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Short Communication

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

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Abstract

High-resolution mass spectrometry indicates that the isotopic abundance of ⁵⁰V of the Late Cretaceous La Luna petroleum asphaltenes of marine origin (highly enriched with V > 2000 ppm) is higher by about 3.5% than that of the inorganic source (VOSO₄ × 5H₂O, Merck). We propose that the difference in the ⁵⁰V/⁵¹V values between the La Luna petroleum asphaltenes and the inorganic source can be best ascribed to the biological processing of seawater vanadium. The fact that the V isotopic compositions of petroleum asphaltenes vary over a very narrow range (2.46–2.52) suggests essentially the same (or similar) and fixed biological source of vanadium. ©2000 Elsevier Science Inc. All rights reserved.

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1. Introduction

Apart from artificial short-lived radioactive nuclides, the element V consists of a mixture of two stable naturally occurring V isotopes, ⁵⁰V and ⁵¹V, whose relative abundances in geochemically undifferentiated carbonaceous material come close to 0.250 and 99.750%, respectively (with a corresponding isotopic ratio ⁵⁰V/⁵¹V = 2.51 × 10⁻³). The various geochemical considerations suggest that V of petroleum asphaltenes arising from a non-endemic source should have a ⁵⁰V/⁵¹V ratio similar to that of an inorganic source. V of petroleum asphaltenes arising directly from a biological material (endemic source) should have a ⁵⁰V/⁵¹V isotopic ratio larger than the inorganic source due to isotopic effects during biological processing [1]. 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 [2]. In view of this, the V contents and isotopic compositions of V in five asphaltenes of the La Luna asphaltic petroleum were determined. For comparison, isotopic data for two source kerogens are also included. The

object of this study was to gain some further insight into the general biogeochemistry of V during the source kerogen/asphaltic petroleum-forming processes. Interest was particularly centred on the possible direct biological source of V.

2. Experimental*2.1. Samples*

Five petroleum samples (DM-115, -116, -118, -119, -120) were obtained from two different West Mara oil fields. Brief geological descriptions and the V analyses are given in Table 1.

2.2. Isolation of asphaltene

The isolation procedure and analysis of various organic fractions of petroleum have been presented in a previous publication [3].

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Table 1
 $^{50}\text{V}/^{51}\text{V}$ isotope ratios and the V contents in the La Luna asphaltene/kerogen and inorganic samples

Sample	Well	V (± 20 ppm)	$^{50}\text{V}/^{51}\text{V} \times 10^3$ ^a (± 0.07)
La Luna asphaltene	DM-115	5300	2.46
	DM-116	4900	2.48
	DM-118	5000	2.52
	DM-119	5500	2.49
	DM-120	4800	2.50
La Luna kerogen	QM-6	2300	2.48
	QM-8	4000	2.46
Inorganic source: VOSO ₄ × 5H ₂ O			2.41

^a These ratios have not been corrected for source/multiplier discriminations. The errors given for the $^{50}\text{V}/^{51}\text{V}$ ratios of the individual samples include the standard deviation $\sigma = [\sum_i (\Delta_i)^2 / (N-1)]^{1/2}$, as well as the errors arising from correction of the $^{50}\text{V}/^{51}\text{V}$ isotope ratio for the inorganic standard. Average value: 2.49 (La Luna petroleum asphaltenes) and 2.47 (La Luna kerogen).

2.3. Vanadium isotopic composition

Geochemical techniques/methods have already been described earlier [4]. 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, we shall only briefly outline our techniques here.

The mass spectrometer used in this investigation was a 12-inch radius 90° sector, magnetic instrument of home design, equipped with a surface ionization/Nier-type ion source. Pressure in the analyser region was maintained below 10^{-8} Torr and the operating pressure in the source region was below 5×10^{-7} Torr. The beam of molecules to be investigated was generated by heating a sample in a rhenium (Re) canoe in the vicinity of a Re ionizing filament. The Re filament was replaced for each run and a 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

The measured V isotope ratios of the geological materials/inorganic source investigated are given in Table 1. These values are also graphically presented in Fig. 1. It is evident from Table 1 and Fig. 1 that none of the asphaltene samples investigated have a $^{50}\text{V}/^{51}\text{V}$ ratio significantly different from the average value: all asphaltene $^{50}\text{V}/^{51}\text{V}$ ratios agree with the average value to within 1.5%. In Table 1 the $^{50}\text{V}/^{51}\text{V}$ abundance ($2.41 \pm 0.07 \times 10^{-3}$) ratio of the inorganic source (Merck: VOSO₄ × 5H₂O) is also given. Our results show that, within the limits of error, the isotopic abundance of ^{50}V of petroleum asphaltenes studied is higher by about 3.5% than that of the inorganic source. Table 1 also shows that the isotopic composition of V in the asphaltenes extracted from the La Luna asphaltic petroleum varies over a very narrow range (2.46–2.52). A summary of some published $^{50}\text{V}/^{51}\text{V}$ ratios of terrestrial/meteoritic inorganic sources containing V in nature pertinent to this report is also depicted graphically in Fig. 1, where the average values for each of these categories are indicated. Although the respective record for terrestrial/meteoritic (inorganic) V displays a large scatter, the average seems to be tethered to a mean somewhere between 2.35 and 2.55.

In the second part of this communication, we report 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. Previous work has shown that La Luna immature source kerogen is highly enriched with V (> 5000 ppm) [5]. Our results (Table 1, 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

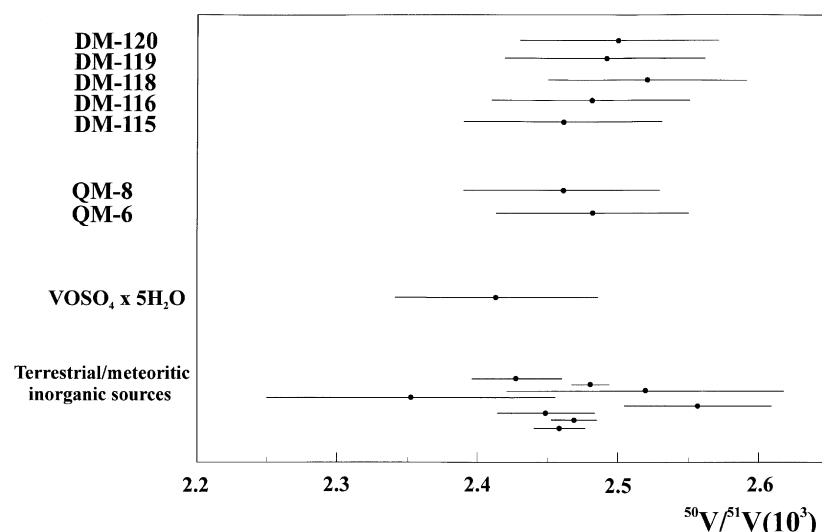


Fig. 1. Vanadium isotope spreads of the La Luna petroleum asphaltenes and the source kerogen and terrestrial/meteoritic sources.

similar, i.e., the relationship between the V isotope ratios of the source kerogen and the associated petroleum asphaltenes can be used to correlate petroleum with the source rocks.

We regard the V isotopic difference between the La Luna petroleum asphaltenes/source kerogen and the inorganic source as highly significant. It is likely that the ultimate source of V in La Luna petroleum asphaltenes were V species soluble in seawater such as the vanadate ion H_2VO_4^- , which is by far the predominant V ion in seawater [4]. In this case, in order to account for the difference in the V isotopic composition between the La Luna petroleum asphaltenes/source kerogen 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 of the source kerogen, or (b) there was an isotopic discrimination during the 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. Consequently, the isotopic difference observed cannot be attributed to isotopic effects associated with diagenesis. Since V is an essential trace element for even procaryotic organisms [6], the incorporation of V into the source kerogen might be subject to biological control and not the kinetic/equilibrium processes that organic geochemists typically consider. From this, it would appear that the difference in the $^{50}\text{V}/^{51}\text{V}$ values

between the La Luna petroleum asphaltenes and the inorganic source can be best ascribed to the biological processing of (inorganic) seawater V by a specific type of marine organism.

The relatively narrow range of the $^{50}\text{V}/^{51}\text{V}$ ratio values for the La Luna petroleum asphaltenes and their source kerogen (Table 1, Fig. 1) indicates essentially the same (or similar) and fixed marine biological source of V. In contrast, the relatively wide range of the $^{50}\text{V}/^{51}\text{V}$ ratio values for the La Luna source kerogens/associated petroleum asphaltenes would be expected for various biological sources of V with variable isotopic compositions. We believe that a single species of marine organism 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 structures (i.e. those parts of its macromolecular skeleton which are enriched with V).

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