finally, we have also measured anomalous V-isotopic compositions in asphaltenes of the floating asphalts from Dead Sea. These asphaltenes are enriched with V (>800 ppm) and their VO^{2+}-P concentrations were found to be >7000 ppm. Also it is noteworthy that in these materials (as in the La Luna methanol-soluble fractions) $>80\%$ of total V is associated with the porphyrin structures, Table 1. These results infer that alleged biologically controlled fractination of porphyrin V is not solitary or sporadic phenomenon and is not confined only to the Late Cretaceous La Luna Basin.

3.4. Biological progenitor of VO^{2+}-P and Cretaceous–Tertiary event: a final note

The high VO^{2+}-P (>100 ppm) kerogens of marine bituminous rocks studied in this Laboratory (and other laboratories) occur on all continents, in rocks of widely varied ages, at various depths, with various temperatures and pressure histories, Table 2 and Fig. 3. Organic geochemical studies have shown that the sedimentary carbonaceous rocks containing VO^{2+}-P rich kerogens/asphaltenes have specific characteristics. They contain an abundant organic matter of phytoplanktonic/bacterial origin, preserved and deposited in a reducing environment. However, the cause for accumulating large quantities of these pigments over wide areas during certain periods of geologic time was not clear. According to Premović et al. [3], many kerogens of marine origin are characterized by high absolute concentrations (>100 ppm) of VO^{2+}-P. This is expected since for marine carbonaceous rocks, there is an abundant input of porphyrin-precursor chlorophylls to bioorganic matter (marine humics) derived from phytoplanktons/bacteria where rich carbonaceous rocks are developed, and physicochemical conditions favor both VO^{2+} and its incorporation into porphyrins. In general, kerogen of terrestrial origin shows the absence of VO^{2+}-P. This is probably a consequence of a relatively lower-chlorophyll-porphyrin contribution to a terrestrial kerogen and an insufficient preservation of any phytoplanktonic/bacterial materials derived chlorophyll-porphyrins under more oxidizing conditions experienced by terrestrial bioorganic matter. In addition, the conclusion towards which the evidence appears to lead is that a high VO^{2+}-P content of a marine kerogen reflects the influence of a certain type of source phytoplanktonic/bacterial materials which was particularly predominant in near-shore anoxic marine deposits, and was much less common or less abundant in terrestrial deposits.

Available evidence indicates that kerogen (rich in VO^{2+}-P) of petroleum source rocks of marine origin is unevenly distributed among geological time. Fig. 3 shows the stratigraphic distribution of this kerogen, plotted in terms of total marine kerogen (enriched with VO^{2+}-P) stored in petroleum source rocks of the world normalized to 100%. Prolific petroleum source rocks, deposited over part of Jurassic and Cretaceous (from 150 to 100 Myr) are responsible for about 65% of marine kerogen (rich in VO^{2+}-P) in these rocks; however, this interval amounts to $<10\%$ only of the time elapsed since the Precambrian.

Finally, geochemical studies indicate that high (>100 ppm) VO^{2+}-P are virtually absent in marine kerogens of Tertiary or younger rocks. It is likely that this general absence is compatible with the massive extinction of specific microorganism(s) during terminal Cretaceous/Tertiary (KT) event that was responsible for generation of marine kerogens enriched with VO^{2+}-P during Paleozoic.

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