

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 ⁵⁰vanadium (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 (VOSO₄·5H₂O, 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 ⁵⁰V/⁵¹V 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 (VO²⁺-P). This analysis shows that the isotopic abundance of ⁵⁰V for the methanol-soluble fractions agrees (within the limits of experimental error) with those of the asphaltenes/kerogens. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Vanadium; Isotopes; Petroleum; Asphaltenes; Kerogen

1. Introduction

The origin of high ⁵⁰vanadium (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) V⁵⁺.

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 (VO²⁺-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 fractionated 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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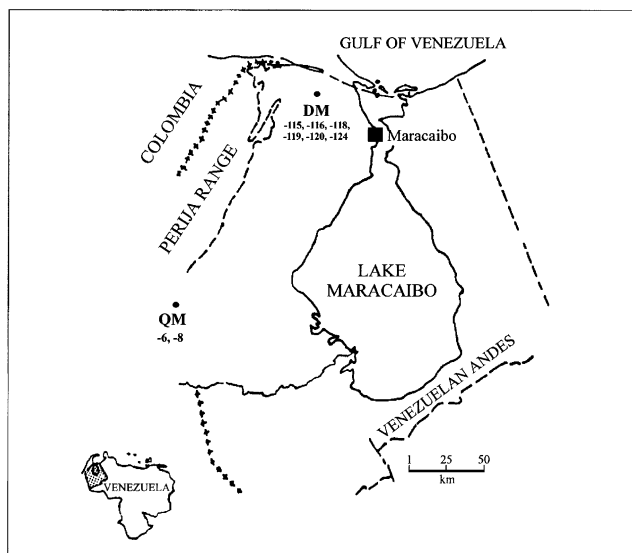


Fig. 1. Geological map indicating the La Luna sample locations: crude oils (West Mara fields) and the source kerogens (Maraca).

Previously, we noted that the V isotopic compositions of the La Luna petroleum asphaltenes differed by as much as 2–5% from inorganic source ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, 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 petroleum 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 asphaltens 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 petroleum/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 rhenium (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 $^{50}\text{V}/^{51}\text{V}$ 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 $^{50}\text{V}/^{51}\text{V}$ isotope ratio for the inorganic standard ($\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$, 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 $^{50}\text{V}/^{51}\text{V}$ ratio significantly different from the average value: all asphaltene $^{50}\text{V}/^{51}\text{V}$ ratios agree with the average value to within

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