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New Vanadium Compounds in Venezuela Heavy Crude Oil Detected by Positive-ion Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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Metalloporphyrins are ubiquitous in nature, particularly iron porphyrins (hemes) and magnesium dihydroporphyrins or chlorophylls. Oxovanadium (IV) complexes of alkyl porphyrins are widely distributed in petroleum, oil shales and maturing sedimentary bitumen. Here we identify new vanadium compounds in Venezuela Orinoco heavy crude oil detected by Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS). These compounds likely have the main structure of porphyrin, with the addition of more aromatic rings, thiophene and amino functional groups, corresponding to molecular series of $C_nH_{2n-40}N_4V_1O_1$ ($36 \leq n \leq 58$), $C_nH_{2n-42}N_4V_1O_1$ ($37 \leq n \leq 57$), $C_nH_{2n-44}N_4V_1O_1$ ($38 \leq n \leq 59$), $C_nH_{2n-46}N_4V_1O_1$ ($43 \leq n \leq 54$), $C_nH_{2n-48}N_4V_1O_1$ ($45 \leq n \leq 55$), $C_nH_{2n-38}N_4V_1S_1O_1$ ($36 \leq n \leq 41$), $C_nH_{2n-40}N_4V_1S_1O_1$ ($35 \leq n \leq 51$), $C_nH_{2n-42}N_4V_1S_1O_1$ ($36 \leq n \leq 54$), $C_nH_{2n-44}N_4V_1S_1O_1$ ($41 \leq n \leq 55$), $C_nH_{2n-46}N_4V_1S_1O_1$ ($39 \leq n \leq 55$), $C_nH_{2n-27}N_5V_1O_1$ ($29 \leq n \leq 40$), $C_nH_{2n-29}N_5V_1O_1$ ($34 \leq n \leq 42$), $C_nH_{2n-33}N_5V_1O_1$ ($31 \leq n \leq 38$), $C_nH_{2n-35}N_5V_1O_1$ ($32 \leq n \leq 41$), $C_nH_{2n-27}N_5V_1O_2$ ($32 \leq n \leq 41$) and $C_nH_{2n-29}N_5V_1O_2$ ($33 \leq n \leq 42$). These findings are significant for the understanding of the existing form of vanadium species in nature, and are helpful for enhancing the amount of information on palaeoenvironments and improving the level of applied basic theory for the processing technologies of heavy oils.

The reserves of heavy petroleum are 8.90 trillion barrels, much larger than the 1.64 trillion barrels of conventional crude oil^{1,2}. Understanding of the molecular structures of heavy fossil feedstocks is valuable for their utilization, but characterization of these ultra-complex materials is very challenging. Vanadium compounds are present in heavy petroleum as porphyrins³. Porphyrins have been extensively studied since their discovery in crude oils and shales as “molecular fossils” by Treibs^{4,5}. They provide palaeoenvironmental information on the deposition environment^{6–10}. A portion of the vanadium compounds give strong optical absorption in the Soret band at circa 400 nm, but the remainder do not, likely due to formation of complexes or due to chemical modification of the porphyrin ring¹¹.

Six series of petroporphyrins have been identified in fossil fuels using mass spectrometry^{12–17}; Qian et al.¹⁵ successfully identified vanadyl porphyrins in unfractionated asphaltenes for the first time, and gave the primary evidence of cycloalkane-substituted and sulfur-containing vanadyl porphyrins. The more complex vanadyl compounds have not been identified. This is due to the low concentration of metalloporphyrins and the complexity of asphaltenes in heavy crude oil. Effective separation and ultra-high mass resolution are needed to resolve these vanadium compounds.

The heavy crude oil used in our studies was obtained from the Orinoco Basin in Venezuela, which was of particular interest, including large accumulations of conventional and medium oil, while at the same time possessing an immense resource of both heavy oil and natural bitumen¹. The sulfur and nitrogen elemental contents of the crude oil were 3.90 wt% and 0.74 wt%, respectively. The density was 1.03 g/cm³ at 20°C. Vanadium concentration was 513.31 ppm. The crude oil sample was subjected to solvent extractions and silica

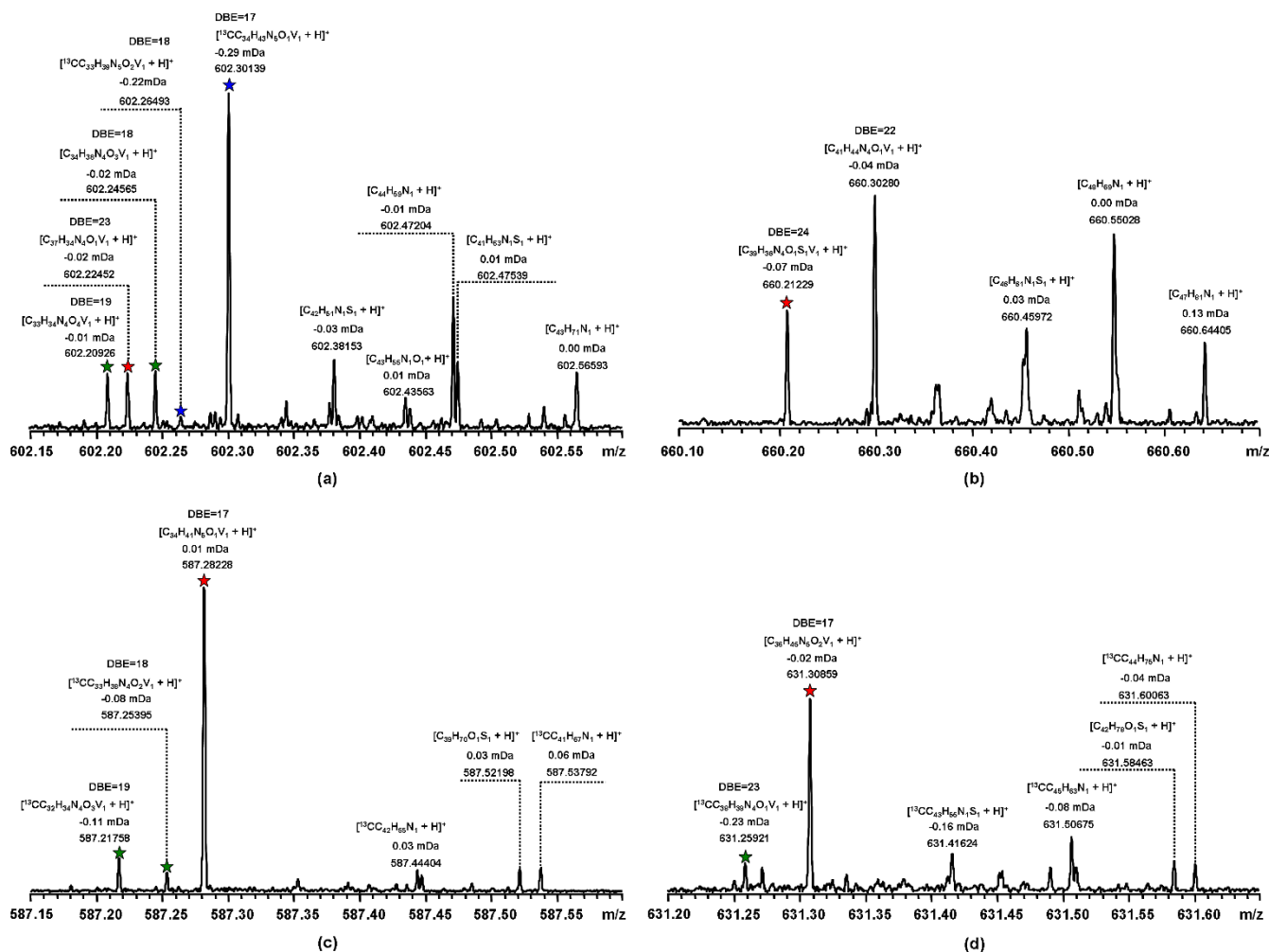


Figure 1 | Expanded mass scale spectra of fractions from the positive-ion ESI FT-ICR MS analysis (a) For fraction M6 at m/z 602, the mass peak with a red star was one of the new vanadyl porphyrins with DBE=23, and the green stars show the derivative intermediate of chlorophyll or heme, which corresponding to $[C_{33}H_{34}N_4V_1O_4+H]^+$ and $[C_{34}H_{38}N_4V_1O_3+H]^+$ described elsewhere¹⁷; (b) For fraction M5 at m/z 660, the mass peak with a red star corresponds to $[C_{39}H_{36}N_4V_1O_1S_1+H]^+$ with DBE=24; (c) For fraction M6 at m/z 587, the mass peak with a red star corresponds to $[C_{34}H_{41}N_5V_1O_1+H]^+$ with DBE=17, the green stars show the isotopic mass peak of $[C_{33}H_{34}N_4V_1O_3+H]^+$ and $[C_{34}H_{38}N_4V_1O_2+H]^+$ described elsewhere¹⁷; (d) For fraction M6 at m/z 631, the mass peak with a red star corresponds to $[C_{36}H_{45}N_5V_1O_2+H]^+$ with DBE=17, the green star shows the isotopic mass peak of $[C_{39}H_{38}N_4V_1O_1+H]^+$ with DBE=23.

gel chromatographic separations which have been described elsewhere¹⁸. The vanadium-rich fractions, named M4, M5, and M6, respectively were investigated by positive-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). All experiments were conducted on a Bruker apex-ultra FT-ICR MS equipped with a 9.4 T actively shielded superconducting magnet. FT-ICR MS has the highest available broadband mass resolution, mass resolving power, and mass accuracy, which enables the assignment of a unique elemental composition to each peak in the mass spectrum^{19,20}.

In an earlier paper¹⁸, in addition to the six known types of vanadyl porphyrins, etio porphyrins (ETIO), deoxophylloerythroio porphyrins (DPEP), dicyclic-deoxophylloerythroio porphyrins (Di-DPEP), Rhodo-etio porphyrins (Rhodo-ETIO), Rhodo-deoxophylloerythroio porphyrins (Rhodo-DPEP), and Rhodo-dicyclic-deoxophylloerythroio (Rhodo-Di-DPEP), three kinds of vanadyl porphyrins corresponding of molecular formula $C_nH_mN_4VO_2$, $C_nH_mN_4VO_3$, $C_nH_mN_4VO_4$, respectively, were detected by positive-ion ESI FT-ICR MS in the Venezuela Orinoco heavy crude oil for the first time. These formulae were consistent with intermediate derivatives of chlorophyll or heme, with functional groups of carbonyl and/or carboxyl at the periphery of porphyrin structures. This

evidence for $C_nH_mN_4V_1O_2$, $C_nH_mN_4V_1O_3$, and $C_nH_mN_4V_1O_4$ class species in crude oil adds further support to the hypothesis that petroporphyrins were derived from chlorophylls and hemes by indicating intermediate structures.

In this study, we found that some vanadium compounds existed with the main structure of porphyrin, but combined with other functional groups containing oxygen atoms, sulfur atoms and nitrogen atoms. In addition, the evidences of ultra-high resolution mass spectrometry and the possible structures were also provided. The vanadium compounds with O, S and N should associate more strongly with the asphaltenes than the less polar components. Formation of complexes with other components would shift and attenuate the Soret absorption in UV-visible spectroscopy.

Results

Ultra-high resolution mass spectra for the new vanadium compounds. Figure 1 shows the close-up view of expanded mass scale spectra of fractions M5 and M6. Figure 1 (a) is for fraction M6 at m/z 602, which was internally calibrated with $[C_{43}H_{71}N_1+H]^+$. Mass peaks were assigned base on the high mass resolution and mass accuracy. The mass peak marked with a red star was one of the new vanadyl

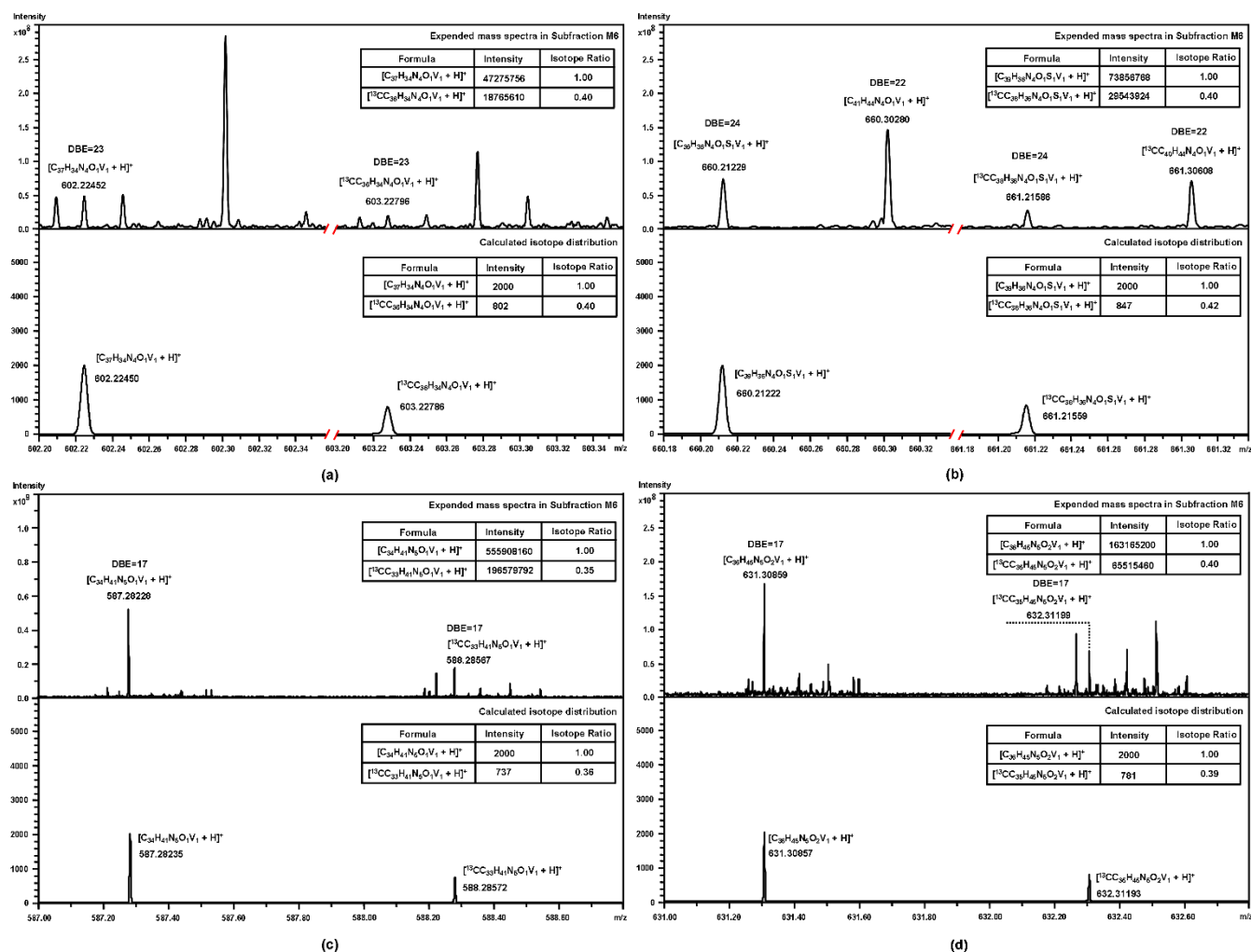


Figure 2 | The comparison chart between the real and calculated mass spectra. (a) For fraction M6 at m/z 602, 603; (b) For fraction M5 at m/z 660, 661; (c) For fraction M6 at m/z 587, 588; (d) For fraction M6 at m/z 631, 632.

porphyrins $[C_{37}H_{34}N_4V_1O_1 + H]^+$ with DBE=23, and the green stars indicate the derivative intermediate of chlorophyll or heme, which correspond to $[C_{33}H_{34}N_4V_1O_4 + H]^+$ and $[C_{34}H_{38}N_4V_1O_3 + H]^+$ described elsewhere¹⁸. Common vanadyl porphyrins contained six types of DBE (Double Bond Equivalence), from 17 to 22 shown in Supplementary Figure 1. In this work, the $C_nH_mN_4V_1O_1$ compounds with DBE=24, 25, 26, and 27 were also detected, which was shown in Supplementary Figure 2.

Figure 1 (b) is for fraction M5 at m/z 660, which was internally calibrated with the known adjacent peak of $[C_{48}H_{69}N_1 + H]^+$. The mass peak with a red star was the $[C_{39}H_{36}N_4V_1O_1S_1 + H]^+$ with DBE=24, its mass error was only 0.07 mDa. These series of vanadium compounds with sulfur atoms show continuous distribution. The $C_nH_mN_4V_1O_1S_1$ series with DBE=22, 23, 25, and 26 were also detected and shown in Supplementary Figure 3 and 4.

Figure 1 (c) and (d) is for M6 at m/z 587, 631, which were internally calibrated with $[C_{42}H_{67}N_1 + H]^+$ and $[C_{45}H_{75}N_1 + H]^+$. The mass peak with a red star in Figure 1 (c) was the $[C_{34}H_{41}N_5V_1O_1 + H]^+$ with DBE=17, which had a mass error of only 0.01 mDa. These series of vanadium compounds with five nitrogen atoms show the same DBE values with ETIOs. The mass peak with a red star in Figure 1 (d) corresponds to $[C_{36}H_{45}N_5V_1O_2 + H]^+$, which has a DBE value of 17. These series also show the same DBE with that of ETIOs. That means if these series of compounds contain the similar structure of vanadium porphyrin, the excess nitrogen atom and oxygen atom should locate on the side-chains. The N and O

adducted species were extensive, the $C_nH_mN_5V_1O_1$ compounds with DBE=18, 20, and 21; $C_nH_mN_5V_1O_2$ compounds with DBE=18 were detected and shown in Supplementary Figure 5 and 6.

Comparison of the isotope ratio between the real and calculated mass spectra. Identification of these vanadium compounds were performed by assigning the spectrum peaks to accurate mass values and isotopic masses, and by observing their characteristic serial distribution at the large mass range. An exact mass match (within 0.5 mDa) is not sufficient to unambiguously identify the presence of vanadium compounds. The isotope ratio is critical to confirm the identification in addition to matching molecular mass¹⁷. Figure 2 shows the comparison chart between the real and calculated mass spectra, which covers these new series of vanadium compounds and their substitution for one ^{13}C , the theoretical prediction of the isotope distribution generated by Bruker DA software. For example, Figure 2 (a) shows the isotope ratio of $[C_{37}H_{34}N_4O_1V_1 + H]^+$, the mass error is only 0.02 mDa, both of the real and calculated isotope ratios for $[^{13}CC_{36}H_{34}N_4O_1V_1 + H]^+$ are 0.40. Therefore, good agreements were not only found in the accuracy mass, but also in the isotope ratios. They were the powerful and significant evidences for these new vanadium compounds.

Types and distributions of these new vanadium compounds. All of these new series vanadyl porphyrins show continuous distributions.

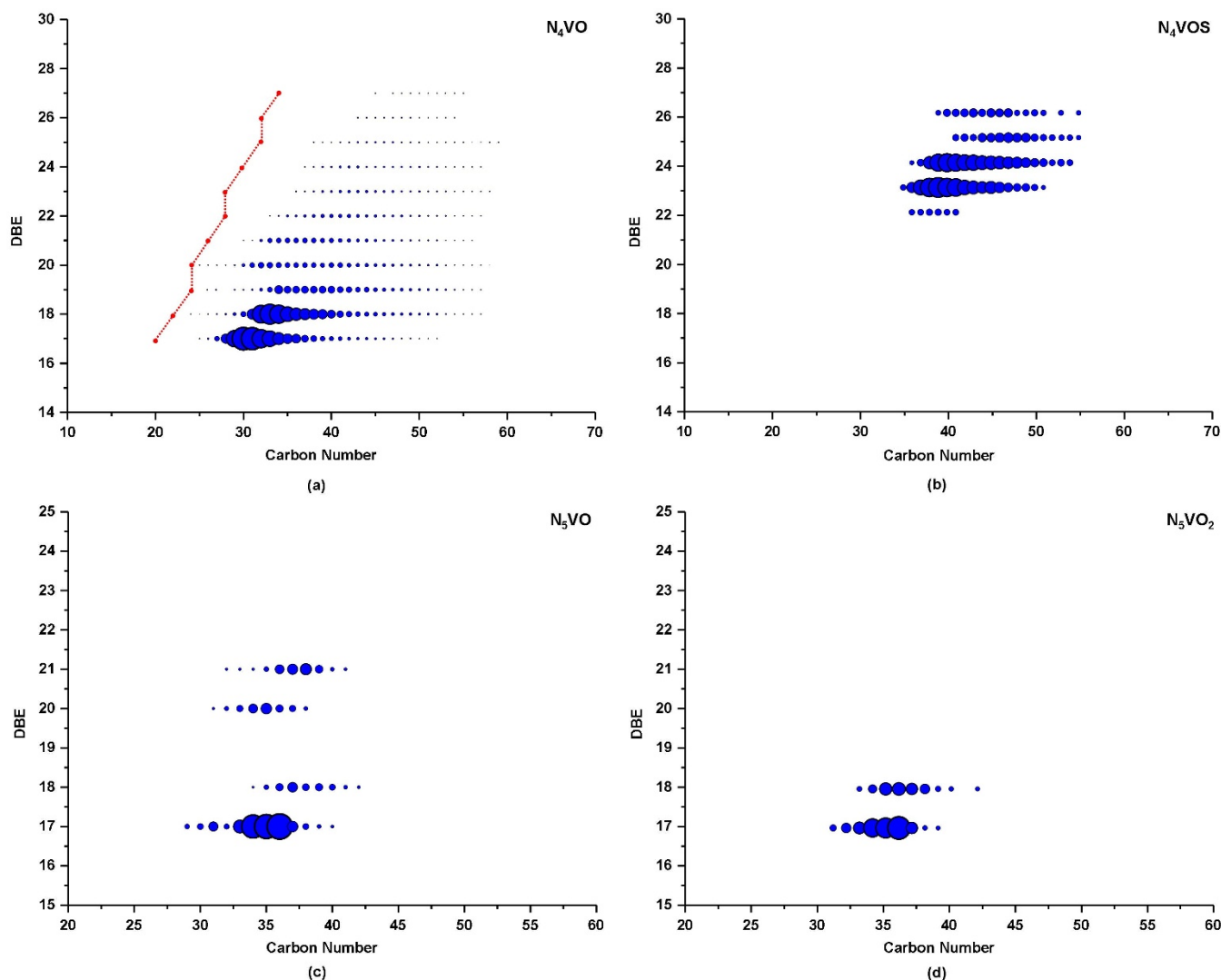


Figure 3 | Iso-abundant plots of double bond equivalents (DBE) as a function of carbon number for each type of vanadium compounds derived from positive-ion ESI FT-ICR MS. (a) For the vanadyl porphyrins in fraction M5, containing eleven types with DBEs from 17 to 27; (b) For the vanadium compounds with one sulfur atom in fraction M5, containing five types with DBEs from 22 to 26; (c) For the vanadium compounds with five nitrogen atoms and one oxygen atom in fraction M6, containing four types with DBEs, 17, 18, 20, and 21 respectively; (d) For the vanadium compounds with five nitrogen atoms and two oxygen atoms in fraction M6, containing two types with DBE of 17 and 18.

Figure 3 shows the iso-abundant plots of DBE as a function of carbon number for each type of vanadium compounds derived from positive-ion ESI FT-ICR MS. The red line in Figure 3 (a) is the absolute upper limit of planar aromatic compounds as found in petroleum, as opposed to curved or fullerene structures which have not been detected²¹. These new series of vanadium compounds detected in Venezuela heavy crude oil are divided into three classes. (1), with the basic porphyrin structure and high DBEs, corresponding to molecules $C_nH_{2n-40}N_4V_1O_1$ ($36 \leq n \leq 58$), $C_nH_{2n-42}N_4V_1O_1$ ($37 \leq n \leq 57$), $C_nH_{2n-44}N_4V_1O_1$ ($38 \leq n \leq 59$), $C_nH_{2n-46}N_4V_1O_1$ ($43 \leq n \leq 54$), and $C_nH_{2n-48}N_4V_1O_1$ ($45 \leq n \leq 55$); (2), with the basic porphyrin structure and one more sulfur atom, corresponding to molecules $C_nH_{2n-38}N_4V_1S_1O_1$ ($36 \leq n \leq 41$), $C_nH_{2n-40}N_4V_1S_1O_1$ ($35 \leq n \leq 51$), $C_nH_{2n-42}N_4V_1S_1O_1$ ($36 \leq n \leq 54$), $C_nH_{2n-44}N_4V_1S_1O_1$ ($41 \leq n \leq 55$), $C_nH_{2n-46}N_4V_1S_1O_1$ ($39 \leq n \leq 55$); (3), with five nitrogen atoms, one or two oxygen atoms corresponding to molecules $C_nH_{2n-27}N_5V_1O_1$ ($29 \leq n \leq 40$), $C_nH_{2n-29}N_5V_1O_1$ ($34 \leq n \leq 42$), $C_nH_{2n-33}N_5V_1O_1$ ($31 \leq n \leq 38$), $C_nH_{2n-35}N_5V_1O_1$ ($32 \leq n \leq 41$), $C_nH_{2n-27}N_5V_1O_2$ ($32 \leq n \leq 41$) and $C_nH_{2n-29}N_5V_1O_2$ ($33 \leq n \leq 42$).

Discussion

Based on the accurate molecular weight and the DBEs, the experiments of collision induced dissociation (CID) were conducted to determine the structures of these new compounds. Supplementary Figure 7 and Figure 8 were the extended mass spectrums of CID experiments. In Supplementary Figure 7, $[C_{44}H_{48}N_4O_1V_1+H]^+$ and $[C_{41}H_{42}N_4O_1S_1V_1+H]^+$ could still be detected with the increasing of collision voltages (CV) from -1.5 eV to -20 eV, -30 eV, we proposed the reasonable structures of these new compounds, which was shown in Figure 4 (a) and (b). They are the vanadyl porphyrins containing more fused aromatic rings and the functional groups of thiophene, which existed stably. These new vanadium compounds with sulfur atoms may be generated from organic sulfur in the source kerogens, or could be added by thermochemical sulfate reduction (TSR)/bacterial sulfate reduction (BSR) during the process of petroleum generation²²⁻²⁵, which would convert side chains into condensed aromatic rings. In Supplementary Figure 8, the mass peak of $[C_{35}H_{43}N_5V_1O_2+H]^+$ at m/z 617 was isolated with the window width of 1 Da under the model of CID, following by the spectra collecting at eight different collision voltages (CV). The peaks at

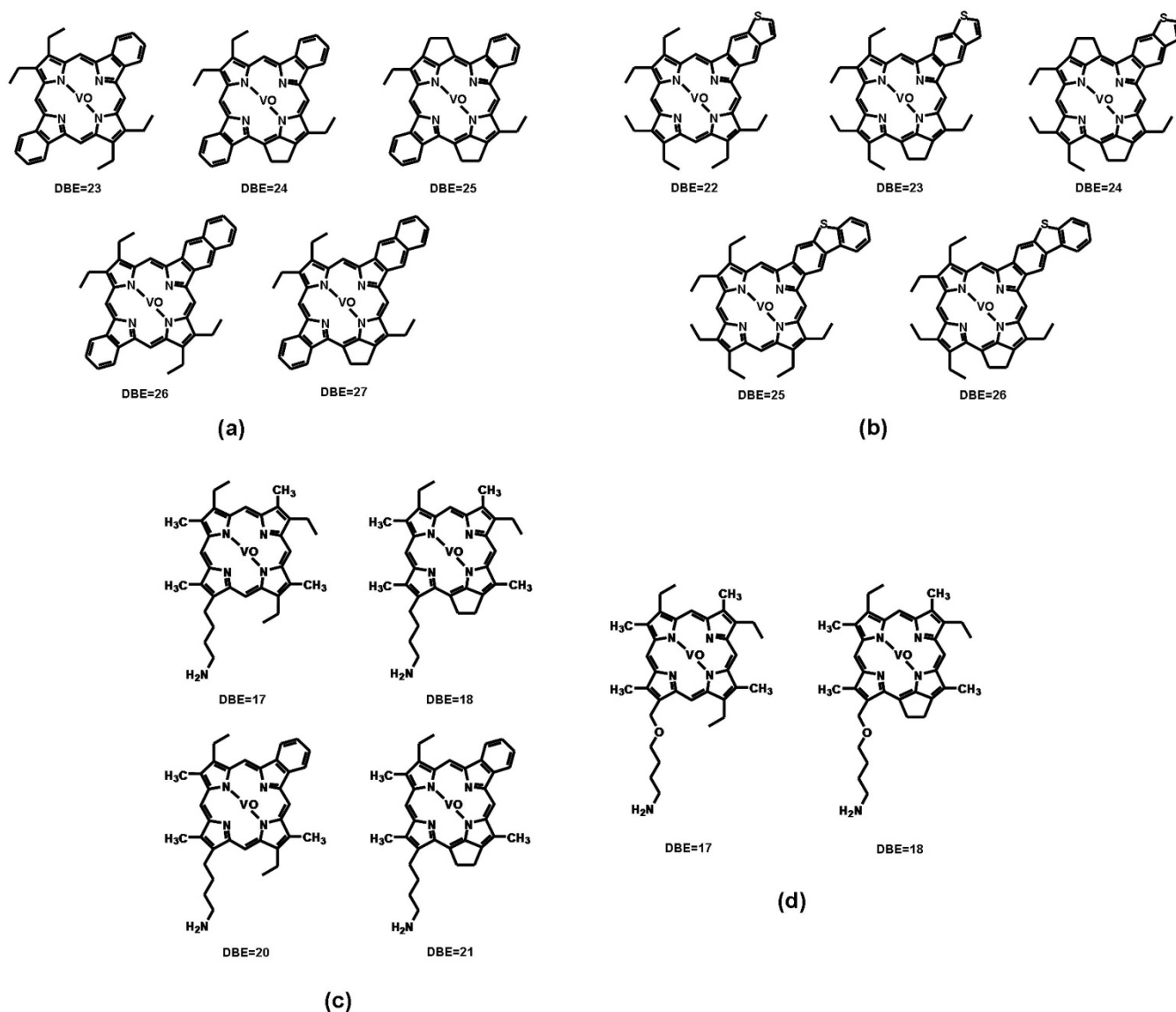


Figure 4 | The reasonable structure of new class species of vanadium compounds in Venezuela Orinoco crude oil detected in purified fractions.

(a): For the vanadyl porphyrins in fractions M5 and M6, with different DBEs from 23 to 27, containing more benzene rings linked the porphyrin ring; (b): For the vanadium compounds with one sulfur atom in fractions M5 and M6, with different DBEs from 22 to 26, containing the function group of thiophene; (c): For the vanadium compounds with five nitrogen atoms and one oxygen atom in fractions M5 and M6, with different DBEs, 17, 18, 20, and 21 respectively, containing the function group of amino; (d): For the vanadium compounds with five nitrogen atoms and two oxygen atoms in fractions M5 and M6, with different DBEs, 17 and 18, containing the function groups of amino and ether.

m/z 530 and 516, corresponded to the vanadyl porphyrins $[C_{31}H_{34}N_4V_1O_1+H]^+$ and $[C_{30}H_{32}N_4V_1O_1+H]^+$, with loss of the functional group of $C_4H_9N_1O_1$ due to breakage of a side chain, which had a DBE of zero, that meant there was no double band in $C_4H_9N_1O_1$. Hence, we suggested that the structure of $C_4H_9N_1O_1$ contained the amine function group and/or the ether link, connected with the ETIO and DPEP porphyrin rings, rather than an amide which has a DBE of one. Figure 4 (c) and (d) shows the possible structures of the new vanadium compounds with five nitrogen atoms and one or two oxygen atoms. Hodgson²⁶ gave preliminary evidence for protein fragments associated with porphyrins, based on which the structures are reasonable. These new compounds contain N, S, and O atoms which would enhance aggregation with asphaltene molecules in heavy oils.

To verify these possible structures, the molecular level structural optimization had been investigated using the density functional theory (DFT) of quantum chemical method, calculating at the B3LYP and B3LYP/LanL2DZ/6-31 G++ level of theory by Gaussian soft-

ware. The calculation results showed that these possible structures of new vanadium compounds could be existed stably, which were shown in Supplementary Figure 9 and Supplementary Table 1 and Table 2.

In summary, we have found sixteen new series of vanadium compounds in Venezuela heavy crude oil and provided the evidences of ultra-high resolution mass spectrometry. The suggested structures are significant for the better understanding of the existing form of vanadium compounds in the heavy fossil fuels, and initiate the recognition of the broad range of porphyrins that can occur.

Methods

Sample Pretreatment. Venezuela Orinoco heavy crude oil sample was obtained from the PetroChina Liaohe Petrochemical refinery. The crude oil sample was subjected to solvents and silica gel chromatographic separations described specifically elsewhere¹⁸. Briefly highlight the points of separation method here, firstly, the oil sample was dissolved in chloroform, followed by adding silica gel to form a slurry mixture; after evaporating at room temperature in a fume hood, the remaining oil/silica gel mixture was transferred into the thimble of Soxhlet extractor; then the Soxhlet extractions



were performed using methanol and toluene sequentially as solvents for 40 h and 24 h, respectively, yielding the methanol solubles and toluene solubles. The methanol soluble fraction was separated into various subfractions by introducing the methanol soluble fraction on top of silica gels in a glass column and sequentially eluting with solvents of increasing polarity to yield various silica gel chromatography subfractions, named M1 to M7. The toluene soluble fraction was divided into nC7 insolubles and solubles. The nC7 solubles were fractionated into various subfractions by introducing the nC7 solubles on top of silica gels in a glass column and sequentially eluting with solvents of increasing polarity to yield various silica gel chromatography subfractions, named T1 to T7.

The vanadium concentrations in the silica gel chromatographic subfractions of methanol soluble and toluene soluble were determined by graphite furnace atomic absorption spectrometer (GFAAS, Beijing Puxi General Analytical Instrument Co. Ltd. TAS990). The results showed majority of vanadium compounds were enriched in M4, M5 and M6 of methanol soluble subfractions, 2116.9 wppm, 3113.6 wppm, and 4380.2 wppm, respectively. The UV-vis spectra of silica gel chromatographic M4 to M6 subfractions showed the characteristic UV-vis absorption band for vanadyl porphyrins at the Soret band of 410 nm, β -bands of 533 nm, and α -band of 572 nm¹⁸. Therefore, M4, M5, and M6 subfractions were investigated by ESI FT-ICR MS.

ESI FT-ICR MS Analysis. Ten milligrams of crude oil sample and its fractions were diluted with 1 mL of toluene. Two to fifteen micro-liters of each diluted sample was further diluted with 1 mL of toluene/methanol (1 : 1, v/v) solution to yield 0.02 to 0.15 mg/mL solutions. Five micro-liters of formic acid were added to the solutions prior to the positive-ion ESI FT-ICR MS analysis. A Bruker apex-ultra FT-ICR MS equipped with a 9.4 T actively shielded superconducting magnet was used.

The analytes were infused through an Apollo II electrospray source at 180 μ L/h using a syringe pump. The operating conditions for positive ion formation were -4.0 kV emitter voltage, -4.5 kV capillary column front end voltage, and 320 V capillary column end voltage. Ions accumulated for 0.1 s in a hexapole with 2.4 V DC voltage and 500 Vp-p RF amplitude. The quadrupole (Q1) was optimized to obtain a broad range for ion transfers. An argon-filled hexapole collision cell was operated at 5 MHz and 700 Vp-p RF amplitude, ions accumulated for 0.6 s and collision voltage was set to -1.5 eV. The extraction period for ions from the hexapole to the ion cyclotron resonance cell was set to 1.5 ms. The rf excitation was attenuated at 11.75 dB. A 4M datasets were acquired for a corresponding mass range of 200 Da to 1000 Da. A total of 128 scans were co-added to enhance the signal-to-noise ratio and dynamic range.

ESI FT-ICR MS Data Processing. The FT-ICR MS was internally calibrated using a N₁ class homologous series which were [C_nH_{2n-17}N₁+H]⁺ and [C_nH_{2n-19}N₁+H]⁺. The internal quadratic calibration was also performed. Peaks with relative abundance greater than six times the standard deviation of the baseline noise level were exported to a spreadsheet. Data analysis was performed by selecting a two-mass scale-expanded segment in the middle of the mass spectrum, followed by the detailed identification of each peak. The peak of at least one of each heteroatom class species was arbitrarily selected as a reference. Species with the same heteroatom class and their homologs with different double bond equivalent (DBE) values and carbon numbers were searched within a set of 0.002 Kendrick mass defect tolerance. The details of data analysis procedure have been described elsewhere²⁷.

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Author contributions

X.Z., C.X. and Q.S. designed all experiments. X.Z. performed the experiments. C.X., M.G. and Q.S. contributed to manuscript preparation. X.Z. wrote the manuscript. All authors contributed to data analysis, discussed the results and implications and commented on the manuscript at all stages.

Additional information

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