

Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks

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Abstract—Enriched concentrations of vanadium and nickel have been noted in a variety of naturally occurring organic substances including crude oils, asphalts, and organic matter in some sedimentary rocks. Vanadium and nickel concentrations in bitumens extracted from a variety of organic sedimentary rock types of different geological ages and geographical areas range from less than 0.2 to 4760 ppm and less than 7 to 1240 ppm, respectively. Vanadium concentrations showed a polymodal frequency distribution, while nickel concentrations showed a near-normal frequency distribution. The concentrations of these two metals showed no significant correlations with bitumen content, organic carbon content, or proportionality between bitumen and organic carbon contents. Enriched vanadium and nickel concentrations greater than 100 ppm are only observed in bitumens that are associated with Type II and Type I kerogens. Conversely, bitumens associated with Type III kerogens contained vanadium and nickel concentrations less than 100 ppm.

The high stability of vanadium and nickel in crude oils, asphalts, and bitumens suggest that they occur in tetrapyrrole complexes. These complexes may occur as free molecules or assimilated subunits in macromolecules within the bitumen. Vanadium and nickel are preferentially concentrated in tetrapyrrole complexes because of their availability in anaerobic systems, small atomic radii, and favorable electron configurations. The potential for an organic sediment to be enriched in these two metals depends upon the amount of tetrapyrroles preserved in its organic matter. Tetrapyrrole preservation preferentially decreases in organic matter as exposure time to aerobic conditions increases. The potential for vanadium and nickel enrichment is therefore the highest in organic matter derived from algae that encountered anaerobic conditions early in their depositional history. Metallation of tetrapyrrole complexes appears to occur within sediments prior to their lithification, and interstitial waters are the most likely source for enriched concentrations of vanadium and nickel. The amount of metal enrichment in a sediment depends upon the diffusion of metal cations from its overlying water body, and this source is only effective as long as the sediment system remains open. The complete metallation of tetrapyrroles is most favorable under conditions of slow sedimentation rates, which would allow open sediment systems to be maintained for long durations.

INTRODUCTION

ABNORMALLY high concentrations of vanadium and nickel have been noted in some crude oils (Hodgson, 1954; Bonham, 1956; Witherspoon and Nagashima, 1957; Ball and Wenger, 1960; and others), asphalts (Erickson *et al.*, 1954), and black shales (Krauskopf, 1955; Vine and Tourtelot, 1970). Although the chemistry of vanadium and nickel in crude oil has been studied extensively (*e.g.* Yen, 1975), investigations concerned with these metals in the organic matter of sedimentary rocks have not received much attention, with the exception of the study by Hodgson and others (1968). Direct evidence is not available on when metallo-organic complexes of vanadium and nickel develop, but their absence in recent surface sediments (Baker and Hodgson, 1968; Shiobara and Taguchi, 1975) and their presence in buried sediments (Louda and Baker, 1981) and in thermally immature sedimentary rocks (Hodgson and others, 1968; Shiobara and Taguchi, 1975) suggests that metallation occurs in unconsolidated sediments prior to lithification.

Vanadium and nickel in crude oil is strongly bound to metallo-organic complexes that have high

molecular weights ($MW > 400$; Yen, 1975). The unlikelihood of these bonds cleaving under diagenetic conditions is evident by their high thermal stability (Constantinides *et al.*, 1959) and their resistance to microbial degradation, water washing, and weathering (Brunnock *et al.*, 1968; Davis and Gibbs, 1975). Once metallo-organic complexes of vanadium and nickel develop, their high stability assures that they will remain during lithification and at higher levels of diagenesis. Their high stability also suggests that generation, migration, and entrapment of crude oil are not likely to affect these bonds (Lewan, 1980), and their enrichment in the organic matter of a source rock may be reflected in part in its expelled crude oil.

The objectives of this study are (1) to report the vanadium and nickel contents of bitumens from a variety of organic sedimentary rock types, and (2) to examine the factors that control the enrichment of these two metals in the bitumens of organic sedimentary rocks. The factors examined include the mode of metal occurrence, reasons for metal preference, preservation of tetrapyrroles, and source of enriched metals.

Table 1: Description of Rock Units Sampled for this Study

ROCK UNIT (AGE)	SAMPLING LOCALITIES	MAJOR ROCK TYPES*	NUMBER OF SAMPLES	KEROGEN TYPE
Monterey Fm. (Miocene)	Ventura Basin, Santa Maria Basin, and Los Angeles Basin, California	Argillaceous and Siliceous Claystone; Calcitic and Argillaceous Marlstone	10	II
Cozy Dell Fm. (Eocene)	Santa Ynez Mts., California	Argillaceous Mudstone	1	II
Kreyenhagen Sh. (Eocene)	San Joaquin Valley, California	Siallitic and Argillaceous Claystone	5	II
Green River Fm. (Eocene)	Uinta Basin, Utah and Green River Basin, Wyoming	Dolomitic and Calcitic Marlstone	37	I
Ferris Fm. (Paleocene- Cretaceous)	Carbon Co., Wyoming	Coal	1	III
Frontier Fm. (Cretaceous)	Uinta Basin, Utah	Coal	2	III
Mowry Sh. (Cretaceous)	Powder River Basin, Wyoming and Uinta Basin, Utah	Quartzose Claystone and Mudstone	24	II-III
Carbondale Fm. (Pennsylvanian)	Illinois Basin, Illinois	Coal	1	III
Breathitt Fm. (Pennsylvanian)	Appalachian Basin, Kentucky	Coal	2	III
Manning Canyon Fm. (Mississippian)	Uinta Basin, Utah	Argillaceous and Quartzose Claystone; Coal	3	III
Bakken Sh. (Dev.-Miss.)	Williston Basin, N. Dakota	Quartzose Claystone	2	II
Woodford Sh. (Dev.-Miss.)	Arbuckle Mts., Oklahoma	Quartzose Claystone	2	II
Chattanooga Sh. (Dev.-Miss.)	Appalachian Basin, Tennessee	Quartzose Claystone	12	II
New Albany Sh. (Dev.-Miss.)	Illinois Basin, Kentucky, Indiana and Illinois; Appalachian Basin, Kentucky	Quartzose Claystone and Mudstone	23	II
Woodruff Fm. (Devonian)	Pinon Range, Nevada	Dolomitic Mudstone	3	II
Maquoketa Fm. (Ordovician)	Illinois Basin, Indiana	Dolomitic Marlstone and Argillaceous Claystone	2	II

* Very-fine-grained rocks classified in accordance with Lewan (1978).

METHODS AND RESULTS

Sample description

This study is based on the vanadium and nickel concentrations in bitumens that were extracted from a wide variety of fine-grained organic sedimentary rocks, which represent different geological ages, geographic locations, and kerogen types (Table 1). The samples have organic carbon contents that range from 0.7 to 77.1 weight percent, and a mean organic carbon content of 11.6 weight percent. Although most of the samples were collected from outcrops, the evaluation of surface weathering and pedogenic weathering as described by Lewan (1980) insured that the effects of weathering on these samples were minimal. A complete description of the sampling localities, stratigraphic positions, petrography, mineralogy, organic carbon contents, kerogen analyses (*i.e.*, visual, elemental and carbon isotopes), bitumen contents, and metal concentrations of the samples used in this study are presented elsewhere by Lewan (1980).

Vanadium and nickel determinations

Vanadium and nickel concentrations in extracted bitumens were determined by neutron activation analysis, which is discussed in detail by Filby and Shah (1975). The analyses were performed at the Nuclear Research Labora-

tory, Virginia Polytechnic Institute and State University under the direction of T. F. Parkinson. The samples were subjected to a thermal flux of 1.3×10^{12} neutrons per centimeter squared per second, and the maximum detection sensitivities for vanadium and nickel are 0.0017 and 1.3 micrograms, respectively. The results of these analyses are summarized in Fig. 1a. The vanadium concentrations have a polymodal distribution that ranges from less than 0.2 to 4760 ppm, and the nickel concentrations have a more normal distribution that ranges from less than 7 to 1240 ppm. These metal concentrations in the bitumens have also been calculated on a whole-rock basis. The results are summarized in Fig. 1b, and the difference between the two metal distributions is similar to that in Fig. 1a. On a whole-rock basis, vanadium concentrations range from less than 0.2 to 19040 ppb, and nickel concentrations range from less than 42 to 19825 ppb.

Extraction of bitumen

The bitumen is extracted by refluxing 200 ml of a benzene/methanol mixture (60/40 volume percent, pesticide grade) through pulverized rock for 20 hours in a Soxhlet apparatus. Afterwards the resulting solution is filtered through a 0.5 μ m Teflon filter. The bitumen is then isolated by evaporating the solvent in a rotary vacuum evaporator,

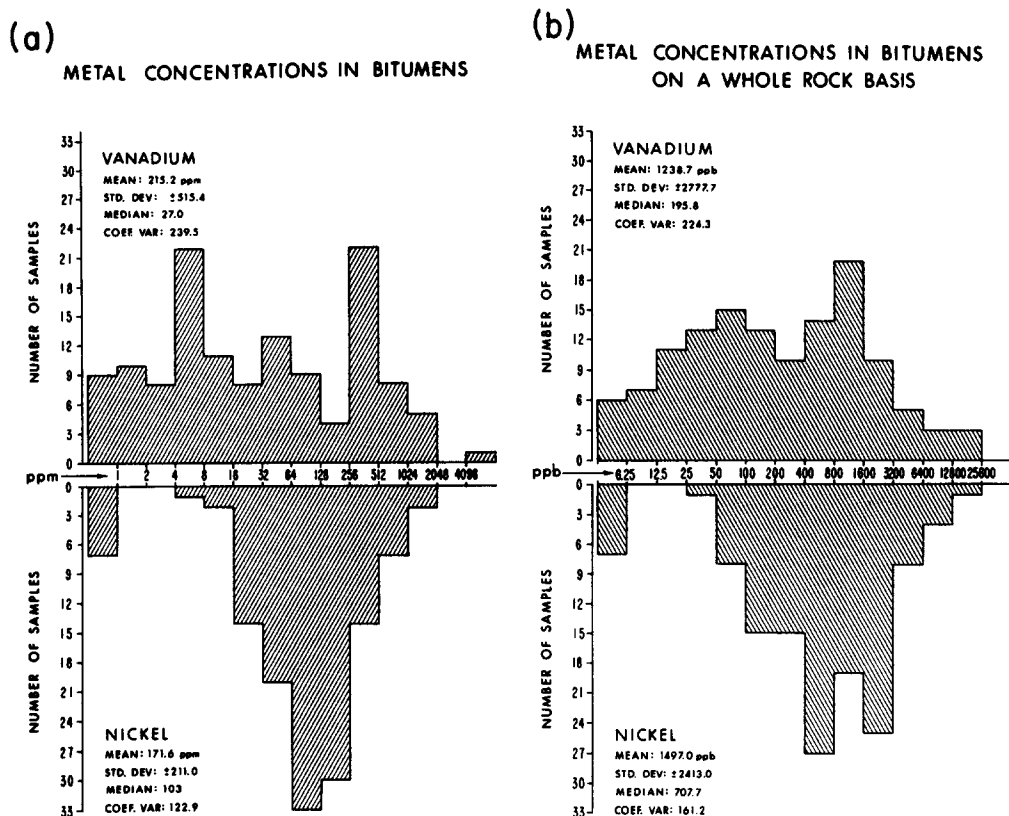


FIG. 1. Histograms of vanadium and nickel concentrations in a) bitumen (ppm) and b) bitumen on a whole rock basis (ppb).

and then heated in an oven at 84°C for 12 hours. This final heating step removes the highly volatile components in the bitumen, which helps stabilize the weight of the bitumen and thus improves the precision of the vanadium and nickel determinations. Rocks that were past the oil generation stage of thermal maturation were not included in this study because their extraction yielded small quantities of bitumen that usually contained large quantities of inorganic contaminants (e.g., sulfur and gypsum). The bitumen contents of the rocks used in this study range from 0.07 to 6.70 weight percent with a mean value of 1.21 weight percent. Linear regression analysis indicated that bitumen content, organic carbon content, and proportionality of bitumen to organic carbon have no significant correlation with the vanadium and nickel concentrations (Fig. 2).

Kerogen isolation and typing

The kerogen was isolated by subjecting pulverized rock to a series of acid treatments and a heavy-liquid separation. The samples are first placed in a warm 18 percent solution of hydrochloric acid for 4 hours, followed by a warm 52 percent solution of hydrofluoric acid for 20 hours, and then placed in a hot (100°C) concentrated solution of hydrochloric acid for 1 hour. The remaining residue is then centrifuged in a zinc bromide solution with a specific gravity of 2.00. The float material is removed and extracted with dichloromethane for 20 hours in a Soxhlet apparatus. The resulting kerogen is dried in a vacuum oven at 69°C for at least 24 hours.

In this study, kerogens were typed on the basis of their elemental analyses, visual analysis, and to a lesser extent their stable carbon isotopes. A detailed discussion on the integrated use of these analyses in kerogen typing is given by Lewan (1980, pp. 12–33), and the typing is in accordance

with the three kerogen types proposed by Tissot and Welte (1978; Chpt. 4). Type I kerogen is considered to be derived from highly aliphatic material of algal origin, and commonly occurs in lacustrine environments. Type II kerogen is considered to be derived from mixtures of phytoplankton, zooplankton, and microorganisms, and commonly occurs in marine environments. Type III kerogen is considered to be derived from vascular plants, and commonly occurs in terrestrial and marginal-marine environments. Comparison of kerogen types with the metal concentrations of their associated bitumens shows that metal concentrations in excess of 100 ppm only occur in bitumens associated with Type II and Type I kerogens (Fig. 3). Relative to the bitumens associated with Type III kerogens, all of the bitumens associated with Type II and Type I kerogens show a higher concentration of nickel by almost one order of magnitude. Similarly, high vanadium concentrations also occur in bitumens associated with Type II kerogens, but unlike the nickel concentrations, not all of these bitumens have higher concentrations than the bitumens associated with Type III kerogens.

DISCUSSION

Mode of occurrence of vanadium and nickel

Naturally occurring metallo-organic complexes of vanadium and nickel may be classified into three basic groups: 1) mixed-ligand tetradendates, 2) humate complexes, and 3) tetrapyrrole complexes (Fig. 4). This simple classification is based on the types of ligands involved in the metallo-organic complex and their coordination with the bound metal. Although

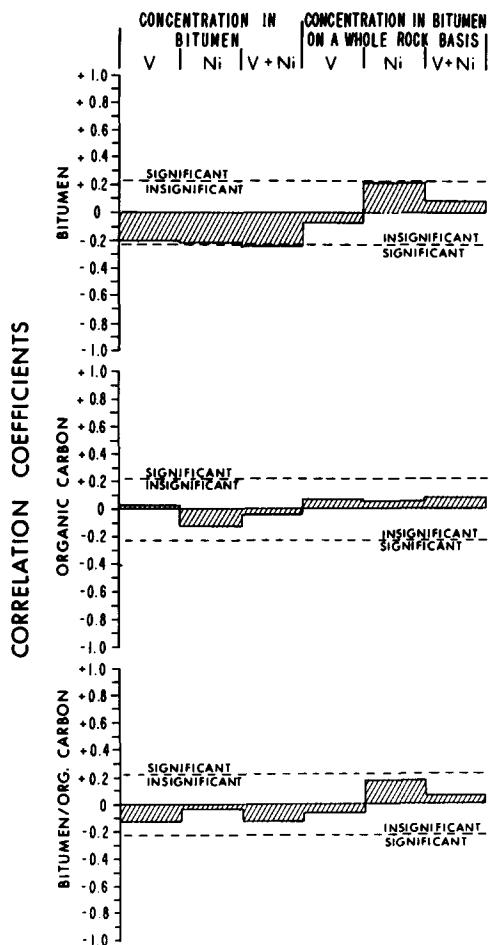


FIG. 2. Correlation coefficients based on linear regression analysis between metal concentrations and bitumen content, organic carbon content, and bitumen:organic carbon ratio. Critical correlation coefficients defining significant and insignificant correlations at the 99 percent confidence level are based on the F-test as described by Crow and others (1960).

the precise chemical and structural character of an entire metallo-organic complex is not always decipherable because of its high molecular weight and structural complexity, the stability of a metal bound to the complex is indicative of the type of ligands and their coordination.

Mixed-ligand tetradentates involve the bonding of a metal to four ligands, which may consist of numerous combinations of sulfur, oxygen, and nitrogen (Yen, 1975; Fig. 4). These complexes require bivalent metal cations, and their coordination is not a stable square planar or octahedral form (Martin and Ramaiah, 1965; Boucher and Yen, 1968 and 1969; Boucher *et al.*, 1968), but rather the ligands are distorted around the metal in less stable tetrahedral or square-pyramidal coordinations. As a result, the stability of vanadium and nickel in mixed-ligand tetradentates is low, and their demetallation may occur in dilute acids (Yen, 1975). Studies concerning mixed-ligand tetradentates in nature are scarce, and

their occurrence in nature appears to be limited to a minor constituent in a few crude oils (Yen, 1975).

Humate complexes are defined in this study as metallo-organic complexes in which oxygen atoms act as the bonding ligands (Fig. 4). Naturally occurring complexes of this type are common in humic substances and usually involve the oxygen in carboxyl or phenolic hydroxide functional groups (van Dijk, 1971; Schnitzer and Khan, 1972; Gamble and Schnitzer, 1973; MacCarthy and Mark, 1976). Although evidence suggests phenolic hydroxide functional groups are involved to some degree in the bonding of metals (MacCarthy and Mark, 1976), it is generally accepted that the oxygen atoms in the carboxyl functional groups are the primary ligands in humate complexes (Vinkler *et al.*, 1976). Vanadyl (VO^{2+}) and nickelous (Ni^{2+}) cations may form humate complexes at low pH values (Szalay and Szilagyi, 1967; Szabo, 1958; McBride, 1978), but their stabilities are considerably lower than the preferred trivalent aluminum and ferric cations (van Dijk, 1971; Schnitzer and Khan, 1972; Kribek *et al.*, 1977). This is supported by the observation that aluminum and iron concentrations in naturally occurring humic substances are considerably higher than vanadium and nickel concentrations (Nissenbaum and Swaine, 1976; Nissenbaum *et al.*, 1972; Cheshire *et al.*, 1977; Knezevic and Chen, 1977). Exceptions to this observation have been noted in some marine humic substances which have higher concentrations of divalent cations than trivalent cations (Rashid, 1971). These exceptions appear to be the result of more nitrogen and sulfur functional groups in some marine humic substances, which act as ligands in addition to the oxygen functional groups (Nissenbaum and Swaine, 1976). These ligands may form mixed-ligand tetradentates, which would prefer divalent cations. In addition to vanadium and nickel not being preferred in humate complexes, their instability within such a complex suggests that they are not likely to survive under diagenetic conditions. Pauli (1975) has shown that demetallation of humate complexes occurs in the presence of hydrogen sulfide and results in the precipitation of metal sulfides. Thermal maturation of organic matter during early diagenesis is also likely to cause demetallation of humate complexes as a result of decarboxylation.

Tetrapyrrole complexes are defined in this study as metallo-organic complexes with four pyrrole-nitrogen atoms acting as ligands (Fig. 4). In addition to including the extensively studied metallated porphyrins, this definition also includes pseudo-aromatic and highly aromatic tetrapyrroles (Fig. 4). These structures may occur as free molecules in an organic medium or as assimilated subunits in macromolecules (Blumer and Rudrum, 1970; Oehler *et al.*, 1974). Unlike the other metallo-organic complexes, tetrapyrrole complexes form tenacious covalent bonds with vanadyl and nickelous cations, which have a high thermal stability (Hodgson and Baker, 1957;

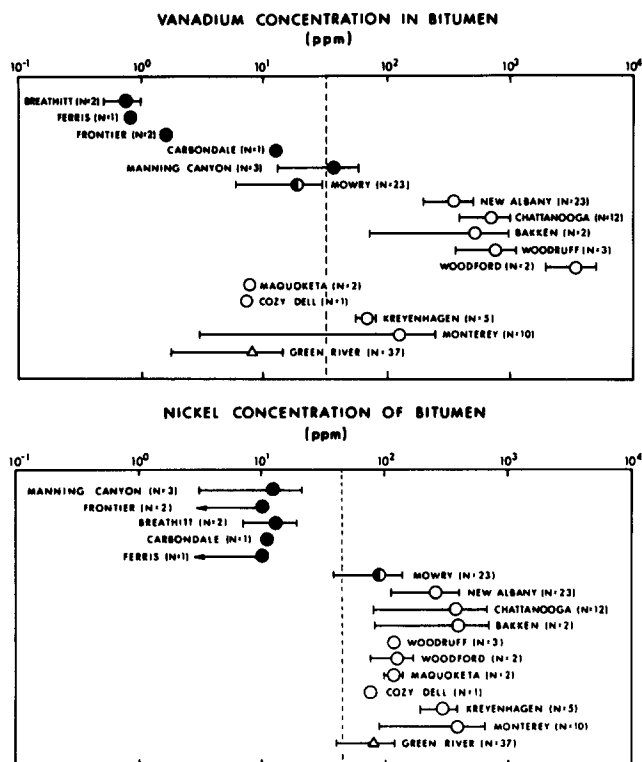


FIG. 3. Mean and standard deviation of vanadium and nickel concentrations in bitumens associated with Type-I (Δ), Type-II (\circ), and Type-III (\bullet) kerogens. The dashed lines represent the division between endemic and enriched concentrations as defined in Figs. 7 and 8.

Rosscup and Bowman, 1967), a resistance to strong acids (Caughey and Corwin, 1955; Dean and Girdler, 1960), and an inertness to cation exchange reactions (Barnes and Dorough, 1950). Although identification of all the metallo-organic complexes involving vanadium and nickel in natural organic substances is currently not feasible, the tenacious bonding of these two metals in crude oils (Constantinides *et al.*, 1959), asphalts (Brunnock *et al.*, 1968), and bitumens (Lewan, 1980) suggests that they are most likely to occur in tetrapyrrole complexes. The following discussion presents a first approximation of the factors influencing the enrichment of vanadium and nickel in bitumens, and is based on the premise that these two metals are primarily bound to some form of tetrapyrrole complexes.

Preference of tetrapyrroles for vanadium and nickel

The stability of tetrapyrroles is enhanced by metallation (Hodgson and Baker, 1957; Corwin, 1959), and small, bivalent cations form the most stable bonds (Dunning *et al.*, 1953; Caughey and Corwin, 1955; Erdman *et al.*, 1957). Although all the cations of the first transition-series of elements meet these requirements, naturally occurring tetrapyrrole complexes are almost exclusively bound to nickel or vanadium cations (Hodgson *et al.*, 1968; Filby, 1975). Nickel is bound as a bivalent nickelous cation

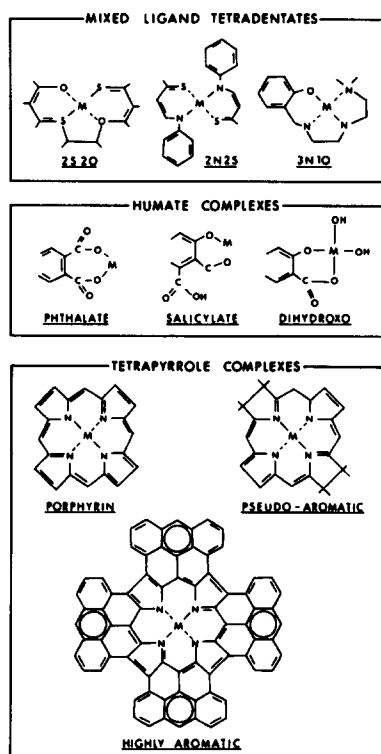


FIG. 4. Examples of metallo-organic complexes of vanadium and nickel (M) that are likely to occur in natural organic substances.

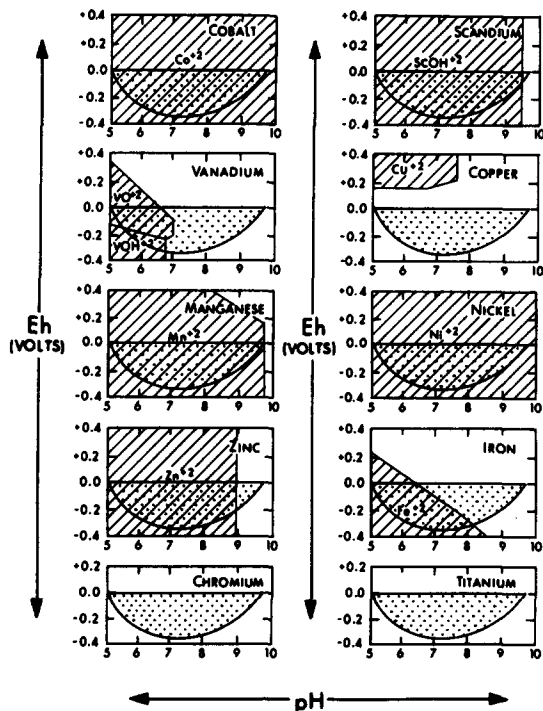


FIG. 5. Eh-pH diagrams showing approximate stability field for tetrapyrrole preservation (stippled area) and stability field for bivalent cations of the first transition-series of elements (hatched area). Diagrams were constructed from thermodynamic data compiled by Garrels and Christ (1965) at 25°C and 1 atm. Total metal concentrations are equal to those reported by Goldberg (1961) for average sea water.

(Fleischer, 1963) and quadrivalent vanadium is bound as a bivalent vanadyl cation (Erdman *et al.*, 1956) within the tetrapyrrole complexes. The stability and preference of these two metals in tetrapyrrole complexes appears to be the result of three factors: 1) their availability in nature as bivalent cations, 2) their small ionic radii, and 3) their favorable electron configuration.

All of the elements of the first transition-series form bivalent cations, but only certain ones exist under conditions favorable for the preservation of organic matter. Anaerobic conditions in accumulating sediments are the most favorable for the preservation of tetrapyrroles (Brongersma-Sanders, 1951; Gorham and Sanger, 1967; Drozdova and Gorskiy, 1972; Drozdova, 1975) and their accompanying organic matter (Zobell, 1946; Koyama and Tomino, 1967; Didyk *et al.*, 1978). These conditions are characteristic of reducing environments with Eh values usually less than zero (Krumbein and Garrels, 1952). An Eh-pH stability field for the preservation of tetrapyrroles and organic matter in nature may be approximated by superimposing the upper Eh limit of zero on the Eh-pH field for marginal marine and marine sediments as reported by Baas Becking and others (1960). This approximate stability field can be compared with Eh-pH conditions necessary for the stability of bivalent cations of the first transition-series

of elements in seawater (Fig. 5). This series of Eh-pH diagrams indicates that bivalent cations of chromium and titanium are not available, whereas bivalent cations of vanadium, nickel, cobalt, scandium, manganese, zinc, and iron are available for bonding with tetrapyrroles. The Eh-pH diagram for copper indicates that it is only available under oxidizing conditions, which is in agreement with the interpretation made by Palmer and Baker (1978) for deep-sea sediments. The restricted availability of bivalent vanadium cations and the overall availability of nickelous cations in these diagrams may account for the polymodal distribution of vanadium and the near-normal distribution of nickel observed in the bitumens (Fig. 1).

The distance between opposite nitrogen atoms in a tetrapyrrole ranges from 3.66 to 3.91 angstroms (Robertson, 1936; Robertson and Woodward, 1937; Crute, 1959; Fleischer, 1963), and because of the limited space the size of a bonding bivalent cation becomes important. In general, the smaller the size of a bivalent cation, the greater its stability and preference within a tetrapyrrole complex (Dunning *et al.*, 1953; Caughey and Corwin, 1955; Erdman *et al.*, 1957). As shown in Table 2, the small ionic radii of the metals in the vanadyl and nickelous cations suggests that these two cations have a distinct physical advantage over the other cations.

In addition to this physical advantage, vanadyl and nickelous cations are also more advantageous from an energy standpoint. Although the Gibbs free energies for metallation of the different bivalent cations would be more informative than their ligand field

Table 2:
Ionic Radii of Metals (6-Fold Coordination) in Bivalent Cations of the First Transition Series. Values are from Ahrens (1952, Table 16).

Bivalent Cations	Ionic Radii of Metal (Å)
V ⁺⁺	0.88
ScOH ⁺⁺	0.81
Mn ⁺⁺	0.80
Fe ⁺⁺	0.74
Zn ⁺⁺	0.74
VOH ⁺⁺	0.74
Co ⁺⁺	0.72
Cu ⁺⁺	0.72
Ni ⁺⁺	0.69
VO ⁺⁺	0.63

stabilization energies (Glasby, 1975; McKenzie, 1975), the lack of thermodynamic data on the metallation of tetrapyrroles encourages the use of the ligand field theory. The weak ligand field produced by a tetrapyrrole suggests that all of the d orbitals of a cation will be filled before electron pairing commences (Hodgson *et al.*, 1967) and this constitutes a high spin state. The coordination of a bivalent cation in a tetrapyrrole may be considered either octahedral or square planar. Both types of coordination have been considered, and their ligand field stabilization energies for the bivalent cations of the first transition-series of elements were calculated as decimal fractions of the octahedral coordination. The results in Table 3 indicate that vanadyl, nickelous, and VOH^{+2} cations have the highest ligand stabilization energies in the octahedral and square planar coordination, which indicates they have the most favorable electron configurations for tetrapyrrole complexes.

Preservation of tetrapyrrole complexes

Chlorophyll and heme pigments in living matter appear to be the most likely precursors of tetrapyrrole complexes found in sediments, sedimentary rocks, and crude oils (Hodgson *et al.*, 1960; Blumer and Snyder, 1967; Yen, 1975). Heme pigments are present in most organisms with a few exceptions such as anaerobic clostridia and lactic acid bacteria (Metzler, 1977, p. 563), but their most significant concentrations occur in animals. Conversely, chlorophyll pigments predominate in plants, where they are more prevalent than the heme pigments. Although heme pigments have been reported from some sediments (*e.g.* Shiobara and Taguchi, 1975), the wider distribution and higher concentrations of chlorophyll pigment in the biosphere suggest it is the more common precursor of tetrapyrrole complexes (Corwin, 1959).

Conversion of chlorophyll pigments to tetrapyrrole complexes similar to those found in sediments, sedimentary rocks, and crude oils involves a series of reactions in the water column and during burial in the sediment (Orr *et al.*, 1958; Baker and Smith,

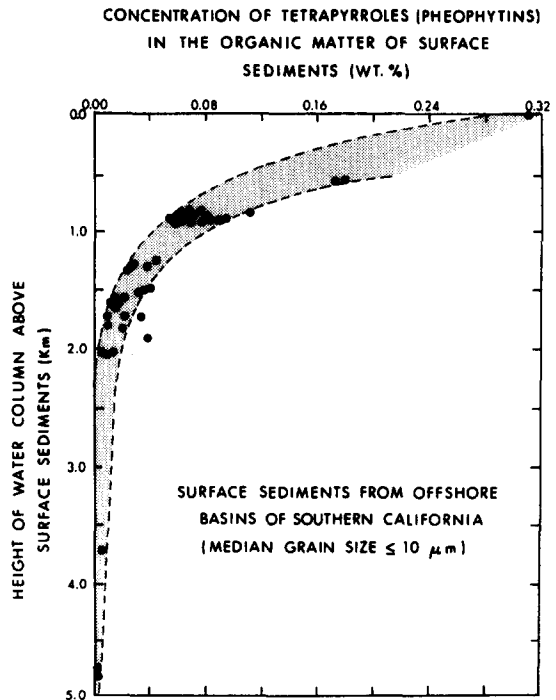


FIG. 6. Plot of concentration of tetrapyrroles (pheophytins) in organic matter from surface sediments of offshore southern California versus height of water column above sediment. The data are from Orr and others (1958), and include only those sediments with median grain diameters equal to or less than 10 microns.

1973; Yen, 1975; Lewan, 1980). Except for the early loss of magnesium (Yentsch, 1965; Lorenzen, 1967), these diagenetic reactions result in modifications to the periphery of a tetrapyrrole (*e.g.* allomerization, dealkenylation, decarboxylation, and ring scission) and do not appear to influence its ability to metallate with vanadyl or nickelous cations (Orr *et al.*, 1958; Hodgson *et al.*, 1967, p. 239; Shiobara and Taguchi, 1975). The most critical diagenetic reaction is the decomposition of chlorophyll pigments, which results in the complete destruction of the tetrapyrrole structure (Daley and Brown, 1973). Although the actual mechanism for this decomposition is not completely understood, anaerobic (Brongersma-Sanders, 1951; Gorham and Sanger, 1967; Drozdova and Gorskiy, 1972; Drozdova, 1975; Didyk *et al.*, 1978) and aphotic conditions (Daley and Brown, 1973) appear to be critical to the preservation of tetrapyrroles.

The preservation of organic matter accompanying tetrapyrroles is also favored under anaerobic conditions (Zobell, 1946; Koyama and Tomino, 1967; Didyk *et al.*, 1978), but data on marine water columns (Vallentyne, 1960; Holm-Hansen, 1969; Gagosian and Heinzer, 1979), lake sediments (Koyama *et al.*, 1973), decaying leaves (Sanger, 1968, 1971a, 1971b) and experimental degradation of algae (Daley and Brown, 1973) show that tetrapyrroles decompose at a significantly higher rate than the bulk organic matter accompanying them. Preferred decomposi-

Table 3: Ligand Stabilization Energies for High Spin, Bivalent Cations of the First Transition Series of Elements in Different Coordinations. All Values Expressed as Decimal Fractions of the Ligand Field Stabilization Energy for Octahedral Coordination (Δ_0).

Number of 3d Electrons	Bivalent Cations	Ligand Field Stabilization Energies			
		Octahedral	Square Planar	Cubic	Tetrahedral
0	Ca ⁺⁺	0.00	0.00	0.00	0.00
1	ScOH ⁺⁺	0.40	0.37	0.53	0.26
2	Ti ⁺⁺	0.80	0.75	1.07	0.53
3	VO ⁺⁺ , VOH ⁺⁺	1.20	1.06	0.71	0.35
4	Cr ⁺⁺	0.60	0.89	0.36	0.17
5	Mn ⁺⁺	0.00	0.00	0.00	0.00
6	Fe ⁺⁺	0.40	0.37	0.53	0.26
7	Co ⁺⁺	0.80	0.75	1.07	0.53
8	Ni ⁺⁺	1.20	1.06	0.71	0.35
9	Cu ⁺⁺	0.60	0.89	0.36	0.17
10	Zn ⁺⁺	0.00	0.00	0.00	0.00

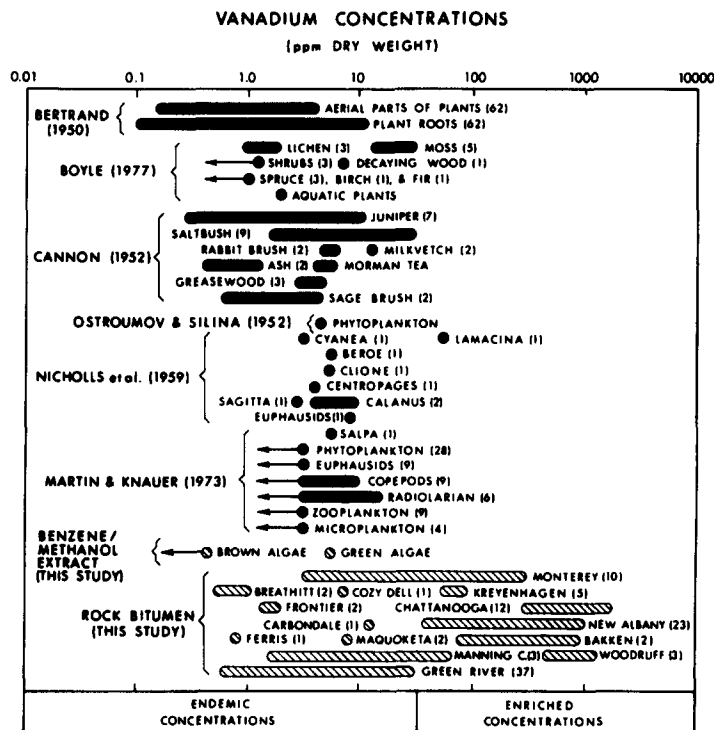


FIG. 7. Range of vanadium concentrations in living matter and in bitumens extracted from sedimentary rocks. Number of samples given in parentheses.

tion of this type suggests that the amount of tetrapyrroles retained in an organic accumulation of organic matter is a function of its exposure time to aerobic conditions and the oxygen content of the aerobic conditions encountered. Thus, the tetrapyrrole content should be low in organic matter that has settled through long aerobic water columns or that has been exposed to aerobic conditions on sediment-water interfaces for long durations. Conversely, the tetrapyrrole content should be high in organic matter that has encountered anaerobic waters early in its descent through a water column or that has been rapidly buried to anaerobic conditions within a sediment column. This may be demonstrated in part by examining the offshore basins of southern California. The height of the water columns overlying these basins varies with basin depth, which may range from 627 meters in the Santa Barbara basin to 4800 meters or more in the open ocean basin (Emery, 1960). Data from Orr and others (1958) in Fig. 6, show that the concentration of tetrapyrroles (*i.e.* pheophytins) in the organic matter from the surface sediments of these basins decrease as their settling distance through the aerobic and dysaerobic portions of the water column increase. The scatter in this general trend may be explained by two additional factors that were not considered in the plot: 1) the oxygen contents of the water columns are not the same over all of the basins, and 2) the exposure time of organic matter on the sediment-water interfaces may vary with the sedimentation rates, which are also not the same in all of the basins.

Phytoplankton and higher plants both contain significant quantities of chlorophyll (3000–67,000 ppm; Vallentyne, 1960; Pace, 1941; Sanger, 1968), but unlike the subaqueous habitat of phytoplankton, the intense light and highly aerobic subarial habitat of higher plants results in rapid and complete decomposition of chlorophylls prior to their deposition. Preferential decomposition of chlorophyll occurs during the late stages of senescence before the death of higher plants (Bidwell, 1974, pp. 483–493), and as a result complete decomposition of chlorophyll usually occurs before a plant is masticated, uprooted, or macerated. Studies on deciduous trees by Sanger (1968, 1971a, 1971b) have shown that decomposition of chlorophyll in leaves is rapid and essentially complete before the leaves are detached from their stems. This suggests that Type III kerogens and associated bitumens derived from higher plants are likely to be deficient in tetrapyrroles and as a result are not likely to be enriched in vanadium and nickel. This is supported by the data presented in Fig. 3, which shows that bitumens associated with Type III kerogens are usually not enriched in vanadium or nickel. Conversely, metal-enriched bitumens are associated with Type II and Type I kerogens, which are considered in part to be derived from phytoplankton. Although subaqueous conditions will not always be conducive for the preservation of tetrapyrroles, this environment in which phytoplankton exist provides a more probable setting for the preservation of tetrapyrroles, which appears to be an important prerequisite for the enrichment of vanadium and nickel.

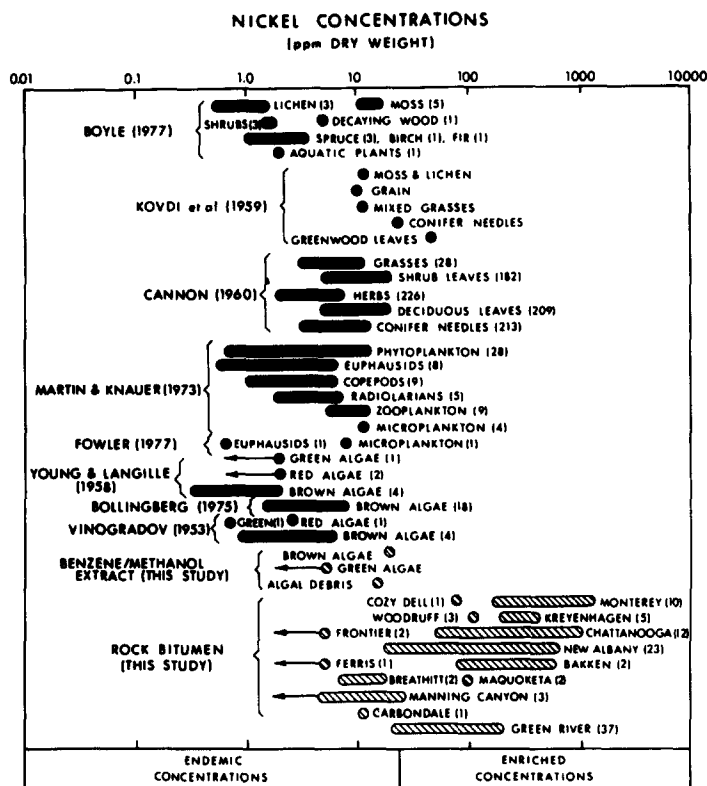


FIG. 8. Range of nickel concentrations in living matter and in bitumens extracted from sedimentary rocks. Number of samples given in parentheses.

Unlike nickel, Fig. 3 shows that vanadium is not always enriched in bitumens associated with Type II kerogens (e.g., Maquoketa, Cozy Dell, and Monterey). This may be explained by the restriction of the vanadyl cation to low pH conditions, while the stability field of the nickelous cation extends over a wide range of pH conditions (Fig. 5). Although hydroxides and biogenic sulfide may reduce the activity of vanadyl and nickelous cations, respectively (Lewan, 1980), the general relationships suggest that vanadium is more likely to be enriched under acidic conditions, whereas nickel may be enriched under basic, as well as acidic conditions.

Source of vanadium and nickel

The source of vanadium and nickel in the organic matter of sediments and sedimentary rocks is critical to understanding the factors controlling their concentrations. The two most likely sources of these two metals are the endemic metals in the living matter from which an organic accumulation was derived (e.g., Vinogradov, 1936; Manskaya and Drozdova, 1968, p. 219; Yen, 1975) or the dissolved metals in the interstitial waters of the sediments with which the organic matter is deposited.

Endemic metal concentrations have been shown to be variable for different types of organisms (Noddack and Noddack, 1939; Martin and Knauer, 1973), for organisms growing in different media (Cannon,

1963; Bertrand, 1950; Riley and Roth, 1971; Brooks et al., 1977), for the same species at different seasons (Black and Mitchell, 1952), and for individuals of the same species (Bertrand, 1950). Review of such data (Figs. 7, 8) suggests that 32 and 45 ppm are the maximum endemic concentrations for vanadium and nickel, respectively. The marine organism that is often cited as a possible cause of vanadium enrichment is the tunicate, ascidia (Vinogradov, 1936; Manskaya and Drozdova, 1968, p. 219; Yen, 1975). Although the presence of this type of tunicate would increase the endemic vanadium concentration significantly (166 to 1860 ppm, Vinogradov, 1953, p. 425), the presence of this sessile, aerobic respiring organism is highly improbable in the anaerobic bottom waters that are usually required for the preservation of organic accumulations. It is for this reason that the endemic concentrations of ascidia were not included in Fig. 7. The ranges of vanadium and nickel concentrations in extracts from algae and bitumens from different formations considered in this study (Figs. 7, 8) indicate that endemic metal concentrations may be the source of vanadium and nickel in some bitumens (e.g., Breathitt, Frontier, Ferris, and Carbondale), but the enriched concentrations of these two metals in the other bitumens require another source. The other source of the two metals is the dissolved vanadium and nickel species in the interstitial waters accompanying the organic matter in a sediment. In a closed sediment system this source of metals is lim-

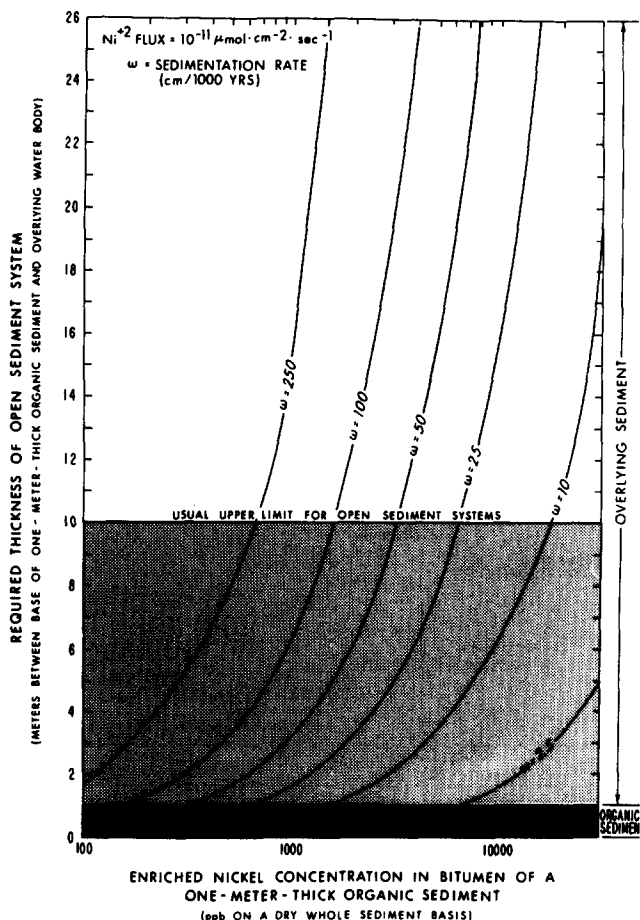


FIG. 9. Graph showing the thickness of an open sediment system that is necessary to assure different degrees of nickel enrichment in the bitumen of a one-meter-thick organic sediment at different rates of sedimentation. The calculations assume that all of the nickel that diffuses into the organic sediment forms metallo-organic complexes. Other considerations include a mean dry sediment density of 2.38 g cm^{-3} and a Ni^{+2} flux of $10^{-11} \mu\text{mol cm}^{-2} \text{ sec}^{-1}$. The mean water content of the sediment is considered to be 50 percent by volume and compaction of sediment with burial is not considered. The dashed portions of the sedimentation rate curves indicate conditions under which nickel enrichment is completed by the end of the deposition of the one-meter-thick organic sediment.

ited and is not likely to be an adequate source for enriched concentrations. As an example, the nickel concentrations in the interstitial waters from the continental borderland off the coast of Southern California (Brooks *et al.*, 1968) and the Saanich Inlet of British Columbia (Presley *et al.*, 1972) range from 1.4 to 20.8 ppb with a mean of 5.6 ± 3.5 ppb. Using the maximum value (20.8 ppb) and assuming that 50 volume percent of a sediment is water and that the remaining sediment has a mean specific gravity of 2.65, the amount of nickel available to enrich the accompanying bitumen is only 7.9 ppb on a dry whole-rock basis. This amount is more than two orders of magnitude smaller than the mean value of 1497 ppb reported for nickel in the bitumens of this study on a whole rock basis (Fig. 1b).

Interstitial waters are more effective sources of metals in open sediment systems where the overlying water body may provide a vast supply of vanadium and nickel. In this type of system, the vanadium and

nickel that are removed from the interstitial waters by metallation of tetrapyrroles are replaced by the downward diffusion of dissolved vanadium and nickel from the overlying water body. This source of vanadium and nickel will only remain effective as long as the sediment system remains open to the overlying water body. The adequacy of this source of vanadium and nickel can be tested by using data on Ni^{+2} in the interstitial waters of Santa Barbara Basin. A linear nickel concentration gradient of $-1.53 \times 10^{-5} \mu\text{ moles cm}^{-4}$ was computed from sediments in the Santa Barbara Basin, on the basis of nickel concentrations in their interstitial water reported by Brooks and others (1968) and the sediment properties reported by Emery (1960). A sediment diffusion coefficient of $6.8 \times 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ was calculated for a temperature of 6°C from data presented by Li and Gregory (1974). Using these values, the flux of nickel through the sediment was calculated to be $10^{-11} \mu\text{ moles cm}^{-2} \text{ sec}^{-1}$ from Fick's first law (Crank, 1975):

$$J_{\text{Ni}^{+2}} = -D_{\text{Ni}^{+2}} \frac{\partial C_{\text{Ni}^{+2}}}{\partial X},$$

where $J_{\text{Ni}^{+2}}$ is the flux of Ni^{+2} through the sediment, $D_{\text{Ni}^{+2}}$ is the diffusion coefficient of Ni^{+2} in sediment and includes corrections for porosity and tortuosity (Li and Gregory, 1974), and $\partial C_{\text{Ni}^{+2}}/\partial X$ is the concentration gradient on Ni^{+2} in sediment. This flux has been used to calculate the burial depths necessary to maintain an open sediment system for different degrees of nickel enrichment at different rates of sedimentation (Fig. 9). Using a nickel concentration in bitumen of 2000 ppb on a whole rock basis, an open sediment system would have to be maintained to depths of 1.3 and 3.2 meters for sedimentation rates of 10 and 25 cm per 1000 years, respectively. It would appear reasonable to assume that diffusion through sediment would remain operative as long as the interstitial water remained a continuous phase in the sediment column, and porosities greater than 60 percent are likely to insure such a condition. Fine grained sediments with porosities greater than 60 percent are common down to burial depths of 5 to 10 meters (Emery, 1960, p. 258; Meade, 1966; Bennett *et al.*, 1981) and in some cases down the depths in excess of 100 meters (Manheim and Waterman, 1974; McDuff and Gieskes, 1976). Although Fig. 9 should only be considered a first approximation, it does suggest that diffusion of dissolved metals in interstitial waters is an adequate source of enriched vanadium and nickel concentrations in bitumens, and that increasing sedimentation rates have an adverse effect on the adequacy of this source.

CONCLUSIONS

The amount of vanadium and nickel concentrated in the organic matter of sedimentary rocks appear to be dependent on two factors: 1) preservation of tetrapyrroles, and 2) persistence of an open sediment system. Preservation of tetrapyrroles is determined by the source of organic matter and the water column conditions, while the persistence of an open sediment system is determined by the character of the sediment column and the rate of sedimentation. The rapid decomposition of tetrapyrroles in terrestrial plants prior to their occurrence as suspended load in fluvial, lacustrine, or marginal marine water bodies, indicates that enriched concentrations of vanadium and nickel are not likely to occur in organic matter derived from this source. Conversely, algae in subaqueous environments are a more probable source of tetrapyrroles, but the amount of preservation is a function of exposure time to aerobic conditions. As the exposure time increases the potential of algal derived organic matter to be enriched in vanadium and nickel decreases because of the increasing preferential decomposition of tetrapyrroles. Diffusion of dissolved metals from an overlying water body into the interstitial waters of a sediment column is critical to maintaining a viable source of vanadium and nickel for the me-

tallation of preserved tetrapyrroles. The feasibility of this process is dependent on the persistence of an open sediment system, which in turn is dependent on slow rates of sedimentation and the character of the sediment. In general, enrichment of vanadium or nickel in the organic matter of a sedimentary rock suggests that within its environment of deposition, algal derived organic matter encountered anaerobic conditions early in its settling, or burial histories and sedimentation rates were slow enough to insure the persistence of an open sediment system. Future studies dealing with the total amount of tetrapyrroles, as well as the vanadium and nickel concentrations in the organic matter of sedimentary rocks may reveal additional information on water column conditions and sedimentation rates of ancient depositional environments.

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