

Vanadium isotope composition of crude oil: effects of source, maturation and biodegradation

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Abstract: We present a study of vanadium (V) isotope compositions for 17 crude oils spanning a wide range of concentrations and formation ages. Bulk organic geochemical and biomarker compositions are investigated for 11 co-genetic crude oils from the Barbados oil field. About 2‰ V isotope fractionation was observed and they are primarily correlated with V/Ni ratios and most likely reflect the depositional environment of the petroleum source rocks. Factors such as the lithology of the source rocks, Eh and pH of the depositional environment, and possibly the V isotope composition of seawater could all play a role in the V isotope composition. The Eh and pH conditions determine the speciation and coordination of V ions in fluids, whereas the lithology of the source rock defines the competing phases for available V ions in solution. The V isotopes are significantly modified by maturation and biodegradation. The V isotope fractionation during biodegradation has most probably resulted from the microbial activity-induced changes in the species and coordination geometries of V ions in fluids. The progressive decrease of $\delta^{51}\text{V}$ with the increase of maturation might suggest a preferential loss of ^{51}V during de-metalation and/or a preferential incorporation of ^{50}V in the newly formed V-organometallic compounds.

The inorganic component in crude oil is generally less than 1 wt%, but it can be important because it influences both the refining process and investigations into oil–oil or oil–source rock correlations in exploration (Filby 1994). Among the inorganic elements in petroleum, vanadium (V) is recognized as the most abundant trace metal constituent whose concentration can range upwards to more than 2000 mg kg⁻¹, although some crude oils contain as little as 0.1 mg kg⁻¹ (Amorim *et al.* 2007). The abundances of V and nickel (Ni), as well as the V/Ni ratio in crude oils, vary widely depending on the source-rock composition, depositional environment and the nature of organic matter (Lewan & Maynard 1982; Lewan 1984; Barwise 1990; Filby 1994). The concentrations of these metals can be influenced by secondary processes, such as thermal alteration, deasphalting (a process in which the asphalt content of crude oil is removed or reduced), biodegradation and water washing or during migration. However, the V/Ni ratio itself tends to be nearly constant due to the structural similarities among organometallic compounds that contain V and Ni (Galarraga *et al.* 2008). Vanadium occurs in crude oil predominantly as vanadyl ions (VO²⁺) in the form of organometallic pyrole complexes of porphyrins in which V substitutes for Mg in plant chlorophylls or Fe in haem. Vanadium also occurs as other largely

unknown non-porphyrins or as the cation of organic acids (e.g. Curiale 1987; Filby 1994; Amorim *et al.* 2007; Zhao *et al.* 2014). It has been shown that VO (II) porphyrins tend to predominate over Ni (II) in more anoxic marine environments, and that Ni (II) porphyrins predominate over VO (II) under more oxic marine and non-marine conditions (Lewan 1984). Hence, the V/Ni ratio has been successfully used to characterize the redox conditions of the depositional environment of petroleum source rocks (Moldowan *et al.* 1986; Barwise 1990; Sundaraman *et al.* 1993; Galarraga *et al.* 2008).

Stable isotope studies of V could provide important information additional to elemental studies, which are prone to more uncertainties such as initial source concentration and H₂O content. Mass-dependent stable isotope fractionation is fundamentally driven by the differences in chemical and physical properties of the atoms arising from the relative mass difference among different atoms of a given element, the so-called isotope effect (Hoefs 2008). The magnitude of isotope fractionation is inversely related to the temperature and diminishes to zero at very high temperatures (Urey 1947). Mass-dependent isotope fractionation between different phases/species is mainly affected by the valence states and the chemical binding environment, where the heavier isotope generally preferentially accumulates in the

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species or compound with higher bonding strength or higher oxidation state (e.g. Urey 1947; Schauble *et al.* 2001). Vanadium exists in multiple valence states (V^{2+} , V^{3+} , V^{4+} and V^{5+}). First-principle calculations predict that the heavy V isotope (^{51}V) is enriched in a more oxidized valence state with an equilibrium isotope fractionation factor of 6.3‰ at 25°C between $[V^{5+}O_2(OH)_2]^-$ and $[V^{3+}(OH)_3(H_2O)_3]$ (Wu *et al.* 2015). Theoretical calculations also show that V isotope fractionation occurs among different species with the same valence state caused by the differences in bond lengths and coordination numbers (Wu *et al.* 2015). This makes the V isotope system particularly important in tracking depositional or post-sedimentary environments, which can lead to a better understanding of the biogeochemical cycles and the near-surface and subsurface pathways that lead to oil formation and possibly the oil degradation processes. This is especially true when hydrocarbon biomarker indices using steranes, hopanes or terpanes have been altered by biodegradation. It has been proposed that biological processing of V by marine life prior to diagenesis may also introduce fractionation (Premović *et al.* 2002). Vanadium has been identified as an essential trace element for plants and animals (Amorim *et al.* 2007) and is thought to be important for bacterial nitrogen fixation (Anbar & Knoll 2002; Bellenger *et al.* 2008; Kraepiel *et al.* 2009). Hence, V isotopes might also have the potential to track the source of biomass within the depositional environment and eventually be developed as a regular biomarker in low-maturity crude oils.

The first attempts to resolve the systematics of the distribution of V isotopic compositions in petroleum systems was conducted on crude oils and kerogens from the Cretaceous La Luna Formation of Venezuela, but using thermal ionization mass spectrometry (TIMS) (Premović *et al.* 2002). This work revealed that the $\delta^{51}V$ values of petroleum asphaltenes and source-rock kerogens appeared to be significantly lighter than that of the inorganic matrix of the La Luna Formation, and was postulated to result from the biological processing of seawater V (Premović *et al.* 2002). In contrast, TIMS analyses of the V isotope compositions of sea squirts that take up significant V from seawater suggested that no notable isotope fractionation between sea squirt and seawater occurred during the biological V uptake process, which had been indicated by their overlapping $^{50}V/^{51}V$ ratios within the analytical uncertainty of ± 0.04 (Nomura *et al.* 2012). However, these earlier TIMS studies all suffer unfortunately from low precision with errors up to $\pm 0.3\%$ (2 SE) of the absolute $^{51}V/^{50}V$ ratios due to the incomplete removal of polyatomic or isobaric interferences and the lack of a well-characterized reference standard (Zhang 2003).

Thus, high precision analysis on V isotopes in crude oil is required to correctly assess the significance of its fractionation. Precise V isotope analyses in geological materials have been only reported recently because of major analytical challenges that occurred prior to the recent advancements in multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) and the development of more specific chemical separation techniques for V isotopes (Nielsen *et al.* 2011; Prytulak *et al.* 2011, 2013; Nielsen 2015; Ventura *et al.* 2015; Wu *et al.* 2016). The $^{51}V/^{50}V$ ratio of the only two stable isotopes of V, ^{51}V (99.76%) and ^{50}V (0.24%), is c. 420 and the minor ^{50}V isotope has direct isobaric interferences from isotopes of chromium (Cr) and titanium (Ti) – specifically ^{50}Cr and ^{50}Ti . Improvements in both MC-ICP-MS and separation protocols have greatly improved analytical precision and made it possible to investigate V isotopes to precisions of about 0.10‰ (2 σ) in silicate matrices (Nielsen *et al.* 2011, 2014, 2016; Prytulak *et al.* 2011, 2013; Wu *et al.* 2016). However, crude oils are more challenging for precise analysis of V isotopes because of their heavy organic matrix, high sulphur (S) content and wide variations in V content. The complex organic matrix may not only introduce various polyatomic interferences that could form isobars on target analytes, but also cause significant instability of the plasma. Sulphur is abundant in many marine-sourced crude oils and its concentration can vary from below 0.05 wt% up to c. 6 wt% or more (Khuhawar *et al.* 2012). Removal of isobaric interferences on V isotopes from sulphur oxide molecules using ion exchange chemical separation techniques described below have been investigated here. Sulphur interferences were initially reported by us when describing a $\delta^{51}V$ value for the NIST 8505 crude oil standard value (Casey *et al.* 2015); they have also recently been reported using higher resolution modes in MC-ICP-MS analyses (Nielsen 2015, 2016; Wu *et al.* 2016).

Ventura *et al.* (2015) recently published V isotope compositions for a suite of 11 crude oils from various basins based on the analytical method established by Nielsen *et al.* (2011) and aided by microwave-assisted digestion (Ventura *et al.* 2015). The V isotope compositions of these crude oils with V concentrations ranging from 5 to 335 ppm spanned a range of -1.64% to -0.22% , somewhat less than the range reported here. Based on the first-order source lithological dependence of $\delta^{51}V$, Ventura *et al.* (2015) proposed that the isotopic compositions in crude oils are primarily inherited from the initial sedimentary organic matter or metal-bearing fluids present during the time of sediment deposition. According to these authors, V stable isotopic composition of crude oils were unlikely to have resulted from mass-dependent fractionation

associated with the generation, expulsion or migration of petroleum (Ventura *et al.* 2015). Nonetheless, the lack of a co-genetic sample set, and the absence of organic geochemical parameters (e.g. the maturation index and biodegradation index) to help constrain processes related to fractionation, may have hindered the detection of other controlling factors and various processes that can result in V isotope fractionation in crude oils.

Here we present a detailed study of V isotope compositions coupled with certain trace and/or major element abundances (V, Ni, S) in 17 crude oils using newly developed procedures. The methods used are capable of yielding external precisions in the V isotope ratio measurement of better than $\pm 0.3\%$ (2σ) for crude oils. The crude oils were selected from eight localities from the worldwide crude oil library of the Center for Petroleum Geochemistry at the University of Houston. They were chosen because of their highly variable V content, ranging from as little as $0.71 \mu\text{g g}^{-1}$ up to $391 \mu\text{g g}^{-1}$ (Table 1) and strongly contrasting V/(V + Ni) ratios; this ratio constitutes a well-known redox index for crude oils (Lewan 1984). The selected samples were used to investigate the first-order primary controlling factor for V isotope variability of crude oils from various depositional environments. Among the 17 crude oils analysed here, a subset of 11 samples have been chosen from a single restricted location and represent a co-genetic set of marine crude oils from multiple wells from the Barbados oil field. Detailed bulk organic geochemical and biomarker analyses had been conducted earlier on the Barbados set of samples in connection with a study to assess the process of hydrocarbon generation, expulsion, migration and preservation in Barbados (Repsol, pers. comm.). The Barbados oils are interpreted to be generated within siliciclastic marine source rocks that reached the early part of the oil-generation window, although small differences in the maturity level can be recognized between the oils. Other differences in the Barbados oil properties appear to be related to strong post-accumulation processes such as biodegradation and possibly some evaporative fractionation in some of the samples. The sample set was therefore deemed useful to further evaluate the potential isotopic fractionation associated with depositional and post-depositional maturation and biodegradation processes. This restricted field locality approach for high precision V isotope measurements coupled with organic geochemistry studies to assess maturity, biodegradation and depositional environment effects on V fractionation has not been previously attempted.

We aim to evaluate the methodology and the validity of using V isotope as a fingerprint for oil–oil and oil–source rock correlation and geochemical inversion studies (Bissada *et al.* 1993) for a range

of crude oils including those variably biodegraded or of variable maturity. The results of this work may contribute to a host of current postulates involving interaction of source, maturation, and migration parameters, and their influences on oil composition. They could ultimately provide insight into some of the biogeochemical cycles, the importance of redox conditions and the variations in pathways that lead to oil formation. The importance of minerals, transition metal catalysis and water in petroleum generation is yet not completely understood (Goldstein 1983; Seewald 1994; Mango 1996; Lewan 1997).

Method

Samples

The basic geological origin, formation age and chemical compositions of all samples are given in Table 1. The detailed information for the studied samples is as follows.

Sample TP-1 is a heavy crude oil (20°API gravity) from the Timan Pechora Province, Russia. This high S crude is generally thought to be generated from Paleozoic anoxic marine carbonate source rocks at low to moderate maturity levels (Requejo *et al.* 1995).

NIST RM8505 is a Venezuelan heavy crude oil (15°API gravity) generated from the Cretaceous La Luna marly source rocks that were deposited under marine anoxic conditions (Galarraga *et al.* 2008).

Sample BFW-1 is a relatively light crude oil (35°API gravity) from the northwestern part of the Bend Arch, Fort Worth Basin in Texas, USA. The oils in this region are thought to have been generated from Pennsylvanian clastic rocks deposited in settings ranging from oxic marine to marginal marine to continental deltaic systems (Thompson 1982; Pollastro *et al.* 2003, 2007).

Sample BFW-2 (36°API gravity) and sample BFW-3 (38°API gravity) are relatively light oils from the northeastern part of the Bend Arch, Fort Worth Basin in Texas, USA. These oils are believed to be generated primarily from marine shales deposited during the Late Mississippian on a continental shelf under dysoxic conditions (Jarvie *et al.* 2001; Pollastro *et al.* 2003, 2007; Hill *et al.* 2007).

Sample PB-1 is a relatively light oil (32°API gravity) from the eastern margin of the Permian Basin adjacent to the Eastern Shelf, in Texas, USA. The source rocks for the oils in this region could be the Lower Mississippian Barnett Shale or the Upper Devonian Woodford Shale or a composite Woodford–Barnett source deposited under marine to marginal marine conditions (Comer 1991; Pollastro *et al.* 2003).

Table 1. Geochemical properties and V isotope compositions of crude oil samples

Sample	Origin	Source-rock age*	Isotope composition				Trace element				API gravity	Biomarker		
			$\delta^{51}\text{V}$ (‰)	2 sd	n	N	S (wt%)	V (mg/g)	Ni (mg/g)	V/ (V + Ni)	API ^o	Pr/ nC17	Ts/ (Ts + Tm)	Tricyclic Index
RM 8505	Venezuela	Cretaceous/Tertiary	-0.02	0.30	17	6	2.17	391	48.6	0.89	15	NA	NA	NA
TP-1	Timan Pechora Province, Russia	Paleozoic	-0.46	0.31	4	2	1.67	119	73.4	0.62	20	NA	NA	NA
PB-1	Tom Green Co. TX, USA	Lower Mississippian or Upper Devonian	-0.62	0.25	6	2	0.18	0.71	0.95	0.43	32	NA	NA	NA
BFW-1	Foard Co. TX, USA	Pennsylvanian	-1.76	0.04	3	1	0.26	1.48	11.3	0.12	35	NA	NA	NA
BFW-2	Grayson Co. TX, USA	Late Mississippian	-0.44	0.13	3	1	0.30	18.3	7.44	0.71	36	NA	NA	NA
BFW-3	Grayson Co. TX, USA	Late Mississippian	-0.11	0.11	3	1	0.20	5.41	2.24	0.71	38	NA	NA	NA
BBD-01	Barbados	Cretaceous	-0.25	0.09	3	1	1.25	80.1	74.2	0.52	19	ND	0.36	0.14
BBD-02	Barbados	Cretaceous	-0.84	0.30	1	1	0.75	82.4	76.0	0.52	20	ND	0.37	0.14
BBD-03	Barbados	Cretaceous	-0.63	0.30	1	1	0.80	44.0	41.9	0.51	25	38.6	0.39	0.14
BBD-04	Barbados	Cretaceous	-1.26	0.27	3	1	0.92	51.6	49.1	0.51	25	10.8	0.38	0.14
BBD-05	Barbados	Cretaceous	0.40	0.30	1	1	0.37	23.3	21.6	0.52	25	29.0	0.42	0.15
BBD-06	Barbados	Cretaceous	-0.67	0.30	1	1	0.98	179	172.8	0.51	19	1.03	0.37	0.13
BBD-07	Barbados	Cretaceous	-0.66	0.30	1	1	0.70	40.1	39.0	0.51	27	0.77	0.38	0.14
BBD-08	Barbados	Cretaceous	-1.60	0.30	1	1	0.21	5.54	7.39	0.43	35	0.83	0.46	0.18
BBD-09	Barbados	Cretaceous	-0.56	0.30	1	1	0.80	57.0	55.8	0.50	24	0.87	0.37	0.13
BBD-10	Barbados	Cretaceous	-1.10	0.30	1	1	0.33	18.6	20.1	0.48	31	0.73	0.43	0.17
BBD-11	Barbados	Cretaceous	-0.95	0.30	1	1	0.48	17.8	18.9	0.49	30	0.78	0.43	0.16

*Source for ages: Thompson 1982; Larue *et al.* 1985; Comer 1991; Speed *et al.* 1991a, b; Babaie *et al.* 1992; Requejo *et al.* 1995; Jarvie *et al.* 2001, 2007; Pollastro *et al.* 2003, 2007; Hill & Schenk 2005; Hill *et al.* 2007; Galarraga *et al.* 2008.

Elemental concentrations were analysed by ICP-OES and ICP-MS. Biomarker data were analysed with GC-MS, and V isotope compositions were analysed with a Nu Plasma II MC-ICP-MS at University of Houston.

NA: not available for publication; ND: not detectable.

Sample BD01 through BD11 are a set of 11 crude oils from the island of Barbados, part of the forearc accretionary prism in the eastern Caribbean, which is underlain by sedimentary rocks and mélanges that include those rocks accreted to the hanging wall of the Caribbean plate, which have been detached from the lower footwall South Atlantic oceanic plate with its Mesozoic and Cenozoic cover sequences. The source-rock ages for these crude oils are a subject of active debate. The crude oils have been suggested to be generated either from Cretaceous marine shales deposited under normal salinity and dysoxic conditions (Burggraf *et al.* 2002; Lawrence *et al.* 2002; Leahy *et al.* 2004; Hill & Schenk 2005) or from marine turbiditic shales of Tertiary age deposited under similar marine conditions (Larue *et al.* 1985; Speed *et al.* 1991a; Babaie *et al.* 1992). The Tertiary interpretation is based, in part, on similarities between whole oil gas chromatograms, carbon isotopes and other geochemical data of Barbados Tertiary shale extracts and crude oils (Babaie *et al.* 1992). Cellulose higher plant debris in wells suggest Tertiary sources were derived from the ancestral Orinoco deltaic systems (Speed *et al.* 1991a; Babaie *et al.* 1992) accreted to the front of the Caribbean arc as it migrated eastwards. Evidence to suggest a Cretaceous source rock for Barbados oils includes: (1) that most of the potential source rocks sampled at the surface or in drill holes on Barbados did not reach the oil window with $R_o < 0.6$ implying deeper, more mature sources (Babaie *et al.* 1992; Hill & Schenk 2005); (2) that a Barbados mud diapir contains not only Paleogene lithic clasts, but a Cretaceous clast (Joes River Formation), which probably indicates a deeper, more mature Cretaceous source (Speed *et al.* 1991a; Deville *et al.* 2003); (3) that direct oil–oil correlations yielded similarities between Barbados oils and some oils from eastern Venezuela and Trinidad that are from Upper Cretaceous La Luna-like source rocks based on their organic geochemistry (Zumberge 1987; Lawrence *et al.* 2002; Hill & Schenk 2005); and (4) that in the Barbados oils there is an absence of the higher plant biomarkers oleanane and lupanes typically associated with Tertiary terrestrial organic matter (Hill & Schenk 2005; our unpublished data). It is also well documented that the basal décollement in Trinidad has penetrated into the Cretaceous section (Wood 2000) and similarly Cretaceous fossils have been sampled from mud-diapir clasts of Trinidad (Speed *et al.* 1991b; Deville *et al.* 2003). Like Trinidad, Barbados is underlain by multiple accreted thrust slices that can repeat stratigraphy and effectively structurally thicken and bury Tertiary and/or Tertiary/Cretaceous stratigraphic sections, with Tertiary only of Tertiary/Cretaceous sections dependent on the depth of the basal décollement.

Barbados crude oil could be interpreted to be co-genetically formed at multiple stratigraphic/structural levels of strictly Tertiary or Tertiary/Cretaceous sections creating the variable thermal maturities down-section indicated by the Barbados crude oil geochemistry (e.g. Hill & Schenk 2005; this study). Drilling has only penetrated immature Paleocene-aged sediments and/or mélanges in Barbados (Speed *et al.* 1991a; Babaie *et al.* 1992), but similar deeper and/or older stratigraphic sections in the oil window underlying Barbados could be possible. Deeper penetration of the basal décollement into the Cretaceous at the time when Eocene–Paleocene subsurface assemblages of Barbados were accreted cannot be precluded at this time. Because there is no measured age-related geochemical biomarker in the crude oil datasets available from various geochemical studies of Barbados oils that could reliably distinguish Tertiary from Cretaceous sources (Hill & Schenk 2005; J.M. Moldowan pers. comm. 2015), we regard Tertiary and Cretaceous source-rock models as both permissible with the current published data and assessment of the internal data available.

The Barbados crude oils have API gravities ranging from 19° to 35°. In spite of the large variations in the elemental concentrations of V and Ni, these oils have a relatively narrow range of $V/(V + Ni)$ ratio of 0.50 ± 0.03 (Table 1), suggesting a small range of source-rock characteristics. Some of these crude oils have also been subjected to variable degrees of biodegradation. Oils range from severely altered in shallow reservoirs to completely unaffected in deeper reservoirs (Hill & Schenk 2005). All of these characteristics of varying biodegradation and maturity are reflected in the compositional data of the 11 wells sampled in this study (Table 1).

Mineralization to remove organic matrix

Crude oils are very complex in composition, viscosity and phase relationships. Direct injection of crude oils into ICP-MS may influence the stability of the plasma or even cause plasma extinction. The analytical challenge for both elemental and isotopic composition of metal elements in crude oils also comes from the various polyatomic and isobaric interferences due to their heavy organic matrix. A mineralization procedure has been developed to destroy the organic structures of crude oils with strong oxidizing acids in pressurized vessels with either the Parr high-pressure acid digestion bomb (Parr 4749) or the single reaction chamber microwave digestion system (Milestone Ultrawave®). These techniques have proved effective to extract metal elements from crude oils with recovery of better than $98 \pm 5\%$ (Yang 2014; Casey *et al.* 2016). Special precautions have been taken to minimize

sampling heterogeneity of high viscosity crude oils by shaking in capped glass vessels while heating at *c.* 80°C on a hot plate. For Parr bomb digestion, precisely weighed crude oil of *c.* 100 mg or *c.* 400 mg was loaded into the Teflon cup of the digestion bomb; 3 ml of 16N HNO₃ was then added to the cup which was then capped and heated on a hot plate at 150°C for 2 h. The cap was then removed and its contents evaporated down to incipient dryness. This pre-oxidizing treatment can destroy some part of the organic matrix and thus help reduce the pressure that can develop inside the Parr bomb during the following heating step. After dry-down, 3 ml of 16N HNO₃ and 1 ml of 12N HCl were added to the Teflon cup; the cup was loaded into the bomb, which, after assembly, was heated at 160°C inside a Lindberg/Blue M oven for 12 h. After the apparatus had cooled down, the inner Teflon cup was taken out of the bomb and the digested solution was then transferred into a Savillex PFA beaker. The Teflon cup was repeatedly washed with 2% HNO₃ to ensure 100% transfer. The solution inside the PFA beaker was then dried down on a hot plate at 150°C. Finally, the digested sample was re-dissolved with 5 ml of 0.2N HNO₃. For microwave digestion, *c.* 400 mg of precisely weighed crude oils were loaded into 40 ml quartz digestion tubes and then 5 ml of 16N HNO₃, 1 ml of 12N HCl and 1 ml of 30% H₂O₂ were added to the digestion tubes for digestion. A five-step microwave irradiation programme was used for digestion: (i) 5 min to 120°C; (ii) 10 min to 160°C; (iii) 10 min to 180°C; (iv) 8 min to 260°C; and (v) hold at 260°C for 15 min. After digestion the resultant solutions were transferred into PFA beakers, dried down to incipient dryness on a hot plate and then re-dissolved with 5 ml of 0.2N HNO₃. Total carbon content of the resultant sample solution was no more than 0.1% (g/g) analysed by a LECO® CS230 Carbon/Sulfur Analyzer. Near-complete recovery of V in crude oils by this mineralization procedure has been demonstrated by repeated digestion experiments on two NIST reference materials for oil (NIST RM 8505 and NIST 1634c) The analysed V concentrations are 390 ± 0.8 µg g⁻¹ (2σ, *n* = 25) for NIST RM 8505 and 28.9 ± 2.3 µg g⁻¹ (2σ, *n* = 10) for NIST 1634c, both being in good agreement with the recommended values by NIST of 390 ± 10 and 28.2 ± 0.4 µg g⁻¹, respectively (Yang 2014; Casey *et al.* 2016). The complete recovery of V during the digestion steps is important to eliminate a potential cause of isotopic fractionations of V. To achieve adequate V (minimum = 1000 ng) for isotope measurements in the method described below, solutions from multiple digestions of low-abundance crude oils were combined before purification, with the number of digestions dependent on V abundance measurements.

Chemical purification

We use a modified approach from that of Nielsen *et al.* (2011) to isolate V from other elements, especially from S, Ti and Cr. To achieve near-quantitative removal of S for successful V isotope analysis, our chemical purification protocol for crude oils uses a multi-step liquid chromatography process with combined cation and anion exchange columns. It has been demonstrated that S molecules can interfere with both V isotopes and ⁴⁹Ti – which is a monitor for Ti levels in solution for isobar correction (Nielsen *et al.* 2011, 2016; Nielsen 2015). To minimize these interferences, our changes to the existing methods include an added column for removal of S, as well as other, more specific, slight modifications to previous column procedures involving somewhat different resins, and achieving reduction in some reagents and modest increases in efficiencies of some column steps, as described below.

First column chemistry. First, 5 ml of wet Bio-Rad AG 50W X-12 (200–400 mesh) cation exchange resin was packed into a quartz glass column with an internal diameter of 10 mm. Before loading the resin, all the columns were repeatedly acid-leached with 8N HNO₃ and 6N HCl. The resin was subsequently washed with 6N HCl and Milli-Q H₂O, and conditioned with 0.2N HNO₃. Next, a 5 ml sample solution in 0.2N HNO₃ was loaded onto the resin. The resin was then washed with Milli-Q H₂O and 1N HNO₃ to remove S and major and trace elements such as Na and Li. The V was then completely washed out of the column with 40 mL of 1N HNO₃. The analysis of the collected solution for the V fraction using ICP-MS indicated that V was 100 ± 5% recovered from the column together with Ti, K and minor amounts of Na. Other cations, such as Mg, Ca, Fe, Al, Si and Cr were all effectively separated from the V fraction by being held in the resin due to them having higher distribution coefficients than V coefficients (Strelow *et al.* 1965). Sulphur (mainly existing as the anion SO₃²⁻) was almost completely removed from the sample matrix. To achieve a complete removal of S, a second pass through this cation exchange column was required for samples with high S content. The removal of Mg, Ca and the majority of other cations by this step makes it possible to use small columns and also to use further separation columns that involve HF to remove Ti and other cations (avoiding the formation of Mg and Ca insoluble fluorides). The collected V fraction in 1N HNO₃ was then evaporated and refluxed with 6N HCl to reduce V⁵⁺ to V⁴⁺; the V was then picked up with 1 ml 0.3N HCl in 1.0N HF mixed acids for the second column.

Second column chemistry. Initially, 1 ml of anion exchange resin AG1 X8 (200–400 mesh) was packed

in a polypropylene column (Bio-Rad, USA). This column was used to separate Ti from V based on the method reported by Makishima *et al.* (2002) and Nielsen *et al.* (2011). Before loading the sample, the columns were cleaned with 6N HCl, 2N HF and Milli-Q H₂O and then conditioned with eluent (0.3N HCl in 1.0N HF mixed acid); a 1 ml sample solution in mixed 0.3N HCl and 1.0N HF prepared from the first column was then loaded onto the column. Finally, the V was eluted with 20 ml of eluent, which left Ti in the column.

Third column chemistry. As with the second polypropylene columns, the third set of columns were repeatedly acid-leached with 8N HNO₃, 6N HCl and 10N HF before filling with 1 ml AG1 X8 resin. These columns were designed to further purify V from other cations remaining in the V fraction after the first and second columns, i.e. mainly K and minor Cr. For this column procedure, V remained absorbed strongly in the band at the top of the column due to the formation of a polyvanadate complex inside the anion exchange resin particles with a matrix of weak acid containing H₂O₂, whereas all the cations have no absorption to the resin (Strelow & Bothma 1967; Kiriyaama & Kuroda 1983). The V fraction obtained from the second column was dried down and then refluxed with 15N HNO₃ – to oxidize all V to the V⁵⁺ form – and then re-dissolved in 1 ml of a mixture of 0.01N HNO₃ and 1.0% H₂O₂. The resin was washed with 2N HNO₃ and Milli-Q H₂O and conditioned with a mixed solution of 0.01N HNO₃ and 1.0% H₂O₂. The sample solution was then loaded onto the column and the resin washed with 10 ml of the mixed solution (0.01N HNO₃ and 1.0% H₂O₂) to remove K, Cr and possibly other cations. Finally, the V was collected with 14 ml of 1N HNO₃.

The chemical separation procedure described above resulted in ⁵⁰Ti/⁵⁰V, ⁵⁰Cr/⁵⁰V and S/V ratios of less than 0.06, 0.04 and 0.1, respectively. The full procedural blank for V from this separation technique was less than 10 ng.

Elemental analysis

Concentrations of V, Ni and S in the crude oils were determined by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry, Agilent 725) or triple quadrupole (QQQ) ICP-MS (Inductively Coupled Plasma Mass Spectrometry, Agilent 8800), depending on their concentrations after digestion, at the University of Houston. The long-term precision of this method in terms of reproducibility of V, Ni and S concentrations is generally about or better than 1% (1σ) evaluated by repeated analysis on multiple full replicates of the NIST RM8505 standard. As to accuracy, the V concentration on NIST RM8505 determined by this method is 391 ± 2 μg g⁻¹

(2σ, n = 17), which is within 1% of the NIST recommended value of 390 ± 10 ppm.

Mass spectrometry for V isotope analysis

For V isotope analysis, we utilized the high resolution Nu Plasma II MC-ICP-MS at the University of Houston. The samples were introduced through a Cetac Aridus II desolvating nebulizer at a concentration of 1000 ng g⁻¹ of V in 2% HNO₃. Sample analyses were bracketed by a 1000 ng g⁻¹ in-house V single-element standard ('UH') prepared from the V ICP standard from Inorganic Ventures, USA (IVU). Isotope compositions in δ notation were first calculated relative to this University of Houston in-house standard (δ⁵¹V_{UH}) in parts per 1000 (δ⁵¹V per mille):

$$\delta^{51}\text{V}_{\text{UH}} = 1000 \times [({}^{51}\text{V}/{}^{50}\text{V})_{\text{sample}}/({}^{51}\text{V}/{}^{50}\text{V})_{\text{IVU}} - 1] \quad (1)$$

The δ⁵¹V_{UH} compositions were all converted and reported relative to the Alfa Aesar (AA) V standard of Nielsen *et al.* (2011) by:

$$\delta^{51}\text{V} = \delta^{51}\text{V}_{\text{UH}} - \Delta \quad (2)$$

where Δ is the average measured per mil difference between the IVU and the AA standards of -0.1 ± 0.02‰ (SE; n = 82).

Masses of 49, 50, 51, 52 and 53 were collected in five Faraday cups (L4, L1, H2, H5 and H7, respectively) fitted with 10¹¹ Ω resistors. For a solution with 1000 ng g⁻¹ V and an uptake rate of 40 μl min⁻¹, the typical intensity of ⁵¹V is about 40 volts. Isobaric interferences from ⁵⁰Ti and ⁵⁰Cr on ⁵⁰V were corrected by monitoring masses 49 and 53, respectively. Values for ⁵⁰Ti/⁴⁹Ti and ⁵⁰Cr/⁵³Cr used for the isobaric interference corrections are 0.9725 (Niederer *et al.* 1985) and 0.4574 (Shields *et al.* 1966), respectively. These values were corrected for instrumental mass fractionation using an exponential law. An exponential mass fractionation factor (β value) was applied to correct for instrumental mass fractionation of the ⁵⁰Ti/⁴⁹Ti and ⁵⁰Cr/⁵³Cr ratios used for isobaric corrections according to the equation:

$$R_{\text{M}} = R_{\text{T}}/(m_1/m_2)^{\beta} \quad (3)$$

where R_T and R_M are the true and measured isotope ratios for a given element and m₁/m₂ is the mass ratio of ⁵⁰Ti/⁴⁹Ti and ⁵⁰Cr/⁵³Cr. The calculated ratio R_M is used for isobaric interference corrections. Dynamic determination of β values for Ti and Cr during an analysis is impossible even with the wide collector array of the Nu Plasma II. Therefore, prior to an analytical session, the β values for Cr and Ti were

independently determined and these fixed values were applied to the online data correction protocol. Overall, $\beta_{(\text{Ti})}$ and $\beta_{(\text{Cr})}$ were *c.* -1.7 and drift during an analytical session (typical of about 20 to 24 hours) was less than ± 0.01 . Maximum $^{50}\text{Ti}/^{50}\text{V}$ and $^{50}\text{Cr}/^{50}\text{V}$ ratios for samples analysed were 0.02 and 0.03, respectively, and the magnitude of offset in the corrected $\delta^{51}\text{V}$ derived from such a small variation of β values was less than 0.002% . Doping experiments with Ti, Cr and S confirm that the relative levels of these particular elements in the purified V solutions result in no systematic bias in the V isotope ratio measurements (Fig. 1). Our tests on natural crude oils with high and low V and S abundances indicate that this method yields a 2σ precision of $\pm 0.30\%$ and is applicable to, and suitable for, crude oils with a wide range of V concentrations (Table 1). It is worth noting that this precision is comparable to that obtained by Ventura *et al.* (2015) but with five times less material (1 ppm v. 5 ppm), mostly owing to the high sensitivity of the Nu Plasma II used for this study. The analysed V isotope compositions of the BDH V standard solution over a 6-month period yielded a mean value of $-1.15\% \pm 0.3\%$ (2σ) which is comparable to the values of -1.19 ± 0.12 (2σ) published by Nielsen *et al.* (2011). The accuracy on the V isotope analysis was further checked by repeated analyses on two NIST reference materials – NIST RM 8505 and NIST SRM 1634c. Repeated analyses (six analyses for two digestions and separations) of NIST SRM 1634c, which is a residual fuel oil with $28.2 \mu\text{g g}^{-1}$ V and 2 wt% of S, yielded a mean $\delta^{51}\text{V}$ value of $-1.41 \pm 0.11\%$ (2σ). Repeated analyses (17 runs from six digestions and separations) of NIST RM 8505, which is a Venezuelan crude oil with $390 \mu\text{g g}^{-1}$ V and 2.2 wt% of S, yielded a mean $\delta^{51}\text{V}$ value of $-0.02 \pm 0.3\%$ (2σ). Both values are in good agreement within the quoted uncertainties with their reported values of -1.49% and $-0.33 \pm 0.36\%$ for NIST SRM 1634c and NIST RM 8505, respectively (Ventura *et al.* 2015). It is interesting to note that our $\delta^{51}\text{V}$ values for NIST RM 8505 and NIST 1634c, although within uncertainties, were both slightly heavier than those obtained by Ventura *et al.* (2015), which might be related to the S effect on the V isotope analysis as stated in the above section.

Results

The V isotope compositions of the 17 crude oils are compiled in Table 1 and Figure 2. The $\delta^{51}\text{V}$ compositions of these oils showed a wide variation, ranging from -1.76% to $+0.40\%$, which is wider than the reported range from -0.27% to -1.29% in mantle-derived mafic and ultramafic rocks from diverse localities and of various degrees of alteration (Prytulak *et al.* 2013). The V isotope composition of these

crude oils indicated that they have been fractionated to be both heavier and lighter compared to that of Bulk Silicate Earth (BSE) ($\delta^{51}\text{V}_{\text{BSE}} = -0.7 \pm 0.2\%$, Prytulak *et al.* 2013). The crude oils analysed here define a slightly broader range compared with the previous results (Ventura *et al.* 2015), though the two datasets largely overlap (Fig. 2). Most strikingly in this study, the 11 co-genetic crude oils from Barbados have almost the same degree of V isotope fractionation defined by the globally distributed sample sets used in both studies, but surprisingly very restricted ratios of V/Ni and V/(V = Ni) compared with the global values (Table 1; Fig. 2).

Discussion

Source and reservoir

The crude oils in this study have a broad range of V isotope compositions (-1.76% to $+0.40\%$, Table 1). The observed total V isotope fractionation of about 2.2% is smaller than the predicted equilibrium fractionation at 25°C of 6.3% between V(V) and V(III) species and of 3.9% between V(V) and V(IV) species for inorganic V species in an aqueous system (Wu *et al.* 2015). However, it is somewhat close to the predicted equilibrium fractionation at 25°C between V(IV) and V(III) species of 2.5% , and that of 1.5% between two V (V) species in an aqueous system (Wu *et al.* 2015). There is a first-order correlation between the V isotope composition and the V/(V + Ni) ratio in the regionally distributed datasets (Fig. 3). As shown in Figure 3, isotopically heavy crude oils are generally associated with high V/(V + Ni) ratios, whereas isotopically light crude oils tend to have low V/(V + Ni) ratios. Such an overall positive correlation between $\delta^{51}\text{V}$ values and the V/(V + Ni) ratio in crude oils has also been reported previously (Ventura *et al.* 2015). We, however, also observed significant variation in $\delta^{51}\text{V}$ values at a given V/(V + Ni) ratio when examining the Barbados dataset from a single locality (Fig. 3) where a large number of more regionally discrete samples from different wells were available for study.

The primary prevalence and proportionality of Ni and V in crude oils are believed to be controlled by the Eh–pH conditions, the availability of S and the lithology of the source rock in the depositional environment (Lewan & Maynard 1982; Lewan 1984; Barwise 1990). The metallo-porphyrins of V and Ni are formed during early diagenesis of source rocks through the metalation of free-based porphyrins which form during a series defunctionalization and conversion of chlorophyll (Baker & Louda 1986; Filby & Van Berkel 1987; Keely *et al.* 1990; Filby 1994). In general, oils of marine origin in more anoxic environments have higher concentrations of trace elements predominated by V porphyrins

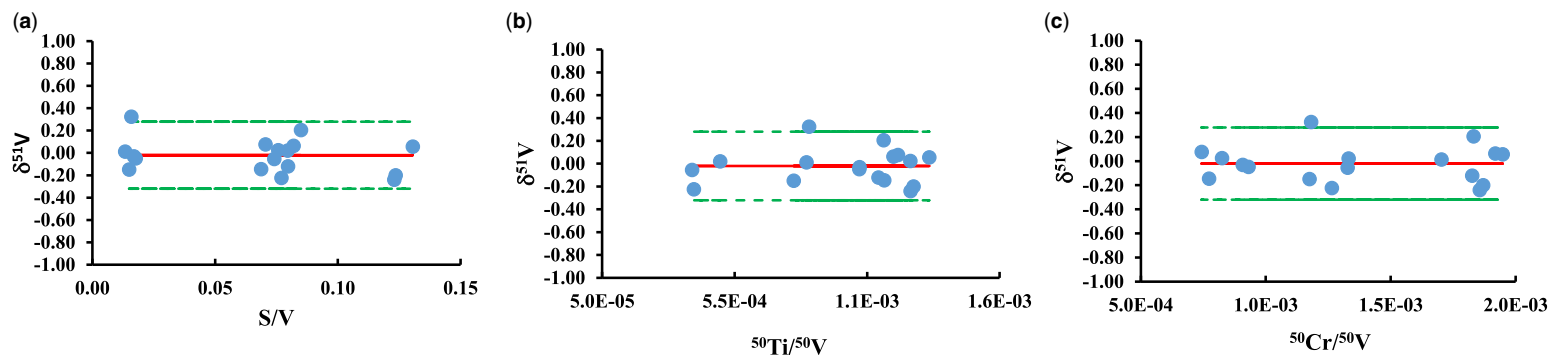


Fig. 1. Measured V isotope compositions for NIST Crude Oil Reference Material RM 8505, reported relative to the AA V standard solution defined as 0‰ (Nielsen *et al.* 2011). Dashed green lines represent the 2 σ error of $\pm 0.3\%$, and the solid red line represents the average value of -0.02% . This shows that multi-step column chemistry can efficiently remove S (a), Ti (b) and Cr (c), and their presence in the purified V solutions results in no systematic bias in the V isotope ratio measurements.

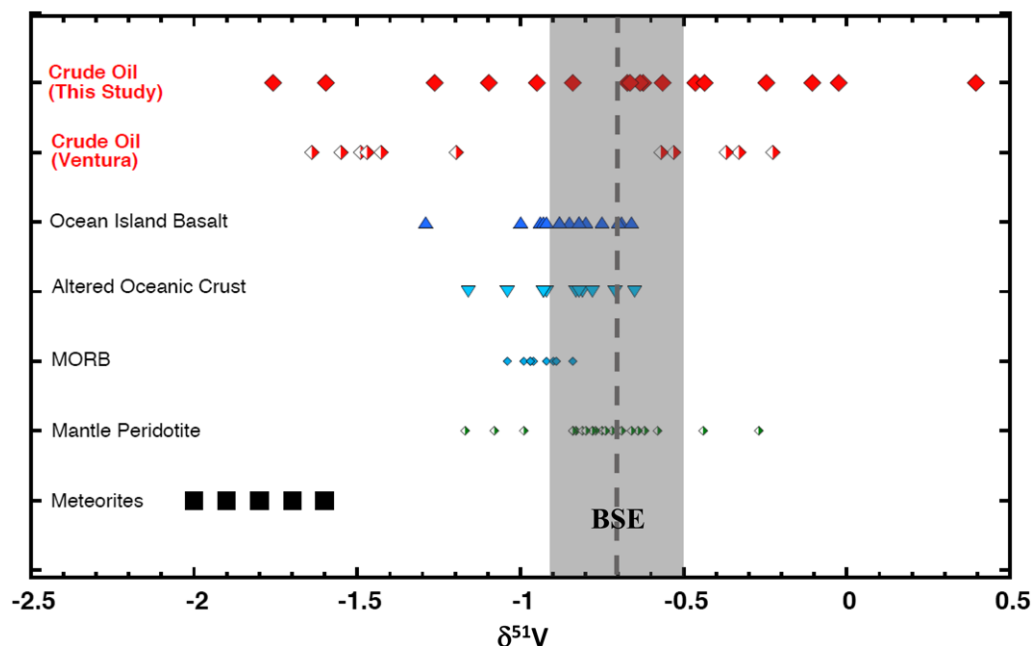


Fig. 2. V isotopic compositions of crude oils (top two rows) as reported here and by Ventura *et al.* (2015) compared with all other data available from terrestrial and meteorite reservoirs (Prytulak *et al.* 2011, 2013; Nielsen *et al.* 2014). Values of $\delta^{51}\text{V}$ are reported relative to the AA V solution standard defined as 0‰ (Nielsen *et al.* 2011). Shaded area is the reported range for Bulk Silicate Earth (BSE): $(-0.7 \pm 0.2\text{‰})$; Prytulak *et al.* 2013).

over Ni, whereas oils derived from terrestrial sources under more oxic conditions have lower concentrations of trace elements predominated by Ni porphyrins over V (Lewan 1984; Barwise 1990; Filby 1994). Hence, both the $\text{V}/(\text{V} + \text{Ni})$ and V isotopic compositions of crude oils might be primarily controlled by the depositional environment of the petroleum source rocks where the V was incorporated into organic matter during sediment deposition and early diagenesis. It is worth noting that the observed correlation trend between V isotope composition and the oxidizing conditions indicated by the $\text{V}/(\text{V} + \text{Ni})$ ratio (Fig. 3) seems to somewhat contradict the theoretical predictions that the heavy V isotope (^{51}V) should be enriched in a more oxidized valance state (Wu *et al.* 2015). However, it should also be noted that validation of the observed first-order correlation between the V isotope compositions and the $\text{V}/(\text{V} + \text{Ni})$ ratios for globally distributed crude oils (Ventura *et al.* 2015; this study) requires further detailed organic geochemical data to support their pristine nature (i.e. these oils were not altered by any secondary process). As discussed in the following sections, secondary processes, such as maturation and biodegradation, can significantly shift the primary V isotope compositions, because in crude oil V mainly occurs as vanadyl ions (VO^{2+}) in the form of organometallic complexes (Branthaver &

Filby 1987; Filby & Van Berkel 1987; Filby 1994). The observed overall correlation between the V isotope compositions and the $\text{V}/(\text{V} + \text{Ni})$ ratios, if proven, might indicate that the V isotope compositions in crude oils are primarily controlled by factors other than the valance status of V in crude oils. It has been shown that the V isotope could fractionate between different species with the same valance status due to the differences in bond lengths and coordination numbers (Wu *et al.* 2015). However, this could also indicate that the dominant speciation and/or the valance status of the V-organometallic complexes could be different in crude oils generated under different depositional environments. For instance, the V in crude oils originated from strongly reducing, H_2S -rich marine, carbonaceous, sedimentary environments mainly exists as vanadyl (VO^{2+}) porphyrins, whilst the V in crude oils from less anoxic, H_2S -poor, non-marine, clay-rich siliciclastic environments might dominantly exist as V (III) in non-porphyrins or as the cation of organic acids. The V in clay minerals that is present mainly as V (III) (Maylotte *et al.* 1981; Premović 1984; Wanty *et al.* 1990) could potentially be leached into interstitial water and be incorporated into crude oils. Further detailed work on the relationship between V isotopes and its speciation in crude oils will be required to resolve this question.

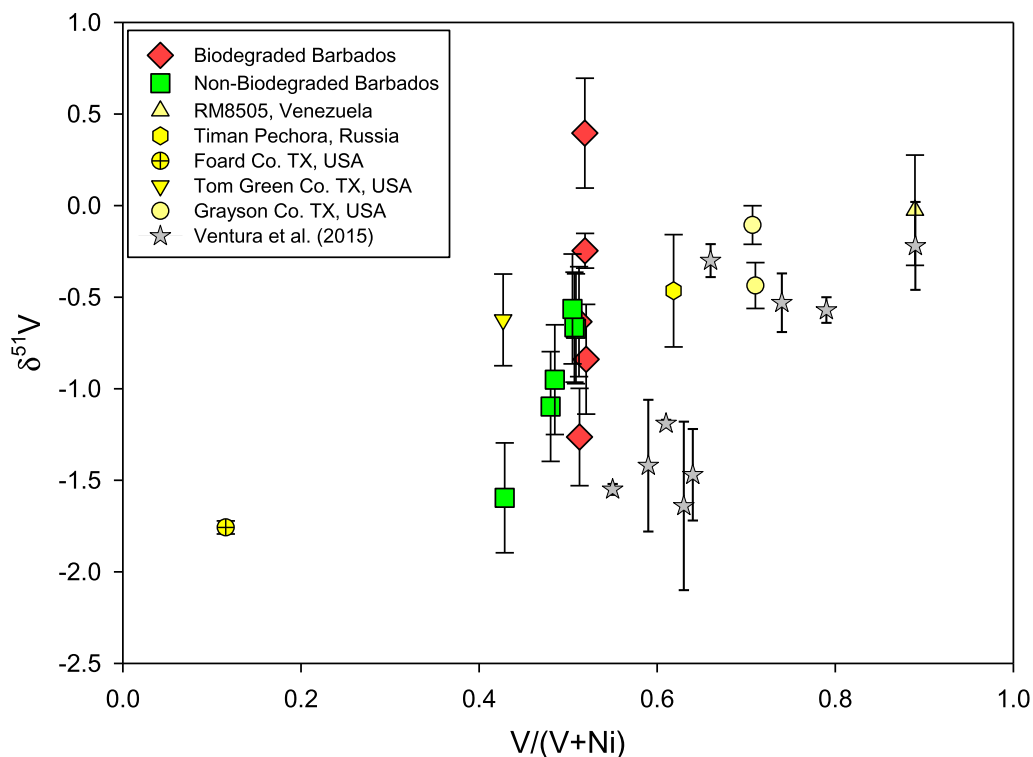


Fig. 3. V isotopic compositions of crude oils from this study and Ventura *et al.* (2015) plotted against V/(V + Ni) ratios. Error bars are 2 SD listed in Table 1. Values of $\delta^{51}\text{V}$ are reported relative to the AA V solution standard defined as 0‰ (Nielsen *et al.* 2011).

The source of V in organic-rich sediments is a matter of controversy and is far from being solved. Two plausible sources have been postulated: (i) the buried remains of V-rich marine organisms (Premović *et al.* 1986); or (ii) preferential adsorption and reduction of V from the water column, from the water/sediment depositional surface, or from subsurface pore water (Szalay & Szilágyi 1967; Bloomfield & Kelso 1973; Cheshire *et al.* 1977; McBride 1978; Premović 1978).

Despite being toxic in humans, V is categorized as an essential trace element for plants and other animals. It stimulates the synthesis of chlorophyll and promotes the growth of young animals (Amorim *et al.* 2007). It is found in marine algal haloperoxidase enzymes (Butler 1998). It also accumulates in Tunicata (Crans *et al.* 2004) that first appear in the fossil record in the early Cambrian period (Fedonkin *et al.* 2012). 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 (Maréchal *et al.* 1999; Premović *et al.* 2002). Premović *et al.* (2002) proposed that the

difference in the $^{50}\text{V}/^{51}\text{V}$ values between the La Luna petroleum asphaltenes/source kerogens and inorganic sources can be ascribed to biological processing of seawater V. In contrast, direct comparison of the V isotope composition of sea squirts and that of seawater appears to show that no notable isotope fractionation occurs during the biological V uptake process, admittedly at the given analytical precision (errors up to $\pm 5\%$ for $^{51}\text{V}/^{50}\text{V}$ ratio, Nomura *et al.* 2012). Obviously, better and more precise investigations are required to resolve the observed controversy. Wedepohl (1971) demonstrated by mass balance calculation that the mechanism for the enrichment of V by V-rich marine organisms must have been of only minor importance. This would indicate that the large V enrichments observed in organic material/crude oil are largely the consequence of adsorption and reduction during deposition and early diagenesis and lithification. This is consistent with V being preferentially concentrated in sediments overlain by anoxic waters through diffusion across the sediment–water interface and immobilization within sediments (Emerson & Huested 1991).

Normal seawater has a V content of only *c.* 2 ppb (Wedepohl 1971), but enrichment of V at the sea bottom may occur under highly reducing conditions associated with organic-matter scavenging action within enriched V solutions (Premović *et al.* 1986). The ultimate sources of V in seawater include hydrothermal solutions related to submarine volcanism (Boström & Fisher 1971), and continental runoff (Wedepohl 1964). Laboratory experiments suggest that V is not leached from basalt during hydrothermal alteration (Seyfried & Mottl 1982). As with serpentinization and seafloor weathering, there is little evidence for elemental V addition or removal during low-temperature hydrothermal alteration (Kelley *et al.* 2003). It has also been reported that the hydrothermal fluids show little overall change in concentration in comparison to seawater (Jeandel *et al.* 1987), which suggests that high-temperature hydrothermal processes cannot be very important in determining the concentration of V in the ocean.

The oceanic residence time of V has been calculated as *c.* 50 kyr (Tribouillard *et al.* 2006), which is significantly longer than the mixing time of the global oceans (*c.* 2000 years; Palmer *et al.* 1988). This would be sufficient for the ocean to have an isotopically homogenous V composition at any given geological time. Hence, one possible explanation of the observed variations in V isotope composition of crude oil would be a simply inheritance from a variable V isotope composition of seawater at the time of source-rock deposition. Theoretical calculations suggest that the V isotope composition of seawater might vary with change of ambient oxygen levels (Wu *et al.* 2015). However further work is required to establish such a speculative control mechanism.

Due to the limitation on high precision age constraints on the crude oils investigated in this study, it is not possible or prudent to conduct a detailed investigation on the age dependence of the V isotope compositions in crude oils. Although under debate because the Barbados source-rock age is less resolvable, the Venezuelan heavy crude oil (NIST RM8505) and the crude oils from Barbados have been interpreted by various investigators to be generated from similar Cretaceous source rocks under marine conditions (Hill & Schenk 2005; Galarraga *et al.* 2008). We note that the NIST RM 8505 crude oil from Venezuela has a very different average $\delta^{51}\text{V}$ value ($-0.02 \pm 0.30\%$) from the average value ($-0.61 \pm 0.07\%$) for crude oils from Barbados that have been least altered (e.g. oils with $\text{Pr}/n\text{C}_{17} < 1.0$ and $\text{Ts}/(\text{Ts} + \text{Tm}) < 0.38$; Table 1 and Fig. 3), although age-related differences are a possibility. If indeed these two sets of crude oils were actually formed at near-similar ages in the Cretaceous, the differences might indicate that the pristine V isotope composition of crude oil is controlled by factors

other than the speculated $\delta^{51}\text{V}$ fluctuation of seawater. The possible factors that can affect the V isotope composition of crude oils other than the temporal variation of V isotope composition of seawater are the depositional environment-dependent speciation of V and their coordination geometries in aqueous solutions (Wu *et al.* 2015). Theoretical calculations showed that V isotope fractionation could occur between different species with the same valence state due to their different bond lengths and coordination numbers (Wu *et al.* 2015).

In aqueous solution, both V (III) and V (IV) species are cationic while V (V) species are anionic (Baes & Mesmer 1976; Zhang 2003). In aqueous solutions, both vanadate (V^{4+}) and vanadyl (V^{5+}) ions undergo a number of the self-condensation reactions. These reactions are very sensitive to the pH of the solution and the presence of potential ligands which can coordinate to the vanadyl and form a number of complexes with different coordination geometries (Baes & Mesmer 1976; Zhang 2003). Vanadium in oxic seawater should be present as V (V) and be hydrolyzed to $\text{VO}_2(\text{OH})_3^{2-}$ at neutral pH, whilst under more acidic conditions (below pH of *c.* 3) the dioxovanadium cation VO_2^+ is the stable species due to the increased coordination number of its hydrated form (Baes & Mesmer 1976; Seewald 2003). Under moderately reducing conditions V (IV) is stable as the oxovanadium cation VO^{2+} , which should also hydrolyze at seawater pH to $\text{VO}(\text{OH})_3^-$ (Baes & Mesmer 1976).

Theoretical calculations show that V isotopes can also be significantly fractionated due to mineral adsorption (Wu *et al.* 2015). Both V(IV) and V(V) are surface-reactive and thus subjected strongly to adsorption processes in natural waters (Wehrli & Stumm 1989). Adsorption of V to biogenic or terrigenous detritus is the most commonly considered mechanism of V removal from seawater and enrichment (Amdurer *et al.* 1983; Prange & Kremling 1985). In the pH range of most natural waters, vanadate strongly adsorbs to ferric and aluminum oxides (Honeyman 1984; Micera & Dallochia 1988; Shieh & Duedall 1988; Wehrli & Stumm 1989) and kaolinite (Breit & Wanty 1991). The vanadyl ion adsorbs more strongly than vanadate, but its stability as an adsorbed species is limited in oxic-water environments (Wehrli & Stumm 1989). Vanadyl (VO^{2+}) ions in nature are characteristically associated with organic ligands and humic and fulvic acids (Cheshire *et al.* 1977; Wehrli & Stumm 1989). In aqueous solutions, therefore, competition for the V (IV) species exists between dissolved organic matter and solid surfaces, such as clays and iron oxides (Shieh & Duedall 1988; Trefry & Metz 1989). Adsorption of vanadyl ions to oxides is preferred over complexation by dissolved organic ligands, except at high ligand concentrations (Micera & Dallochia 1988;

Wehrli & Stumm 1989). In crude oil, V mainly occurs as vanadyl ions (VO^{2+}) in the form of organometallic complexes with porphyrins (vanadyl porphyrins) for the substitution of the Mg of plant chlorophylls, and with other largely unknown non-porphyrins or as the cation of organic acids (Branthaver & Filby 1987; Filby & Van Berkel 1987; Filby 1994). The metalation of organometallic complexes occurs in early diagenesis where metal ion speciation in interstitial water is controlled by the Eh–pH conditions during sedimentation as the buried sediment may not be in open contact with the water column above the sediment (Lewan 1984; Filby 1994).

Hence it is reasonable to expect a first-order dependence of $\delta^{51}\text{V}$ in crude oils on the depositional environment of petroleum source rocks. During the deposition and early diagenesis, the Eh–pH conditions determine the speciation and coordination of V ions in the water column or pore water, whilst the lithology of the source rock (i.e. the relative abundance of carbonate, clay and iron oxides) defines the co-existing phases that are competing with organic molecules (e.g. porphyrins) for the available V ions in solution. The observed overall correlation between the V isotope compositions and the V/(V + Ni) ratios (Fig. 3) indicate that the crude oils originated from strongly reducing, H_2S -rich, marine, carbonaceous sedimentary environments tend to have heavier $\delta^{51}\text{V}$ values compared with those from the less anoxic, H_2S -poor, non-marine siliciclastic environments.

Biodegradation

As shown in Figure 3, the co-genetic crude oils from Barbados have a wide variation of $\delta^{51}\text{V}$ values ranging from -1.60‰ to $+0.40\text{‰}$ (Fig. 3; Table 1). This clearly indicates that the pristine V isotopic compositions of crude oils can be significantly modified by secondary processes, such as migration, maturation or biodegradation in a single location. These secondary processes may result in the gain or loss of V during the petroleum system evolution through burial, catagenesis, migration and entrapment (e.g. Filby 1994).

Based on the measured ratio of Pr/ $n\text{C}_{17}$ and the shape of the chromatograms of light organic compounds in the samples – which are reliable indicators for biodegradation (Peters & Moldowan 1993) – the analysed crude oils from Barbados are subdivided into two groups: biodegraded crude oils (Pr/ $n\text{C}_{17}$ > 1.0) and non-biodegraded crude oils (Pr/ $n\text{C}_{17}$ < 1.0). Compared to the average $\delta^{51}\text{V}$ value of $-0.61 \pm 0.07\text{‰}$ for the most pristine crude oils (samples BBD-7 and BBD-9, Table 1), the V isotope composition of the biodegraded crude oils appears to be fractionated significantly to both heavier and lighter values (Fig. 4).

Bacteria in the reservoir utilize nutrients such as phosphate ions and any oxidants to oxidize hydrocarbons and non-hydrocarbons and create altered petroleum. It is generally accepted that most surface and subsurface biodegradation is caused by aerobic bacteria (e.g. Palmer 1993), with sufficient oxygen and nutrient supply provided by moving water within the reservoir (Connan 1984; Volkman *et al.* 1984; Larter *et al.* 2006). It has now been recognized, however, that anaerobic sulphate-reducing and fermenting bacteria also can degrade petroleum where oxygen is not available (Connan *et al.* 1995; Coates *et al.* 1996; Caldwell *et al.* 1998; Zengler *et al.* 1999). Under anoxic conditions, NO , SO_4^{2-} , Mn^{4+} , Fe^{3+} and CO_2 as well as vanadate can all potentially act as alternative electron acceptors (oxidants) to oxidize organic compounds during biodegradation (Rehder 1991; Crans *et al.* 2004; Huang 2004; Winter & Moore 2009). With increasing biodegradation, oils become more viscous, richer in resins, asphaltenes, S and metals (Connan 1984; Volkman *et al.* 1984; Palmer 1993; Peters & Moldowan 1993; Meredith *et al.* 2000). It therefore seems logical to expect a fractionation of V isotopes associated with the modification of its concentration during biodegradation. If organic V bonds are ruptured, kinetic isotope effects favouring the lighter ^{50}V would increase the $\delta^{51}\text{V}$ value of the unreacted material. An alternative explanation is that the change in $\delta^{51}\text{V}$ values is due to microbial activity-induced changes of the species of V ions (and their coordination geometries in the waters) that are ready to be added to the oils. Generally, biodegradation does not involve major V bond changes because the V complexes usually have high molecular weight and are aromatic in structure, and thus are resistant to bacterial attack (Palmer 1983; Strong & Filby 1987; Sundararaman & Hwang 1993). The pH of the solution and the presence of potential ligands, however, are very sensitive to biodegradation which can simultaneously lead to elevated contributions of organic acids that act as ligand binding sites (Hughey *et al.* 2007; Skaare *et al.* 2007).

Maturation

As shown in Figure 5, the $\delta^{51}\text{V}$ values of the non-biodegraded crude oils from Barbados are negatively correlated with the Ts/Tm maturation indices ((Ts)/(Ts + Tm)) and the Tricyclic Index (Peters & Moldowan 1993). This observed correlation thermal maturity index is significant ($R^2 = 0.87$ with Ts/(Ts + Tm) and $R^2 = 0.93$ with the Tricyclic Index), though it is based only on a small dataset with a total variation on $\delta^{51}\text{V}$ of *c.* 1‰. With increasing burial, the temperatures in the source rocks rise and the chemically labile portions of the crude oil begin to crack. As shown in Figure 6, the V

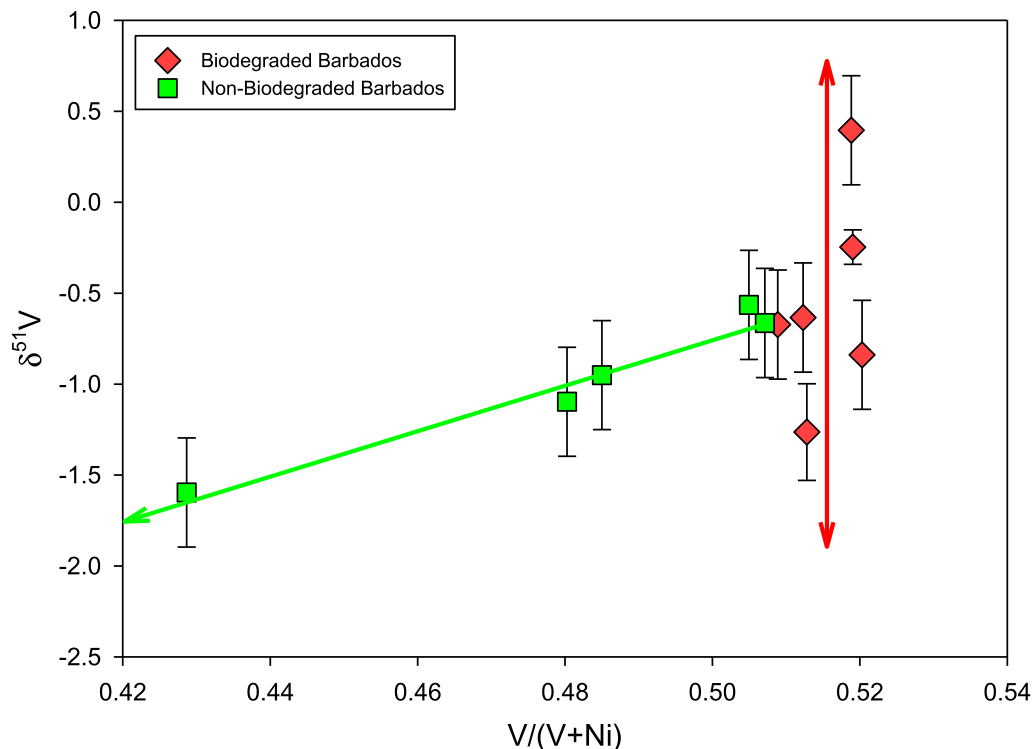


Fig. 4. V isotopic compositions of non-biodegraded vs. biodegraded crude oils from Barbados plotted against $V/(V + Ni)$ ratios. Error bars are 2 SD as listed in Table 1. Values of $\delta^{51}V$ are reported relative to the AA V solution standard defined as 0‰ (Nielsen *et al.* 2011). Note the small change (c. 20%) in $V/(V + Ni)$ in the most mature sample.

concentrations of the non-biodegraded crude oils generally decrease with the increase of maturation as measured by these indices. The V in crude oils exists as both vanadyl-porphyrin compounds and non-porphyrin compounds with various chemical structures (Branthaver & Filby 1987; Filby & Van Berkel 1987; Filby 1994; Amorim *et al.* 2007). In the porphyrin complexes, V is bound by four N donor atoms while in the non-porphyrin compounds N, O and S can all act as donor atoms in various combinations (Dickson *et al.* 1972; Sebor *et al.* 1975). The bonds between C and heteroatoms (N, S and O) are more labile and hence easier to break (Mackenzie & Quigley 1988). Bonding of V to sulphur ligands in organic matter has been reported (Yen 1975; Baker & Louda 1986). Though vanadyl porphyrins are stable up to 400°C during laboratory heating (Premović *et al.* 1996), it has been shown that the type of V porphyrins could change from deoxyphylloerythroetioporphyrin (DPEP) to etio-porphyrin (ETIO) at lower temperatures during thermal maturation of crude oils (Didyk *et al.* 1975; Mackenzie *et al.* 1980; Barwise & Park 1983; Barwise & Roberts 1984; Barwise 1987; Sundararaman

et al. 1988; Sundararaman & Hwang 1993). Increasing maturity has also been shown to change the distribution of VO^{2+} ETIO porphyrins towards lower carbon numbers (Gallango & Cassani 1992; Sundararaman & Moldowan 1993) indicating that for a given porphyrin type, the thermal degradation rate is higher for higher carbon-number species. It has also been speculated that during maturation of a crude oil, decomposition of the metallo-porphyrins would lead to a free cation, e.g. Ni^{2+} or VO^{2+} , which would either be complexed by an asphaltene functionality (or other polar molecules, e.g. naphthenic acids), or form a metal sulphide molecule that would be trapped in asphaltene micelles (Filby 1994). Day & Filby (1992) have shown that de-metalation–metalation of VO^{2+} porphyrins on montmorillonite is also reversible. The exchange and/or transformation of V between different species during these processes are all potentially able to cause V isotope fractionation due to the variation of the V bonding strength among different chemical structures.

Thus, the observed progressive decrease of $\delta^{51}V$ values and changes in V abundance in the co-genetic

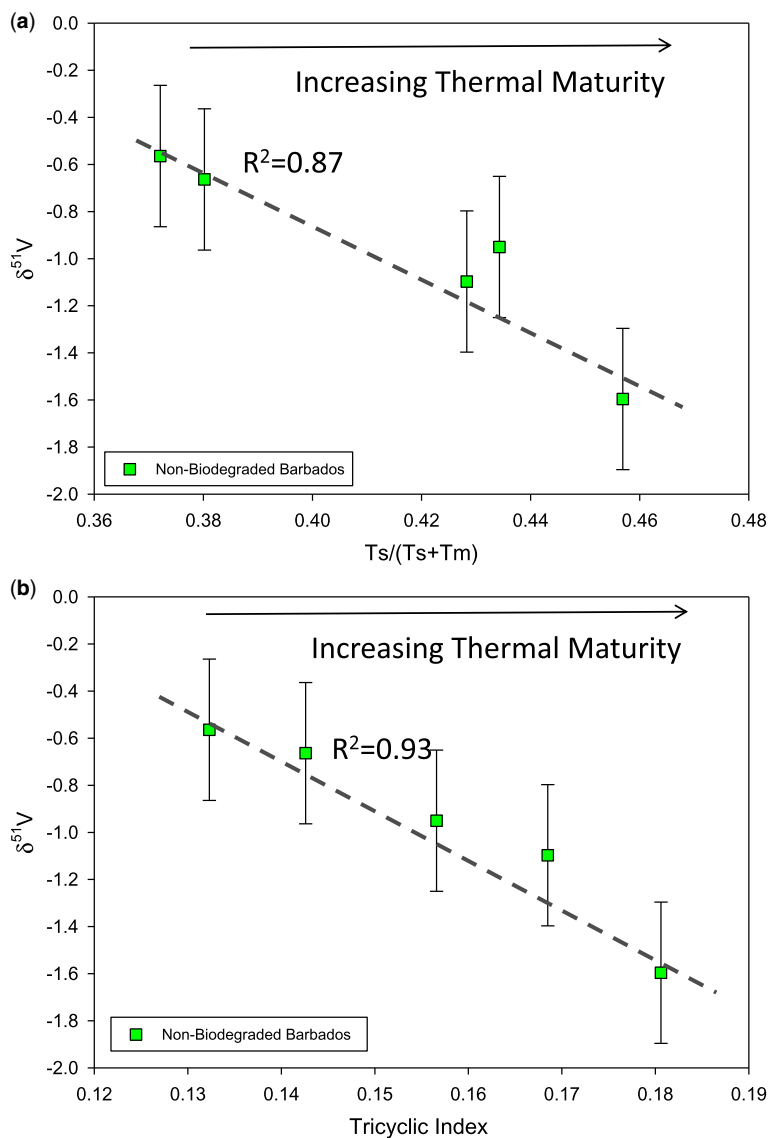


Fig. 5. Correlation of V isotope compositions of non-biodegraded crude oils from Barbados with thermal maturities defined by the $Ts/(Ts + Tm)$ ratio (a) and Tricyclic Index (b). Error bars are 2 SD given in Table 1. Note the decreasing $\delta^{51}\text{V}$ values with increasing thermal maturation. Values of $\delta^{51}\text{V}$ are reported relative to the AA V solution standard defined as ‰ (Nielsen *et al.* 2011).

Barbados crude oils with maturation (Fig. 5) might indicate a preferential loss of ^{51}V during de-metalation and/or a preferential incorporation of ^{50}V in the newly formed V-organometallic compounds. Alternatively, the observed variation of $\delta^{51}\text{V}$ values with maturation might be simply caused by a temperature-dependent isotope fractionation process. The typical oil window is *c.* 50–150°C, depending on how quickly the source rock is heated (Tissot & Welte

1984). Theoretical calculations have shown that the V isotope fractionation between different species varies with temperature in the oil window temperature range (Wu *et al.* 2015). However, the magnitude of temperature-induced isotope fractionation diminishes along with the increase of temperature (Wu *et al.* 2015) and is contradictory to the observed trend with increasing fractionation away from its pristine value (Fig. 5); it is therefore unlikely to be

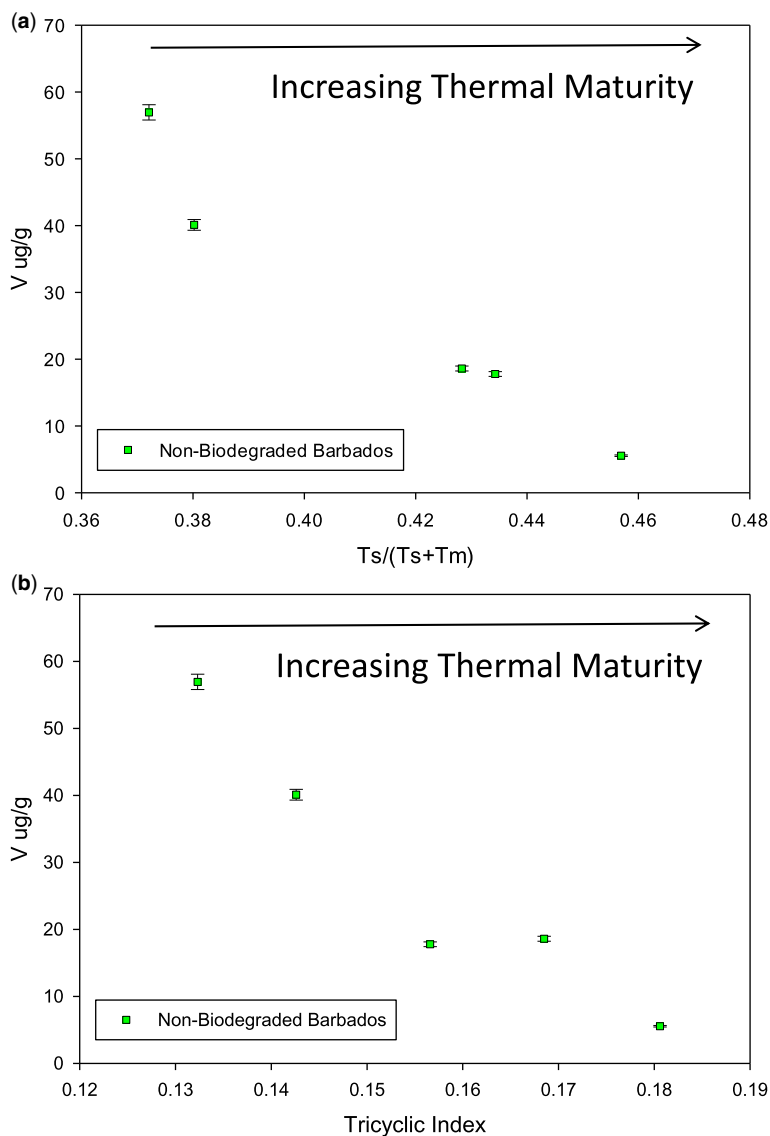


Fig. 6. Correlation of V isotope compositions of only non-biodegraded crude oils from Barbados with thermal maturity indices defined by the $Ts/(Ts + Tm)$ ratio (a) and Tricyclic Index (b). Error bars are calculated based on 2 RSD of 2%. Note the de-metalation trend with increasing thermal maturity. Values of $\delta^{51}V$ are reported relative to the AA V solution standard defined as 0‰ (Nielsen *et al.* 2011).

the actual driver of the V isotope fractionation during maturation.

Conclusions

We have presented a detailed study on the V isotope composition of 17 crude oils spanning a wide range of V concentrations, localities, and variable

formation ages using a procedure capable of yielding external precisions of better than $\pm 0.3\%$. Notable V isotope fractionation exists in these globally distributed crude oils.

The $\delta^{51}V$ isotope compositions in the unaltered crudes are primarily correlated with Ni/V ratios and are most likely determined by the depositional environment of petroleum source rocks. The Eh–pH conditions determine the speciation and

coordination of V ions in the water column or pore water, whereas the lithology of the source rocks (i.e. the relative abundance of carbonate, clay and iron oxides) defines the co-existing phases that are competing with organic molecules (e.g. porphyrins) for the available V ions in solution.

Correlations between $\delta^{51}\text{V}$ composition and biomarkers indicate that V isotope compositions are subjected to significant modification by both maturation and biodegradation.

V isotope fractionation during biodegradation may depend on the conditions of biodegradation, i.e. aerobic v. anaerobic. The most likely explanation for this dependence is the change of the species of V ions and their coordination geometries induced by the microbial activity at the water/oil interface.

Significant modification of V content in crude oils occurs as a result of de-metallation–re-metallation processes of VO^{2+} porphyrins and/or non-porphyrins during the progressive thermal maturation of crude oils. The observed progressive decrease of $\delta^{51}\text{V}$ values and V content in the co-genetic Barbados crude oils with increasing maturation might suggest a preferential loss of ^{51}V during de-metallation and/or a preferential incorporation of ^{50}V in the newly formed V-organometallic compounds.

The combination of V isotope data with traditional biomarker and multi-elemental analysis data on crude oils could potentially become a powerful new geochemical marker and exploration tool. However, more complete understanding of the fundamental mechanisms that control V isotope fractionation in crude oils requires further investigation of crude oils from restricted localities and source rocks. Systematic, coupled organic/inorganic geochemical investigations of crude oils generated under specific, well-understood conditions will be essential for more complete understanding of these processes. Correlation studies of V isotope data with other elemental and biogeochemical data, as well as high precision constraints on oil formation age are essential to more completely understand V fractionation in crude oils.

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