

Factors controlling the proportionality of vanadium to nickel in crude oils

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Abstract—The proportionality of V to Ni in crude oils is determined by the environmental conditions in which their source rocks were deposited. Thermal maturation, migration, and reservoir alterations may change the concentrations of these two metals by addition or subtraction of more labile portions of a crude oil, but their tenacious bonding with high-MW organics suggests that their proportionality to one another should remain unchanged. Eh-pH diagrams offer an explanation of the factors controlling their proportionality and its relationship with S contents. Three Eh-pH regimes are proposed for the natural system. Regime I represents conditions under which Ni^{+2} is available for bonding and vanadium is unavailable because of its quinivalent state. Crude oils expelled from source rocks deposited within this regime are expected to have $V/(Ni + V)$ less than 0.10 and low S (<1 weight percent). Regime II represents conditions under which Ni^{+2} -Nickelous cations and vanadyl cations are available with vanadyl cations being hindered in part by the formation of hydroxides and nickelous cations being hindered in part of metastable sulfide ions. Source rocks deposited within this regime expel crude oils with low S contents and V-Ni fractions that range from 0.10 to 0.90. Regime III represents conditions under which vanadyl and trivalent vanadium cations are available for bonding but Ni^{+2} may be partially hindered by sulfide complexing. Source rocks deposited within this regime expel crude oils that have high S contents and V-Ni fractions greater than 0.50.

INTRODUCTION

THE PROPORTIONALITY of vanadium to nickel in crude oils has been examined by many investigators (e.g., WITHERSPOON and NAGASHIMA, 1957; BALL and WENGER, 1960; KATCHENKOV, 1979) and used in oil-to-oil correlations (HODGSON, 1954; AL-SHAHRISTANI and AL-ATYIA, 1972; MCKIRDY and HORVATH, 1976) and to a lesser extent in oil-to-source rock correlations (TAGUCHI, 1975). Vanadium and nickel form tenacious bonds with metallo-organic complexes in the high-molecular weight fraction of crude oils (CORBETT, 1967; DWIGGINS *et al.*, 1969; FILBY, 1975), that are not likely to demetallate until metamorphic conditions are encountered. Cleavage of vanadium and nickel bonds in crude oils occurs at temperatures in excess of 300°C, but even at temperatures in excess of 350°C the proportionality of these two metals remains constant in natural crude oils (CONSTANTINIDES *et al.*, 1959) and laboratory pyrolysates (LEWAN, 1980). Crude oils degraded by the collective processes of water washing, microbial degradation, oxidation, and inspissation showed no obvious demetallation and the proportionality of vanadium to nickel remained constant in natural settings (BRUNNOCK *et al.*, 1968) and open-tank experiments (DAVIS and GIBBS, 1975). Although the addition or subtraction of more labile components in a crude oil during its expulsion, migration, or entrapment may cause variations in its vanadium and nickel concentrations, the proportionality of the two metals is likely to remain constant.

The high stability of the vanadium to nickel proportionality and its characteristic range of values for crude oils from a particular rock unit, stratigraphic

section, or area within a basin (HODGSON, 1954; WITHERSPOON and NAGASHIMA, 1957; AL-SHAHRISTANI and AL-ATYIA, 1972) suggests that this proportionality may be determined by the source rocks from which the crude oils were derived. LEWAN and MAYNARD (1982) showed that it is feasible for vanadium and nickel to be preferentially enriched in metallo-organic complexes by diffusion of these metals into an organic-sediment column from the overlying water body. Vanadium and nickel will continue to concentrate in the organic matter until the bonding sites are completely filled or the sediment column becomes closed to the overlying water body as a result of compaction. Once the metallation is terminated, the proportionality of vanadium to nickel is likely to remain fixed as the lithification of the sediment proceeds. During thermal maturation of the resulting rock, the proportionality is expected to be maintained in its expelled crude oil. This has been demonstrated in part by pyrolysis experiments in which the proportionality in bitumens extracted from Green River Shale and Woodford Shale was the same as the proportionality in their expelled pyrolysates (LEWAN, 1980).

This study examines three factors that are most likely to control the proportionality of vanadium to nickel during metallation in organic sediments. These factors are redox potential, hydrogen ion activity, and sulfide activity. The influence and interrelationships of these factors are most easily envisaged with Eh-pH diagrams. Although these diagrams offer only a thermodynamic perspective and neglect kinetic considerations, the results obtained from them present a reasonable interpretation of vanadium to nickel proportionalities observed in crude oils. These dia-

grams are not intended to predict precise Eh and pH values of environments in which oil-source rocks were deposited, but rather, they are used to illustrate general relationships among the variables.

Eh-pH diagram considerations

The total dissolved element concentrations used in the construction of the Eh-pH diagrams of this study are those found in average sea water as reported by GOLDBERG (1961; *i.e.*, in moles per liter $\Sigma V = 10^{-7.41}$, $\Sigma Ni = 10^{-7.48}$, $\Sigma S = 10^{-1.56}$, and $\Sigma C = 10^{-2.63}$). The diagrams constructed with these concentrations are also applicable to fresh and interstitial waters whose small deviations from these values do not cause appreciable variations in the stability fields. The diagrams represent conditions at 25°C and 1 atmosphere, but appreciable variations in the stability fields are not expected for temperatures between 0 and 50°C (EVANS and GARRELS, 1958) and pressures within tens of atmospheres (GARRELS and CHRIST, 1965, p. 261). The natural limits for diagenetic conditions in organic sediments is considered to be the negative portion of the Eh-pH fields of open marine and marginal marine sediments as reported by BAAS BECKING *et al.* (1960).

The Gibbs free energies of the different species considered in the diagrams and their source are given in the Appendix. Sulfide and carbonate reactions were considered in constructing the diagram for nickel but not for vanadium. This is because vanadium carbonates and sulfides are rare and as a result no thermodynamic data are available on their formation. Although α -NiS is considered a high temperature polymorph of millerite (β -NiS; KULLERUD and YUND, 1962), its higher Gibbs free energy of formation was used in constructing the diagram for nickel. The choice of this α -polymorph is based on the premise that nickel sulfides behave similar to iron sulfides under diagenetic conditions. BERNER (1964a,b, 1967) has shown that metastable iron sulfides (black precipitate and mackinawite) precipitate before the more stable forms (pyrite and marcasite), and their Gibbs free energies of formation are similar to the high temperature polymorph (troilite).

The Eh-pH diagram representing the different species of vanadium is shown in Fig. 1. Vanadium in crude oils occurs

as a quadrivalent metal (MAROV *et al.*, 1972) in the form of vanadyl (VO^{+2} ; SARACENO *et al.*, 1961; ROBERTS *et al.*, 1961). As shown in Fig. 1, the stability field for the vanadyl species becomes tapered with increasing pH and consists of two species; (1) as a free cation and, (2) as a hydroxide. Under acid conditions (pH < 6.9) within the quadrivalent stability field, the free vanadyl cation would be readily available for the formation of vanadyl-organic complexes. Conversely, under basic conditions (pH > 6.9) the formation of vanadyl-organic complexes could be partially hindered by the association of hydroxide with vanadyl cations. The Eh-pH diagram indicates that vanadyl hydroxides should precipitate under these basic conditions, but kinetic considerations suggest that this would be unlikely because of the very dilute concentrations. It is more likely that vanadyl cations within this stability field would form aqueous hydroxides (*e.g.*, $VO(OH)^+$, $VO(OH)_2^0$, $VO(OH)_3^-$, and $V_4O_7^{2-}$; IANNUZZI and RIEGER, 1975), which would become more of a hindrance to the formation of vanadyl-organic complexes with increasing pH.

The Eh-pH diagram representing the different species of nickel are shown in Fig. 2. Nickel in metallo-organic complexes occurs as a bivalent nickelous cation (Ni^{+2}). This species of nickel predominates in marginal and marine sediments, but may become unavailable for bonding with metallo-organic complexes under reducing conditions when bacterial sulfate reduction is operative. Although bacterially generated sulfide may not precipitate NiS as shown in Fig. 2, an aqueous NiS species is likely to occur and inhibit the bonding of nickelous cations to metallo-organic complexes. Under these conditions, the availability of nickelous cations in organic sediments is limited to a stability field that becomes tapered with decreasing pH values. It should be noted that the unlikelihood of inorganic reduction of sulfate indicates that in environments where bacterial sulfate reduction is minimal because of low sulfate concentrations (*e.g.*, lacustrine and fresh-water swamps), nickelous cations will be available over the entire field for organic sediments.

RESULTS AND DISCUSSION

The proportionality of vanadium to nickel in the organic matter of sediments and their later expelled

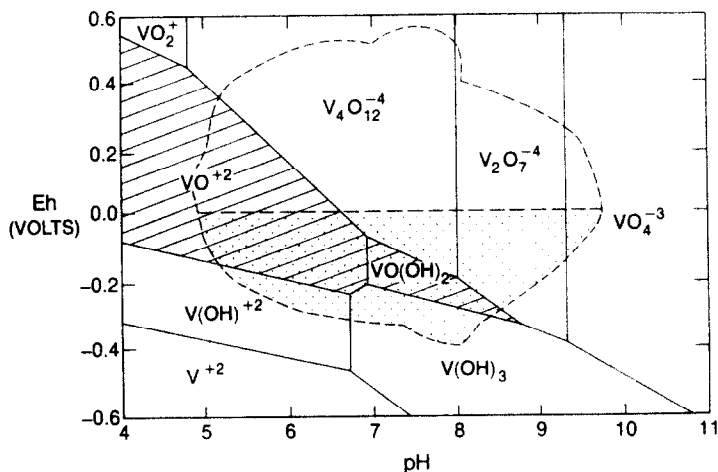


FIG. 1. Eh-pH diagram for vanadium species at seawater concentrations ($\Sigma V = 10^{-7.41}$, $\Sigma S = 10^{-1.56}$, and $\Sigma CO_2 = 10^{-2.63}$ mol/liter), 25°C, and 1 ATM. Hatched area represents the stability field for vanadyl species. Dashed outline represents natural stability field for marginal and open marine sediments (BAAS BECKING *et al.*, 1960), with the stippled portion representing the field for organic sediments (KRUMBEIN and GARRELS, 1952).

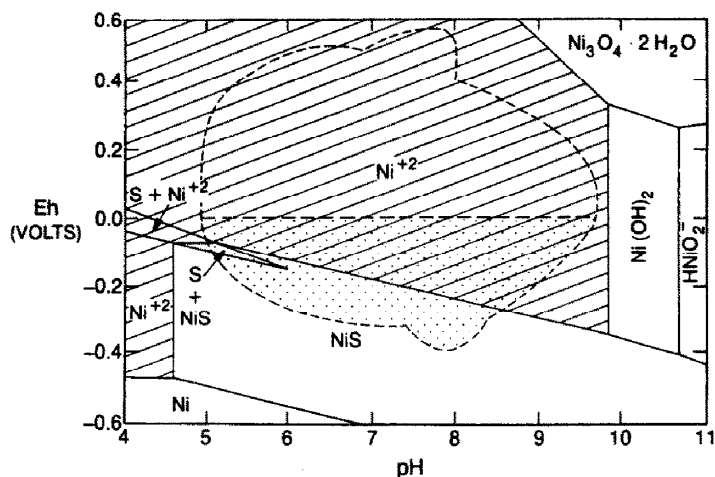


FIG. 2. Eh-pH diagram for nickel species at seawater concentrations ($\Sigma N = 10^{-7.48}$, $\Sigma S = 10^{-1.56}$, and $\Sigma CO_2 = 10^{-2.63}$ mol/liter), 25°C, and 1 ATM. Hatched area represents the stability field for nickelous cations. The explanation of the dashed outline and stippled area is the same as that given for Fig. 1.

crude oils may be discussed in terms of three Eh-pH regimes, by combining Figs. 1 and 2 as shown in Fig. 3. The proportionality of vanadium to nickel will be expressed as a decimal fraction, which is defined as the quotient of vanadium divided by the sum of nickel plus vanadium on a weight percent basis [$V/(Ni + V)$]. This expression is referred to as the vanadium-nickel fraction. The finite limits (0.0 to 1.0) and equal interval scale of this expression make it more useful in comparing and mathematical processing of data than the V/Ni ratio. In addition to accessing the vanadium-nickel fractions from Fig. 3,

some generalizations about the sulfur content in the organic matter of sediments and their expelled crude oil may also be proposed. Similar to vanadium and nickel, sulfur content of unaltered crude oils is usually considered to be the result of the environment in which a source rock was deposited (GRANSCH and POSTHUMA, 1974).

Although initially Fig. 3 may appear complex, three distinct regimes within the stability field for organic sediments may be defined. Regime I represents conditions where vanadium occurs as quinquivalent anions ($V_4O_{12}^{4-}$, $V_2O_7^{4-}$, and VO_4^{3-}) and as a result,

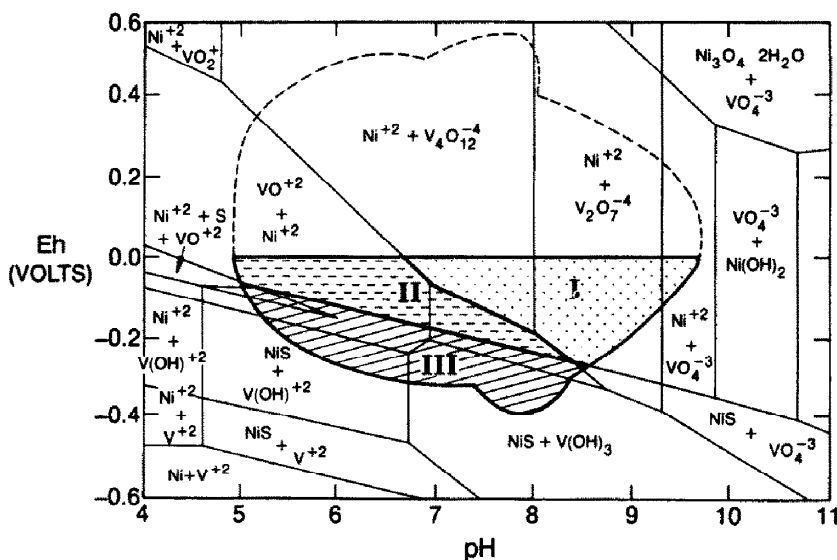


FIG. 3. Eh-pH diagram resulting from superimposing the Eh-pH diagrams for vanadium and nickel in Figs. 1 and 2 on one another. Stippled area represents the proposed stability field for Regime I, dashed area represents the proposed stability field for Regime II, and hatched area represents the proposed stability field for Regime III.

TABLE 1. Organic Sedimentary Rocks and Crude Oils Considered to be Related to Regime I

DESCRIPTION	V-Ni FRACTION (V/(Ni+V))	SULFUR (wt.%)
CRUDE OILS		
Tertiary Reservoirs in the Unita Basin (N=8; Lewan, 1980).	0.03	0.24
Mesozoic Reservoirs in the Unita Basin (N=2; Lewan, 1980)	0.02	0.30
Tertiary Reservoir in Duri, Indonesia (N=1; Wilson et al., 1975).	0.08	0.17
Tertiary Reservoir in Anse La Butte, Louisiana (N=1; Weeks and McBride, 1979).	<0.01	0.65
EXTRACTABLE ORGANIC MATTER		
Evaporitic Facies of the Wilkins Peak Member, Green River Fm., Big Island Mine, Wyo. (N=6; Lewan, 1980)	0.02	n.d.
Maquoketa Fm., Newton Quarry, Indiana (N=2; Lewan, 1980).	0.06	n.d.
Miocene-Cretaceous, Blake-Bahama Basin, DSDP LEG 44, Site 391 (N=6; Baker et al., 1978).	0.00*	n.d.
Quaternary-Miocene, San Miquel Gap, DSDP LEG 63, Site 467. (N=15; Louda and Baker, 1981).	0.01*	n.d.
Cretaceous, Bay of Biscay, DSDP LEG 48, Site 402A, (N=5; Baker and Palmer, 1979).	0.00*	n.d.

* Based only on metal content of porphyrins.
n.d. = Not Determined
N = Number of Samples Included in Average.

vanadyl cations would not be available for metallation. Conversely, nickelous cations would be available for metallation and the proportionality of vanadium to nickel would be low ($V/(Ni + V) < 0.10$) in the organic matter and its later expelled crude oil. Many of the organic sediments encountered by the Deep Sea Drilling Project appear to occur within Regime I. The pH values of these sediments are usually greater than 7 and the vanadium-nickel fraction of the extractable tetrapyrroles is usually less than 0.10 (Table 1). Organic matter deposited under the con-

ditions of Regime I and its later expelled crude oil are also expected to have low sulfur contents. As shown in Fig. 4, the boundary separating equal portions of sulfide from sulfate ions is below Regime I. Although bacterially generated sulfide ions may occur in Regime I, their availability to react with the organic matter is likely to be hindered by sulfide-oxidizing bacteria or the precipitation of iron sulfides. The open lacustrine and playa facies of the Green River Formation appear to have been deposited under the conditions of Regime I, with pH values exceeding 9 in the playa facies. Vanadium-nickel fractions of the extractable organic matter from these facies are less than 0.05 (Table 1). It should also be noted that crude oils considered to be expelled from the Green River Formation have vanadium-nickel fractions less than 0.05 and sulfur contents less than 1 weight percent (Table 1).

In Regime II, both vanadyl and nickelous cations should be available for metallation. In the basic portion of this regime, the nickelous cation is expected to become more competitive for metallation because of the increasing hindrance of vanadyl cations by the formation of aqueous hydroxides. The vanadium-nickel fraction under these conditions is expected to be less than 0.50. Vanadyl hydroxides should not occur in the acidic portion of Regime II, and as a result, both vanadyl and nickelous cations should be available. This suggests that the proportionality of vanadium to nickel in the interstitial waters is likely to play an important role in determining the proportionality of the two metals acquired by metallo-organic complexes in the sediments. According to the average sea water concentrations reported by GOLDBERG (1961), the vanadium to nickel proportionality should be near unity ($V/(Ni + V) \cong 0.50$) for marine systems, but this proportionality may be altered in the interstitial waters by sorption-desorption

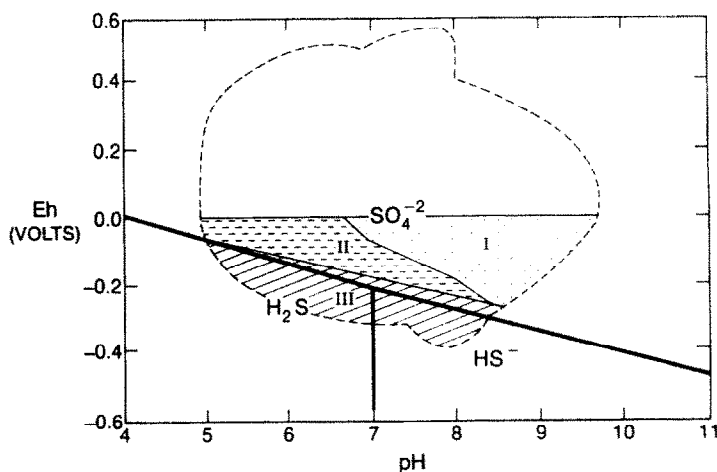


FIG. 4. Eh-pH diagram showing the relationship between the three proposed stability regimes in Fig. 3 and the stability field for sulfide ions in seawater ($\Sigma S = 10^{-1.56}$ mol/liter) at 25°C and 1 ATM.

TABLE 2. Organic Sedimentary Rocks and Crude Oils Considered to be Related to Regime II

DESCRIPTION	V-Ni FRACTION (V/(Ni+V))	SULFUR (wt.%)
CRUDE OILS		
Carboniferous Reservoirs of the Ouachitas, Oklahoma (N=3; Curiale, 1981).	0.74	0.37
Lower Cretaceous Reservoirs of the Western Desert, Egypt (N=4; Abu-Elgheit et al., 1979).	0.53	0.19
Cretaceous Reservoirs of Gabon (N=5; Whisman and Cotton, 1971).	0.28	0.51
Upper Cretaceous Reservoirs of the Pembina Field, Alberta (N=63; Hodgson and Baker, 1959).	0.41	0.17
Devonian Reservoirs of the Redwater Field, Alberta (N=37; Hodgson and Baker, 1959).	0.31	0.50
Pennsylvanian Reservoirs of Oklahoma (N=4; Hyden, 1956).	0.68	0.26
Tertiary Reservoirs of the Eastern Region of Nigeria (N=4; Whisman and Cotton, 1971).	0.29	0.21
EXTRACTABLE ORGANIC MATTER		
New Albany Shale of the Illinois Basin (N=23; Lewan, 1980).	0.59	n.d.
Chattanooga Shale of the Southern Appalachian Basin (N=12; Lewan, 1980).	0.67	n.d.
Kreyenhagen Shale of the San Joaquin Basin, California (N=5; Lewan, 1980).	0.20	n.d.
Mowry Shale of the Powder River Basin (N=17; Lewan, 1980).	0.22	n.d.

n.d. = Not Determined

N = Number of Samples Included in Average.

or precipitation-dissolution reactions of particulate matter or minerals within the sediment. The vanadium-nickel fraction within this regime may also be altered by the presence of bacterially generated sulfide ions. As shown in Fig. 4, the instability of sulfide ions in Regime II suggests that the quantities produced would be insufficient to generate high sulfur contents in the organic matter of a sediment, but may be sufficient to form aqueous NiS ions that would hinder the availability of nickelous cations. Rate of sulfide generation relative to rate of its consumption, either by bacterial oxidation or iron-sulfide precipitation, may govern the degree to which nickelous cations are hindered from metallation. The variety of controls on the vanadium-nickel fraction of crude oils expelled from rocks deposited in Regime II suggests that a high variability of vanadium-nickel fractions may be expected not only from different rock units, but also from different horizons of the same rock unit (LEWAN, 1980). Crude oils expelled from rocks deposited in Regime II are expected to have vanadium-nickel fractions between 0.10 and 0.90, and low sulfur contents (Table 2).

Regime III will only be present if a significant quantity of sulfate-reducing bacteria are operating in the sediment. The amount of sulfate reduction depends primarily on the availability of metabolites (KAPLAN and RITTENBERG, 1964; MCCREADY, 1975;

GOLDHABER and KAPLAN, 1975; and LYONS and GAUDETTE, 1979) and sulfate in the sediment. Energetically, Regime III would be expected to exist regardless of sulfate reducing bacteria, but the abiotic reduction of sulfate is slow and not likely to occur until higher temperatures or unnaturally low Eh values are reached in the sediments. The limits of Regime III in Fig. 3 represent conditions under which essentially all of the sulfate in a marine system has been reduced. Within this regime, the availability of nickelous cations would be reduced by the formation of aqueous sulfide complexes. This reduction in the activity of nickelous cations and the availability of vanadyl and trivalent vanadium hydroxide cations suggests that within this regime the vanadium-nickel fraction of metallo-organic complexes should be greater than 0.50. Although trivalent vanadium has not been reported in natural organic substances, it may account for the non-quadrivalent portion (11 to 20 wt%) that has been noted in some crude oils (e.g., Bachaquero and Lagunillas crude oils, SARACENO *et al.*, 1961). LEWAN and MAYNARD (1982) have shown that trivalent vanadium hydroxide (VOH²⁺) could be accommodated in tetrapyrroles on the basis of its favorable ligand field stabilization energy. As shown in Fig. 3, the availability of trivalent hydroxide cations would only occur under the most reducing conditions of Regime III.

It is critical to the existence of Regime III that bacterially generated sulfide ions persist and are not removed from solution by oxidation or by precipitation of iron sulfides. Figure 4 shows that oxidation of sulfide is not likely because the regime occurs within the stability field of sulfide ions. Therefore, it becomes imperative that iron is not available or the amount of bacterially generated sulfide exceeds the amount of available iron. Oxide coatings on detrital

TABLE 3. Crude Oils Considered to be Expelled from Sedimentary Rocks Related to Regime III

DESCRIPTION	V-Ni FRACTION (V/(Ni+V))	SULFUR (wt.%)
Cretaceous Reservoirs of Kuwait (N=4; Whisman and Cotton, 1971; Brunnoek et al., 1968; Wilson et al., 1975).	0.74	2.46
Jurassic Reservoirs of Saudi Arabia (N=5; Whisman and Cotton, 1971).	0.83	1.91
Lower Cretaceous Reservoirs of the Lloydminster Field, Alberta (N=12; Hodgson and Baker, 1959).	0.64	3.38
Miocene Reservoirs of the Gulf of Suez (N=3; Abu-Elgheit et al., 1979).	0.77	1.69
Miocene Reservoir of Bachaquero, Venezuela (N=1; Wilson et al., 1975).	0.88	2.68
Phosphoria and Tensleep Reservoirs of the Big Horn Basin, Wyoming (N=9; This Study).	0.79	3.13
Reservoir of Lagunillas, Venezuela (N=1; Bieber et al., 1960).	0.88	2.20

N = Number of Samples Included in Average.

matter is the major source of iron in sediments. Sediments composed primarily of biogenic pelagic matter (e.g., calcareous and siliceous oozes) will be low in iron and capable of supporting conditions necessary for Regime III. In addition to the available sulfide ions hindering the availability of nickelous cations to form metallo-organic complexes, the sulfides may also react with portions of the accumulating organic matter. Crude oils expelled from rocks deposited in Regime III are expected to have high sulfur contents in addition to high vanadium-nickel fractions (≥ 0.50 , Table 3).

The Eh-pH regime of the source rock from which a crude oil has been expelled may be approximated by plotting the vanadium-nickel fraction vs. the sulfur content of a crude oil (Fig. 5). The division between high and low sulfur contents was chosen as 1 wt% on the basis of the frequency distribution of 9315 crude oils compiled by TISSOT and WELTE (1978; p. 356). It should be emphasized that the vanadium-nickel fraction is not likely to change in a crude oil as a result of thermal maturation, migration, or reservoir alterations, but these processes may influence the sulfur content of a crude oil. Biodegradation of

crude oils has been shown to increase the sulfur content by removing the more labile portions of a crude oil (BAILEY *et al.*, 1973; HUNT, 1979, p. 483). Therefore, interpretations should be limited to non-biodegraded crude oils. The crude oils plotted in Fig. 5 are from a variety of sources. Although the amount of biodegradation on many of the crude oils used from the literature could not be assessed, only those with $^{\circ}$ API gravities greater than 20 were plotted in Fig. 5. Crude oils that plot outside of the suggested Eh-pH regimes may be interpreted as resulting from the mixing of crude oils from sources with different Eh-pH regimes or addition of sulfur during migration or entrapment. It should be noted that at low metal concentrations (<5 ppm) the precision of the vanadium and nickel analyses is essential. At these low concentrations, a statistical mean of several analyses should be used in calculating the vanadium-nickel fraction.

The Eh-pH regimes in Fig. 5 offer a means of classifying crude oils on the basis of the depositional conditions of the source rocks from which they were expelled. In addition to using this classification in oil-to-source rock correlations, it may also prove to

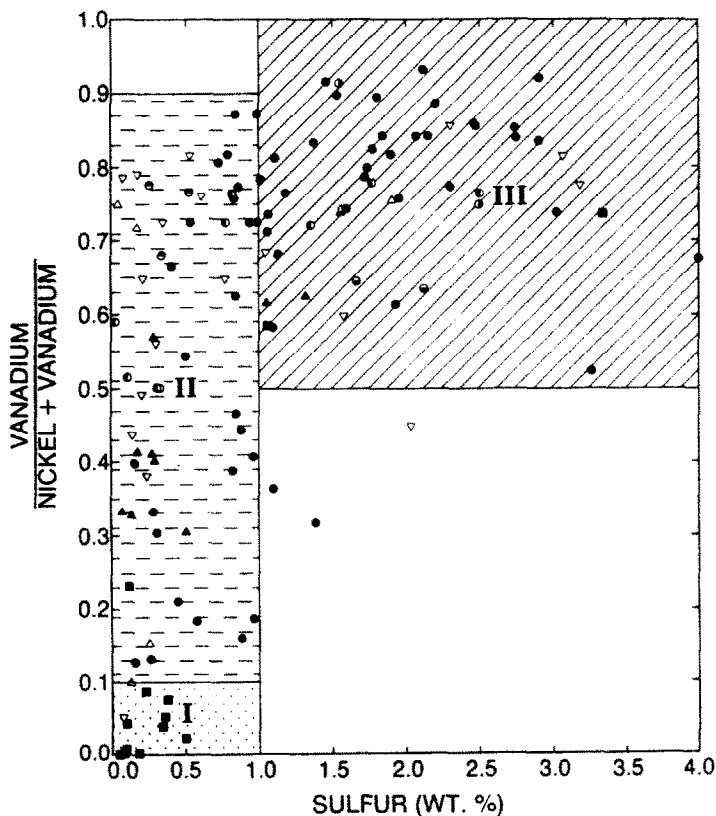


FIG. 5. Vanadium-nickel fraction versus sulfur content of crude oils from WHISMAN and COTTON, 1971 (●); BRUNNOCK *et al.*, 1968 (○); ABU-ELIGHEIT *et al.*, 1979 (◐); CURIALE, 1981 (◑); WILSON *et al.*, 1975 (◒); BIEBER *et al.*, 1960 (△); HYDEN, 1956 (▽); HODGSON and BAKER, 1959 (▲); and LEWAN 1980 (■). Roman numerals and shaded area correspond to the stability regimes proposed in Fig. 3. The data points plotted are only for crude oils with API $^{\circ}$ gravities equal to or greater than 20.

be useful in identifying crude oils from different depositional facies of the same source rock.

CONCLUSIONS

The proportionality of vanadium to nickel in crude oils may be attributed to the Eh, pH, and sulfide activity of the environment in which their source rocks were deposited. Three basic Eh-pH regimes have been defined. Regime I represents conditions under which nickelous cations are available for bonding, but vanadium is not available because of its occurrence as a quinquevalent anion. Crude oils expelled from source rocks that were deposited in this regime will have low vanadium-nickel fractions (<0.10) and low sulfur contents. Regime II represents conditions under which nickelous and vanadyl cations are available, but the presence of sulfide or hydroxide ions may hinder their availability for bonding. Source rocks deposited in this regime are expected to expel crude oils with a wide range of vanadium-nickel fractions (0.10–0.90) and low sulfur contents (<1 weight percent). Regime III represents conditions under which vanadyl or trivalent vanadium cations are available with the availability of nickelous cations being hindered by the presence of sulfide ions. Crude oils expelled from source rocks deposited in this regime are expected to have high vanadium-nickel fractions (>0.50) and high sulfur contents (>1 weight percent).

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APPENDIX

Gibbs Free Energies at 25°C and 1 ATM for the Formation of Species Considered in the Construction of Eh-pH Diagrams Shown in Figures 1 and 2

SPECIES	PHASE*	ΔG_f° (KCAL·MOL ⁻¹)	SOURCE**
V	s	0.0	1
V ⁺²	aq	-54.2	1
V ⁺³	aq	-60.1	1
VO ⁺²	aq	-109.0	1
VO ₂ ⁺	aq	-142.0	1
V ₂ O ₂	s	-189.0	1
V ₂ O ₃	s	-271.0	1
V ₂ O ₄	s	-318.0	1
V ₂ O ₅	s	-344.0	1
V ₂ O ₇ ⁻⁴	aq	-417.3	2
VO ₄ ⁻³	aq	-219.2	2
V ₄ O ₉ ⁻²	aq	-665.3	1
V ₄ O ₁₁ ⁻²	aq	-774.9	2
V ₁₀ O ₂₈ ⁻⁸	aq	-1862.4	1
HV ₁₀ O ₂₈ ⁻⁸	aq	-1870.3	1
H ₂ V ₁₀ O ₂₈ ⁻⁸	aq	-1875.2	1
V(OH) ⁺²	aq	-112.8	1
(VO) ₂ (OH) ₂ ⁺²	aq	-322.28	3
VO(OH) ⁺	aq	-157.96	3
VO(OH) ₂	s	-213.5	1
V(OH) ₃	s	-218.0	1
Ni	s(II)	0.0	4
Ni ⁺²	aq	-11.53	4
HNiO ₂	aq	-83.46	4
NiCO ₃	s	-147.0	4
NiSO ₄	s	-184.9	4
NiSO ₄ ·6H ₂ O	s(Retgersite)	-531.7	5
NiSO ₄ ·7H ₂ O	s(Morendsite)	-588.4	5
α-NiS	s	-17.7	4
β-NiS	s(Millerite)	-20.6	5
γ-NiS	s	-27.3	4
NiS ₂	s(Vaesite)	-34.0	6
NiO	s(Bunsenite)	-51.3	4
Ni(OH) ₂	s	-108.3	4
Ni ₃ O ₄ ·2H ₂ O	s	-283.53	4
Ni(OH) ₃	s	-129.5	4
Ni ₂ O ₃ ·H ₂ O	s	-169.96	4
NiO ₂	s	-47.5	4
NiO ₂ ·2H ₂ O	s	-164.8	4
S	s(Orthorhombic)	0.0	4
S ⁻²	aq	21.96	4
HS ⁻	aq	3.01	4
H ₂ S	aq	-6.54	4
HSO ₄ ⁻	aq	-179.94	4
SO ₄ ⁻²	aq	-177.34	4
H ₂ O	l	-56.69	4
H ₂ CO ₃	aq	-149.0	4
HCO ₃ ⁻	aq	-140.31	4
CO ₃ ⁻²	aq	-126.22	4

* aq = Aqueous; s = Solid; and l = Liquid.

** 1. Evans and Garrels (1958); 2. Calculated from equilibrium constants presented by Evans and Garrels (1958); 3. Postulated hydrolyzed species that exist within a pH range of 2.69 to 3.30 (Henry et al., 1973); 4. Garrels and Christ (1965); 5. Robie and others (1978); and 6. Calculated by extrapolating temperature function presented by Schiffman and Miller (1978).