Chemical Geology, 91 (1991) 83–97
Elsevier Science Publishers B.V., Amsterdam

Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis

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(Accepted for publication November 13, 1990)

ABSTRACT

Breit, G.N. and Wanty, R.B., 1991. Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis. In: J.F. Branthaver and R.H. Filby (Guest-Editors), Trace Metals in Petroleum Geochemistry. Chem. Geol., 91: 83–97.

Published data relevant to the geochemistry of vanadium were used to evaluate processes and conditions that control vanadium accumulation in carbonaceous rocks. Reduction, adsorption, and complexation of dissolved vanadium favor addition of vanadium to sediments rich in organic carbon. Dissolved vanadate (V(V)) species predominate in oxic seawater and are reduced to vanadyl ion (V(IV)) by organic compounds or H_2S. Vanadyl ion readily adsorbs to particle surfaces and is added to the sediment as the particles settle. The large vanadium concentrations of rocks deposited in marine as compared to lacustrine environments are the result of the relatively large amount of vanadium provided by circulating ocean water compared to terrestrial runoff.

Vanadium-rich carbonaceous rocks typically have high contents of organically bound sulfur and are stratigraphically associated with phosphate-rich units. A correspondence between vanadium content and organically bound sulfur is consistent with high activities of H_2S during sediment deposition. Excess H_2S exited the sediment into bottom waters and favored reduction of dissolved V(V) to V(IV) or possibly V(III). The stratigraphic association of vanadiferous and phosphatic rocks reflects temporal and spatial shifts in bottom water chemistry from suboxic (phosphate concentrated) to more reducing (euxinic?) conditions that favor vanadium accumulation.

During diagenesis some vanadium–organic complexes migrate with petroleum out of carbonaceous rocks, but significant amounts of vanadium are retained in refractory organic matter or clay minerals. As carbon in the rock evolves toward graphite during metamorphism, vanadium is incorporated into silicate minerals.

1. Introduction

Vanadium contents of carbonaceous sedimentary rocks can be used as a guide for petroleum exploration (Curiale, 1987), for the evaluation of ancient depositional environments (Lewan, 1984), and for the estimation of vanadium resources (Kuck, 1985; Breit, 1991). Using vanadium concentrations of these rocks and in petroleum evolved from them requires a thorough understanding of geochemical controls that affect accumulation of vanadium in the rock and its retention during diagenesis. The large vanadium abundances in many carbonaceous rocks, relative to average shale (Table 1), have been explained as syngenetic (Brumsack and Lew, 1982; McKelvey et al., 1986; Breit, 1991), diagenetic (Vine and Tourtelot, 1970) and epigenetic (Coveney et al., 1987) enrichments. In most of these evaluations, however, geochemical processes such as reduction–oxidation, adsorption, and complexation and their effect on vanadium transport and accumulation commonly are not critically evaluated. This paper reviews the controls on vanadium cycling and the implications of these controls on syngenetic accumulation of vanadium.

TABLE 1

Range of vanadium abundances in carbonaceous accumulations

	Vanadium (ppm)
(1) Petroleum	<0.1–1,600
(2) Tar sands	14–300
Oil shales:	
(3) Marine	110–5,000
(4) Lacustrine	50–250
(5) Black shales	20–16,000
(6) Sapropelic coal	as much as 3 wt.%
(7) Coal	0–1,300
(8) Asphaltite deposits (Peru and Argentina)	2,000–10,000
(9) Average shale	130

(1) Whisman and Cotton, 1971; Kuck, 1985. (2) Harrison et al., 1981; Peer, 1981. (3) Robl et al., 1983; Derkey et al, 1985; Glikson et al., 1985. (4) Tuttle et al., 1983; Glikson et al., 1985; Tuttle, unpublished data. (5) Vine and Tourtelot, 1970; McKelvey et al., 1986. (6) Zhang 1985. (7) Valkovic, 1983. (8) Larson and Welker, 1947; Kett, 1948; Aguije, 1954. (9) Turekian and Wedepohl, 1961.

A relation between vanadium and organic carbon is evident by their strong correlation in marine oil shales and black shales (Fig. 1). This association reflects either an affinity of vanadium for organic matter or the favorability of conditions that preserve organic matter to partition dissolved vanadium into the sediment. The variable slopes of the regression lines in Fig. 1 can be explained as differences in the composition of organic matter (Lewan and Maynard, 1982), variable chemical conditions in the depositional environments (Lewan, 1984), variations in the rates of vanadium supply or sedimentation, or changes in the composition of the sediment during diagenesis. Our evaluation of these factors has led to a model that describes vanadium accumulation in carbonaceous rocks.

Published data on carbonaceous shales and fossil fuels, the geochemistry of vanadium in modern depositional environments, and our research on vanadium deposits were used to identify conditions that favor vanadium accumulation. Based on this analysis, geochemical conditions and the supply of vanadium to depositional basins were determined to be the major controls on vanadium accumulation in carbonaceous sediments. Our model is consistent with most observations of vanadium-enriched rocks and provides a conceptual framework that we hope will be tested by future research.

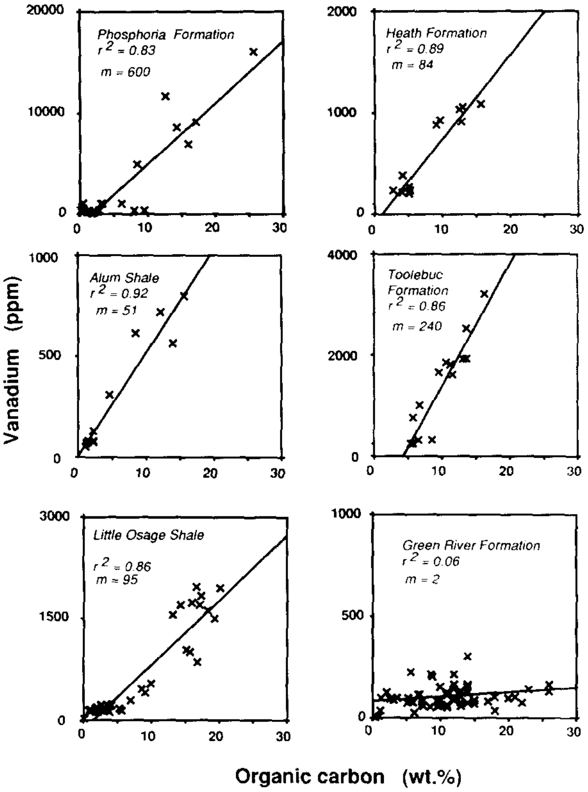

Fig. 1. Organic carbon vs. vanadium content of oil shales and black shales. All shales except the lacustrine Green River Formation were deposited in marine environments. Lines were calculated by simple linear regression. r^2 = (correlation coefficient)^2; m = slope of the regression lines. Data: Phosphoria Formation, Idaho and Wyoming: Gulbrandsen (1966) and McKelvey et al. (1986); Heath Formation, Montana: Derkey et al. (1985); Alum Shale, Sweden: Andersson et al. (1985); Toolebuc Formation, Australia: Riley and Saxby (1986); Little Osage Shale, Oklahoma: Wenger (1987); Green River Formation, Colorado: M.L. Tuttle, unpublished data.

2. Transport and supply of vanadium

Syngenetic accumulation of vanadium in carbonaceous rocks requires transfer of dissolved vanadium from the overlying water column into accumulating sediments. Redox conditions, adsorption, and complexation are the main controls on the solubility of vanadium in natural waters. In addition to these geochemical controls on transport, the vanadium abundance in carbonaceous rocks also reflects the supply of vanadium and the rate of sedimentation.

2.1. Dissolved vanadium

Transport of dissolved vanadium in modern surface waters is strongly dependent on oxidation state and water composition. Three oxidation states of vanadium are possible in sedimentary environments (Fig. 2): V(V) as vanadate species ($H_nVO_4^{n-3}$, $n=0$ to 4), V(IV) as vanadyl ion ($VO(OH)_n^{2-n}$, $n=0$ to 2), and V(III) as $V(OH)_n^{3-n}$ ($n=0$ to 3). Vanadate species (V(V)) are anions in the range of natural pH and the amount dissolved in oxic waters is rarely limited by solubility of V(V) species. Both V(IV) and V(III) are less soluble than V(V) because of their tendency to form insoluble oxyhydroxides in the pH range of natural waters (Wanty, 1986; Wehrli and Stumm, 1989).

Dissolved vanadium does not form strong complexes with common inorganic ligands but may be complexed by organic compounds. Vanadium(V) forms only weak complexes with carboxylic acids at pHs less than 7 (Bartusek and Sustacek, 1983; Tracey et al., 1987). Relative to vanadate ion and most other 2+ transition metal ions, vanadyl ion forms strong bonds with organic complexes (Perrin, 1979; Wehrli, 1987). These complexes increase the stability field of vanadyl species relative to V(V) and V(III), as illustrated by vanadyl–salicylate (Fig. 2). Salicylic acid was used in this example because it is a good analog for the bonding of vanadyl ion to humic acids (Mangrich and Vugman, 1988; Goncalves and Mota, 1987). Relatively little is known about the complexation of V(III) with organic compounds. Organic compounds such as those found in humic acids are not only effective at complexing V(IV) but can reduce V(V) to V(IV) (Szalay and Szilagyi, 1967; Goodman and Cheshire, 1975; Wilson and Weber, 1979). Therefore, dissolved vanadate in contact with natural organic compounds is likely to be reduced and complexed.

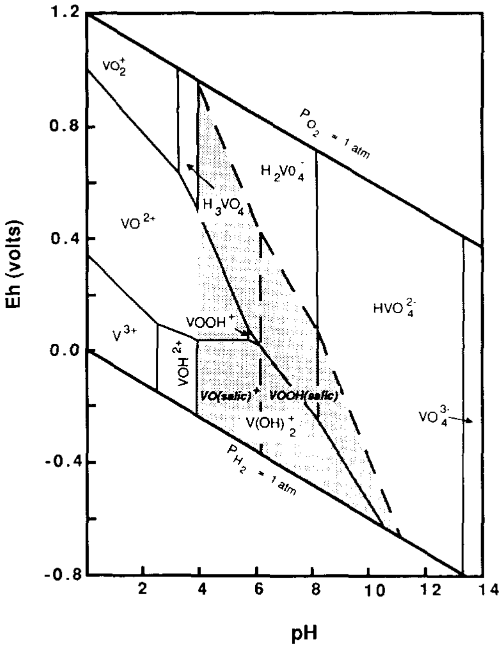

Fig. 2. Eh vs. pH diagram of vanadium-H_2O (solid lines) and vanadyl-H_2O--salicylate(salic) at 25°C and 1 atm., [salicylate] = 10^{-5} *M*. Vanadium species calculated for [V] less than 10^{-5} *M* to avoid polymeric species (Ehde et al., 1985). Vanadyl salicylate stability field (stippled area) was calculated for pH 4 to 11. Boundaries calculated from thermodynamic data reviewed by Wanty (1986). Data for stability of vanadyl--salicylate compounds from Goncalves and Mota (1987).

Dissolved organic complexes might affect the concentration of vanadium in natural waters. Sugimura et al. (1978), Orivini and Lodola (1979), and Amdurer et al. (1983) determined that 20 to 80% of dissolved vanadium in fresh waters and seawater is bound to organic compounds; however, Shiller and Boyle

(1987) and Jeandel et al. (1987) did not detect any organically bound vanadium in their investigations. In pore waters from anoxic sediments in the Gulf of California, Brumsack and Gieskes (1983) noted that the abundances of organic compounds and vanadium correlate. The association with dissolved organic compounds and the large concentration of vanadium (as much as 1,300 ppb V) are best explained by vanadyl–organic complexes. In these reducing pore waters, vanadium is likely to be V(IV) and is present in concentrations 2,000 times greater than predicted for a vanadyl–H_2O system (calculated using data from Wanty, 1986). Heggie et al. (1986) measured a tenfold enrichment of vanadium in very shallow pore waters relative to adjacent bottom waters. They attributed the higher concentrations to complexes of vanadium with dissolved organic matter, which inhibit diffusion of vanadium into the sediment.

2.2. *Supply*

Sources of vanadium proposed to explain syngenetic accumulation include hydrothermal solutions related to submarine volcanism (Bostrom and Fisher, 1971), seawater (Holland, 1979), and continental runoff (Wedepohl, 1964). Hydrothermal fluids are unlikely to result in unusual vanadium abundances because they have vanadium contents similar to those of seawater (Jeandel et al., 1987). In addition, iron oxides that precipitate from the hydrothermal solutions are an important sink of vanadium in seawater (Dymond and Roth, 1988; Metz et al., 1988; Trocine and Trefry, 1988; Trefry and Metz, 1989). The relative amounts of vanadium supplied by seawater and continental runoff were evaluated using box models (Figs. 3 and 4) that are designed to be analogs of modern marine and lacustrine systems. In evaluating these models, the amount of vanadium trapped in a sediment was calculated to be independent of processes that control accumulation. The impact of these processes is discussed later.

The marine model (Fig. 3) assumes that the depositional basin is open to seawater circulation similar to the model proposed by Heckel (1977) to explain deposition of Pennsylvanian black shales in the Midcontinent, U.S.A. We used an average rate of oceanic mixing to estimate the volume of water circulated through the basin (based on an oceanic circulation time of 1,000 years; Broecker and Peng, 1982). This requires that 2.8 million tons of vanadium is supplied to the basin per year. The sedimentation rate (0.3 mm/yr.) was selected to mimic the rate in the modern Black Sea (Degens et al., 1978). With these assumptions the solid phase of the sediment within the basin is enriched by 800 ppm vanadium if two percent of the dissolved vanadium is added to the sediment.

The modeled marine basin is similar to the geometry of the Eromanga basin, Australia in which the Cretaceous Toolebuc Formation was deposited. This calcareous oil shale averages 1500 ppm V (Riley and Saxby, 1986) and contains a total of 0.5 billion tons of vanadium (estimated from data of Doutch and Saxby, 1983, and Patterson et al., 1986). The Toolebuc was deposited in approximately 1 million years (Burger, 1986) at a calculated rate of 0.04 mm/yr. (original porosity estimated at 80%). If the supply of vanadium to the Eromanga basin was similar to that modelled in Fig. 4, only 0.6% of the dissolved vanadium was fixed by the sediment. Although this seems like a low extraction efficiency, the amount of vanadium in the Toolebuc Formation represents two percent of the total vanadium cycled through the ocean over one million years (assuming an oceanic residence time of vanadium of 100,000 years; Shiller and Boyle, 1987).

Accumulation of vanadium from continental runoff was evaluated by modeling a closed-basin lake similar to Great Salt Lake, Utah (Fig. 4). A closed basin lake was selected to

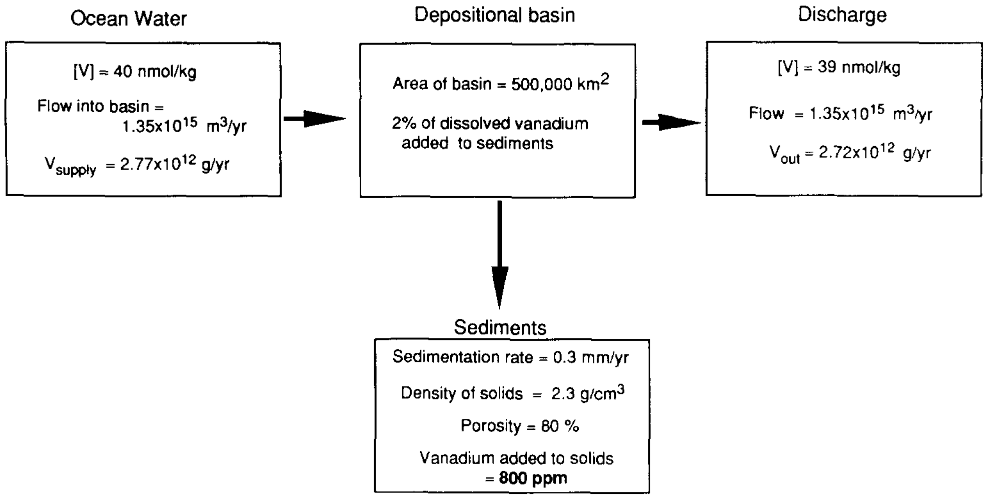

Fig. 3. Box model of syngenetic vanadium accumulation in marine carbonaceous sediments. Concentration of vanadium from Jeandel et al. (1987). Basin is open to average oceanic circulation (Broecker and Peng, 1982). Sediment characteristics are similar to those measured by Degens et al. (1978) in Black Sea sediments.

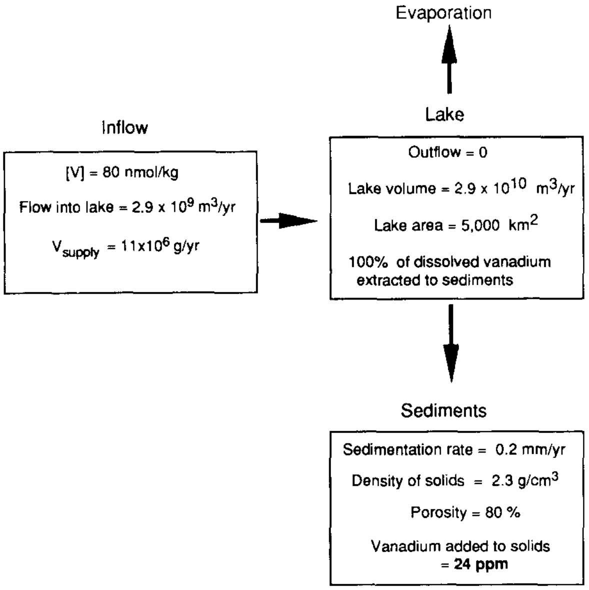

Fig. 4. Box model of vanadium accumulation in sediments within a closed basin lake. All recharge to the lake is due only to evaporation. The lake is similar in scale and vanadium budget to Great Salt Lake, Utah. Physical chacteristics of the lake were compiled from Arnow (1980) and Stauffer (1980); inflow concentration of vanadium estimated from analyses of recharge rivers (D. Stevens, written communication, 1989).

mimic the depositional conditions thought to be characteristic of most lacustrine oil shales. In this example, all of the vanadium in recharge water, 11 tons per year, is deposited with the accumulating sediment. Because the mass of vanadium per unit area of the lake is 2000 times less than in the marine model, relatively small amounts of vanadium will be added to the lake sediment. The calculated concentration of vanadium added to the sediment, 24 ppm, is close to the measured concentration of extractable (nondetrital) vanadium in Great Salt Lake sediments (Domagalski et al., 1990). This slight enrichment is despite the larger concentrations of vanadium in the inflow waters compared to average river water (40 nmol/kg; Shiller and Boyle, 1987). Slightly increased vanadium concentrations in the sediment could result by increasing the recharge rate or the concentration of vanadium in the inflow water. Although the concentration of vanadium in the inflow waters could be higher, concentrations greater than 1000 nmol/kg would be necessary to result in sediment vanadium abundances comparable to marine carbonaceous rocks. Such large dissolved vanadium abundances have not been detected in surface waters unaffected by anthropogenic activities.

Comparison of the box models for the marine and lacustrine settings emphasizes that differences in vanadium supply can cause major differences in vanadium concentrations of sediments and resulting rocks (Table 1). This conforms to the consistently low vanadium content of lacustrine compared to marine oil shale. Anomalous, syngenetic enrichments of vanadium and other metals are unlikely in lacustrine sediments because the rate of metal supply from incoming water is many orders of magnitude lower than for the modelled marine system. Even if the drainage basin is composed of vanadium-rich rock, the increase in total amount of vanadium supplied is typically small. Consistent with the conclusions of Brumsack and Lew (1982), seawater is a better supplier of vanadium in carbonaceous sediments than continental runoff.

3. Accumulation of vanadium in sediments

Extraction of dissolved vanadium from the water column and addition to carbonaceous sediments is the result of physical, chemical and possibly biological processes. Processes such as adsorption, particle settling and diffusion are considered along with the variables that affect the efficiency of these processes.

3.1. Biota

Organisms may play an active role in vanadium cycling, either by accumulating vanadium as part of their life cycle or by excreting compounds that reduce or bind vanadium (Krauskopf, 1956; Lee, 1983; Boyd and Kustin, 1984; Nechay, 1984). Lee (1983) noted that algae passively adsorb vanadium and this adsorption may be important in the flux of vanadium into lake sediments. Some ascidians (a class of filter-feeding Urochordates) have been proposed to explain vanadium enrichments because of their large vanadium contents (Lee, 1983; Zhang 1985; Glikson et al., 1985). However, these sessile benthic organisms are unlikely to survive in the anoxic conditions ambient during accumulation of carbonaceous sediments (Lewan and Maynard, 1982). An alternative explanation was presented by Brumsack (1983) who determined that a mixture of metals contained in plankton and average shale could explain the abundance of metals, including vanadium (<200 ppm V), in most modern carbonaceous marine sediments. However, vanadium abundances in metal-rich sediments and rocks, such as the Black Sea sediments, require an additional mechanism of vanadium enrichment. Although the process(es) by which vanadium is added to the sediment may be abiogenic, organisms control vanadium accumulation by providing the organic matter that ultimately creates chemical environments favorable for vanadium accumulation (Brumsack, 1983).

3.2. Adsorption and particle settling

Adsorption of vanadium to biogenic or terrigenous detritus is the most commonly considered mechanism of vanadium removal from seawater (Amdurer et al., 1983; Prange and Kremling, 1985). In the pH range of most natural waters, vanadate strongly adsorbs to ferric and aluminum oxides (Honeyman, 1984; Micera and Dallocchia, 1988; Shieh and Duedall, 1988; Wehrli and Stumm, 1989) and kaolinite (Breit and Wanty, unpublished data). Vanadyl ion adsorbs more strongly than vanadate, but its stability as an adsorbed species is limited in oxic waters (Wehrli and Stumm, 1989). Adsorption of vanadyl to oxides is even preferred over complexation by dissolved organic ligands except at high ligand concentrations (Micera and Dallocchia, 1988; Wehrli and Stumm, 1989). For example, Shiller and Boyle (1987) determined that as much as 40% of the vanadium transported by the Mississippi River is bound to suspended particles. They also experimentally determined that vanadate adsorption increased when pH increased above

4.5. In oxic basins, iron oxides adsorb significant amounts of vanadium from seawater (Shieh and Duedall, 1988) and may be an important sink of dissolved vanadium (Trefry and Metz, 1989).

Collier (1984) noted a 10% depletion of dissolved vanadium in ocean surface waters. This depletion decreases slowly with depth and at approximately 500 m depth the dissolved vanadium concentration reaches a constant value, near 36 nmol/kg. This concentration profile can be attributed to binding of vanadium to biogenic particles and its release as the particles are altered during settling. A portion of the vanadium held by the particles might be bound to the particles by adsorption. The maximum vanadium flux calculated by Collier is 15 nmol cm^{-2} $yr.^{-1}$ and would result in only 80 ppm vanadium in solids of a sediment that has an accumulation rate of 0.5 mm/yr. (assuming initial porosity is 80% and the mass of the particles is preserved). Approximately 90% of the particle mass (organic carbon) must be lost with complete retention of vanadium to explain carbonaceous rocks containing vanadium concentrations near 1000 ppm, which seems unlikely. Thus, removal of dissolved vanadium onto settling biogenic particles in oxic waters cannot easily account for the vanadium contents of carbonaceous rocks.

Some investigators have noted a decrease in the abundance of dissolved vanadium in anoxic waters that is best explained by adsorption. Van der Sloot et al. (1985) attributed the 70% decrease in dissolved vanadium in anoxic estuary waters to reduction of V(V) to V(IV). Although Van der Sloot et al. suggested that solubility of oxyhydroxides might limit the concentration of dissolved vanadium, Wehrli and Stumm (1989) argued that adsorption is more likely the limiting factor. Consistent with the observations of Van der Sloot et al., Collier (1984) noted a slight depletion of vanadium in anoxic water at Saanich Inlet. Fowler and Knauer (1986) noted that while little vanadium was scavenged from surface waters, particles passing through an anoxic zone adsorbed significant amounts of vanadium. Adsorption of vanadium will increase if vanadate is reduced to V(IV) species. Stratified water columns containing anoxic waters favor this reduction because reducing organic compounds are preserved and the absence of oxygen favors V(IV). Reduction on particle surfaces is also possible because most of the adsorptive properties of solids are controlled by organic coatings (Balistrieri et al., 1981). The 10% depletion of dissolved vanadium detected by Collier (1984) in oxic surface waters may be a minimum indication of the effectiveness of adsorption.

3.3. Diffusion

Above we speculated on a particle scavenging model of vanadium accumulation; an alternative explanation for the enrichment is diffusion (Brumsack, 1986; Jarvis and Higgs, 1987; Francois, 1988). Diffusion of vanadium into carbonaceous sediment from bottom waters is favored by a decreasing concentration of V(V) species in pore waters due to reduction, complexation and adsorption within the sediment. Brumsack (1986) invoked diffusion to explain enrichment of vanadium in anoxic sediments from the Gulf of California. The vanadium concentration in these sediments increases linearly from 80 ppm at the sediment surface to 110 ppm at a depth of 30 cm. Assuming the increase of 30 ppm V is the result of diffusion (sediments have 70% porosity and a solid phase density of 2.0 g/cm^3) and a sedimentation rate of 1 mm/yr. (Wang and Yeh, 1985), the vanadium flux into these sediments is estimated to be 1.0 $\mu g\, cm^{-2}\, yr.^{-1}$. This flux could account for sediments with vanadium contents of 500 ppm only if the sediments were deposited at very slow rates (less than 0.05 mm/yr.) and diffusion of vanadium was possible to a depth of at least 1 m. The apparent absence of modern carbonaceous sediments having vanadium concentrations that exceed 300 ppm suggests that diffusion alone cannot explain large vanadium concentrations (> 500 ppm) detected in many carbonaceous rocks, or that modern sedimentation rates are too rapid.

3.4. Redistribution of vanadium within sediments

Chemical changes within sediments modify the abundance of contained vanadium. Reworking of typical sediments under oxic conditions result in high contents of vanadium in the shallowest pore waters presumably because vanadium is mobilized from degrading biogenic particles (Shaw et al., 1990). This vanadium may diffuse upward into the bottom waters (Heggie et al., 1986; Shaw et al., 1990) or downward toward preserved reducing zones where it reprecipitates (Colley et al., 1984; Jarvis and Higgs, 1987). Shaw et al. (1990) compared the vanadium contents of pore waters in anoxic and oxic sediments and determined that vanadium is not redistributed in anoxic sediments.

4. Associations with other elements

Geochemical conditions that favor vanadium accumulation can be further constrained by evaluating the abundance and geochemical controls on elements associated with vanadium in carbonaceous rocks. We specifically considered organically bound sulfur, phosphate and nickel because of the consistent positive relation between the abundance of these components and vanadium content.

4.1. Vanadium–organically bound sulfur

The geochemical association of vanadium and sulfur is apparent in the large vanadium abundances in sulfur-rich petroleum (Lewan, 1984; Tissot and Welte, 1984) and in the contents of vanadium in carbonaceous rock rich in organic-sulfur (Patterson et al., 1986). This association has been speculated to be the result of preferential bonding of vanadium to sulfur ligands on the organic matter (Yen, 1975; Baker and Louda, 1986) or chemical conditions operative during sediment deposition (Lewan, 1984). Sulfur–organic compounds are still poorly characterized and the extent and type of bonding with vanadium is unknown. Lewan (1984) argued that vanadium is preferentially enriched in carbonaceous sediments with large H_2S activities because H_2S favors formation of V(IV) and inhibits competing ions, such as nickel, from bonding with organic complexes. Lewan's analysis is consistent with geochemical characteristics of most carbonaceous sediments.

Large contents of organically bound sulfur are expected in carbonaceous marine sediments with low contents of reactive iron, because iron normally buffers the H_2S activity to low values by forming iron sulfide minerals (Canfield, 1989). Most reactive iron is supplied to sedimentary basins as iron oxide coatings on detrital grains. Thus carbonaceous sediments with low contents of terrestrial detritus, those dominated by chemical and biogenic sediments, contain excess H_2S. This H_2S reacts slowly with the organic matter to form organically bound sulfur (Orr and Sinninghe Damste, 1990). In typical marine sediments, the weight ratio of sulfide sulfur to organic carbon ranges between 0.2 and 0.5 (Sweeney, 1972). However, in iron-deficient sediments this ratio is typically lower. Vanadium-rich carbonaceous rocks typically have low S/C ratios (Patterson et al., 1986; Wenger, 1987; Beier and Hayes, 1989), but had large H_2S concentrations in their depositional pore waters.

Some hydrogen sulfide will diffuse into the overlying water column as available iron is depleted. Therefore, bottom waters over these sediments are likely to be strongly reducing and favorable for reduction of V(V) to V(IV) or possibly V(III). Wanty (1986) experimentally verified the reduction of V(IV) to V(III) by H_2S under a range of conditions. Rates of reduction are sufficiently rapid to produce V(III) during earliest diagenesis. Although this reduction may be inhibited in carbonaceous sediments by stable vanadyl–organic complexes (Fig. 2), the abundance of V-enriched clay minerals (which contain mainly V(III)) in many carbonaceous rocks (Breit, 1991) are consistent with reduction.

4.2. Vanadium–phosphorus association

Vanadium-rich carbonaceous rocks are commonly interbedded with or laterally associated with phosphate-rich rocks (Bliskovsky, 1969; McKelvey et al., 1986; Patterson et al., 1986; Wenger, 1987; Beier and Hayes, 1989). Rocks enriched in phosphate are typically stratigraphically above or below the carbonaceous units with the greatest vanadium content. The spatial association suggests that vanadium and phosphorus accumulations are genetically related but resulted from slightly different depositional environments.

An association of vanadium and phosphorus is consistent with the behavior of vanadium in the water column. Depletion of dissolved vanadium in near-surface ocean waters (Collier, 1984; Sherrell and Boyle, 1988) and in some estuaries (Shiller and Boyle, 1987) parallels concentration profiles of phosphate. Vanadium may be tied to the phosphate cycle either through biogenic assimilation, adsorption to biogenic particles, or substitution of vanadate for phosphate (Jeandel et al., 1987). Collier (1984) measured a molar V/P ratio of 4×10^{-3} in >53-μm particles. If these particles were reworked to form a phosphorite while retaining vanadium, a deposit composed of 85% apatite should contain 1,000 ppm vanadium. However, reworking of biogenic particles to form a phosphorite can result in loss of vanadium relative to phosphorus, as exemplified by the low vanadium content of organic carbon-poor phosphorites, which typically contain <100 ppm vanadium (Bliskovsky, 1969; Riggs et al., 1985). Thus vanadium is decoupled from the phosphate cycle under conditions in which organic matter is consumed.

Phosphorus and presumably vanadium are added to the sediment by settling of mainly biogenic particles. Their spatial separation within a carbonaceous sequence is consistent with the geochemical conditions that favor accumulation of vanadium or phosphorus. Arguments presented above suggest vanadium is concentrated in strongly reducing sediments while phosphate accumulations are the result of sediment reworking under less reducing conditions (Glenn et al., 1988). Therefore, shifts in bottom water composition controlled which element was concentrated. The vanadium released by suboxic reworking of the sediments may have moved downward or laterally into more strongly reducing sediments.

4.3. Vanadium and nickel

Carbonaceous rocks are commonly enriched in Ag, Cr, Mo, Ni, U, and Zn in addition to vanadium (Holland, 1979; Brumsack and Lew, 1982). The abundance of nickel relative to vanadium has been particularly useful and applied to describing depositional conditions (Lewan, 1984) and for petroleum–source rock correlation (Curiale, 1987). Lewan (1984) argued that vanadium accumulates relative to nickel (high V/Ni) in strongly reducing, H_2S-rich environments. Consistent with this analysis, Wenger and Baker (1986) determined that greater levels of anoxia favored large V/Ni mole ratios (maximum value ~5), as well as larger contents of both metals.

Most of the discussion of V and Ni in carbonaceous rocks is the result of their large contents in petroleum. Their enrichment in petroleum is partly because they form very stable porphyrin complexes (Lewan and Maynard, 1982). Lewan (1984) pointed out that the V/Ni ratios are largest in sulfur-rich petroleum because of the reduction of vanadium by H_2S and inhibition of Ni by NiS complexes. However, the V/Ni ratio does not increase systematically with increasing sulfur content. Above approximately 1 wt.% sulfur an average maximum V/Ni ratio is between 4 and 5 (Lewan, 1984), which is similar to the ratio in modern ocean water ([V] = 40 nmol/kg, Jeandel et al., 1987; [Ni] = 8.2 nmol/kg, Bruland, 1980). The similarity of the two ratios can be explained by the complete or equivalent extraction of both Ni and V in strongly reducing (H_2S-rich) environments.

The V/Ni ratios measured in petroleum are consistent with the ratios detected in bitumens remaining in the probable source rocks, but are quite different from the whole-rock V/Ni ratios. Deviations of the V/Ni ratio from the values measured in bitumen reflect vanadium in silicate minerals and nickel in sulfides. For example, V/Ni ratios of organic extracts in the Toolebuc Formation are approximately 1, while the whole-rock ratios are between 5 and 8. Most of the vanadium in this oil shale (1500 ppm) is contained in silicate minerals, while most of the nickel (300 ppm) is in sulfide minerals (Glickson et al., 1985; Patterson et al., 1986).

5. Changes during diagenesis

Diagenetic changes to organic and mineral constituents of carbonaceous rocks are the result of complex processes related to changes in pressure, temperature, and chemical environment. These changes alter both the abundance and residence of vanadium in these rocks as indicated by the variations of vanadium-rich rocks from immature oil shales to graphitic schists. During and soon after sediment deposition, vanadium is likely to be complexed by functional groups on organic macromolecules. Studies of soil and estuarine humic substances indicate that vanadium readily coordinates with organic acid groups (Templeton and Chasteen, 1980; Goncalves and Mota, 1987; Mangrich and Vugman, 1988). With progressive maturation and condensation, organic matter looses some of these functional groups (Tissot and Welte, 1984). Vanadium is probably redistributed as the functional groups are lost into more stable complexes such as porphyrins and asphaltenes. The progressive increase in the percentage of porphyrins metallated with increasing diagenesis is consistent with redistribution (fig. 4.17 in Baker and Louda, 1986).

As temperature increases into the oil window, vanadyl porphyrin and other unidentified vanadium complexes are cleaved from macromolecules and enter migrating petroleum. Along the transport path, vanadium concentrations in heavy petroleum may increase because of biodegradation or loss of light oil components (Filby and Van Berkel, 1987). Asphaltite deposits having high vanadium contents are products of accumulation of metal-rich heavy oil components (Table 1). In many carbonaceous rocks, however, much of the vanadium originally deposited with the sediments remains in the rock during diagenesis and metamorphism (Sozinov, 1982).

Conditions that favor retention of vanadium in carbonaceous rocks are poorly understood but are probably influenced by the composition of the organic matter and the abundance of clay minerals. Marine carbonaceous rocks, including oil shales and sapropelic coals, typically contain vanadium-rich clay minerals (Norrish and Patterson, 1976; Zhang, 1985; Coveney et al., 1987). Vanadium in clay minerals is present mainly as V(III), although some V(IV) has been detected (Maylotte et al., 1981; Premovic, 1984; Wanty et al., 1990). Vanadium(III) formed by reaction of V(IV) with H_2S (Wanty, 1986), or possibly through reaction with residual organic matter at high temperatures. Because V(III) readily substitutes for aluminum in the octahedral sites of clays, clay recrystallization (smectite to illite) or authigenesis would include V(III) in the forming clay. Vanadium(III) is stable in the clay structure and will survive extensive weathering as well as recrystallization to coarse-grained micas in graphitic schists such as those in Alabama (Pallister and Thoenen, 1948).

6. General model of vanadium accumulation

A summary model of processes that result in high concentrations of vanadium in carbonaceous rocks and resulting petroleum is presented in Fig. 5. Conditions favorable for accumulation of vanadium to large concentrations include an adequate supply of vanadium from circulating seawater, a slow rate of sedimentation, and a stratified, partially anoxic water column. These conditions are best satisfied using a depositional model similar to that proposed by Heckel (1977), which combines aspects of the barred stratified basin (Brumsack, 1983) and upwelling environments (Pederson and Calvert, 1990) to explain metalliferous carbonaceous rocks.

Some vanadium in shallow water is adsorbed to biogenic particles; in the present-day ocean, this adsorption is insufficient to result in high vanadium concentrations in sediments. The apparent low efficiency of adsorption reflects the relative lack of extensive anoxic waters in modern unrestricted marine basins. As the particles settle through oxic water, vanadium is redissolved as organic components are oxidized. Particles that settle through anoxic water, are capable of adsorbing vanadyl ion, formed by reduction of V(V) by dissolved organic compounds or hydrogen sulfide produced within the sediment. Vanadyl ion is stable in these environments because of strong organic complexes and adsorption. The relative importance of particle settling and diffusion in concentrating vanadium is controlled by the sedimentation rate and the extent of anoxic water in the overlying water column.

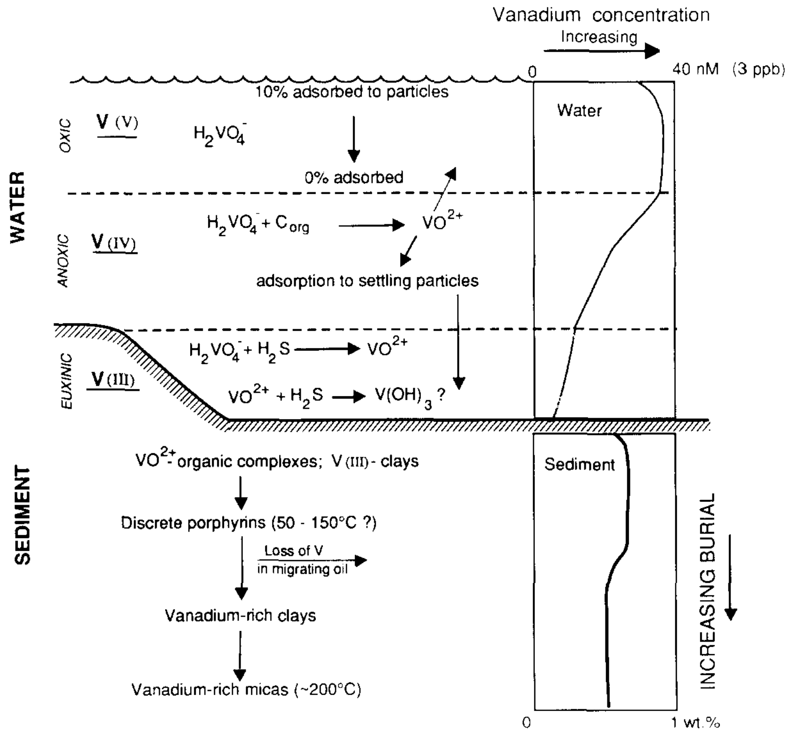

Fig. 5. Summary of processes proposed to explain vanadium accumulation in carbonaceous sediment and subsequent changes during diagenesis.

Within the carbonaceous sediment, vanadium, mainly as vanadyl ion, is initially bound to organic compounds such as carboxylic acids. Hydrogen sulfide in the pore waters may reduce some of the V(IV) to V(III), favoring partition of some of the vanadium into clay minerals. Maturation during early diagenesis destroys organic acid ligands that complex vanadium. Vanadium released from these complexes enters unmetallated porphyrins and other poorly understood refractory complexes. Increased burial and temperature result in the partition of some organically complexed vanadium into migrating petroleum. Depending on the composition of the rock, most of the vanadium remains in the rock by entering clay minerals.

Acknowledgements

This paper was improved substantially by the comments of J.D. Domagalski, D.Z. Piper, M.L. Tuttle, and two anonymous reviewers.

References

Aguije, S.H., 1954. El vanadio en el Peru. Mineria (Organo del Instituto de Ingenieros des Minas del Peru), 2: 19–30.

Amdurer, M., Adler, D. and Santschi, P.H., 1983. Studies of chemical forms of trace elements in sea water using radiotracers. In: C.S. Wong, E. Boyle, K.W. Bruland, J.D. Burton and E.D. Goldberg (Editors), Trace Metals in Sea Water. Plenum Press, New York, N.Y., pp. 537–562.

Andersson, A., Dahlman, B., Gee, D.G. and Snall, S., 1985. The Scandinavian Alum Shales. Nor. Geol. Unders., 56: 16.

Arnow, T., 1980. Water budget and water-surface fluctuations of Great Salt Lake. In: J.W. Gwynn (Editor), Great Salt Lake, A Scientific, Historical and Economic Overview. Utah Geol. Miner. Surv. Bull., 116: 255–263.

Baker, E.W. and Louda, J.W., 1986. Porphyrins in the Geological record. In: R.B. Johns (Editor), Biological Markers in the Sedimentary Record: Methods in Geochemistry and Geophysics, 24. Elsevier, Amsterdam, pp. 126–225.

Balistrieri, L., Brewer, P.G. and Murray, J.W., 1981. Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep ocean. Deep-Sea Res., 28: 101–121.

Bartusek, M. and Sustacek, V., 1983. Chelates of vanadium(V) with organic hydroxy compounds in aqueous solutions. Coll. Czech. Chem. Commun., 48: 2785–2797.

Beier, J.A. and Hayes, J.M., 1989. Geochemical and isotopic evidence for paleoredox conditions during deposition of the Devonian–Mississippian New Albany Shale, southern Indiana. Geol. Soc. Am. Bull., 101: 774–782.

Bliskovskiy, V.Z., 1969. Molybdenum, chromium and vanadium in phosphorites. Geochem. Int., 6: 878–887.

Bostrom, K. and Fisher, D.E., 1971. Volcanogenic uranium, vanadium and iron in Indian Ocean sediments. Earth Planet. Sci. Lett., 11: 95–98.

Boyd, D.W. and Kustin, K., 1984. Vanadium: a versatile biochemical effector with an elusive biological function. In: G.L. Eichhorn and L.I. Marzilli (Editors), Advances in Inorganic Biochemistry, 6. Elsevier, Amsterdam, pp. 311–365.

Breit, G.N., 1991. Vanadium—Resources in fossil fuels. In: J. DeYoung Jr. and J. Hammerstrom (Editors), Contributions to Commodity Geology Research. U.S. Geol. Surv. Bull., 1877 (in press).

Broecker, W.S. and Peng, T-H., 1982. Tracers in the Sea. Lamont-Doherty Geological Observatory, Columbia University, New York, N.Y., 690 pp.

Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel, and copper in the north Pacific. Earth Planet. Sci. Lett., 47: 176–198.

Brumsack, H.J., 1983. A note on Cretaceous black shales and recent sediments from oxygen deficient environments: Paleoceanographic implications. In: E. Suess and J. Theide (Editors), Coastal Upwelling, Its Sedimentary Record, Part A. Plenum Press, New York, N.Y., pp. 471–483.

Brumsack, H.J., 1986. The inorganic geochemistry of Cretaceous black shales (DSDP Leg 41) in comparison to modern upwelling sediments from the Gulf of California. In: C.P. Summerhayes and N.J. Shackleton (Editors), North Atlantic Paleoceanography. Geol. Soc., Spec. Publ., 21: 447–462.

Brumsack, H.J. and Gieskes, J.M., 1983. Interstitial water trace-metal chemistry of laminated sediments from the Gulf of California, Mexico. Mar. Chem., 14: 89–106.

Brumsack, H.J. and Lew, M., 1982. Inorganic geochemistry of Atlantic Ocean sediments with special reference to Cretaceous black shales. In: U. von Rad, K. Hinz, M. Sarnthein and E. Seibold (Editors), Geology of the Northwest African Continental Margin. Springer-Verlag, New York, N.Y., pp. 661–685.

Burger, D., 1986. Palynology, cyclic sedimentation, and paleo environments in the Late Mesozoic of the Eromanga Basin. In: D.I. Gravestock, P.S. Moore and G.M. Pitt (Editors), Contributions to the Geology and

Hydrocarbon Potential of the Eromanga Basin. Geol. Soc. Aust., Spec. Publ., 12: 53–70.

Canfield, D.E., 1989. Reactive iron in marine sediments. Geochim. Cosmochim. Acta, 53: 619–632.

Colley, S., Thomson, J., Wilson, T.R.S. and Higgs, N.C., 1984. Post-depositional migration of elements during diagenesis in brown clay and turbidite sequences in the northeast Atlantic. Geochim. Cosmochim. Acta, 48: 1223–1235.

Collier, R.W., 1984. Particulate and dissolved vanadium in the North Pacific ocean. Nature (London), 309: 441–444.

Coveney, R.M., Jr., Leventhal, J.S., Glascock, M.D. and Hatch, J.R., 1987. Origins of metals and organic matter in the Mecca Quarry Shale Member and stratagraphically equivalent beds across the midwest. Econ. Geol., 82: 915–933.

Curiale, J.A., 1987. Distribution and occurrences of metals in heavy crude oils and solid bitumen – implications for petroleum exploration. In: R.F. Meyer (Editor), Exploration of Heavy Crude Oil and natural bitumen. Am. Assoc. Pet. Geol., Stud. Geol., 25: 207–219.

Degens, E.T., 1978. Varve chronology: estimated rates of sedimentation in the Black Sea deep basin. In: P. Stoffers, S. Glaubic and M. Dickman (Editors), Initial Reports of the Deep-Sea Drilling Project. U.S. Government Printing Office, Washington, D.C., 42: 499–508.

Derkey, P.D., Abercrombie, F.N., Duke, S.M. and Daniel, J.A., 1985. Geology and oil shale resources of the Heath Formation, Fergus County, Montana. Montana Bur. Min. Geol. Mem., 57, 100 pp.

Domagalski, J.D., Eugster, H.P. and Jones, B.F., 1990. Trace metal geochemistry of Walker, Mono, and Great Salt Lakes. In: R.J. Spencer and I-Ming Chou (Editors), Fluid Mineral Interactions: A Tribute to H.P. Eugster. Geochem. Soc., Spec. Publ., 2: 315–354.

Doutch, H.F. and Saxby, J., 1983. Oil shale methodology. Yearbook of the Bureau of Mineral Resources and Geophysics, Canberra, Australia, Australian Government Publishing Service, pp. 93–95.

Dymond, J. and Roth, S., 1988. Plume dispersed hydrothermal particles: A time-series record of settling flux from the Endeavor Ridge using moored sensors. Geochim. Cosmochim. Acta, 52: 2525–2536.

Ehde, P.M., Andersson, I. and Petterson, L., 1986. Multicomponent polyanions. 40. A potentiometric and ^{51}V NMR study of equilibria in the H^+–$H_2VO_4^-$–$C_2O_4^{2-}$ system in 0.6 M NaCl medium. Acta Chem. Scand., A4: 489–499.

Filby, R.H. and Van Berkel, G.J., 1987. Geochemistry of metal complexes in petroleum, source rocks and coal: An overview. In: R.H. Filby and J.F. Branthaver (Editors), Metal Complexes in Fossil Fuels. Am. Chem. Soc. Symp. Ser., 344: 2–39.

Fowler, S.W. and Knauer, G.A., 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Progr. Oceanogr., 16: 147–194.

Francois, R., 1988. A study of the regulation of the concentrations of some trace metals (Rb, Sr, Zn, Pb, Cu, V, Cr, Ni, Mn, and Mo) in Saanich Inlet, British Columbia, Canada. Mar. Geol., 83: 285–308.

Glenn, C.R., Arthur, M.A., Yeh, H-W. and Burnett, W.C., 1988. Carbon isotopic composition and lattice bound carbonate of Peru–Chile margin phosphorites. In: W.C. Burnett and P.N. Froelich (Editors), The Origin of Marine Phosphorite. The Results of the R.V. *Robert D.Conrad* Cruise to the Peru Shelf. Mar. Geol., 80: 287–307.

Glikson, M., Chappell, B.W., Freeman, R.S. and Webber, E., 1985. Trace elements in oil shales, their source and organic association with particular reference to Australian deposits. Chem. Geol., 53: 155–174.

Goncalves, M.L.S. and Mota, A.M., 1987. Complexes of vanadyl and uranyl ions with the chelating groups of humic matter. Talanta, 34: 839–847

Goodman, B.A. and Cheshire, M.V., 1975. The bonding of vanadium in complexes with humic acid: an electron paramagnetic resonance study. Geochim. Cosmochim. Acta, 39: 1711–1713.

Gulbrandsen, R.A., 1966. Chemical composition of phosphorites of the Phosphoria Formation. Geochim. Cosmochim. Acta, 30: 769–778.

Harrison, W.E., Mankin, C.J., Weber, S.J. and Curiale, J.A., 1981. Oil sands and heavy oil potential of Oklahoma. In: R.F. Meyer and C.T. Steele (Editors), The Future of Heavy Crude Oils and Tar Sands, First International Conference. McGraw-Hill, New York, N.Y., pp. 83–89.

Heckel, H.D., 1977. Origin of phosphatic black shale facies in Pennsylvanian cyclothems of mid-continent North America. Am. Assoc. Pet. Geol. Bull., 61: 1045–1068.

Heggie, D., Kahn, D. and Fischer, K., 1986. Trace metals in metalliferous sediments, MANOP site M: interfacial pore water profiles. Earth Planet. Sci. Lett., 80: 106–116.

Holland, H.D., 1979, Metals in black shales—a reassessment. Econ. Geol., 74: 1676–1679.

Honeyman, B.D., 1984. Cation and Anion Adsorption at the Oxide/Solution Interface in Systems Containing Binary Mixtures of Adsorbents: An Investigation of the Concept of Adsorptive Additivity. Ph.D. thesis, Stanford University, Stanford, Calif. (unpublished).

Jarvis, I. and Higgs, N., 1987. Trace element mobility during early diagenesis in distal turbidites: late Quaternary of the Madeira Abyssal Plain, N. Atlantic. In: P.P.E. Weaver and J. Thomson (Editors), Geology and Geochemistry of Abyssal Plains. Geol. Soc. Spec. Publ., 31: 179–213.

Jeandel, C., Cassio, M. and Minster, J.F., 1987. Vanadium behavior in the global ocean and in the Mediterranean Sea. Mar. Chem., 21: 51–74.

Kett, F.F., 1948. The vanadium-bearing solid bitumens of the Argentine. The Vancorum Review, 5: 3–21

Krauskopf, K.B., 1956. Factors controlling the concentrations of thirteen rare metals in sea water. Geochim. Cosmochim. Acta, 9: 1–32.

Kuck, P.H., 1985. Vanadium. In: Mineral Facts and Problems. U.S. Bur. Min. Bull., 675: 895–915.

Larson, C.B. and Welker, K.K., 1947. Vanadium Resources of Peru. U.S. Bur. Min., Mineral Trade Notes, Spec. Suppl., 16, 58 pp.

Lee, K., 1983. Vanadium in the aquatic ecosystem. In: J.O. Nriagu (Editor), Aquatic Toxicology, Vol. 13. Wiley, New York, N.Y., pp. 155–187.

Lewan, M.D., 1984. Factors controlling the proportionality of vanadium to nickel; ratios in crude oils. Geochim. Cosmochim. Acta, 48: 2231–2238.

Lewan, M.D. and Maynard, J.B., 1982. Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. Geochim. Cosmochim. Acta, 46: 2547–2560.

Mangrich, A.S. and Vugman, N.V., 1988. Bonding parameters of vanadyl ion in humic acid from the Jucu River estuarine region, Brazil. The Science of the Total Environment, 75: 235–241.

Maylotte, D.H., Wong, J., St. Peters, R.L., Lytle, F.W. and Greegor, R.B., 1981. X-ray absorption spectroscopic investigation of trace vanadium sites in coal. Science, 214: 554–556.

McKelvey, V.E., Strobell, J.D., Jr. and Slaughter, A.L., 1986. The Vanadiferous Zone of the Phosphoria Formation in Western Wyoming and Southeastern Idaho. U.S. Geol. Surv. Prof. Pap., 1465, 27 pp.

Metz, S., Trefry, J.H. and Nelsen, T.A., 1988. History and geochemistry of a metalliferous sediment core from the Mid Atlantic Ridge at 26°N. Geochim. Cosmochim. Acta, 52: 2369–2378.

Micera, G. and Dallocchia, R., 1988. Metal complex formation of the surface of amorphous aluminum hydroxide. Part IV. Interactions of oxovanadium(IV) and vanadate(V) with aluminum hydroxide in the presence of succinic, malic and 2-mercaptosuccinic acids. Colloids Surfaces, 34: 185–196.

Nechay, B.R., 1984. Mechanisms of action of vanadium. Annu. Rev. Pharmacol. Toxicol., 24: 501–24

Norrish, K. and Patterson, J.H., 1976. Characterization of vanadiferous clays, Julia Creek, Queensland. Int. Geol. Congr., Abstr., 25 (3): 756–757.

Orivini, E. and Lodola, L., 1979. Determination of the chemical forms of dissolved vanadium in freshwater as determined by ^{48}V radiotracer experiments and neutron activation analysis. Sci. Total Environ., 13: 195–207.

Orr, W.L. and Sinninghe Damste, J.S., 1990. Geochemistry of sulfur in petroleum systems. In: W.L Orr and W.L. White (Editors), Geochemistry of Sulfur in Fossil Fuels. Am. Chem. Soc. Symp. Ser., 429: 2–29.

Pallister, H.D. and Thoenen, J.R., 1948. Flake-Graphite and Vanadium Investigation in Clay, Coosa and Chilton Counties, Alabama. U.S. Bur. Min., Rep. Invest., 4366, 84 pp.

Patterson, J.H., Ramsden, A.R., Dale, L.S. and Fardy, J.J., 1986. Geochemistry and mineralogical residences of trace elements in oil shales from Julia Creek, Queensland, Australia. Chem. Geol., 55: 1–16.

Pederson, T.F. and Calvert, S.E., 1990. Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks? Am. Assoc. Pet. Geol. Bull., 74: 454–466.

Peer, E.L., 1981. United States refineries and their adaptability to process heavy crude oil. In: R.F. Meyer and C.T. Steele (Editors), The Future of Heavy Crude Oils and Tar Sands, First International Conference. McGraw-Hill, New York, N.Y., pp. 663–669.

Perrin, D.D., 1979. Stability Constants of Metal Ion Complexes, Part B. Organic Ligands. IUPAC Chem. Data Ser., 22. Pergamon Press, New York, N.Y., 1264 pp.

Prange, A. and Kremling, K., 1985. Distribution of dissolved molybdenum, uranium and vanadium in Baltic Sea waters. Mar. Chem., 16: 259–274.

Premovic, P.I., 1984. Vanadyl ions in ancient marine carbonaceous sediments. Geochim. Cosmochim. Acta, 48: 873–877.

Riggs, S.R., Snyder, S.W.P., Hine, A.C., Snyder, S.W., Ellington, M.D. and Mallette, P.M., 1985. Geologic framework of phosphate resources in Onslow Bay, North Carolina Continental Shelf. Econ. Geol., 80: 716–738.

Riley, K.W. and Saxby, J.D., 1986. Organic matter and vanadium in the Toolebuc Formation, Northern Eromanga Basin and southern Carpentaria Basin. In: D.I. Gravestock, P.S. Moore and G.M. Pitt (Editors), Contributions to the Geology and Hydrocarbon Potential of the Eromanga Basin. Geol. Soc. Aust. Spec. Publ., 12: 267–272.

Robl, T.L., Bland, A.E., Koppenaal, D.W. and Barron, L.S., 1983. Geochemistry of oil shales in eastern Kentucky. In: F.P. Miknis and J.F. McKay (Editors), Geochemistry and Chemistry of Oil Shales. Am. Chem. Soc. Symp. Ser., 230: 159–180.

Shaw, T.J., Gieskes, J.M. and Jahnke, R.A., 1990. Early diagenesis in differing depositional environments: The response of transition metals in pore water. Geochim. Cosmochim. Acta, 54: 1233–1246.

Sherrell, R.M. and Boyle, E.A., 1988. Zinc, chromium, vanadium and iron in the Mediterranean Sea. Deep-Sea Res., 35: 1319–1334.

Shieh, Chih-Shin and Duedall, I.W., 1988. Role of amorphous ferric oxyhydroxide in removal of anthropogenic vanadium from seawater. Mar. Chem., 25: 121–139.

Shiller, A.M. and Boyle, E.A., 1987. Dissolved vanadium in rivers and estuaries. Earth Planet. Sci. Lett., 86: 214–224.

Sozinov, N.A., 1982. Ore potential of Precambrian black shale formation. Rev. Bras. Geocienc., 12: 506–509.

Stauffer, N.E., 1980. Computer modeling of the Great Salt Lake. In: J.W. Gwynn (Editor), Great Salt Lake, a Scientific, Historical and Economic Overview. Utah Geol. Miner. Surv. Bull., 116: 265–272.

Sugimura, Y., Suzuki, Y. and Miyake, Y., 1978. Chemical forms of minor metallic elements in the ocean. J. Oceanogr. Soc. Jpn., 34: 93–96

Sweeney, R.E., 1972. Pyritization During Diagenesis of Marine Sediments. Ph.D. thesis, University of California, Los Angeles, Calif. (unpublished).

Szalay, A. and Szilagyi, M., 1967. The association of vanadium with humic acids. Geochim. Cosmochim. Acta, 31: 1–6.

Templeton, G.D. and Chasteen, N.D., 1980. Vanadium–fulvic acid chemistry: conformational and binding studies by electron spin probe techniques. Geochim. Cosmochim. Acta, 44: 741–752.

Tissot, B.P. and Welte, D.H., 1984. Petroleum Formation and Occurrence. Springer-Verlag, New York, N.Y., 2nd ed., 699 pp.

Tracey, A.S., Gresser, M.J. and Parkinson, K.M., 1987. Vanadium(V) oxyanions. Interactions of vanadate with oxalate, lactate and gylcerate. Inorg. Chem., 26: 629–638.

Trefry, J.H. and Metz, Simone, 1989. Role of hydrothermal precipitates in the geochemical cycling of vanadium. Nature (London), 342: 531–533.

Trocine, R.P. and Trefry, J.H., 1988. Distribution and chemistry of suspended particles from an active hydrothermal vent site on the Mid-Atlantic Ridge at 26°N. Earth Planet. Sci. Lett., 88: 1–15

Turekian, K.K. and Wedepohl, K.H., 1961. Distibution of elements in some major units of the Earth's crust. Geol. Soc. Am. Bull., 72: 175–191.

Tuttle, M.L., Dean, W.E. and Parduhn, N.L., 1983. Inorganic geochemistry of Mahogany zone oil shale in two cores from the Green River Formation. In: F.P. Miknis and J.F. McKay (Editors), Geochemistry and Chemistry of Oil Shales. Am. Chem. Soc. Symp. Ser., 230: 85–96.

Valkovic, V., 1983. Trace Elements in Coal. CRC Press, Boca Raton, Fla., 121 pp.

Van der Sloot, H.A., Hoede, D., Wijkstra, J., Duinker, J.C. and Nolting, R.F., 1985. Anionic species of V, As, Se, Mo, Sb, Te, and W in the Schledt and Rhine estuaries and the southern Bight (North Sea). Estuarine Coastal Shelf Sci., 21: 633–651.

Vine, J.D. and Tourtelot, E.B., 1970. Geochemistry of black shale deposits—A summary report. Econ. Geol., 65: 253–272.

Wang, Chug-Ho and Yeh, Hsueh-wen, 1985. Oxygen isotope compositions of DSDP Site 480 diatoms: Implication and applications. Geochim. Cosmochim. Acta, 49: 1469–1478.

Wanty, R.B., 1986. Geochemistry of Vanadium in an Epigenetic Sandstone-Hosted Vanadium–Uranium Deposit, Henry Basin Utah. Ph.D. thesis, Colorado School of Mines, Golden, Colo. (unpublished).

Wanty, R.B., Goldhaber, M.B. and Northrop, H.R., 1990. Geochemistry of vanadium in an epigenetic, sandstone-hosted vanadium–uranium deposit, Henry basin, Utah. Econ. Geol., 85: 270–284.

Wedepohl, K.H., 1964. Untersuchungen am Kupferschiefer in Nordwestdeutschland; ein Beitrag zur Deutung der Genese bituminöser Sedimente. Geochim. Cosmochim. Acta, 28: 305–364.

Wehrli, B., 1987. Vanadium in der Hydrosphäre; Oberflachenkomplexe und Oxidationskinetik. Ph.D. Dissertation, Eidgenossischen Technischen Hochschule, Zürich (unpublished).

Wehrli, B. and Stumm, W., 1989. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation. Geochim. Cosmochim. Acta, 53: 69–77.

Wenger, L.M., 1987. Variations in the Organic Geochemistry of Anoxic–Oxic Black Shale–Carbonate Sequences in the Pennsylvanian of the Midcontinent, U.S.A. Ph.D. thesis, Rice University, Houston, Texas (unpublished).

Wenger, L.M. and Baker, D.R., 1986. Variations in organic geochemistry of anoxic–oxic black shale–carbonate sequences in the Pennsylvanian of the Midcontinent, U.S.A.. Org. Geochem., 10: 85–92.

Whisman, M.L. and Cotton, F.O., 1971. BuMines data promise help in identifying petroleum-spill sources. Oil Gas J., 69: 111–113.

Wilson, S.A. and Weber, J.H., 1979. An EPR study of the reduction of vanadium(V) to vanadium(IV) by fulvic acid. Chem. Geol., 29: 345–354.

Yen, T.F., 1975, Chemical Aspects of metals in native petroleum. In: Yen, T.F. (Editor), The Role of Trace Metals in Petroleum. Ann Arbor Science Publishers Inc., Ann Arbor, Mich., pp. 1–30.

Zhang, A., 1985. Geochemistry of vanadium in the marine black rock sequence of Yanjaibao. 10th Int. Congr. Carboniferous Stratigraphy and Geology, 23: 31–42.