J.Serb.Chem.Soc. 65(8)561-569(2000)
JSCS-2777

UDC 546.881:546.027:553.985
Original scientific paper

The vanadium isotopic constitution of petroleum asphaltenes: La Luna Formation (Venezuela)

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(Received 10 November 1999)

High resolution mass spectrometry indicates that the isotopic abundance of ^{50}vanadium (V) of the Late Cretaceous La Luna petroleum asphaltenes and related source kerogen of marine origin (both highly enriched with V > 2000 ppm) is higher by about 3.5 % than that of an inorganic vanadium source ($VOSO_4 \cdot 5H_2O$, Merck). It is proposed that the difference in the $^{50}V/^{51}V$ values between the La Luna source kerogen/the associated petroleum asphaltenes and the inorganic source can be best ascribed to the biological processing of seawater V. The fact that the isotopic compositions of V vary over a very narrow range (2.46–2.50) suggest an essentially same (or similar) and fixed biological source of V.

Keywords: vanadium, isotope, asphaltene, petroleum.

INTRODUCTION

The concept of immature petroleum, involving the first-generation product of a very rich, relatively immature source rock, has existed in one form or another for more than 20 years. Such a material would consist of high-molecular-weight compounds (*e.g.*, asphaltenes), rich in heteroatoms (often including associated V) and would have minor amounts of light hydrocarbons.[1] This material would, therefore, represent a source rock primary product that has not attained the physicochemical properties (characteristics) of mature/light petroleum. Thus, the asphaltene molecules may be regarded as intermediate products along the pathway leading progressively from the source kerogen to normal (conventional), mature/light petroleum. Immature petroleums are low maturity oils because of low thermal exposure (shallow burial for short geologic time) and they are generated as asphaltic oils rich in

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heteroatoms because of an unusually high organic heteroatom content (including V) in the immature source kerogens.[2] In general, marine carbonate/siliceous rocks are the source of large quantities of immature, non-biodegraded heavy petroleum deposits that occur as liquids/semisolids in porous/fractured media.[1] These non-biodegraded asphaltic petroleums (rich in V) found, for example, in northwestern Venezuela (the La Luna Formation) are considered to be the products of oil-prone, V-rich (immature) source kerogen of marine origin.[3,4]

The overall composition of the source kerogen (including its V) depends firstly on the nature of the original organic materials and in part on its progress towards the final stage of maturation (catagenesis). It is suggested that the bulk of the La Luna source kerogen (abundant in V) are derived from the organic remains of phytoplankton, which gives rise to humics enriched by non-endemic V during diagenesis.[5]

The origin of V associated with the asphaltenes in asphaltic petroleums of marine origin, in general, is one of the intriguing problems of petroleum geochemistry since its origin is undoubtedly closely related to the origin of the immature source kerogen itself and the associated asphaltic petroleum.[1] In fact, V bound in the asphaltene matrix may have originated into two ways: a) through incorporation into the humic progenitors (humics) of the immature source kerogen during the diagenesis of the original bioorganic material in the early sediment from interstitial seawater and b) through incorporation into humics and diagenesis of the (endemic) V compounds of the original bioorganic material.[6] Although there is no general agreement on the issue, majority opinion seems to incline towards a non-endemic origin of V associated with the immature source kerogen structure. A few earlier researchers expressed the view that V in a geoorganic accumulation (including the source kerogen) was derived from biological precursors.[7–10] In most cases, V incorporation into the immature source kerogen is essentially due to abiotic, diagenetic reactions of the initial humic substances with the associated seawater (inorganic) V.[5] Thus, it is not unreasonable to suggest that the La Luna immature source kerogen abundant in V (or, at least, those parts of its macromolecular skeletons which are highly enriched with V) are relics of initial marine humic substances which were also enriched with V. However, as Premović *et al.*[5] pointed out, the relative V abundances in the La Luna source kerogen and related petroleum asphaltenes obviously require an additional source of V enrichment besides common seawater.

Whilst considerable attention has been paid to the isotopic composition of the various forms of non-metals (especially carbon) in petroleum,[11] less regard has been given to the metals. Apart from artificial short-lived radioactive nuclides, the element V consists of a mixture of two stable naturally occurring V isotopes, ^{50}V and ^{51}V, whose relative abundances in geochemically undifferentiated carbonaceuos material comes close to 0.250 % and 99.750 %, respectively (with a corresponding isotopic ratio $^{50}\mathrm{V}/^{51}\mathrm{V} = 2.50\times10^{-3}$). The above considerations suggest that V of petroleum asphaltenes arising from a non-endemic source should have a $^{50}\mathrm{V}/^{51}\mathrm{V}$ ratio similar to that of an inorganic source. The petroleum asphaltene V arising directly from biological material (endemic source) should have a $^{50}\mathrm{V}/^{51}\mathrm{V}$

isotopic ratio larger than the inorganic source due to kinetic/equilibrium effects during biological processing. Implicit in such an approach is that the ultimate inorganic source of the endemic/non-endemic V was primarily seawater enriched more or less with this metal.[6] In view of this, the V contents and isotopic compositions of V in five asphaltenes of the La Luna asphaltic petroleums were determined with the object of gaining some further insight into the general biogeochemistry of V during the source kerogen-/the asphaltic petroleum forming processes. Interest was particularly centered on the possible direct biological source of V.

Previously we noted that the V isotopic compositions of petroleum asphaltenes differed by as much as 2 % to 5 % from an inorganic source ($VOSO_4 \cdot 5H_2O$, Merck).[12] The possibility that such a difference arose from a different preference for the V isotopes of the original living organisms (the buried remnants of which contributed to the formation of the source kerogen) warrants extension of our previous study of V of the asphaltenes isolated from asphaltic petroleums from the La Luna Formation (Venezuela) containing enhanced concentrations of V ($\geq$3000 ppm). Here our preliminary report is amplified with a description of the employed chemical techniques and additional isotopic measurements for five La Luna petroleum asphaltene samples are reported.

EXPERIMENTAL

Samples

Five petroleum samples (DM-115, 116, 118, 119, 120) were obtained from two different West Mara oil fields. Brief geological discriptions and the V analyses of the samples are given in Table I.

Isolation of asphaltene

The isolation procedure and analysis of various organic fractions of petroleums has been presented in previous publications.[5,13]

Emission spectrometry

A PGS-2 plane gratind 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.[14]

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.

Electron spin resonance (ESR) analysis

The ESR measurements were performed on finely-ground powders of the asphaltene samples that were transfered to an ESR quartz tube. The spectra were recorded on a Bruker ER200 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.

Vanadium isotopic composition

Since it is our intention to extend our measurements to a number of additional asphaltenes/kerogens and to make a complete summary report in the near future, the employed techniques will only be briefly outlined here.

The mass spectrometer used in this investigation was a 12-inch radious 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 after 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.

RESULTS AND DISCUSSION

The measured V isotope ratios of the geological materials/inorganic source investigated are given in Table I. These values are also graphically presented in Fig. 1. They have not been corrected for source/multiplier discriminations. The errors given in Table I/Fig. 1 for the $^{50}V/^{51}V$ ratios of the individual samples include the standard deviation $\sigma = [\Sigma i\,(\Delta i)^2 / (N-1)]^{1/2}$ as well as the errors arising from correction of the 50V/51V isotope ratio for the inorganic standard ($VOSO_4 \cdot 5H_2O$, Merck). These errors serve as an indication of the precision of the individual measurements. It is evident from Table I/Fig. 1 that none of the investigated asphaltene samples 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 < 1.5 %. The $^{50}V/^{51}V$ abundance ($2.41 \pm 0.07\times10^{-3}$) ratio of the inorganic source (Merck, $VOSO_4 \cdot 5H_2O$) is also given in Table I. The results show that, within the limits of error, the isotopic abundance of ^{50}V of the studied petroleum asphaltenes is higher by about 3.5 % than that of the inorganic source. Table I also shows that the isotopic composition of V in the asphaltenes extracted from the La Luna asphaltic petroleums varies over a very narrow range (2.46–2.50). A summary of some published $^{50}V/^{51}V$ ratios of terrestrial sources containing V in nature pertinent to this discussion is, also, depicted graphically in Fig. 1, 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.

In the second part of this communication, the initial results of the V isotopic compositions of the immature source kerogen samples of two source rocks of the La Luna Formation, QM-6/-8, are reported. Previous work has shown that the La Luna immature source kerogen is highly enriched with V (> 5000 ppm).[5] The results (Table I, Fig. 1) show that, within the limits of error, the isotopic abundances of ^{50}V of the La Luna source kerogen and related petroleum asphaltenes are similar. Thus, it may be concluded that the $^{50}V/^{51}V$ ratios of the La Luna petroleum asphaltenes and the source kerogen are similar if the petroleum asphaltenes and the corresponding source kerogen 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 source kerogen/the associated petroleum asphaltenes and the inorganic source as highly significant. If the major source of V in the La Luna source kerogen/the associated petroleum asphaltenes was soluble seawater V (in particular vanadate ions $H_nVO_4^{n-3}$),[15] then, in order to account for the difference in the V isotopic composition between the La

Luna petroleum asphaltenes and inorganic V, either (a) the V isotopic composition of the La Luna petroleum asphaltenes has been uniquely affected by some natural geochemical reaction(s) associated with diagenesis/catagenesis 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/catagenesis (and during migration) should be generally very low and these secondary effects can never obscure seriously the isotopic signature of V associated with the original biological material. Consequently, the isotopic difference observed cannot be attributed to isotopic effects associated with diagenesis/catagenesis (nor with migration). The closely similar V isotopic properties of the La Luna source kerogen and the related petroleum asphaltenes indicate that thermal decomposition of the source kerogen during early catagenesis and migration cannot seriously obliterate the primary V isotopic signature of the original organic material.

TABLE I. $^{50}V/^{51}V$ isotope ratios and the $V/VO^{2+}/VO^{2+}$-P contents in the La Luna asphaltene kerogen and an inorganic sample

Sample	Well	Total V ± 20ppm	VO^{2+}-P ± 50ppm	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 asphaltene	DM-115	5300	–	–	–	2.46
	DM-116	4900	–	–	–	2.48
	DM-118	5000	–	–	–	2.52
	DM-119	5500	14600	1390	25.0	2.49
	DM-120	4800	19000	1810	40.0	2.50
La Luna kerogen	QM-6	2300	–	–	–	2.48
	QM-8	4000	–	–	–	2.46
Inorganic source: $VOSO_4 \cdot 5H_2O$	–	–	–	–	–	2.41

The average value:
2.49 (the La Luna petroleum asphaltene) and 2.47 (the La Luna kerogene).

Since V is an essential trace element for even procaryotic organisms,[16] the incorporation of V into kerogen might be subject to biological control and not the 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 source kerogen/petroleum asphaltenes and the inorganic source could be best ascribed to the biological processing of (inorganic) seawater V by a specific type of marine organisms. In such a circumstance, where the biological processing and accumulation of V is complete, the isotopic composition of a source kerogen/petroleum asphaltene would be invariable and similar to the original biological V. For this interpretation to be invalidated, a geochemical (inorganic) process capable of copying the fractionation typical of biological processing would have to be postulated.

It has been shown that the V concentrations of different types of marine organisms can vary but a review of these data implies that 30 ppm is the maximum concentration for endemic V.[17] A biogenic interpretation of the $^{50}V/^{51}V$ ratios of the source kerogen/petroleum asphaltenes in question is consistent with the fact that

V in some types of marine organisms could be enriched above the levels found in other marine organisms. For example, the accumulation reaches especially 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 1–6500 ppm ondry basis.[18] On the other hand, 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).[19] For example, Goren[20] has coupled iron (Fe)-oxidizing bacteria, such as *Thiobacillus ferrooxidans* and *Ferrobacillus thiooxidanas*, 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 in 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 norrow range of the $^{50}V/^{51}V$ ratio values for the La Luna source koregen/the associated petroleum asphaltenes (Table I, Fig. 1) indicates an essentially same (or similar) and fixed marine biological source of V. In contrast, a relatively wide range of $^{50}V/^{51}V$ ratio values for the La Luna source kerogens/the associated petroleum asphaltenes would be expected for various biological sources of V with variable isotopic compositions. We believe that a single species of marine organisms of the Late Cretaceous La Luna sea played a crucial role in the selective

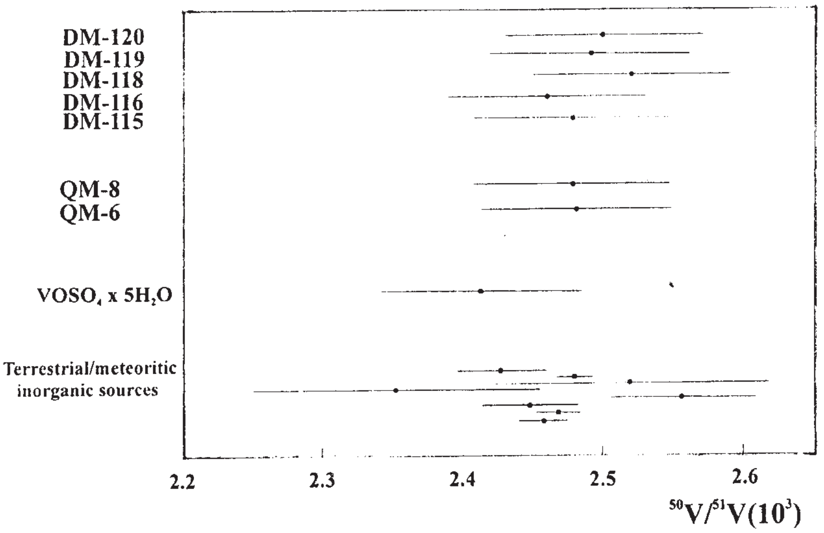

Fig. 1 Vanadium isotope spreads of the La Luna petroleum asphaltenes and the source kerogen and terrestrial/meteoric sources.

V accumulation and that its buried remnants were one of the main sources of V incorporated into the La Luna 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 Late Cretaceous La Luna humics during early diagenesis may be finaly biogenic, an ultimate external inorganic source probably controlled quantitatively the V accumulation. Clearly, the identification of a particular marine biological organism which sourced V in the La Luna source kerogen would greatly advance our efforts of reconstructing the La Luna sedimentary paleoenvironment during the Late Cretaceous.

From the above considerations, it may be concluded that the organically combined V of the La Luna source kerogen/the associated petroleum asphaltenes probably best represents the primary V associated with the original biological material. On the other hand, there are only two major classes of V of primary importance in the source kerogen/the associated petroleum asphaltenes: non-porphyrinic V and vanadyl (VO^{2+})-porphyrins.[4] The kerogen VO^{2+}-porphyrins have been studied extensively in this Laboratory for the last 20 years but nonporphyrinic V have not yet been explored. VO^{2+}-porphyrins are particularly observed in the asphaltene fraction of the La Luna petroleums and in the kerogen of the related rocks, where they are protected by incorporation in their polymeric network. According to Premovic *et al.*,[5] the incorporation of V into porphyrin structures and the formation of the source kerogen VO^{2+}-porphyrins must be a secondary process. Hence, it may be reasoned that biological (nonporphyrinic) V was probably the main source of V of the VO^{2+}-porphyrins within the structures of the La Luna immature source kerogen. However, it should be pointed out that the porphyrin components of the wide spread VO^{2+}-porphyrins in the La Luna petroleums and their source rocks are inherited from the chlorophylls of phytoplanktons living in the Cretaceous La Luna seawater.

Our data (Table I) indicate that in two samples of the La Luna petroleum asphaltenes (DM- 119/- 120) ≥60 % of total V is present as non-porphyrinic V. It could be expected that the biochemically distinctive components of the biological organism (supposedly responsible for the V enrichment of the La Luna source kerogen) may display characteristic (through usually minor) differences in their V isotopic compositions. If the V of the VO^{2+}- porphyrins incorporated into the structures of the La Luna source kerogens/the associated petroleum asphaltenes is derived from the same biological organism as the bulk of the V, then these compounds should have a $^{50}V/^{51}V$ ratio similar to that of V of the source kerogen/the associated petroleum asphaltenes. Initial experiments with alkyl VO^{2+}-porphyrins extracted (isolated) from the La Luna asphaltic petroleums indicate that these compounds have a similar V isotopic composition to the V of the La Luna source kerogen/the associated petroleum asphaltenes. However, at the moment, this data is still insulfficient to establish fully this interpretation and work is still in progress. However, $^{50}V/^{51}V$ ratio studies, in general, promise to be of great value in future research of the source kerogen/the associated asphaltic petroleums highly enriched with V and VO^{2+}- porphyrins.

Acknowledgment: This research was supported by grant number 02E38 from the Ministry of Science and Technology of Serbia. Thank are due to Programa Catedra Conicit and Consejo de

Estudios de Postgrado de la Universidad Central de Venezuela for financing the stay of P. I. P. in Venezuela (Instituto de Ciencias de la Tierra, UCV). Funding support from le Ministére Francais de l'Education Nationale, de l'Enseignement Supérieur et de la Recherche, to P. I. P. for his stay at the Universite Pierre et Marie Curie (Paris) is gratefully acknowledged. I. Tonsa thanks EAOG for the Travel Scholarship at Instituto de Ciencias de la Tierra, UCV.

ИЗВОД

ИЗОТОПСКИ САСТАВ ВАНАДИЈУМА У НАФТНИМ АСФАЛТЕНИМА: ЛА ЛУНА ФОРМАЦИЈА (ВЕНЕЦУЕЛА)

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Масена спектрометрија високе резолуције је показала да је изотопски садржај ^{50}вандијума (V) из Ла Луна нафтних асфалтена (касна креда) и њихових изворних керогена морског порекла (и једних и других обогаћених са V > 2000 ppm) већи за око 3.5 % него у неорганском извору ($VOSO_4 \cdot 5H_2O$, Merck). Предложено је да се разлике у $^{50}V/^{51}V$ вредностима између Ла Луна изворних керогена/придружених нафтних асфалтена и неорганског извора могу приписати микробиолошком процесирању V из морске воде. Чињеница да изотопски састав V варира у уском опсегу (2,46–2,50) сугерише суштински исти (или слични) и одређен биолошки извор V.

(Примљено 10. новембра 1999)

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