

The occurrence of vanadium in nature: its biogeochemical cycling and relationship with organic matter—a case study of the Early Cambrian black rocks of the Niutitang Formation, western Hunan, China

Rizwan Sarwar Awan^{1,2}  · Chenglin Liu^{1,2} · Shangfeng Yang^{1,2} · Yuping Wu^{1,2} · Qibiao Zang^{1,2} · Ashar Khan³ · Guoxiong Li^{1,2}

Received: 11 March 2021 / Revised: 12 April 2021 / Accepted: 1 June 2021 / Published online: 8 June 2021
© Science Press and Institute of Geochemistry, CAS and Springer-Verlag GmbH Germany, part of Springer Nature 2021

Abstract Vanadium in the black rocks has economic and environmental impacts. In sediments, it is broadly disseminated as a multivalent metal element mainly sensitive to redox settings. Globally in petroleum, it is considered an abundant component. Vanadium is an essential tool to determine the relationship of the Earth with extra-terrestrial bodies. In the Yangtze region, the black rocks of the Early Cambrian Niutitang Formation are highly enriched in the concentration of V, Co, Ni and Mo. These sediments are comprised of a high total organic carbon content, and the average concentration of vanadium is over 240 ppm. Here we discuss the mechanisms and conditions that were responsible for the accumulation of vanadium in these black sediments in the Yangtze region. The oxygenated ocean water is favorable for the dissolved vanadate species V(V). Therefore, in oxic ocean-water, it can be reduced by organic matters or by H₂S to vanadyl ions V(IV), which can facilely be adsorbed to the tiny particles and finally deposit into the sediments with the settling of the particles. The presence of V₂O₃ in the Niutitang Formation indicates the isomorphism state of vanadium existence in the clay minerals. Clays and pyrite are the most favorable mineral for vanadium enrichment. However, it is suggested the

quartz of non-biogenic origin might be unfavorable for vanadium enrichment. Vanadium is mainly derived from the diagenetic transformation of its precursor (porphyrin pigments and chlorophyll) from the organism. During the Early Cambrian period, the massive transgression in the sea level created a favorable environment for organisms to survive. Additionally, the hydrothermal activities brought massive nutrient supply in the form of vanadium and other metal elements from the deep Earth. These creatures consumed the vanadium-rich nutrients, which became a part of their bodies in the form of hard and soft parts. Later on, when these organisms died and were submerged in the sediments. After the diagenetic actions, this vanadium became a part of these black sediments along with organic carbon. Therefore, these black rocks in the Yangtze region are enriched in vanadium and organic carbon. It is suggested the various processes such as adsorption, complexation, and reductions are the main factors responsible for the precipitation of dissolved vanadium into the organically rich sediments.

Keywords Vanadium · Organic matter · Chlorophyll · Porphyrin · Anthropogenic · Isomerization

✉ Rizwan Sarwar Awan
rsageoche@gmail.com

✉ Chenglin Liu
liucl@cup.edu.cn

¹ College of Geosciences, China University of Petroleum, Beijing 102249, China

² State Key Laboratory of Petroleum Resource and Prospecting, China University of Petroleum, Beijing 102249, China

³ Water and Power Development Authority, Lahore Pakistan

1 Introduction

The black rock sediments are widely distributed around the globe (Fig. 1). The Early Cambrian is a unique geological span due to diversity in the abundance of ancient remains (fossils), also known as a period of Cambrian Explosion (Amthor et al. 2003; Pi et al. 2013). Variation in the ambient conditions signifies a feasible rationale for evolutionary heterogeneity; nevertheless, it is a subject of discussion. Early Cambrian marine sedimentary rocks are

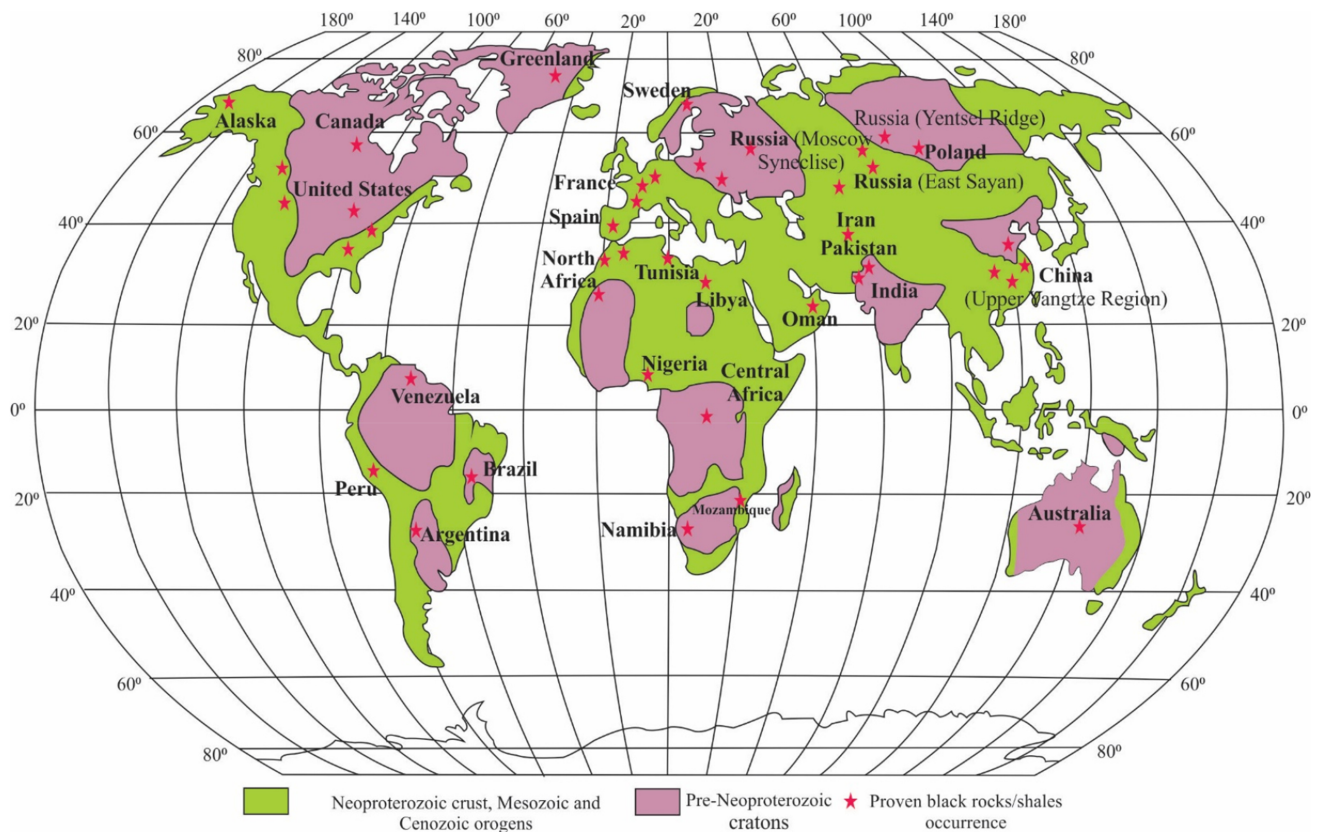


Fig. 1 Global distribution of black rock/shales (Awan et al. 2020)

broadly deposited in entire South China. The Niutitang Formation in South China comprises various types of black sediments, e.g., shale, carbonaceous shale, siliceous shale, sandstone, silty shale, mudstone, and silty mudstone, also known as the black rock series (Awan et al. 2020). These rocks became a new type of mineral resource in China due to the enrichment of some precious elements, e.g., molybdenum, vanadium, and uranium, but so far without substantial exploitation of these elements. In the environment, vanadium is a prevalent metal element. It is widely used nearly in all fields of geochemistry. A Spanish mineralogist, Andres Manuel Del Rio has discovered vanadium in 1801 during working on blue Pb ore ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$) sample from Mexico. That has also been called vanadinite (Weeks 1932). There are two isotopes of indigenous vanadium (i) ^{50}V (radioactive), (ii) ^{51}V (stable). The concentration of vanadium (V) in the Earth's crust is identical to zinc (Zn). It is nearly ten times greater than lead (Pb) and twice copper (Cu). In the Earth's crust, it is the fifth most frequently occurring transitional element. The average amount of vanadium in the ocean, sediments, and in the atmosphere is $1.8 \mu\text{g/L}$, 150 mg/kg , and 1000 ng/m^3 , respectively (Fig. 2) (Imtiaz et al. 2015; Langeslay et al. 2018). Vanadium is broadly disseminated in rocks (igneous and sedimentary) and minerals as moderately incompatible

lithophilic elements. Vanadium has not been studied extensively relative to other transitional metal elements. Vanadium, chiefly in the sediments, can occur in three forms (a) trivalent V (III), (b) tetravalent V (IV), and (c) pentavalent V (V) (Larsson 2014). The enrichment of vanadium has been noticed in oil shale, peat, crude oil, bitumen, and asphalt, and the sediments (rocks and soils) of the volcanic regions. Vanadium, as a VO-porphyrins in crude oils, can reach up to 0.12% (Aydin et al. 2012). In the sediments, the concentration of vanadium is used to examine the mineralogy of the parent rock. Almost 65 minerals in nature contained vanadium. The more significant minerals containing vanadium are vanadinite, carnotite, mottramite, patronite, and roscoelite (Lide 2008). Organic matter (OM) and vanadium have a significant relationship. It is due to its considerable attraction towards OM. The organic matter can form complex aggregates with vanadium or can reduce to its lower valence state, particularly at a lower pH level (Lu et al. 1998). Vanadium could be adsorbed or integrates into clays; therefore, the concentration of vanadium could be higher in organically rich sediments or peats. In metallic form, it can't exist in soils, whereas commonly, it could occur with oxides of aluminium, iron, manganese, lead, copper, calcium, and zinc. In sediments, the most typical form of vanadium is

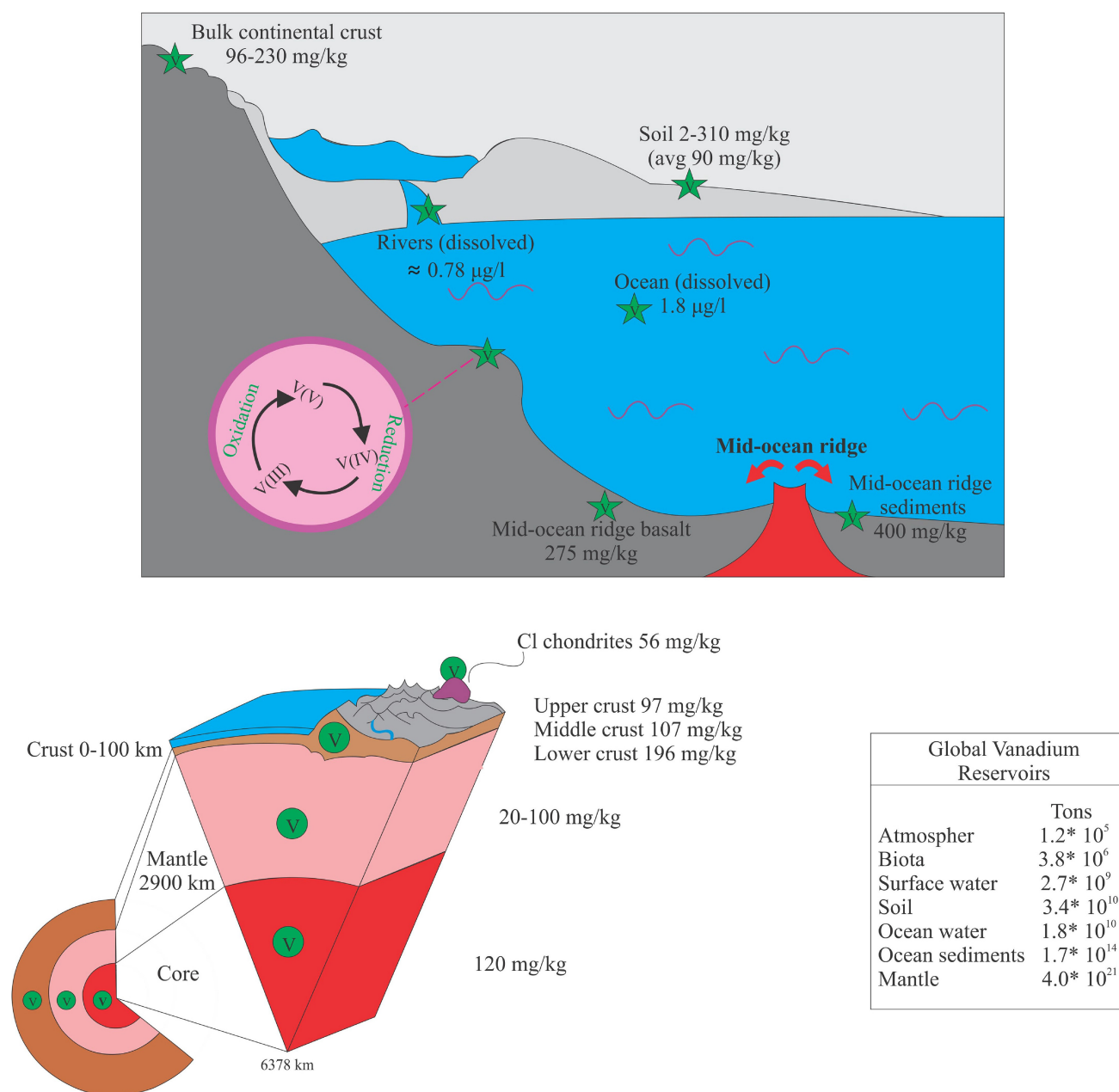


Fig. 2 The accumulation of vanadium on the earth. Modified after Huang et al. (2015)

vanadates (Venkataraman and Sudha 2005). In the oceans, vanadium is the second most abundant transitional element after molybdenum and is found as an ion pair ($\text{Na}^+\text{H}_2\text{VO}_4^-$) with a typical concentration of 30–35 nM. Macroalgae utilize vanadate (V) from the ocean water in the form of vanadium. Marine organisms such as fan worms, sea squirts (ascidians) use vanadate without any distinct biological advantages (Rehder 2015). Currently, the distribution of vanadium under differentiation of magma in elevated temperature and pressure, and the new features to study the stable isotopic composition of vanadium is a hot topic (Nielsen et al. 2014; Prytulak et al. 2013). The

possible distribution and the accumulation of the vanadium in the Earth's interior are shown in Fig. 2. Nearly 80% of the produced world vanadium is chiefly utilized in the steel industry as an additive. As vanadium is an essential raw material, it plays a vital role in the steel-iron industry and other manufacturing units, e.g., shipyard, automobiles, fertilizers, etc. Its complexes are valuable and have a wide range of applications in catalysts-ceramics, industries, batteries, pigments. Vanadium is resistant to rust, utilized in various nuclear applications. It is also utilized in high-speed iron-steel tools and superconductive magnets. In the medical industry, vanadium supplements are being utilized

to remedy various diseases (Emsley 2011). In the past few decades, the occurrence of vanadium (V) in the source rocks containing kerogen, bitumen, and crude oil has become a hot topic in the field of geochemistry. Vanadium is the most prevalent and abundant trace element in petroleum. The relationship of vanadium with the OM relies on various factors related to diagenetic changes, such as biological precursors, water incorporation, or sediments. It can be controlled by sedimentary redox settings (Eh and pH), type of OM, and organometallic compounds (Monaco et al. 2002). The following are the key objectives of this research:

1. This research broadly discusses the geochemical constraints of vanadium under various environments.
2. It is a holistic approach to elucidate the favorable minerals for vanadium accumulation.
3. To determine the biological origin of vanadium in organic-rich black rocks of the Niutitang Formation.

2 Geology and tectonics

A multistage action caused the fragmentations of Rodina during the Neoproterozoic time. The final phase of splitting and drifting took place during the period of 750–690 Ma (Liu et al. 2015). In North China, Cathasian and Yangtze blocks were isolated during the period of Ediacaran–Early Cambrian. The rifted deep marine basin had produced at the surrounding of the Yangtze block's periphery (Liguo 1997). At that period, the Yangtze block was situated at the equatorial zone closer to the S–W of the Australian Plate (Fig. 3) (Liu and Xu 1994). Due to tectonics progression in Ediacaran to the Early Cambrian period, paleo-settings of the research area were transformed from shallow to a deeper marine shelf or slope environment (carbonates to argillaceous rocks) (Liu et al. 2015; Zhu et al. 2003). Recent studies revealed that Early Cambrian was characterized as a maximum flooding span in the Yangtze region. OAE (anoxic ocean event) extensively prevailed during the Early Tommotian and created anoxic bottom water settings on a massive scale (Jiang et al. 2011). Niutitang and its geological equivalent rocks are on a wide-scale comprised of black shale deposits on the Yangtze black, especially on the slope. Generally, it is suggested that phosphorites at the bottom of Cambrian are a clue of strong upwelling (Clark et al. 2004; Wille et al. 2008). Among them, some black shales are related to metallic ores (Fe–Ni–Mo). These ores were deposited due to hydrothermal events in the Cambrian period (Orberger et al. 2007; Steiner et al. 2001). Another indicia to prove Cambrian hydrothermal activity is higher values of Eu anomaly of the phosphate nodules within the

shales (Zhu et al. 2014). Various metallic ratios (Co–Cu–Ni–PGE's) suggest the ultramafic and mafic source for these rocks (Han et al. 2015). Few studies indicate the primary source for these metallic ores in these black sediments is due to seawater in a silled basin via durable stratigraphic condensation (Lehmann et al. 2007; Och et al. 2013). In the eastern Yunnan region, the lower part of the Niutitang Formation's geologic age is 540–536 Ma based on U–Pb dating. The Guizhou area shows relatively younger ages suggesting territorial diachroneity, for instance, 522.7 ± 4.9 Ma (Wang et al. 2012) and 532.3 ± 0.7 Ma (Jiang et al. 2011). The central part of the black Niutitang Formation is dated to 521.0 ± 5.0 Ma using Re–Os (Xu et al. 2011). The deposition age of the Niutitang Formation based on recent researches is 3–12 Ma year, which was started at 532–523 Ma and stopped at approximately 520 Ma years from the bottom to the top. The average thickness of Niutitang Formation in the research area is 76 m, which exhibits the rate of deposition was about 6–7 m/Ma or nearly 25 m/Ma (Xu et al. 2012).

3 Methods and material

In this research, a geological field trip of the Xiangxi area in western Hunan, South China, has been organized to collect samples from two well-exposed outcrop sections Longbizui (LA) and Sancha (CR) section (Fig. 4). Various geochemical experiments were performed on these samples to accomplish this research.

Total organic carbon (TOC) quantifies the total amount of organic carbon in the samples. In this research, the amount of TOC is measured by the LECO CS230. At first, rock specimens were crushed and sieved to a smaller size (< 200) and cleaned with a dilute HCL (5%) for 24 h at 60 °C to eradicate carbonated and inorganic carbon. Subsequently, the treated HCL was eliminated with the purified water. Then the test specimens were desiccated to 50 °C in the oven for 24 h. The samples were combusted at high temperatures (900 °C) using an oxygen-enriched carrier gas. The quantity of organic C was entirely oxidized to CO₂ from a specimen, and the bulk volume of produced CO₂ was utilized to compute TOC.

X-ray diffractometer (XRD) using Bruker D2 PHASER X was applied to determine the mineralogy of the studied samples. A small amount (5 g) of grounded (300 mesh size) samples were utilized. Continuous scanning (183–6) in the device was selected at the step of 0.002 with an accuracy of $\pm 0.1\%$. The quantitative mineralogical results of the specimens were obtained via MacDiff software.

The concentration of trace elements in these sediments was analyzed by incorporating Nex ION300D. Samples

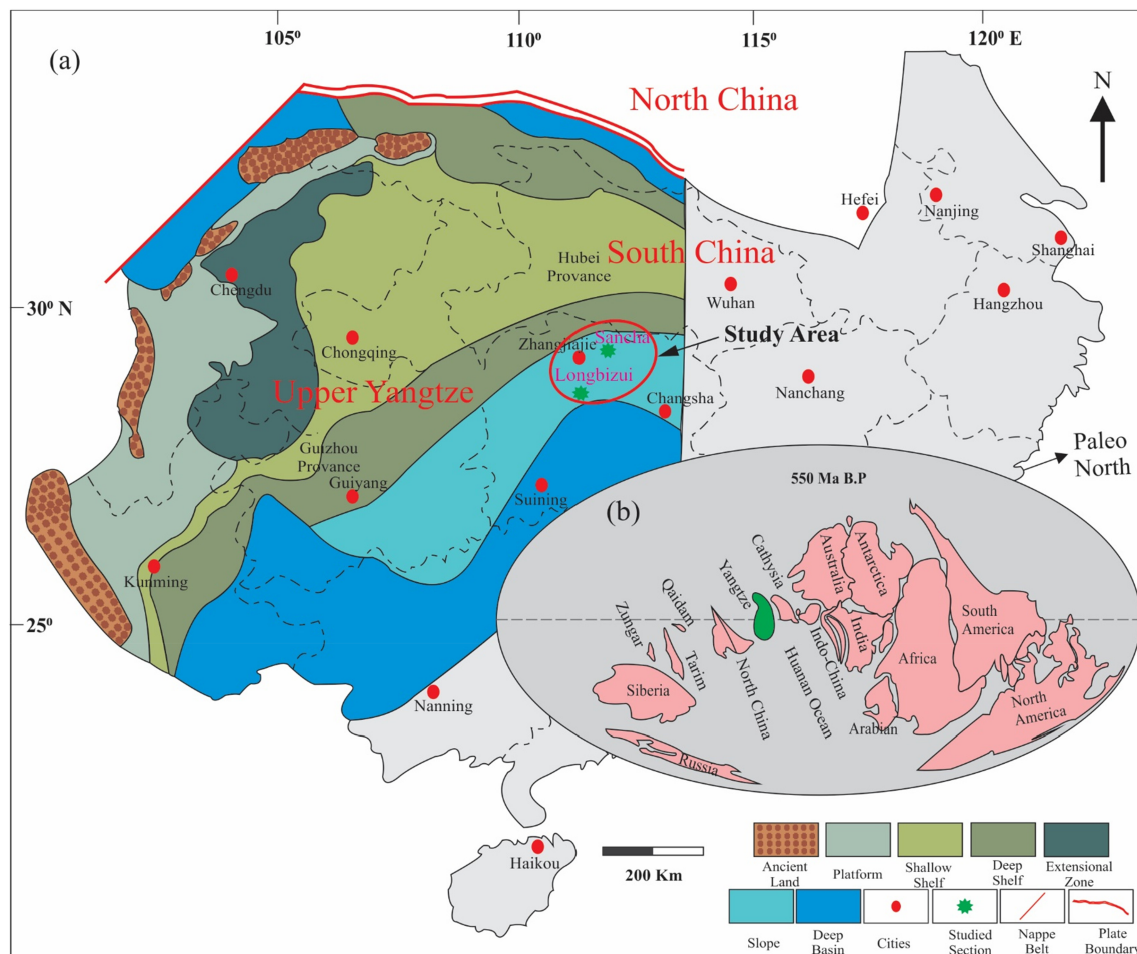


Fig. 3 **a** The Paleogeographic map of the upper Yangtze region, deciphering the different lithofacies (modified after Luo 2014; Steiner et al. 2001; Zhang et al. 2018), **b** displaying global paleogeography during the early Cambrian period (modified after Liu et al. 2015)

were formerly dissolved into an acidic solution. The trace elements were evaluated using the standard internal technique with a relative temperature and humidity below 21 °C and 31%, respectively. The error in this technique was below 10%.

The scanning electron microscope (SEM), with the aid of energy dispersive spectroscopy (EDS), was operated for the examination. The compositional analysis of catalyst, surface morphology, and rock minerals was investigated via Field Emission Microscope (FEI Quanta200F) along with a focused ion beam system. Initially, the surface of the samples was gold-coated. The gold coating process is adopted for a better resolution before the scan with an electrostatic beam positioned in the cylinder. Both the secondary ion and secondary electron produced by the ion beam's bombardment on the sample were gathered and capture a focused ion beam microscopic image.

The electron probe micro-analyzer (EPMA) JEOL EPMA8230 equipment was used to determine various minerals and the concentration of the V_2O_3 in the Hebei

Institute of regional geology and mineral resource survey. The ambient temperature and the relative humidities were 24 °C and 52%, respectively.

4 Discussion

4.1 Mode of vanadium occurrence

Vanadium may have been divided into three primary groups in naturally occurring Metallo-organic compounds. (i). Mixed ligands tetradendate, (ii). tetrapyrrole complexes, (iii). Humate complexes. This basic categorization is following the kinds of ligands that involve the interaction of metal bounding with the Metallo-organic compounds. Due to the structural complexity and the higher molecular weight of the precise structural and chemical nature of Metallo-organic compounds are not always displayed. The stability between the complexes and the metal bounding is an indication of ligands type and their coordination.

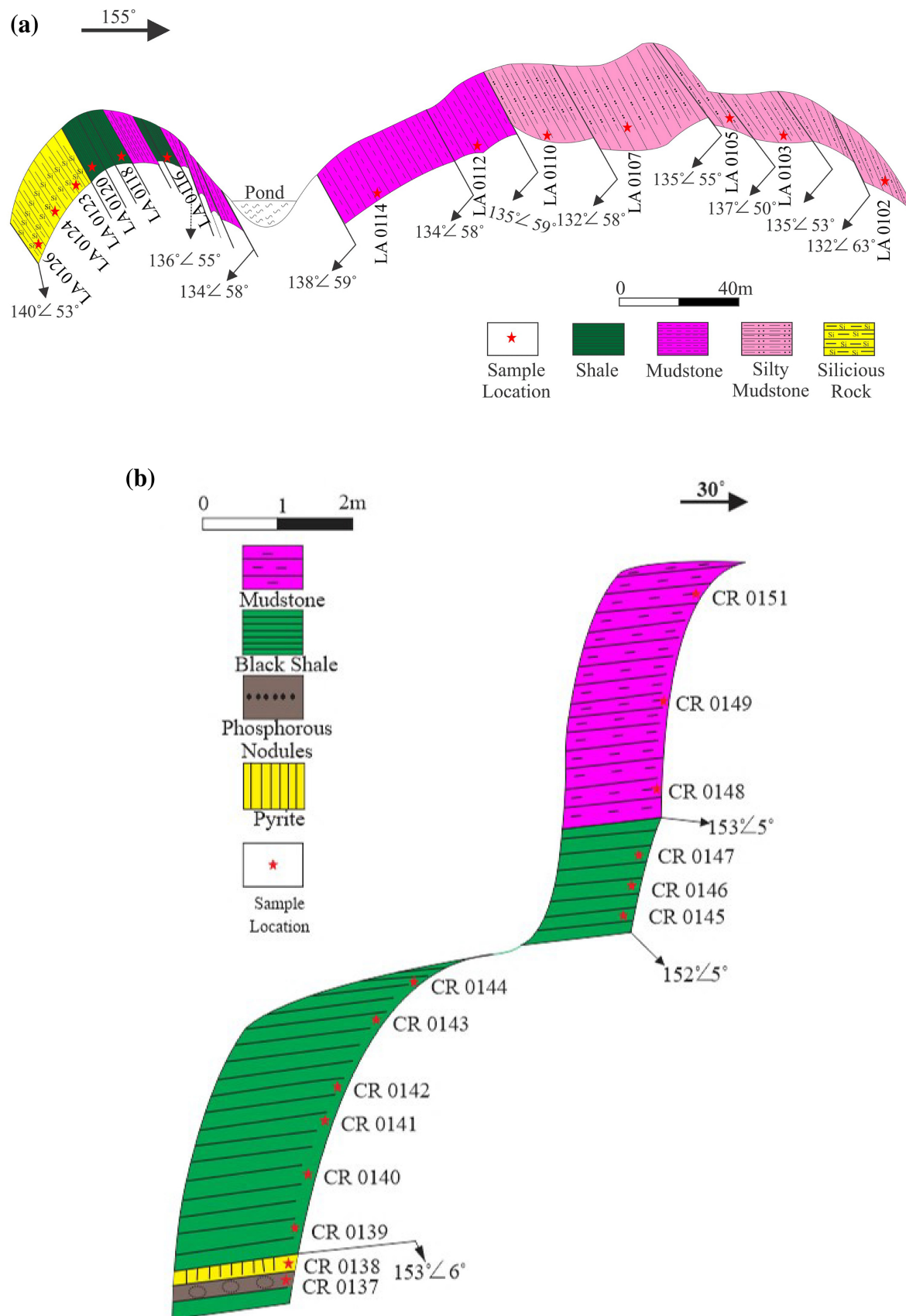
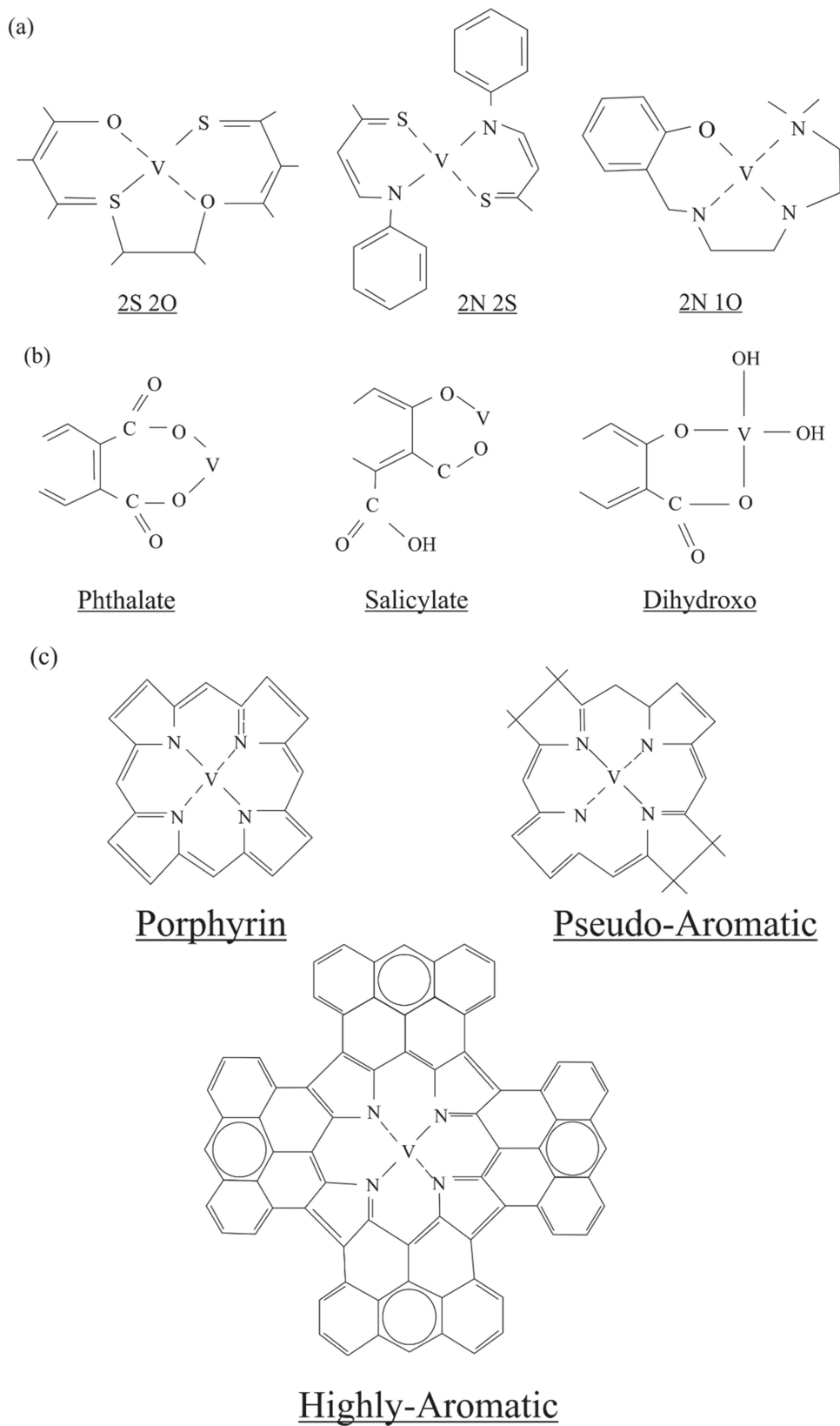


Fig. 4 The studied outcrop sections revealing the lithology and the sample collection points (a). Longbizui section (b). Sancha section

Fig. 5 The Metallo-organic compounds containing vanadium in naturally occurring substances



In mixed-ligands tetradentate, four ligands can be bonded with the metals. It might contain various combinations of oxygen, nitrogen, and sulfur (Fig. 5a) (Yen 1975). Usually, bivalent metallic cations are required in this kind of complex, and their coordination is not an octahedral form of stable square planer (Boucher and Yen 1968). Additionally, these ligands in less stable coordination of square pyramidal or tetrahedral are distorted around the metal. In dilute acids, vanadium demetallation may occur, and it may have low stability in mixed ligand tridentate (Yen 1975).

Humate complexes are defined as Metallo-organic compounds containing oxygen as bonding ligands (Fig. 5b). This kind of compound naturally occurs in humic complexes. Typically they contain oxygen atoms in phenolic hydroxide or carboxyl functional groups (Gamble and Schnitzer 1973; Schnitzer and Khan 1972). It is suggested that the functional group of phenolic hydroxide is bonded with metals up to some degree. In humate compounds, the primary ligands as a carboxyl functional group contain an oxygen atom (Vinkler et al. 1976). At low pH, the humate compounds may form by the cations of vanadyl (VO^{2+}). Its stability is significantly lower than the desired trivalent cations of ferric and aluminum (Křibek et al. 1977), supported by the higher amount of Fe and Al than vanadium in naturally found humic compounds (Cheshire et al. 1977). It is also observed in humic compounds of marine origin, which contains a greater amount of divalent cations relative to trivalent (Rashid 1971). In some marine humic compounds, it is due to the increasing sulfur and nitrogen functional groups that act as a ligand, which contains oxygen atoms as a functional group (Nissenbaum and Swaine 1976). This kind of ligands might preferably form the divalent mixed ligands tetradenates. Moreover, in humate compounds, vanadiums are not preferred due to their instabilities, which suggests they may not survive in diagenetic settings. During early diagenetic conditions, OM's thermal maturation via decarboxylation may result in humate compounds' demetallation.

Tetrapyrrole complexes can be determined as Metallo-organic compounds containing four atoms of pyrrole-nitrogen serving as a ligand (Fig. 5c). Additionally, based on the extensive research of metallated porphyrins, the present definition includes the higher aromatic and the pseudo-aromatic tetrapyrroles (Fig. 5c). This kind of structure may present in the subunits of macromolecules or as a free molecule of OM (Oehler et al. 1974). Tetrapyrrole complexes and the vanadyl cation, in contrast to other Metallo-organic compounds, make tenacious covalent bonds having higher thermal stability, resistance to strong acid, and having inertness behavior to cation exchange reaction (Lewan and Maynard 1982). Even though, it is not possible to identify all the Metallo-organic compounds related to

vanadium. The tenacious bonding of vanadium in asphalt, crude oil, and bitumens is thought to be associated with the tetrapyrrole compounds (Lewan 1981).

4.2 Vanadium occurrence and biogeochemical cycling

The biogeochemical cycling of the vanadium is the natural pathway in which the concentration of vanadium circulates in various environments via chemical, geological, and biological aspects (Fig. 6).

4.2.1 Vanadium in the soil

Vanadium is a unique transitional metal element due to its redox-sensitive nature. It can be found in various rocks, especially in the black rocks under different environments. Vanadium in the soils is primarily derived from the parental rocks (Kabata-Pendias and Pendias 1993). However, recent studies showed that the vanadium in soils could be enriched by anthropogenic activities such as burning fossil fuels, mining, pesticides, industries, fertilizers, and recycling domestic wastes (Nriagu and Pirrone 1998; Taner 2002). Titanomagnetite deposits are considered a fundamental vanadium source in which vanadium minorly substitutes the iron (Evans and White 1987). Similarly, organic fractions, Fe-oxide compounds, and argillaceous minerals are also comprised of vanadium (Kabata-Pendias and Pendias 1979). In soils, the concentration of vanadium ranges from 2–310 mg/kg with a mean concentration of 90 mg/kg (Fig. 2). The global vanadium distribution in soils is presented in Table 1. It has been noticed the soil globally in Japan (Andosols) contains a higher concentration of vanadium 250 mg/kg (Takeda et al. 2004). Vanadium is highly enriched in organically rich-soils, and peats, which shows a strong tendency towards organic matter (OM). Different lithologies contain various concentrations of vanadium, such as shales are abundant in the concentration of vanadium (130 mg V/kg) than carbonates and sandstones (20 mg V/kg) (Adriano 1986; Alloway 1990). In the Earth's continental crust, vanadium is broadly distributed as a vital element that ranges from 96 to 230 mg/kg (Fig. 2). It stands at 22nd in all discovered and at 5th in all transitional elements in the Earth's crust. Furthermore, it is usually found in argillaceous and alkaline rocks as well as in the lithosphere (Adriano 1986; Anke 2004; Baroch 2005). The vanadium's pH and oxidation state are the two significant factors that control vanadium's geochemical attributes. Previous studies describe the higher content of vanadium in limestone soil relative to other soils (Ovari et al. 2001; Połedniok and Buhl 2003).

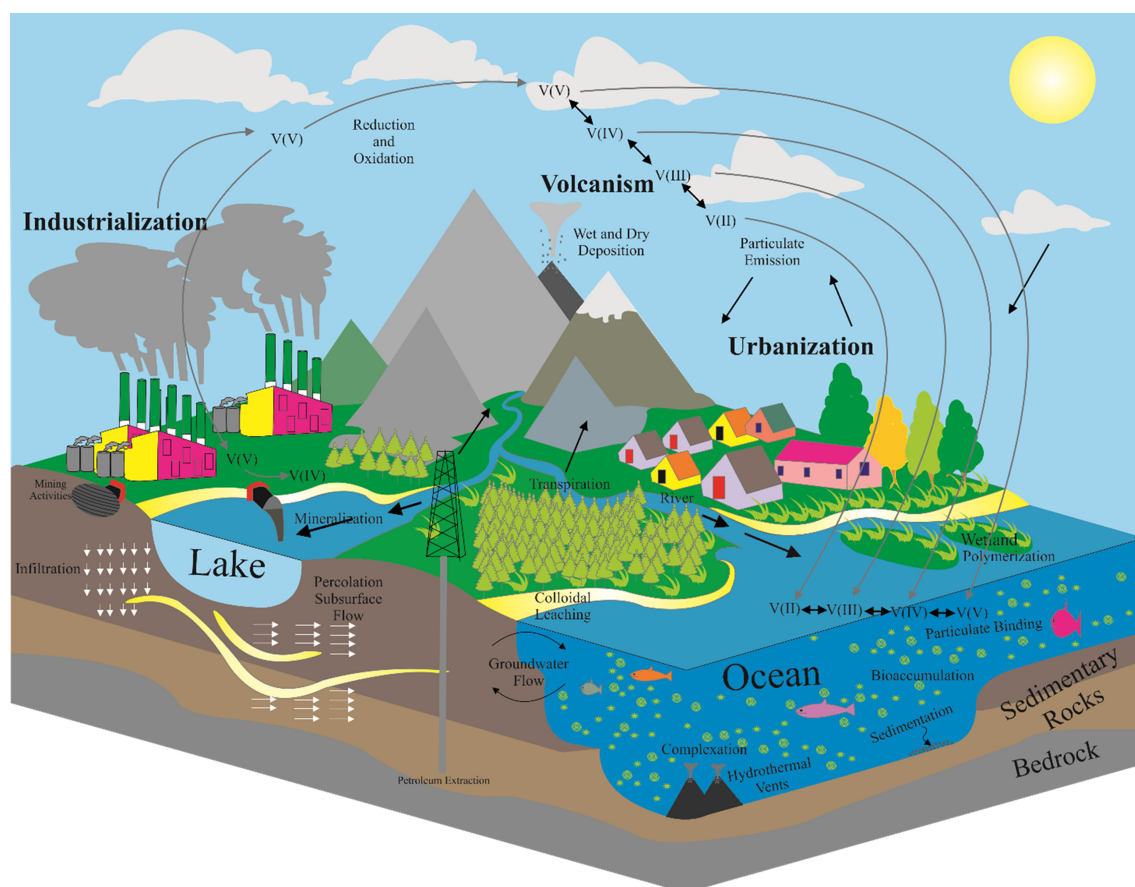


Fig. 6 Schematic diagram revealing the vanadium biogeochemical cycle

Table 1 Global distribution of vanadium in soils

Country/region	Concentration of vanadium (mg/kg)	References
China	82	Chen et al. (1991)
Sweden	69	Eriksson (2001)
Japan	94 (Gleysols)	Takeda et al. (2004)
Japan	250 (Andosols)	Takeda et al. (2004)
Ankara, Turkey	74	Yay et al. (2008)
Poland	18.39	Dudka and Markert (1992)
Russia	79–91	Protasova and Kopayeva (1985)
Italy (Palemo)	58	Manta et al. (2002)
Italy	87	Angelone (1992)
Portugal	32	Ferreira et al. (2001)
England (Northern)	103	Rawlins et al. (2002)
USA	36–150	Govindaraju (1994)
Csepel Island, Hungary	15.2–42.0	Ovari et al. (2001)
Ireland (Galway)	50	Zhang (2006)
Spain (Alcalá de Henares)	6.01	Granero and Domingo (2002)
Spain (Catalonia)	15.2–144.9	Tume et al. (2006)
Lithuania	38	Salminen and Gregorauskien (2000)
Finland	79	Koljonen (1992)

4.2.2 Vanadium in the water sources

Earth is the distinct planet amongst all planets, known as the blue planet. It is due to water's presence in a massive area. Additionally, 97% of the water on the Earth is salty, only 1% useable, and 2% is frozen. The concentration of dissolved vanadium in rivers is 0.78 $\mu\text{g/L}$ (Fig. 2). In different environments, the relationship of various environmental factors and vanadium in solution may fluctuate, e.g., there could be a low content of dissolved vanadium in streams that might be due to a strong relationship with particulate and colloidal Fe (Wällstedt et al. 2010). In contrast, the concentration of dissolved vanadium in major rivers is closely associated with the origin of rock and the weathering. However, it has a weak linkage with colloids or OM (Shiller and Boyle 1987). The concentration of dissolved vanadium in the water close to the mining horizons could be higher up to several hundred; for example, the dissolved vanadium in the Wyoming River of the United States is 30–220 mg/L (Schroeder 1970). In water, the concentration of vanadium is chiefly dependent on seasonal variations. During summer or in warm conditions, the concentration of dissolved vanadium in marine and freshwater systems has been reported at a higher level in Florida Bay (Caccia and Millero 2003), Biwa Lake and Toyko Bay (Sato and Okabe 1978), and Long Island Sound (Wang and Wilhelmy 2009). This seasonal mobility of vanadium could be affected by various factors. The relationship between the water particulates and the vanadium could be due to the substantial dependency of Eh and pH settings, which can vary seasonally. Light as a photoreduction could also impact the fluctuating concentration of vanadium in acidic streams (Kay et al. 2011). In the open ocean, the average dissolved vanadium concentration is thought to be 35–45 nmol/L (Emerson and Husted 1991). Vanadium keeps a conservative form in oceans with its high concentration. However, it exhibits lower concentration and a non-conservative behavior in coastal waters (Wang and Wilhelmy 2009). The suspended particulate form of vanadium reservoir is relatively smaller (1.8×10^{10} g) in the global oceans than the dissolved vanadium reservoirs (2.7×10^{15} g) (Hope 2008). Oceanic sediments are the biggest vanadium pool (1.7×10^{20} g) on the Earth's surface (Hope 2008). Moreover, the ultimate vanadium sink of the global circulated V is the ocean floors (Bengtsson and Tyler 1976; Miramand and Fowler 1998). In marine sediments, volcanic activities play a significant role in vanadium accumulation with a higher concentration (greater than 400 mg/kg) at the active volcanic ridge sediments (Boström and Fisher 1971).

Vanadium in groundwater is considered a significant heavy metal, and the surface water is mainly influenced by vanadium in the mining regions (Ortiz-Bernad et al. 2004).

In the aqua sphere, vanadium is a more abundant transitional element similar to the average concentration of zinc (Rehder 1991). The pollution of vanadium is further noticed in different water resources, such as lakes, rivers, and seas. In oceans, the average amount of vanadium is 1.8 $\mu\text{g/L}$. However, the vanadium quantity at mid-ocean ridge sediments is pretty much higher at 400 mg/kg (Fig. 2). Vanadium concentration at the bottom of the Persian Gulf is higher than 100 $\mu\text{g/g}$, similar to the fresh dry samples (Pourang et al. 2005). The groundwater specimens (about 10%) from the USA (California and some other states) contain more than 25 $\mu\text{g/dm}^3$ of vanadium. It is because of vanadium washout from water-bearing sediments (Wright and Belitz 2010). In oxic water settings, the most dominant form of vanadium is V(V). In contrast, the vanadyl ion VO^{2+} (IV) is more stable in reducing conditions and tends to hydrolyze. In Colorado River Basin, the amount of vanadium is 0.2–49.2 $\mu\text{g/L}$, with its maximum concentration close to the mining region of U-V (Linstedt and Kruger 1969). The most significant freshwater source in China is the Yangtze River, which contains vanadium from 0.24 to 64.5 $\mu\text{g/L}$ (Licheng and Kezhun 1992). In water, the geochemical attributes of vanadium control the biogeochemical cycle of vanadium in the surface environs (Fig. 6). The speciation of V is a composite function of solution chemistry, biology, Eh, pH, and several surface environments. Vanadium in the natural water resources exists in three different states +5, +4, +3. Various vanadate species V(III), V(IV), and V(V) are stable in anoxic, oxic, and suboxic environments, respectively (Sadiq 1988). Different spectroscopic and chemical techniques are shown chiefly V(IV) and V(V) species in a natural aqueous system (Colina et al. 2005; Wann and Jiang 1997; Zhao et al. 2006). Vanadium complexation with both inorganic and organic ligands can enhance its mobility at the surface of the interface (solid-water) (Wanty and Goldhaber 1992). Vanadium (IV) readily forms complexes with a broader range of inorganic and organic ligands relative to vanadium V(V). The typical compounds formed with the inorganic ligands are VSO_4^- for V(III); $\text{VO}(\text{OH})\text{CO}_3^-$, VOCL^+ , VOF_4^{2-} , VOF_3^- , $\text{VO}(\text{CH}_3\text{COO})$, $\text{VO}(\text{CH}_3\text{COO})_2$, VOF^+ , VOF_2 , VOCO_3 , VOSO_4 , $\text{VO}(\text{OH})\text{C}_2\text{O}_4^-$, $\text{VO}(\text{C}_2\text{O}_4)_2^{2-}$, OS_4 , for V(IV); $\text{H}_4\text{VO}_4\text{C}_2\text{O}_4^-$ and $\text{H}_4\text{VO}_4(\text{C}_2\text{O}_4)_2^{3-}$ for V(V) (Wanty and Goldhaber 1992). A wide range of organic substances has an affinity with vanadium comprising humic substances and fulvic acid via oxygen groups. Moreover, the organic substances form comparatively weaker complexes with vanadate oxyanion than oxycation V(IV) (Wehrli 1987). Hence, the V(V) organic compounds are vital to reduce V(V), and vanadium can be stabilized against reductions via binding of humic compounds at pH values (Kustin 1974). The reduction of abiotic and biotic V(V) can

produce both V(III) and V(IV) (Carpentier et al. 2003). Vanadium's organic-metalliferous chemistry is well established, and the typical form is cyclopentadienyl. The most common type of reagent in synthetic organic chemistry is vanadocene dichloride $(C_5H_5)_2VCl_2$. Which can reduce to $C_2H_5)_2V$, and $C_5H_5)_2V$.

4.2.3 Vanadium in the atmosphere

One of the substantial elements of the vanadium cycle is the atmospheric vanadium. Vanadium is substantially increasing in the biosphere since the last few decades that is threatened for the future. The main factors responsible for this uprise are mining activities, wet and dry atmospheric deposition, weathering, etc. (Morrell et al. 1986; Ringelband and Hehl 2000). Vanadium exists in hot-water springs and with volcanic ashes, tephra due to the volcanic actions (Mizuno et al. 2008; Smichowski et al. 2003). The vanadium concentration added to the atmosphere by the natural and anthropogenic sources is comparable (37×10^9 g/year). However, only 10% of the vanadium deposited in the global oceans is by anthropogenic sources (Duce and Hoffman 1976). Vanadium tends to stand for a prolonged time in the water, soil, and air and can react with the other metal elements in its surrounding (Miramand and Fowler 1998). In the contaminant list of Europe, vanadium (144t) ranks at 3rd owing to the combustion of power generation plants after Pb (191.5t) and Zn (341t). Hence due to vanadium, environmental contamination is more significant near oil fires and industries (Sabbioni et al. 1984). The key natural sources which liberate vanadium in the atmosphere are volcanic eruption, marine aerosols, continental dust, fossil fuels, forest fires, soil erosion, and other biogenic activities (Nadal et al. 2004).

It is estimated that almost greater than 64,000 tons of the V are liberated to the atmosphere via anthropogenic and natural sources (Lin et al. 2004). Nearly 58,500 tons (91%) of the global vanadium emission is from oil combustion, heavy oils, coals, and mining activities (Nadal et al. 2004). Russia and Eastern Europe contribute about 14,500 tons of global vanadium emission, whereas the Asian developing countries share greater than 33,500 tons. 85% of the total produced global vanadium is utilized in the steel sector as a ferrovanadium. However, up to 10% of the remaining global vanadium as a V-Al-Ti alloy is utilized for aerospace industries (Moskalyk and Alfantazi 2003). The vanadium uses in various other sectors are glass coating, catalysts, rechargeable batteries, etc. However, its utilization in the generation and storage of energy might be increased in the future. In the ferrous metallurgy sector, the produced vanadium wastes are chiefly in the form of particulate and liquid (WHO 1988). 60%–70% of the vanadium is recovered from these wastes. However, the rest of

them (30%–40%) is liberated into the environment through slag, wastewater, dust, and gas emission (Hope 1997; Jiao and Teng 2008). A significant amount of vanadium (up to several hundred mg/L) may be contained in the plants' wash water and liquid waste. In the mining industry, vanadium-containing leachates and effluents are mainly produced during the processing of Ti and U ores. Additionally, vanadium is a vital element of oxidation reactions and the chemical synthesis of the polymer and chemical industries, which also generates vanadium-containing waste (Nriagu 1998). The combustion of petroliferous fossil fuels rich in vanadium is an important source of V in the atmosphere (Duce and Hoffman 1976; Hope 1997). Only 60%–70% of the vanadium is recovered from refineries, and the remaining 30%–40% is discharged into the environment (Hope 1997). Vanadium (+ 4) is thought to be less toxic than vanadium (+ 5). It is because vanadium (+ 5) could affect certain enzymes' actions (Assem and Levy 2009). Moreover, V (+ 5) harms various animals (Assem and Levy 2009). The amount of vanadium mined every year is about 130,000 tons (Monakhov et al. 2004). Coal exploration also causes a higher annual concentration of vanadium in the atmosphere as coals also contain vanadium traces. In oceans, approximately 100,000 years is the time for vanadium to reside (Whitfield and Turner 1979) and are mainly transported by riverine as particulate vanadium and mechanical weathering. The concentration of vanadium might be lower in various vanadium pools during geohistorical periods. However, the concentration of vanadium in recent sediments and various other vanadium pools could be higher mainly by anthropogenic sources, which also changes the global climatic conditions. Hope (1997) indicated the concentration of vanadium introduced to the environment via anthropogenic sources is significantly higher (230 Gg) and is increasing every year. Moreover, Liu et al. (2017) has also specified the increase of vanadium via anthropogenic activities in recent years is due to vanadium utilization in various industries. Due to these reasons, it is suggested the concentration of vanadium in modern sediments will be higher. However, it will be a hot, and debatable topic for future researchers.

4.2.4 Vanadium in the biological creatures

Some aquatic organisms pile up vanadium in their cells called vanadocytes. The concentration of vanadium in various marine organisms is presented in Table 2. Vanadium can enhance the metabolic action, yield, and size of some plants. Vanadium has similar phosphate characteristics due to its capability to motivate or/and inhibit various metabolizing phosphate enzymes (Rehder 1991). Furthermore, the smaller quantity of vanadium can inhibit the phosphorous transformation of enzymes in the organisms

Table 2 The concentration of vanadium in the marine organisms

Organisms	Vanadium concentration (mg/kg dry weight)	References
Macroalgae	0.4–8.9	Meisch et al. (1977)
Annelids	25–10,000	Michibata (1996)
Fish	0.08–3.0	Soares et al. (2003)
Ascidians	0.7–786	Michibata (1996)
Zooplanktons	0.07–290	Nason (1958) and Vonk et al. (1960)
Phytoplanktons	1.5–4.7	Goc (2006)
Mammals	< 0.01–1.04 (fresh weight)	Llobet and Domingo (1984)
Other invertebrates	0.0004–45.7	Domingo (1996)

Table 3 The average amount of total organic carbon and mineral content in the black rocks of the Niutitang Formation

Sections	TOC (wt.%)	Quartz (%)	Clays (%)	Pyrite (%)
Longbizui	$\frac{0.65-8.16}{3.34(13)}$	$\frac{40.1-85.2}{62.1(11)}$	$\frac{9.18-43.74}{27.37(11)}$	$\frac{2.9-10.3}{6.7(11)}$
Sancha	$\frac{5.37-9.96}{8.09(14)}$	$\frac{40.1-85.2}{64.9(13)}$	$\frac{9.18-43.74}{30.89(13)}$	$\frac{5.3-10.4}{7.55(13)}$

(Cantley et al. 1977). Biological networks, such as the membrane's transport mechanism, can be damaged by the intermingling of several proteins with the vanadium oligomers (Arans 1995). It is noticed the reactive oxygen species (ROS) are regulated by vanadium (Zhang et al. 2001). Certain micro-creatures can respire vanadium (V) or (IV) as an electron acceptor (Ortiz-Bernad et al. 2004; Zhang et al. 2014). The higher redox potentiality of vanadium for V(V/IV), and moderately lower toxicity insinuates that other electron acceptors such as Fe^{+3} would prefer to utilize V. The concentration of vanadium might be higher in the sediments due to vanadium consumption and sorption by microbes that could be the main source of V in fossil fuels (Breit 1989; Lewan 1984).

4.3 Vanadium and the total organic carbon

Total organic carbon (TOC) is the quantity of organic carbon in sediments (Awan et al. 2021; Jian et al. 2021; Tahir et al. 2020). The average quantities of TOC from the Longbizui and the Sancha sections are 3.34 wt.% and 8.09 wt.%, respectively (Table 3). To develop and the relationship between vanadium and organic matter (OM), we have presented the cross plot between vanadium and TOC from various shales around the globe (Fig. 7). In marine shales, it is observed the vanadium has a strong positive relationship with total organic richness, as shown in Fig. 7. However, vanadium's relationship with TOC in the Green River Formation of the lacustrine environment reveals a

weak positive association. The strong positive association of V with the OM might be due to a strong association of vanadium with the microbial shells. This relationship reveals the linkage of vanadium with organic matter (OM) or is a sign of favorable conditions in which OM is preserved on dissolved vanadium and in the sediments. The variation in the slope lines of vanadium and TOC (Fig. 7) may be due to the following factors: (1) compositional discrepancies of the organic matter (OM), (2) variation in the sedimentation rate or the supply of vanadium, (3) during diagenesis compositional variation of the sediments, (4) different depositional environments (Lewan 1984; Lewan and Maynard 1982).

The biological origin of vanadium in organic matter, crude oil, and asphalt in black rocks are unclear (Vine and Tourtelot 1970). Vanadium, as tetrapyrroles in these organic substances, is firmly bonded with the organic-metallic compounds. These tetrapyrroles form covalent bonds with the cations of vanadyl (VO^{2+}). As a result, these macromolecules develop higher thermal stability (Lewan and Maynard 1982). V-porphyrins are structurally comprised of four polypyrrole macrocycles. These polypyrroles are linked with each other via methine bridges. These methane bridges are contained four heterocyclic pyrroles of nitrogen atoms that act as ligands. These macromolecules are mainly derived from the living organism's diagenetic transformation, especially from the precursors of vanadium, such as heme porphyrin pigments and chlorophyll (Blumer and Snyder 1967). The diagenetic pathway of organic-metallic compounds is shown in Fig. 8. Here, the central cation Mg in the porphyrin ring is substituted by other cations, e.g., VO^{2+} . These vanadyl cations are highly enriched in planktonic biomass and organic-rich sediments (Lewan and Maynard 1982). Furthermore, other oxygenated groups and the phytol chains are eliminated after an increase in thermal stresses via different bond cleavages (Fig. 8). Due to the experiences of environmental stresses in algae, the abundant distribution

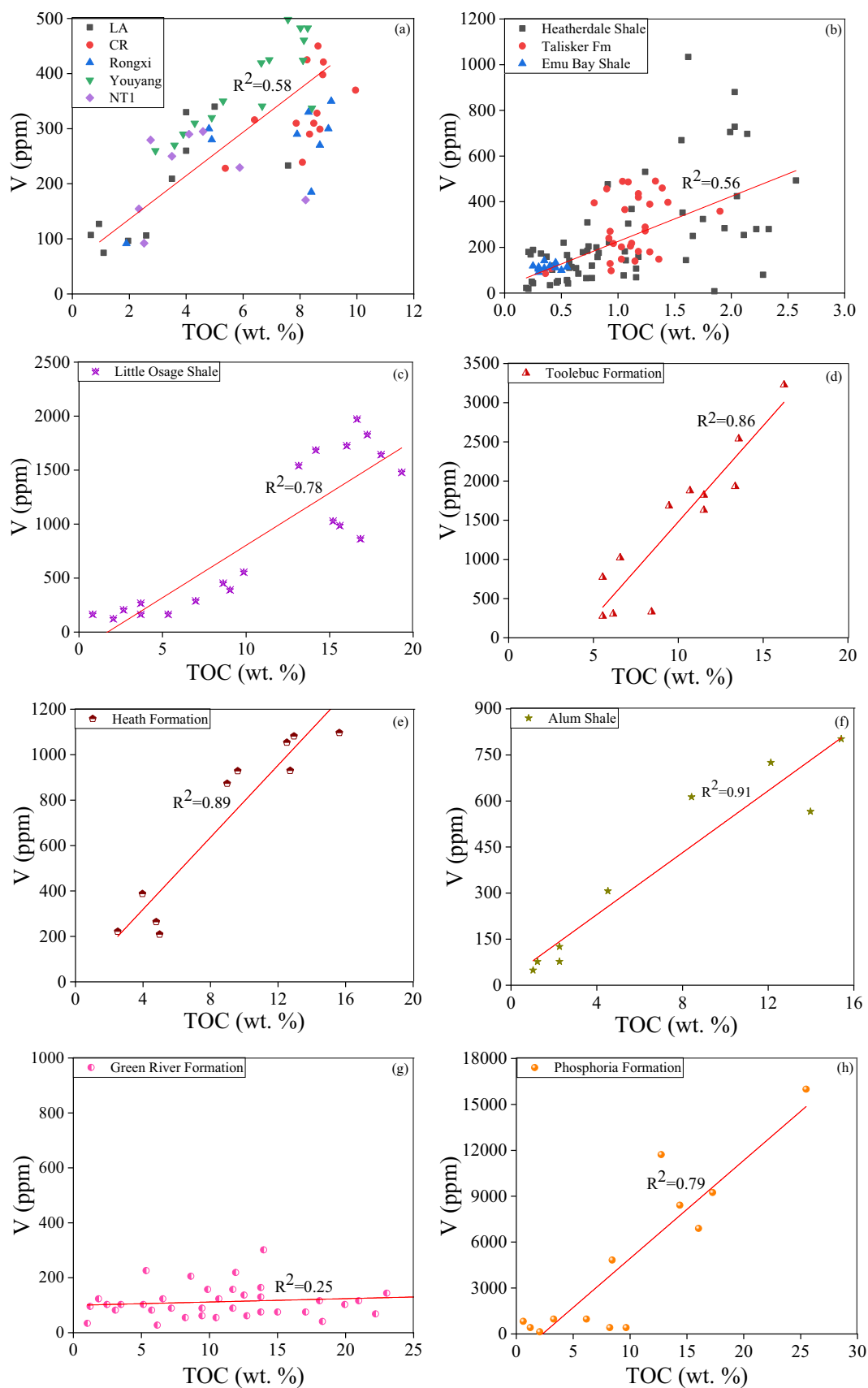


Fig. 7 The relationship of vanadium with the organic carbon in the various black rocks around the globe. The Green River Shale was deposited in a lacustrine environment, whereas the other was deposited in marine settings. Some part of the data is retrieved from Andersson et al. (1985), Derkey (1985), Gao et al. (2018), Gulbrandsen (1966), Hall (2012), McKelvey et al. (1987), Riley and Saxby (1986), Tang et al. (2017), Tuo et al. (2016), Tuttle et al. (1983), Wenger and Baker (1986) and Wu et al. (2016)

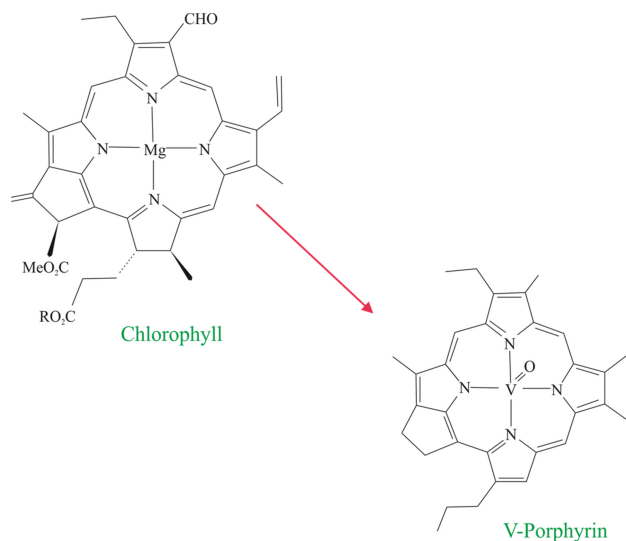


Fig. 8 Diagenetic alteration and the molecular structure of chlorophyll transformation into Vanadium porphyrin

of chlorophyll-carotenoids in the cells actively responds (Minhas et al. 2016; Mulders et al. 2014). As the stress increases, the cysts developed from algae. These cysts comprise a prolific amount of chlorophyll carotenoids bodies. After the deposition of cysts in the sediments, diagenetically chlorophyll-carotenoids altered, leading to vanadium preservation throughout the fossil cysts (Minhas et al. 2016; Mulders et al. 2014). Therefore, it can be suggested that vanadium may be attributed to the organic

walls of acritarchs as a remnant form of chlorophyll, which contains chloroplasts.

4.4 Mineralogy and the vanadium association

Mineralogy plays a key role in vanadium accumulation. Therefore, It is important to discuss various minerals that are favorable for vanadium accumulation in sedimentary rocks. In the studied samples, the heterogenic mineral composition is observed. However, quartz, clays, and pyrite are the main mineral constituents (Table 3). The cross-plot between quartz and V displays a weak positive association (Fig. 9). Previous studies suggested the presence of quartz in the Niutitang Formation is chiefly derived from a biogenic origin (Awan et al. 2020). Some part of vanadium that is consumed by organisms becomes a part of their bodies. In this context, this weak positive association of quartz with vanadium might be due to quartz's biogenic origin. Therefore, this research also suggests the quartz other than biogenic origin might be unfavorable for vanadium enrichment. In contrast, clays and pyrite depict a relatively positive relationship with vanadium. Pyrite is an essential mineral for predicting a reducing-anoxic environment. The anoxic environment is beneficial for the deposition of some trace elements, i.e., V, Ni, and Co. Hence, it can also suggest the higher amount of pyrite mineral in a rock formation is also favorable for the enrichment of vanadium. In various environmental conditions such as hydrothermal, sedimentary, and metamorphic, the clay mineral contains a significant vanadium concentration. The broader occurrence of vanadium in clay minerals suggests that the clay minerals can rapidly incorporate vanadium in nature over a broader range of temperature, pressure, and geochemical conditions. Redox settings mainly control the geochemistry of vanadium in natural water. In dissolved form, vanadium can be transported as V^{4+} and/or V^{5+} , and it can be reduced and precipitated as V^{3+} .

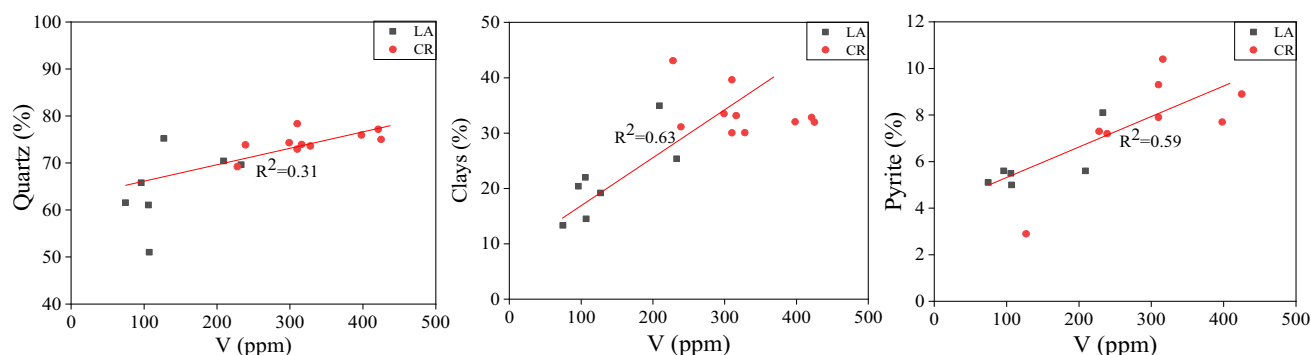


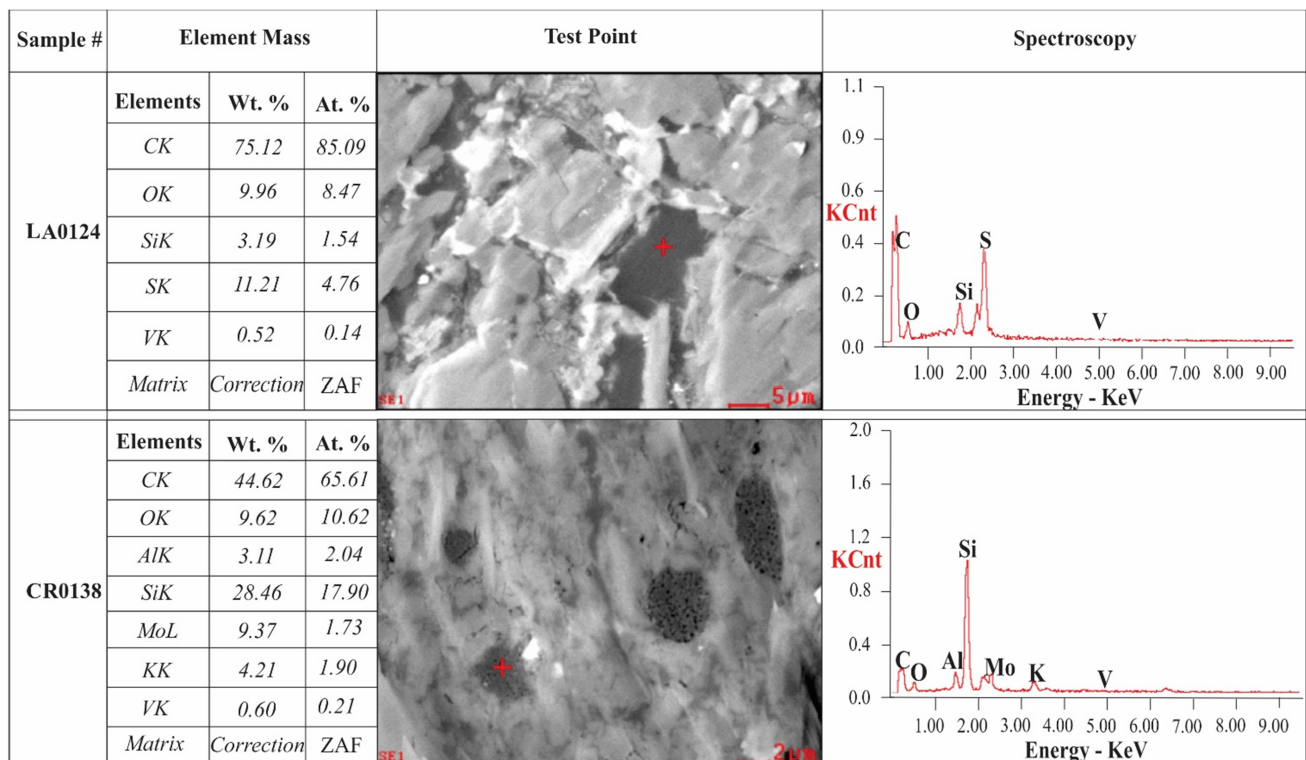
Fig. 9 The relationship of vanadium with various minerals (LA: Longbizui; CR: Sancha)

Table 4 Electron probe micro-analyzer (EPMA) results of the early Cambrian Niutitang Formation

Sample no	K ₂ O (%)	CaO (%)	TiO ₂ (%)	Na ₂ O (%)	MgO (%)	Al ₂ O ₃ (%)	SiO ₂ (%)	Cr ₂ O ₃ (%)	MnO (%)	FeO (%)	NiO (%)	V ₂ O ₃ (%)	Total (%)
LA0112	6.889	0.041	0.363	0.444	1.878	31.885	51.822	0.028	0.011	2.671	0	0.088	96.12
LA0120	8.642	0.063	0.779	0.045	2.217	29.358	51.813	0.066	0.027	3.762	0.001	0.415	97.188
CR0137	4.963	0.235	0.096	0.04	4.298	26.294	55.439	0.292	0.009	0.01	0	3.136	94.812
CR0142	5.589	0.151	0.024	0.006	4.858	26.151	57.341	0.298	0	0.005	0	2.46	96.883
CR0147	8.101	0.057	0.514	0.193	1.63	29.293	53.532	0.029	0.022	3.417	0	0.056	96.844
CR0149	6.496	0.072	0.168	0.095	1.663	32.447	51.503	0.159	0	1.159	0.008	0.068	93.836

In sedimentary rocks, during the diagenetic action, the clay minerals usually incorporate vanadium (Breit and Wanty 1991). In clay minerals, vanadium can persist in its crystalline network as an isomorphism by substituting Al with V(IV) and V(III). However, a tiny quantity of vanadium amalgamates with OM and/or adsorbed on the surfaces of minerals, i.e., clays and pyrite, etc. (Zhang et al. 2011). Hitherto, vanadium has been noticed in three groups of organisms, e.g., ascidians, certain amanita mushrooms (fly agaric), marine Polychaeta fan worms. The specialized blood cells in the ascidian (Vandocytes) take vanadium, with a higher concentration in ascidia gemmate (350 nM).

A wide range of bacteria utilizes vanadium for various biological functions. Vanadium nitrogenase is also termed iron-molybdenum enzymes. It has been commonly utilized to reduce the level of dinitrogen–ammonia in several plants. These vanadium nitrogenase are mainly derived from some specific bacterias nourished in molybdenum lean settings. However, their activity is inferior, then MO-Nase (Sippel and Einsle 2017). In sedimentary rock, vanadium availability is chiefly dependent on the V-bearing minerals, e.g., V-micas, Cr-V garnet, and Ti-V garnet, or it can be adsorbed on clays or organic matters. Vanadium ions (V^{4+} or V^{+3}) in clay minerals substitute the

**Fig. 10** Scanning electron microscopy revealing the distribution of the elemental energy spectrum from the black rocks of the Niutitang Formation

aluminum (Al^{3+}) and become a part of the crystal lattice via isomerization. The presence of vanadium in the black rocks of the Niutitang Formation is displayed in Table 4. These results reveal the presence of V_2O_3 , which indicates the isomorphism state of vanadium existence in the clay minerals. The vanadium presence in the Niutitang Formation is also observed under a scanning electron microscope (Fig. 10) that shows a strong association of vanadium with organic carbon.

4.5 The association of vanadium with other elements

The favorable geochemical settings for the vanadium accumulation can be discussed in the black rocks by determining its enrichment and geochemical constraints on other associated metal elements. This research discussed vanadium's relationship with the presence of various metal elements (Mg, P, Ti, Ni, Cu, and U) in the Niutitang Formation (Fig. 11). Here we noticed the strong positive linkage of vanadium with Ni, Cu, P, and U, and the weak positive association with MgO. However, Vanadium and Ti have a negative relationship in the Niutitang Formation. The black rocks usually contain a higher concentration of metal elements (Awan et al. 2020; Brumsack 1983; Holland 1979). These elements, especially the abundance of Ni and Cr are the significant elements in determining the paleodepositional settings (Awan et al. 2020; Lewan 1984; Tang et al. 2017). Vanadium usually occurs in H_2S rich strongly reducing settings relative to nickel and chromium

(high V/Cr, and V/Ni) (Awan et al. 2020; Tang et al. 2017). The higher values of V/Ni and V/Cr are clues of anoxic settings. The discussion of Ni and V in the black rocks is due to their greater concentration in petroleum. The enrichment of these elements is due to remarkably stable porphyrin compounds in petroleum (Lewan and Maynard 1982). Due to the reduction of V via H_2S and hindrance of Ni by NiS compounds, the ratio of V/Ni in sulfur-rich petroleum is at a higher level (Lewan 1984). However, systematically the ratio of V/Ni doesn't upsurge with the rise of sulfur concentration. The maximum average ratio of V/Ni above 1.0 wt% of sulfur is between 4.0 and 5.0 (Lewan 1984), which is quite analogous to the modern ocean-water (Ni = 8.20 nmol/Kg (Bruland 1980) and V = 40.0 nmol/Kg (Jeandel et al. 1987). The measured ratios of V/Ni in petroleum and bitumen are consistent. However, it is different from the ratio of V/Ni in the whole rock. This fluctuation of V/Ni value in bitumen reveals Ni in sulfides and V in silicates.

The vanadium-rich black rocks are usually associated or interbedded with the phosphatic-rich sediments (Beier and Hayes 1989; Patterson et al. 1986). The phosphate-rich rocks stratigraphically occur above or below in vanadium-rich black rocks. Based on the spatial relationship, phosphorus and vanadium are genetically related. However, these elements accumulate in little diverse depositional settings. The phosphorous and vanadium relationship is persistent with the vanadium behavior in the water column. The vanadium depletion in estuaries water (Collier 1984) and the near-surface water (Shiller and Boyle 1987) are

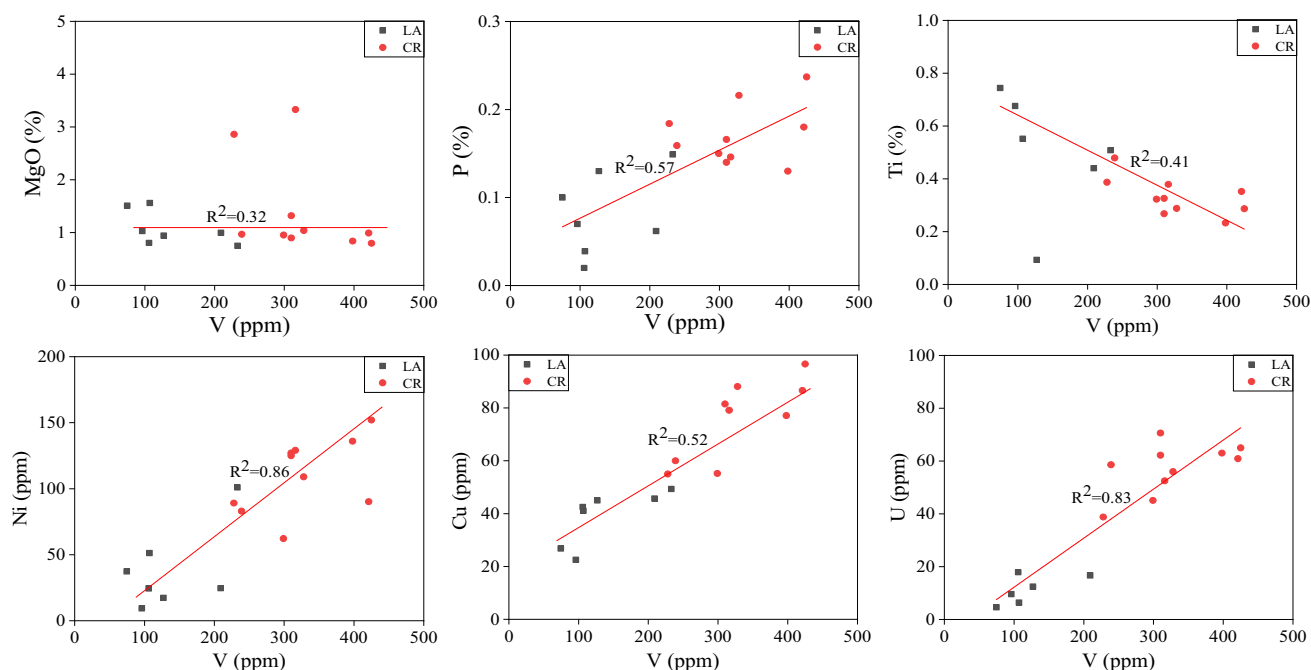


Fig. 11 The relationship of vanadium with various trace elements (LA: Longbizui; CR: Sancha)

analogous to phosphate quantity. In various ways, i.e., adsorption to biogenic particles, biogenic assimilation, vanadium may be linked with the phosphate cycle or via replacement of vanadate to phosphate (Jeandel et al. 1987). The sulfur-rich petroleum contains larger vanadium quantities, revealing an obvious relationship between sulfur and vanadium (Lewan 1984; Tissot and Welte 1984). Similarly, the black sediments with massive organically bound sulfur comprise a substantial amount of vanadium (Patterson et al. 1986). The relationship between vanadium and sulfur in OM is considered due to the vanadium preferred bonding to the sulfur ligands (Baker and Louda 1986; Yen 1975). It might be due to the various chemical processes that occur during the deposition of these sediments (Lewan 1984). The organic-sulfur compounds are so far poorly featured, and the degree of bonding type is still unclear. Lewan (1984) suggests the enrichment of vanadium in carbonaceous black rocks linked with H_2S . It is because the H_2S creates a favorable condition in the formation of V(IV). In the overlying water, some of the H_2S will be diffused due to the depletion of iron. Consequently, the strongly reduced bottom water will be beneficial in the reduction of vanadium from V(V)–V(IV) or to V(III).

4.6 Vanadium accumulation and sources in Niutitang Formation

The enrichment of vanadium in these Early Cambrian sediments might be due to chemical, physical, and biological processes. Various processes like diffusion, adsorption, and particle settling may influence the efficiencies of these progressions. Biotas are thought to play a proactive role in the vanadium cycle. They can accumulate vanadium as their lifecycle or reduced them by excreting (Boyd and Kustin 1984). In the sediments, algae may inactively adsorb vanadium, which plays a vital role in vanadium flux (Lee 1983). A few ascidians are predicted to have an enriched quantity of vanadium, e.g., Urochordates (Zhang 1985). However, In anoxic environments, the assemblage of sessile benthonic creatures in carbonaceous rocks is hard to endure (Lewan and Maynard 1982). Brumsack (1983) suggested the enrichment of metal elements in marine sediments could be determined by the combination of metal elements in the average shales and planktons. However, the abundance of vanadium in metallic-rich rocks and sediments, e.g., sediments of the Black Sea, postulate other processes to enrich vanadium. Those processes may change the chemical environment, which can be beneficial for the enrichment of vanadium in sediments.

The most frequent process for the evacuation of vanadium from the seawater is its adsorption on the terrigenous or biogenic particles. Vanadate in various pH ranges of the

natural waters can vigorously adsorb on the clay minerals and the oxides of Al and Fe, (Wehrli and Stumm 1989). Vanadyl ions adsorbed more powerfully than vanadates. However, its durability as the adsorbed species in the oxic water is modest (Wehrli and Stumm 1989). Besides the higher concentration of ligands, the vanadyl-oxides' adsorption is preferable relative to the complexity of the dissolve organic ligand (Micera and Dallochio 1988). More than 40% of the transported vanadium from the Mississippi River is adsorbed to the detrital particles (Shiller and Boyle 1987). It is experimentally noticed that the adsorption of vanadate exacerbates when the pH raised over 4.5. Iron oxides can substantially adsorb the massive quantity of vanadium from the ocean water in the oxic basins (Shieh and Duedall 1988). These oxic basins may be a vital pool for dissolved vanadium (Trefry and Metz 1989). Another possible mechanism for the enrichment of vanadium in these black rocks of the Niutitang Formation could be due to diffusion phenomena. In these Early Cambrian sediments, vanadium diffusion from the bottom water is preferred by the declining quantity of V(V) species in the pores via complexation, reduction, and adsorption into the sediments. In sediments, due to the chemical transformation, the available concentration of vanadium may alter. The concentration of vanadium in the shallower pore water may increase due to the sediments reworking under the oxic environment or apparently due to vanadium's mobilization from the degraded biogenic particles (Shaw et al. 1990). The reworked vanadium may be diffused upward or downward into the bottom water and reprecipitated into the reduced regions (Colley et al. 1984; Heggie et al. 1986; Jarvis and Higgs 1987; Shaw et al. 1990). However, Shaw et al. (1990) compared the pore water vanadium in oxic and anoxic sediments and suggested the redistribution of vanadium does not occur in anoxic sediments.

Vanadium is extensively used to study ancient marine sediments due to its unique nature and abundance. It can be used to determine some invaluable facts regarding the source, diagenesis, and paleoenvironmental settings. In marine sediments, especially in shales, the origin of vanadium is still a source of contention. The abundance of vanadium in marine sediments is interesting due to the burial of vanadium-rich organisms (Vinogradov 1936). The rapid growth of massive algal-biomass in a specific time window (e.g., 100,000 years) could be a prerequisite in forming polymetallic beds. Li et al. (1999) and Awan et al. (2020) suggested the black shales in the Yangtze region during the Early Cambrian period were developed through massive organic production in an upwelling system. Various forms of algae have revealed a higher biosorption ability of V and Ni (Holan and Volesky 1994). In the photic zone, the annual concentration of green algae production

could be elevated to $48.9 \text{ kg} \cdot \text{m}^{-2}$ (Xu and He 2006), which could enhance the storage of vanadium. Xu and Li (2015) observed algae's presence in the black rocks of Niutitang Formation in the form of heavily squeezed vesicles or tri-lete appearance. The red phosphatized algae were also noticed in the Doushantuo Formation in South China (Xiao et al. 2004). The reduction and adsorption of metal elements on organic substances (such as humic substances) are the probable mechanisms for the enrichment of vanadium in carbonaceous marine shales. Usually, the humic substance in the sediments forms soluble compounds with vanadium, which play a fundamental role in the fixation and transportation of vanadium (Cheshire et al. 1977; McBRIDE 1978). The chemical composition of igneous rocks and the volcanic-clastic material are considered to be identical. Basalts and some other igneous rocks comparatively contain a higher vanadium level (up to 0.11%). Similarly, these rocks contain a higher concentration of other transitional metal elements such as Cu, Mo, Ni, and Cr. Volcanic ash in the Niutitang Formation may be a source of vanadium in the form of VO^{2+} porphyrin. In the marine Niutitang Formation, the VO^{2+} porphyrins can be divided into three groups based on their physicochemical characteristics. (i) VO^{2+} porphyrins are a product of kerogenization and polymerization phenomena with higher aromaticity or molecular weight, (ii) VO^{2+} porphyrins, which reveals the nominal diagenetic evidence, (iii) and the VO^{2+} porphyrins embedded with the kerogen configuration. Incorporating the nuclei of VO^{2+} porphyrins into the matrix's kerogen is certainly an abiotic geochemical alteration of biosynthesize pigmental chlorophyll. The inclusion of VO^{2+} porphyrins into the sediments is not its ultimate fate. Several high aromatics and high /low extractable porphyrins are considered to be a product of kerogen thermal stress (Mackenzie et al. 1980). These processes are considered to be accountable to produce a broader spectrum of aliphatic hydrocarbons from kerogen. Various types of VO^{2+} porphyrins may have been produced from biogenic pigment chlorophyll via diagenetic and catagenetic processes. Previous studies also indicated that volcanic ash in marine shales is an unusual source of metallic enrichment (Leventhal and Kepferle 1982; Wedepohl 1971). The chemical alteration of ash is led by various factors when the ash falls on the bottom of the sea: fine particle size, loose porous nature, broader surface region, and its unstable composition. Under the high reducing setting of vanadium, the chemical solutions of weathering become enriched. V(V) and V(IV) occur in various chemical forms, such as (i) sulfides, (ii) vanadates, or hydro-oxides, which are weakly adsorbed/precipitated on limestones or clays, (iii) vanadium porphyrin or humic compounds. At the bottom of the ocean, the vanadium

could be abundant via the scavenged activity of sulfides and marine organic matter.

4.7 Vanadium accumulation model

The enrichment model of the vanadium in the black rock is presented in Fig. 12. The reason for this enrichment of vanadium in black rocks are (i) higher vanadium supply in the seawater, (ii) stratification, (iii) anoxic water settings, (iv) slow sedimentation rate. In the shallow water, biogenic particles adsorbed some of the vanadium. However, this concentration of adsorbed vanadium is inadequate for the sediments' enrichment in the modern ocean. In the anoxic water column, the sediments adsorbed the vanadyl ion. Moreover, Due to adsorption and strong organic compounds, the vanadyl ion is stable in these settings. During the early diagenesis, organic ligands are destroyed by thermal maturation and consequently form complex vanadium. With an increased burial depth and thermal maturity, the liberated V from organic compounds become a part of petroleum via migration. In the black rocks, the diagenetic alteration to the mineral composition and the OM is due to the intricate mechanisms associated with temperature, pressure, and chemical settings. These variations in the black rocks transform both the existence and the abundance of vanadium that has been suggested by the fluctuations of V-rich sediments graphitic schist to immature oil shales. As the vanadium is deposited into the sediments, it forms complex compounds with the organic macromolecules. Previous research on estuarine humic compounds and soil reveals the rapid association of organic acid compounds with vanadium (Goncalves and Mota 1987; Mangrich and Vugman 1988; Templeton and Chasteen 1980). OM liberates a few functional groups gradually with condensation and maturity (Tissot and Welte 1984). Presumably, the redistributed V as a functional group develops more stable compounds, e.g., asphaltenes and porphyrins. During progressive diagenetic changes, both the increase and redistribution of porphyrins metallated percentages are consistent (Baker and Louda 1986). As the burial temperature upsurges, the vanadium compounds and the vanadyl porphyrins joins the migration hydrocarbons after separation from macromolecules. The concentration of vanadium may increase into the heavy hydrocarbons during the migration of petroleum. It is due to the depletion of light hydrocarbons or the occurrence of biodegradation (Filby and Van Berkel 1987). Most of the vanadium in the black rocks accumulates during sedimentation, and it remains in the sediments even during metamorphism and diagenetic actions (Sozinov 2018). The factors that are beneficial for the preservation and enrichment of vanadium in the black rocks are poorly described. However, the enrichment of vanadium may be affected by clay minerals and the nature

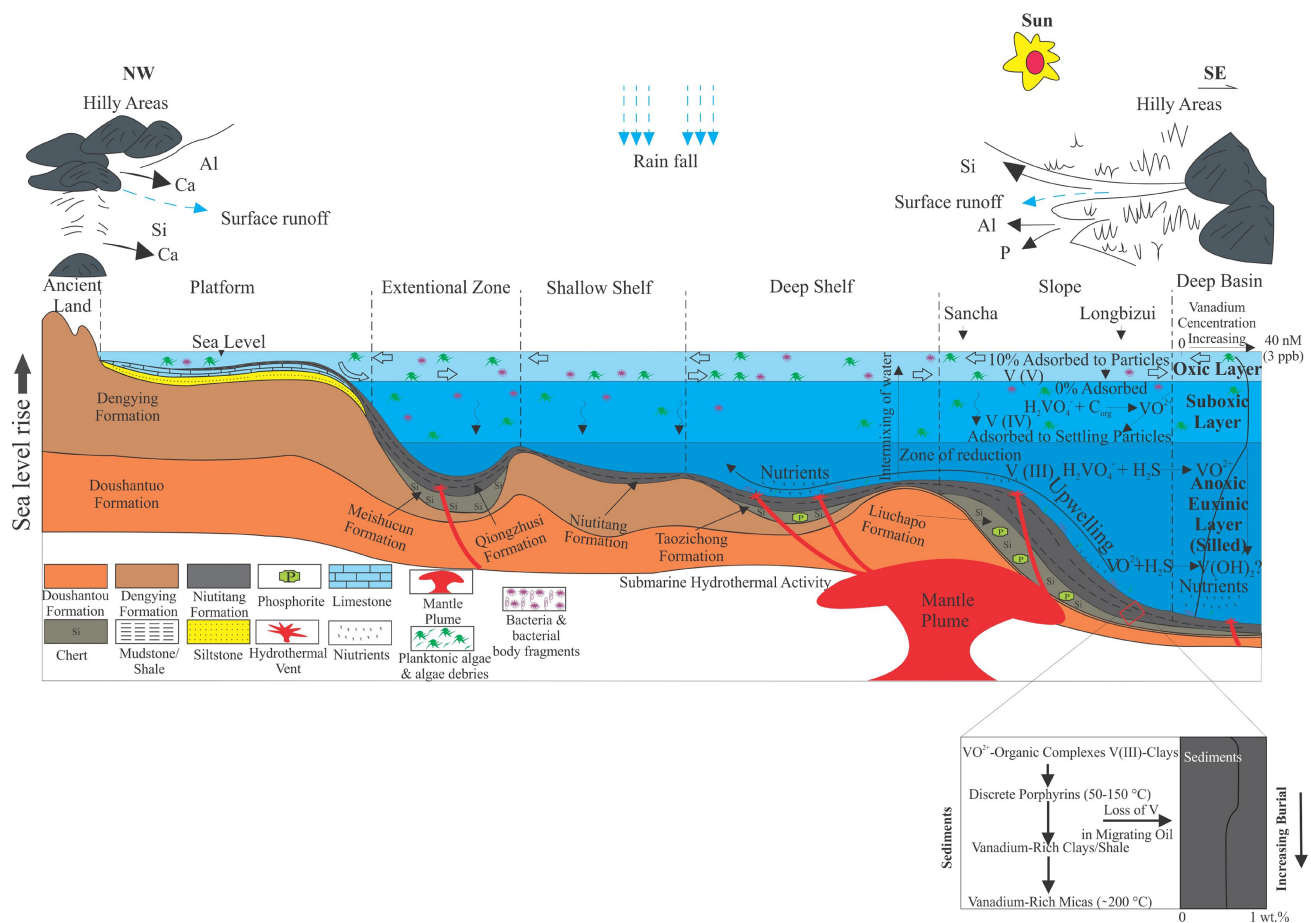


Fig. 12 Vanadium accumulation model in the Niutitang Formation

of OM. Marine black rocks, sapropelic coals, and carbonaceous shale mainly encompass V-rich minerals (Zhang 1985; Coveney et al. 1987). In clay minerals, V chiefly occurs in the form of V(III). However, V(IV) species have also been noticed in the clay minerals (Premović 1984; Wanty et al. 1990). It is thought V(III) might be formed at high temperature via reaction of V(IV) with residual OM or believed to form through the reaction of V(IV) with H_2S (Wanty 1986). In clay octahedral sites AL readily substitutes by V(III). In clay's structure, V(III) is stable, and it can exist also exist in extreme weather conditions. It is suggested the Niutitang Formation is extensively affected by volcanic activity during the Early Cambrian period due to extensional forces (Awan et al. 2020). These volcanic activities brought massive nutrients in the form of the various metal element (V, Ni, Co, Cr) from the deeper Earth through faults and fissures. Moreover, the sea level transgression during the Early Cambrian period enhanced biological activity. These organisms consumed the metal elements, which later become a part of their bodies. Later on, the vanadium and other metal-rich organisms were died and laid down at the bottom of the ocean surface and

deposited in the sediments. Finally, when the initially deposited loose sediments were diagenetically altered, this vanadium became enriched along with organic matter in the Niutitang Formation. In the upper water column or in the photic region where macroalgae and phytoplanktons proliferate is a productive zone for photosynthesis. As a result of OM's higher sedimentation rate, the black shales, phosphates, mudstone, chert, and adsorbed trace metal elements could accumulate onto the seafloor (Li et al. 2013; Piper and Link 2002). Patrick (1978) suggests the growth of green algae and diatoms in the laboratory could be higher with the higher availability of vanadium concentration. Moreover, the favorable amount of the dissolved vanadate for the evolution of nitrogen-fixing bacterias is 10–1000 Nm, while the growth of these bacterias is limited under 10 nM (Bellenger et al. 2008a). However, vanadophores may also be produced and consumed by these bacterias under limited settings (Bellenger et al. 2008b). The previous studies have also explained that marine algae's biomasses, e.g., red, brown, and green algae, have a substantial sorption ability for Ni, V, Cd, Cu, Hg, Pb (Doshi et al. 2006; Prasher et al. 2004). The

dissolved V is enormously found in the seawater. However, the hydrothermal activities could be a source of V. The massive amount of metal elements could accumulate in the algal remanents, which were reduced and fixed via bacterial actions.

5 Conclusion

This article describes the occurrence of vanadium in nature-its biogeochemical cycling and its relationship with organic matter. The following are the conclusive facts that controlled the enrichment of OM in these sediments:

1. There are three naturally occurring Metallo-organic compounds of vanadium, based on the type of ligands, i.e., mixed ligands tetradendate, tetrapyrrole complexes, and humate complexes.
2. The black rocks of the Niutitang Formation deciphered a strong positive association of vanadium with the total organic carbon content. A similar trend is also observed in the various black sediments around the globe. The strong positive association of V with the OM might be due to a strong association of vanadium with the microbial shells.
3. Lithophile is the main geochemical characteristic of vanadium. However, it has a little tendency for siderophile and a biophilic tendency. As vanadium forms various complex ions and exists in three different states, + 5, + 4, and + 3, it has a diadochic replacement tendency of different elements within the mineral structure by vanadium.
4. Vanadium doesn't form an autonomous mineral in igneous rocks, but it has a higher concentration in the basic igneous rocks. It resides in the other mineral structures in the form of V^{4+} by replacing Al^{3+} , Ti^{4+} , and Fe^{3+} . In the sedimentary rocks, the most common vanadium is V^{4+} , and V^{5+} , whereas the V^{3+} is mainly distinctive to the sediments' buried organic matter.
5. Clays and pyrite are the most favorable mineral for vanadium enrichment. However, it is suggested the quartz other than biogenic origin might be unfavorable for vanadium enrichment.
6. During the Early Cambrian period, the massive transgression in the sea level created a favorable environment for organisms to survive. Additionally, the hydrothermal activities brought massive nutrient supply in the form of vanadium and other metal elements from the deep Earth. These creatures consumed the vanadium-rich nutrients, which became a part of their bodies in the form of hard and soft parts. Later on, when these organisms died and were submerged in the sediments. After the diagenetic

actions, this vanadium became a part of these black sediments along with organic carbon. Therefore, these black rocks in the Yangtze region are enriched in vanadium and organic carbon.

Acknowledgements The authors are grateful to the National Natural Science Foundation (NNCF) of China for awarding us pecuniary aid with Grant Numbers 41572099, and 41872127 to accomplish this scientific research.

Declarations

Conflict of interest The authors declare no conflicts of interest.

References

- Adriano DC (1986) Other trace elements. In: Trace elements in the terrestrial environment. Springer, pp 470–501
- Alloway BJ (1990) Heavy metals in soils. Blackie and Son, Ltd. Glas., London
- Amthor JE, Grotzinger JP, Schröder S, Bowring SA, Ramezani J, Martin MW, Matter A (2003) Extinction of cloudina and namacalathus at the Precambrian-Cambrian boundary in Oman. *Geology* 31:431–434
- Andersson A, Dahlman B, Gee DG, Snall S (1985) The Scandinavian alum shales. Sveriges Geol undersökning. Ser Ca Avh och Uppsats I 4 0
- Angelone M (1992) Trace elements concentrations in soils and plants of Western Europe. *Biogeochem trace Met* 19–60
- Anke M (2004) Vanadium: an element both essential and toxic to plants, animals and humans? In: *Anales de La Real Academia Nacional de Farmacia. Real Academia Nacional de Farmacia*, pp 961–999
- Arans DC (1995) Interaction of vanadates with biogenic ligands. *Met Ions Biol Syst* 31:147
- Assem FL, Levy LS (2009) A review of current toxicological concerns on vanadium pentoxide and other vanadium compounds: gaps in knowledge and directions for future research. *J Toxicol Environ Heal Part B* 12:289–306
- Awan RS, Liu C, Gong H, Dun C, Tong C, Chamssidini LG (2020) Paleo-sedimentary environment in relation to enrichment of organic matter of Early Cambrian black rocks of Niutitang Formation from Xiangxi area China. *Mar Pet Geol* 112:104057
- Awan RS, Liu C, Aadil N, Yasin Q, Salaam A, Hussain A, Yang S, Jadoon AK, Wu Y, Gul MA (2021) Organic geochemical evaluation of Cretaceous Talhar Shale for shale oil and gas potential from Lower Indus Basin, Pakistan. *J Pet Sci Eng* 200:108404
- Aydin F, Saydut A, Gunduz B, Aydin I, Hamameci C (2012) Chemical speciation of vanadium in coal bottom ash. *Clean-Soil Air Water* 40:444–448
- Baker EW, Louda JW (1986) Porphyrins in the geological record. *Methods Geochem Geophys* 24:125–225
- Baroch EF (2005) Kirk-Othmer encyclopedia of chemical technology 24
- Beier JA, Hayes JM (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
- Bellenger JP, Wichard T, Kraepiel AML (2008a) Vanadium requirements and uptake kinetics in the dinitrogen-fixing bacterium *Azotobacter vinelandii*. *Appl Environ Microbiol* 74:1478–1484

- Bellenger JP, Wichard T, Kustka AB, Kraepiel AML (2008b) Uptake of molybdenum and vanadium by a nitrogen-fixing soil bacterium using siderophores. *Nat Geosci* 1:243–246
- Bengtsson S, Tyler G (1976) Vanadium in the environment. London, University of London Monitoring and Assessment Research Centre. Marc Report
- Blumer M, Snyder WD (1967) Porphyrins of high molecular weight in a Triassic oil shale: evidence by gel permeation chromatography. *Chem Geol* 2:35–45
- Boström K, Fisher DE (1971) Volcanogenic uranium, vanadium and iron in Indian Ocean sediments. *Earth Planet Sci Lett* 11:95–98
- Boucher LJ, Yen TF (1968) Spectral properties of oxovanadium(IV) complexes. II. Bistrifluoroacetylacetonediethylenediamine. *Inorg Chem* 7:2665–2667
- Boyd DW, Kustin K (1984) Vanadium: a versatile biochemical effector with an elusive biological function. *Adv Inorg Biochem* 6:312–365
- Breit GN (1989) Vanadium: resources in fossil fuels
- Breit GN, Wanty RB (1991) Vanadium accumulation in carbonaceous rocks: a review of geochemical controls during deposition and diagenesis. *Chem Geol* 91:83–97
- Bruland KW (1980) Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth Planet Sci Lett* 47:176–198
- Brumsack HJ (1983) A note on Cretaceous black shales and Recent sediments from oxygen deficient environments: paleoceanographic implications. In: Coastal upwelling its sediment record. Springer, pp 471–483
- Caccia VG, Millero FJ (2003) The distribution and seasonal variation of dissolved trace metals in Florida Bay and adjacent waters. *Aquat Geochem* 9:111–144
- Cantley LC, Josephson L, Warner R, Yanagisawa M, Lechene C, Guidotti G (1977) Vanadate is a potent (Na, K)-ATPase inhibitor found in ATP derived from muscle. *J Biol Chem* 252:7421–7423
- Carpentier W, Sandra K, De Smet I, Brigé A, De Smet L, Van Beeumen J (2003) Microbial reduction and precipitation of vanadium by *Shewanella oneidensis*. *Appl Environ Microbiol* 69:3636–3639
- Chen J, Wei F, Zheng C, Wu Y, Adriano DC (1991) Background concentrations of elements in soils of China. *Water Air Soil Pollut* 57:699–712
- Cheshire MV, Berrow ML, Goodman BA, Mundie CM (1977) Metal distribution and nature of some Cu, Mn and V complexes in humic and fulvic acid fractions of soil organic matter. *Geochim Cosmochim Acta* 41:1131–1138
- Clark SHB, Poole FG, Wang Z (2004) Comparison of some sediment-hosted, stratiform barite deposits in China, the United States, and India. *Ore Geol Rev* 24:85–101
- Colina M, Gardiner PHE, Rivas Z, Troncone F (2005) Determination of vanadium species in sediment, mussel and fish muscle tissue samples by liquid chromatography–inductively coupled plasma-mass spectrometry. *Anal Chim Acta* 538:107–115
- Colley S, Thomson J, Wilson TRS, Higgs NC (1984) Post-depositional migration of elements during diagenesis in brown clay and turbidite sequences in the North East Atlantic. *Geochim Cosmochim Acta* 48:1223–1235
- Collier RW (1984) Particulate and dissolved vanadium in the North Pacific Ocean. *Nature* 309:441–444
- Coveney RM, Leventhal JS, Glascock MD, Hatch JR (1987) Origins of metals and organic matter in the Mecca Quarry Shale Member and stratigraphically equivalent beds across the Midwest. *Econ Geol* 82:915–933
- Derkey PD (1985) Geology and oil shale resources of the Heath Formation. Fergus County, Montana
- Domingo JL (1996) Vanadium: a review of the reproductive and developmental toxicity. *Reprod Toxicol* 10:175–182
- Doshi H, Ray A, Kothari IL, Gami B (2006) Spectroscopic and scanning electron microscopy studies of bioaccumulation of pollutants by algae. *Curr Microbiol* 53:148–157
- Duce RA, Hoffman GL (1976) Atmospheric vanadium transport to the ocean. *Atmos Environ* 10:989–996
- Dudka S, Markert B (1992) Baseline concentrations of As, Ba, Be, Li, Nb, Sr and V in surface soils of Poland. *Sci Total Environ* 122:279–290
- Emerson SR, Husted SS (1991) Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. *Mar Chem* 34:177–196
- Emsley J (2011) Nature's building blocks: an AZ guide to the elements. Oxford University Press
- Eriksson J (2001) Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, precipitation and in oil and crops. Swedish Environmental Protection Agency Stockholm
- Evans HT, White JS (1987) The colorful vanadium minerals: a brief review and a new classification. *Mineral Rec* 18:333–340
- Ferreira A, Inácio MM, Morgado P, Batista MJ, Ferreira L, Pereira V, Pinto MS (2001) Low-density geochemical mapping in Portugal. *Appl Geochem* 16:1323–1331
- Filby RH, Van Berkel GJ (1987) Geochemistry of metal complexes in petroleum, source rocks, and coals: an overview. ACS Publications
- Gamble DS, Schnitzer M (1973) The chemistry of fulvic acid and its reactions with metal ions. In: Metals and metal-organic interactions in natural waters, pp 265–302
- Gao P, He Z, Li S, Lash GG, Li B, Huang B, Yan D (2018) Volcanic and hydrothermal activities recorded in phosphate nodules from the Lower Cambrian Niutitang Formation black shales in South China. *Palaeogeogr Palaeoclimatol Palaeoecol* 505:381–397
- Goc A (2006) Biological activity of vanadium compounds. *Cent Eur J Biol* 1:314–332
- Goncalves MLS, Mota AM (1987) Complexes of vanadyl and uranyl ions with the chelating groups of humic matter. *Talanta* 34:839–847
- Govindaraju K (1994) 1994 compilation of working values and sample description for 383 geostandards. *Geostand News* 18:1–158
- Granero S, Domingo JL (2002) Levels of metals in soils of Alcalá de Henares, Spain: human health risks. *Environ Int* 28:159–164
- Gulbrandsen RA (1966) Chemical composition of phosphorites of the Phosphoria Formation. *Geochim Cosmochim Acta* 30:769–778
- Hall PA (2012) Elemental, isotopic and molecular signatures of Early Cambrian marine sediments and a phantom petroleum system in South Australia
- Han T, Zhu X, Li K, Jiang L, Zhao C, Wang Z (2015) Metal sources for the polymetallic Ni–Mo–PGE mineralization in the black shales of the Lower Cambrian Niutitang Formation. *South China Ore Geol Rev* 67:158–169
- Heggie D, Kahn D, Fischer K (1986) Trace metals in metalliferous sediments, MANOP Site M: interfacial pore water profiles. *Earth Planet Sci Lett* 80:106–116
- Holan ZR, Volesky B (1994) Biosorption of lead and nickel by biomass of marine algae. *Biotechnol Bioeng* 43:1001–1009
- Holland HD (1979) Metals in black shales; a reassessment. *Econ Geol* 74:1676–1680
- Hope BK (1997) An assessment of the global impact of anthropogenic vanadium. *Biogeochemistry* 37:1–13
- Hope BK (2008) A dynamic model for the global cycling of anthropogenic vanadium. *Glob Biogeochem Cycles* 22:GB4021
- Huang J-H, Huang F, Evans L, Glasauer S (2015) Vanadium: global (bio) geochemistry. *Chem. Geol.* 417:68–89
- Imtiaz M, Tu S, Xie Z, Han D, Ashraf M, Rizwan MS (2015) Growth, V uptake, and antioxidant enzymes responses of chickpea (*Cicer*

- arietinum* L.) genotypes under vanadium stress. *Plant Soil* 390:17–27
- Jarvis I, Higgs N (1987) Trace-element mobility during early diagenesis in distal turbidites: Late Quaternary of the Madeira Abyssal Plain, N Atlantic. *Geol. Soc. London. Spec Publ* 31:179–214
- Jeandel C, Caisso M, Minster JF (1987) Vanadium behaviour in the global ocean and in the Mediterranean Sea. *Mar Chem* 21:51–74
- Jian L, Jixian T, Chenglin L, Dehao F, Xu Z, Mai Z, Zeqing G, Hua K, Awan RS, Zhijie L (2021) Geochemical characteristics and source analysis of natural gas in the saline lacustrine basin in the Western Qaidam basin. *J Pet Sci Eng* 201:108363
- Jiang G, Shi X, Zhang S, Wang Y, Xiao S (2011) Stratigraphy and paleogeography of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in south China. *Gondwana Res* 19:831–849
- Jiao XD, Teng Y (2008) Techniques on soil remediation and disposal of vanadium pollution. *Chin J Soil Sci* 39:448–452
- Kabata-Pendias A, Pendias H (1979) Trace elements in the biological environment. In: *Wyd. Geol., Warsaw* 300
- Kabata-Pendias A, Pendias H (1993) *Biochemistry of trace elements*. PWN, Warsaw
- Kay RT, Groschen GE, Cygan G, Dupré DH (2011) Diel cycles in dissolved barium, lead, iron, vanadium, and nitrite in a stream draining a former zinc smelter site near Hegeler. *Illinois Chem Geol* 283:99–108
- Koljonen T (1992) Suomen geokemian atln, wit 2: morceni-Geochemical Atlas of Finland, Part 2 Till. Geological Survey of Finland, Espoo, p 21X
- Křibek B, Kaigl J, Oružinský V (1977) Characteristics of di- and trivalent metal-humic acid complexes on the basis of their molecular-weight distribution. *Chem Geol* 19:73–81
- Kustin K, Liu S, Nicolini C, Toppen D (1974) Interaction of catechol and catechol derivatives with dioxovanadium(V). I. Kinetics of complex formation in acidic media. *J Am Chem Soc* 96:7410–7415
- Langeslay RR, Kaphan DM, Marshall CL, Stair PC, Sattelberger AP, Delferro M (2018) Catalytic applications of vanadium: a mechanistic perspective. *Chem Rev* 119:2128–2191
- Larsson MA (2014) Vanadium in soils
- Lee K (1983) Vanadium in the aquatic ecosystem. *Adv Environ Sci Technol* 13:155–187
- Lehmann B, Nägler TF, Holland HD, Wille M, Mao J, Pan J, Ma D, Dulski P (2007) Highly metalliferous carbonaceous shale and Early Cambrian seawater. *Geology* 35:403–406
- Leventhal JS, Kepferle RC (1982) Geochemistry and geology of strategic metals and uranium in Devonian shales of the eastern interior United States. In: *Synthetic fuels from oil shale, II*. Institute of Gas Technology Chicago, Ill, pp 72–96
- Lewan MD (1981) Geochemistry of vanadium and nickel in organic matter of sedimentary rocks
- Lewan MD (1984) Factors controlling the proportionality of vanadium to nickel in crude oils. *Geochim Cosmochim Acta* 48:2231–2238
- Lewan MD, Maynard JB (1982) Factors controlling enrichment of vanadium and nickel in the bitumen of organic sedimentary rocks. *Geochim Cosmochim Acta* 46:2547–2560
- Li R, Lu J, Zhang S, Lei J (1999) Organic carbon isotopes of the Sinian and Early Cambrian black shales on Yangtze Platform, China. *Sci China Ser D Earth Sci* 42:595–603
- Li Y, Sun S, Chan LS (2013) Phosphogenesis in the 2460 and 2728 million-year-old banded iron formations as evidence for biological cycling of phosphate in the early biosphere. *Ecol Evol* 3:115–125
- Licheng Z, Kezhun Z (1992) Background values of trace elements in the source area of the Yangtze River. *Sci Total Environ* 125:391–404
- Lide DR (2008) *CRC handbook of chemistry and physics*. CRC, Boca Raton
- Liguo C (1997) Evolution and structural styles of the Sichuan foreland basin. In: *Global tectonic zones supercontinent formation and disposal: proceedings of the 30th International Geological Congress, Beijing, China, 4–14 August 1996*. VSP, p 87
- Lin TS, Chang CL, Shen F-M (2004) Whole blood vanadium in Taiwanese college students. *Bull Environ Contam Toxicol* 73:781–786
- Linstedt KD, Kruger P (1969) Vanadium concentrations in Colorado River basin waters. *J Am Water Work Assoc* 61:85–88
- Liu BJ, Xu XS (1994) *Atlas of paleogeography and lithofacies of South China: Sinian-Trias*
- Liu ZH, Zhuang XG, Teng GE, Xie XM, Yin LM, Bian LZ, Feng QL, Algeo TJ (2015) The lower Cambrian Niutitang Formation at Yangtiao (Guizhou, SW China): organic matter enrichment, source rock potential, and hydrothermal influences. *J Pet Geol* 38:411–432
- Liu Y, Liu G, Qu Q, Qi C, Sun R, Liu H (2017) Geochemistry of vanadium (V) in Chinese coals. *Environ Geochem Health* 39:967–986
- Llobet JM, Domingo JL (1984) Acute toxicity of vanadium compounds in rats and mice. *Toxicol Lett* 23:227–231
- Lu X, Johnson WD, Hook J (1998) Reaction of vanadate with aquatic humic substances: an ESR and 51V NMR study. *Environ Sci Technol* 32:2257–2263
- Luo C (2014) Geological characteristics of gas shale in the lower Cambrian Niutitang Formation of the Upper Yangtze Platform. *Chengdu Chengdu University of Technology*, pp 115–132
- Mackenzie AS, Patience RL, Maxwell JR, Vandenbroucke M, Durand B (1980) Molecular parameters of maturation in the Toarcian shales, Paris Basin, France—I. Changes in the configurations of acyclic isoprenoid alkanes, steranes and triterpanes. *Geochim Cosmochim Acta* 44:1709–1721
- Mangrich AS, Vugman NV (1988) Bonding parameters of vanadyl ion in humic acid from the Jucu river estuarine region, Brazil. *Sci Total Environ* 75:235–241
- Manta DS, Angelone M, Bellanca A, Neri R, Sprovieri M (2002) Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci Total Environ* 300:229–243
- McBRIDE MB (1978) Transition metal bonding in humic acid: an ESR study. *Soil Sci* 126:200–209
- McKelvey VE, Strobell Jr JD, Slaughter AL (1987) The vanadiferous zone of the phosphoria formation in western Wyoming and southeastern Idaho
- Meisch H-U, Benzschawel H, Bielg H-J (1977) The role of vanadium in green plants. *Arch Microbiol* 114:67–70
- Micera G, Dallochio R (1988) Metal complex formation on the surface of amorphous aluminium hydroxide. Part IV. Interaction of oxovanadium (IV) and vanadate (V) with aluminium hydroxide in the presence of succinic, malic and 2-mercapto-succinic acids. *Colloids Surf* 34:185–196
- Michibata H (1996) The mechanism of accumulation of vanadium by ascidians: some progress towards an understanding of this unusual phenomenon. *Zoolog Sci* 13:489–502
- Minhas A, Hodgson P, Barrow C, Adholeya A (2016) A review on the assessment of stress conditions for simultaneous production of microalgal lipids and carotenoids. *Front Microbiol* 7(2016):1–19
- Miramand P, Fowler SW (1998) Bioaccumulation and transfer of vanadium in marine organisms. *Adv Environ Sci Technol YORK* 30:167–198
- Mizuno N, Amano Y, Mizuno T, Nanzyo M (2008) Changes in the heavy mineral content and element concentration of Tarumae-a tephra with distance from the source volcano. *Soil Sci Plant Nutr* 54:839–845

- Monaco SL, López L, Rojas H, Garcia D, Premovic P, Briceño H (2002) Distribution of major and trace elements in La Luna Formation, southwestern Venezuelan basin. *Org Geochem* 33:1593–1608
- Monakhov IN, Khromov SV, Chernousov PI, Yusfin YS (2004) The flow of vanadium-bearing materials in industry. *Metallurgist* 48:381–385
- Morrell BG, Lepp NW, Phipps DA (1986) Vanadium uptake by higher plants: some recent developments. *Environ Geochem Health* 8:14–18
- Moskalyk RR, Alfantazi AM (2003) Processing of vanadium: a review. *Miner Eng* 16:793–805
- Mulders KJM, Lamers PP, Martens DE, Wijffels RH (2014) Phototrophic pigment production with microalgae: biological constraints and opportunities. *J Phycol* 50:229–242
- Nadal M, Schuhmacher M, Domingo JL (2004) Metal pollution of soils and vegetation in an area with petrochemical industry. *Sci Total Environ* 321:59–69
- Nason A (1958) The metabolic role of vanadium and molybdenum in plants and animals. *Tract elements*. Academic Press, New York pp 269–296
- Nielsen SG, Prytulak J, Wood BJ, Halliday AN (2014) Vanadium isotopic difference between the silicate Earth and meteorites. *Earth Planet Sci Lett* 389:167–175
- Nissenbaum A, Swaine DJ (1976) Organic matter-metal interactions in recent sediments: the role of humic substances. *Geochim Cosmochim Acta* 40:809–816
- Nriagu JO (1998) History, occurrence, and uses of vanadium. *Vanadium Environ. Chem Biochem* 1–36
- Nriagu JO, Pirrone N (1998) Emission of vanadium into the atmosphere. *Adv Environ Sci Technol YORK* 30:25–36
- Och LM, Shields-Zhou GA, Poulton SW, Manning C, Thirlwall MF, Li D, Chen X, Ling H, Osborn T, Cremonese L (2013) Redox changes in Early Cambrian black shales at Xiaotan section, Yunnan Province, south China. *Precambrian Res* 225:166–189
- Oehler JH, Aizenshtat Z, Schopf JW (1974) Thermal alteration of blue-green algae and blue-green algal chlorophyll. *Am Assoc Pet Geol Bull* 58:124–132
- Orberger B, Vymazalova A, Wagner C, Fialin M, Gallien JP, Wirth R, Pasava J, Montagnac G (2007) Biogenic origin of intergrown Mo-sulphide-and carbonaceous matter in Lower Cambrian black shales (Zunyi Formation, southern China). *Chem Geol* 238:213–231
- Ortiz-Bernad I, Anderson RT, Vrionis HA, Lovley DR (2004) Vanadium respiration by *Geobacter metallireducens*: novel strategy for in situ removal of vanadium from groundwater. *Appl Environ Microbiol* 70:3091–3095
- Ovari M, Csukas M, Zaray GY (2001) Speciation of beryllium, nickel, and vanadium in soil samples from Csepel Island, Hungary. *Fresenius J Anal Chem* 370:768–775
- Patterson JH, Ramsden AR, Dale LS, Fardy JJ (1986) Geochemistry and mineralogical residences of trace elements in oil shales from Julia Creek, Queensland, Australia. *Chem Geol* 55:1–16
- Pi DH, Liu CQ, Shields-Zhou GA, Jiang SY (2013) Trace and rare Earth element geochemistry of black shale and kerogen in the Early Cambrian Niutitang Formation in Guizhou province, South China: Constraints for redox environments and origin of metal enrichments. *Precambrian Res* 225:218–229
- Piper DZ, Link PK (2002) An upwelling model for the Phosphoria sea: a Permian, ocean-margin sea in the northwest United States. *Am Assoc Pet Geol Bull* 86:1217–1235
- Poledniok J, Buhl F (2003) Speciation of vanadium in soil. *Talanta* 59:1–8
- Pourang N, Nikouyan A, Dennis JH (2005) Trace element concentrations in fish, surficial sediments and water from northern part of the Persian Gulf. *Environ Monit Assess* 109:293–316
- Prasher SO, Beauguard M, Hawari J, Bera P, Patel RM, Kim SH (2004) Biosorption of heavy metals by red algae (*Palmaria palmata*). *Environ Technol* 25:1097–1106
- Premović PI (1984) Vanadyl ions in ancient marine carbonaceous sediments. *Geochim Cosmochim Acta* 48:873–877
- Protasova NA, Kopayeva MT (1985) Trace and dispersed elements in soils of Russian Plateau. *Pochvovedeniye* 1:29–37
- Prytulak J, Nielsen SG, Ionov DA, Halliday AN, Harvey J, Kelley KA, Niu YL, Peate DW, Shimizu K, Sims KWW (2013) The stable vanadium isotope composition of the mantle and mafic lavas. *Earth Planet Sci Lett* 365:177–189
- Rashid MA (1971) Role of humic acids of marine origin and their different molecular weight fractions in complexing di- and tri-valent metals. *Soil Sci* 111:298–306
- Rawlinson B, Lister T, Mackenzie A (2002) Trace-metal pollution of soils in northern England. *Environ Geol* 42:612–620
- Rehder D (1991) The bioinorganic chemistry of vanadium. *Angew Chem Int Ed Engl* 30:148–167
- Rehder D (2015) The role of vanadium in biology. *Metallomics* 7:730–742
- Riley KW, Saxby JD (1986) Organic matter and vanadium in the Toolebuc Formation, northern Eromanga Basin and southern Carpentaria Basin
- Ringelband U, Hehl O (2000) Kinetics of vanadium bioaccumulation by the brackish water hydroid *Cordylophora caspia* (Pallas). *Bull Environ Contam Toxicol* 65:486–493
- Sabbioni E, Goetz L, Bignoli G (1984) Health and environmental implications of trace metals released from coal-fired power plants: an assessment study of the situation in the European Community. *Sci Total Environ* 40:141–154
- Sadiq M (1988) Thermodynamic solubility relationships of inorganic vanadium in the marine environment. *Mar Chem* 23:87–96
- Salminen R, Gregorauskiene V (2000) Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. *Appl Geochem* 15:647–653
- Sato Y, Okabe S (1978) Vanadium in sea waters and deposits from Tokyo Bay, Suruga Bay and Harima Nada. *J Fac Mar Sci Technol Tokai Univ* 11:1–19
- Schnitzer M, Khan SU (1972) Reactions of humic substances with metal ions and hydrous oxides. *Humic Subst Environ* 203–251
- Schroeder HA (1970) Vanadium, air quality monographs 70-13. Am. Pet. Institute, Washington, pp 1–32
- Shaw TJ, Gieskes JM, Jahnke RA (1990) Early diagenesis in differing depositional environments: the response of transition metals in pore water. *Geochim Cosmochim Acta* 54:1233–1246
- Shieh CS, Duedall IW (1988) Role of amorphous ferric oxyhydroxide in removal of anthropogenic vanadium from seawater. *Mar Chem* 25:121–139
- Shiller AM, Boyle EA (1987) Dissolved vanadium in rivers and estuaries. *Earth Planet Sci Lett* 86:214–224
- Sippel D, Einsle O (2017) The structure of vanadium nitrogenase reveals an unusual bridging ligand. *Nat Chem Biol* 13:956–960
- Smichowski P, Gómez D, Rosa S, Polla G (2003) Trace elements content in size-classified volcanic ashes as determined by inductively coupled plasma-mass spectrometry. *Microchem J* 75:109–117
- Soares SS, Aureliano M, Joaquim N, Coucelo JM (2003) Cadmium and vanadate oligomers effects on methaemoglobin reductase activity from Lusitanian toadfish: in vivo and in vitro studies. *J Inorg Biochem* 94:285–290
- Sozinov NA (2018) Ore potential of Precambrian black shale formation. *Rev Bras Geociências* 12:506–509
- Steiner M, Wallis E, Erdtmann B-D, Zhao Y, Yang R (2001) Submarine-hydrothermal exhalative ore layers in black shales from South China and associated fossils—insights into a Lower

- Cambrian facies and bio-evolution. *Palaeogeogr Palaeoclimatol Palaeoecol* 169:165–191
- Tahir M, Awan RS, Muzaffar W, Iltaf KH (2020) Organic geochemical evaluation of the lower cretaceous sembar formation to identify shale-gas potential from the southern Indus Basin Pakistan. *N Am Acad Res* 3:54–78. <https://doi.org/10.5281/zenodo.4023378>
- Takeda A, Kimura K, Yamasaki S (2004) Analysis of 57 elements in Japanese soils, with special reference to soil group and agricultural use. *Geoderma* 119:291–307
- Taner MF (2002) Vanadium-geology, processing and applications. In: *Proceedings of international symposium on vanadium*. Can. Inst. Mining, Metall. Pet., p 265
- Tang X, Jiang Z, Li Z, Cheng L, Zhang Y, Sun P, Fan C (2017) Factors controlling organic matter enrichment in the Lower Cambrian Niutitang Formation Shale on the eastern shelf margin of the Yangtze Block, China. *Interpretation* 5:T399–T410
- Templeton GD III, Chasteen ND (1980) Vanadium-fulvic acid chemistry: conformational and binding studies by electron spin probe techniques. *Geochim Cosmochim Acta* 44:741–752
- Tissot BP, Welte DH (1984) *Petroleum formation and occurrence—second revised and enlarged edition*
- Trefry JH, Metz S (1989) Role of hydrothermal precipitates in the geochemical cycling of vanadium. *Nature* 342:531–533
- Tume P, Bech J, Longan L, Tume L, Reverter F, Sepulveda B (2006) Trace elements in natural surface soils in Sant Climent (Catalonia, Spain). *Ecol. Eng.* 27:145–152
- Tuo J, Wu C, Zhang M (2016) Organic matter properties and shale gas potential of Paleozoic shales in Sichuan Basin, China. *J. Nat. Gas Sci. Eng.* 28:434–446
- Tuttle ML, Dean WE, Parduhn NL (1983) Inorganic geochemistry of Mahogany zone oil shale in two cores from the Green River Formation. ACS Publications
- Venkataraman BV, Sudha S (2005) Vanadium toxicity. *Asian J Exp Sci* 19:127–134
- Vine JD, Tourtelot EB (1970) Geochemistry of black shale deposits; a summary report. *Econ Geol* 65:253–272
- Vinkler P, Lakatos B, Meisel J (1976) Infrared spectroscopic investigations of humic substances and their metal complexes. *Geoderma* 15:231–242
- Vinogradov AP (1936) Concerning the origin of vanadium in petroleum and solid bitumens. *Coll. Akad. V. L. Vernadskii* 145
- Vonk HJ, Waterman TH, Talbot H (1960) *Physiology of the Crustacea*, vol 1. Academic Press, New York, pp 291–316
- Wällstedt T, Björkvald L, Gustafsson JP (2010) Increasing concentrations of arsenic and vanadium in (southern) Swedish streams. *Appl Geochem* 25:1162–1175
- Wang D, Wilhelmy SAS (2009) Vanadium speciation and cycling in coastal waters. *Mar Chem* 117:52–58
- Wann CC, Jiang S-J (1997) Determination of vanadium species in water samples by liquid chromatography-inductively coupled plasma mass spectrometry. *Anal Chim Acta* 357:211–218
- Wanty RB (1986) Geochemistry of vanadium in an epigenetic sandstone-hosted vanadium-uranium deposit, Henry basin, Utah
- Wanty RB, Goldhaber MB (1992) Thermodynamics and kinetics of reactions involving vanadium in natural systems: accumulation of vanadium in sedimentary rocks. *Geochim Cosmochim Acta* 56:1471–1483
- Wanty RB, Goldhaber MB, Northrop HR (1990) Geochemistry of vanadium in an epigenetic, sandstone-hosted vanadium-uranium deposit, Henry Basin, Utah. *Econ Geol* 85:270–284
- Wedepohl KH (1971) Environmental influences on the chemical composition of shales and clays. *Phys Chem Earth* 8:307–333
- Weeks ME (1932) The discovery of the elements. VII. Columbium, tantalum, and vanadium. *J Chem Educ* 9:863
- Wehrli B (1987) Vanadium in der Hydrosphäre: Oberflächenkomplexe und Oxidationskinetik
- Wehrli B, Stumm W (1989) Vanadyl in natural waters: adsorption and hydrolysis promote oxygenation. *Geochim Cosmochim Acta* 53:69–77
- Wenger LM, Baker DR (1986) Variations in organic geochemistry of anoxic-oxic black shale-carbonate sequences in the Pennsylvanian of the Midcontinent, USA. *Org Geochem* 10:85–92
- Whitfield M, Turner DR (1979) Water-rock partition coefficients and the composition of seawater and river water. *Nature* 278:132–137
- WHO (1988) *Environmental Health Criteria No. 81*. World Heal. Organ., Geneva
- Wille M, Nägler TF, Lehmann B, Schröder S, Kramers JD (2008) Hydrogen sulphide release to surface waters at the Precambrian/Cambrian boundary. *Nature* 453:767
- Wright MT, Belitz K (2010) Factors controlling the regional distribution of vanadium in groundwater. *Groundwater* 48:515–525
- Wu C, Tuo J, Zhang M, Sun L, Qian Y, Liu Y (2016) Sedimentary and residual gas geochemical characteristics of the Lower Cambrian organic-rich shales in Southeastern Chongqing, China. *Mar Pet Geol* 75:140–150
- Xiao S, Knoll AH, Yuan X, Poeschel CM (2004) Phosphatized multicellular algae in the Neoproterozoic Doushantuo Formation, China, and the early evolution of florideophyte red algae. *Am J Bot* 91:214–227
- Xu SN, He PM (2006) Analysis of phenomena for frequent occurrence of red tides and bioremediation by seaweed cultivation. *J Fish China* 30:554–561
- Xu J, Li Y-L (2015) An SEM study of microfossils in the black shale of the Lower Cambrian Niutitang Formation, Southwest China: IMPLICATIONS for the polymetallic sulfide mineralization. *Ore Geol Rev* 65:811–820
- Xu L, Lehmann B, Jingwen M, Wenjun Q, Andao D (2011) Re-Os age of polymetallic Ni-Mo-PGE-Au mineralization in Early Cambrian black shales of South China—a reassessment. *Econ Geol* 106:511–522
- Xu L, Lehmann B, Mao J, Nägler TF, Neubert N, Böttcher ME, Escher P (2012) Mo isotope and trace element patterns of Lower Cambrian black shales in South China: multi-proxy constraints on the paleoenvironment. *Chem Geol* 318:45–59
- Yay OD, Alagha O, Tuncel G (2008) Multivariate statistics to investigate metal contamination in surface soil. *J Environ Manage* 86:581–594
- Yen TF (1975) Chemical aspects of metals in native petroleum. In: *Trace metals in petroleum*
- Zhang A (1985) The geochemistry of vanadium in the marine black rock sequence of Yangjiabao
- Zhang C (2006) Using multivariate analyses and GIS to identify pollutants and their spatial patterns in urban soils in Galway, Ireland. *Environ Pollut* 142:501–511
- Zhang Z, Huang C, Li J, Leonard SS, Lanciotti R, Butterworth L, Shi X (2001) Vanadate-induced cell growth regulation and the role of reactive oxygen species. *Arch Biochem Biophys* 392:311–320
- Zhang Y-M, Bao S-X, Liu T, Chen T-J, Huang J (2011) The technology of extracting vanadium from stone coal in China: history, current status and future prospects. *Hydrometallurgy* 109:116–124
- Zhang J, Dong H, Zhao L, McCarrick R, Agrawal A (2014) Microbial reduction and precipitation of vanadium by mesophilic and thermophilic methanogens. *Chem Geol* 370:29–39
- Zhang Y-Y, He Z-L, Jiang S, Lu S-F, Xiao D-S, Chen G-H, Zhao J-H (2018) Controls on the organic carbon content of the lower Cambrian black shale in the southeastern margin of Upper Yangtze. *Pet Sci* 15:709–721

- Zhao L, Zhu X, Feng K, Wang B (2006) Speciation analysis of inorganic vanadium (V (IV)/V (V)) by graphite furnace atomic absorption spectrometry following ion-exchange separation. *Int J Environ Anal Chem* 86:931–939
- Zhu M, Zhang J, Yang A, Li G, Steiner M, Erdtmann BD (2003) Sinian-Cambrian stratigraphic framework for shallow-to deep-water environments of the Yangtze Platform: an integrated approach. *Prog Nat Sci* 13:951–960
- Zhu B, Jiang S-Y, Yang J-H, Pi D, Ling H-F, Chen Y-Q (2014) Rare Earth element and SrNd isotope geochemistry of phosphate nodules from the lower Cambrian Niutitang Formation, NW Hunan Province, South China. *Palaeogeogr Palaeoclimatol Palaeoecol* 398:132–143