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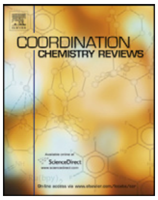

Review

A possible role for extraterrestrial vanadium in the encounter of life

Dieter Rehder*

Chemistry Department, University of Hamburg, D-20146 Hamburg, Germany

Contents

1. Introduction 2227
2. Vanadium in meteorites 2228
3. Vanadium in the coma of comet Wild 2 2228
4. Vanadium oxide in dwarf stars and exoplanets 2229
5. Vanadium oxide based protective and transport systems 2229
6. Conclusion 2230
References 2231

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ABSTRACT

Extraterrestrial vanadium compounds typically contain vanadium in low oxidation states (V^{II}, V^{III}), reflecting anoxic environments (low oxygen fugacities) during genesis. In meteorites, most of which are fragments from asteroids and thus represent samples from the very beginning of our solar system, are found the pyroxenes which are typical V^{II} bearing minerals. In calcium- and aluminium-rich inclusions of dust particles collected from the coma of comet Wild 2, osbornite (TiN) with titanium replaced by up to 63% vanadium has been found. The atmospheres of “hot Jupiter” type exoplanets, as well as the atmospheres of early M type stars (red dwarfs) contain vanadium(II)oxide, which is also likely a constituent in interstellar clouds. The relevance of these vanadium occurrences for the generation of complex molecules out of simple ones under primordial conditions is briefly discussed in light of the catalytic potential of vanadium nitrides and -oxides. At higher oxygen fugacities, oxidic V^{IV} and V^{V} species are available. In this context, the ability of higher valent vanadium oxides to form nano-structured webs of protocells, and the potential of decavanadate and VO^{2+} to interfere with chemical processes in micellar structures and lipid vesicles is addressed.

1. Introduction

“It is not surprising that natural evolution has incorporated many metal ions into performing a wide variety of tasks and playing crucial roles in living systems. One of these metals certainly has been vanadium” [1]. The role of vanadium in life processes pertinent to our planet has become well established during the bygone centenary. In living organisms, vanadium can be present in the oxidation states +III (hydrated V^{3+}), +IV (in the form of coordination compounds of the oxidovanadium ion VO^{2+} or “bare” V^{4+}) and +V ($H_2VO_4^-$ under common physiological conditions) [2]. Some nitrogen fixing bacteria, such as *Azotobacter*, employ vanadium in the $\{Fe_7VS_9\}$ cofactor of the nitrogenase systems, possibly switching the oxidation state of vanadium between +II and +IV in the course of N_2 reduction. Examples for individuals employing vanadium in the oxidation states +IV and +III are certain ascidians (sea squirts) which intermittently “store” VO^{2+} by binding up to 20 of these cations to small proteins termed vanabins, and finally accumulating $[V(H_2O)_5HSO_4]^{2+}$ in specific blood cells called vanadocytes. *Amanita* mushrooms like the fly agaric contain non-oxido vanadium(IV) coordinated to an isopropionic acid derivative of hydroxylamine. A variety of marine algae, along with some fungi and lichen, express a vanadate-dependent haloperoxidase, in which vanadate(V) is linked coordinatively to a histidine side chain of the protein matrix. Finally, bacteria such as *Shewanella oneidensis* (a soil bacterium) [3a] and *Pseudomonas isachenkovii* (isolated from an ascidian) [3b] can employ vanadate(V) as the primary electron acceptor in respiration, reducing vanadate to oxidovanadium(IV) hydroxide and thus initiating processes of vanadium mineralization.

In extent terrestrial minerals, vanadium can occur in the oxidation states +III, +IV and +V. Examples are the minerals roscoelite $K(Al,V^{III})_2(OH,F)_2[AlSi_3O_{10}]$, patronite $V^{IV}(S_2)_2$ and vanadinite $PbCl_2{\cdot}3Pb_2(V^{V}O_4)_4$. Along with monovanadate(V), con-

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* Tel.: +49 40 428486087.
E-mail address: rehder@chemie.uni-hamburg.de

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Table 1
Percentage abundances of vanadium (by atoms).

Universe	20×10^{-9}
Sun (and other comparable stars)	9×10^{-9}
Asteroids, meteorites, dwarf stars, exoplanets	$\approx 20 \times 10^{-6}$[a]
Earth's crust	75×10^{-6}
Sea water	4×10^{-6}

[a] Corresponds to ca. 200 vanadium atoms per 10^6 silicon atoms.

densed water-soluble vanadates such as tetravanadate $V_4O_{12}{}^{4-}$ and, in particular, decavanates $H_nV_{10}O_{28}{}^{(6-n)-}$ ($n = 0$–3) have been shown to take over important roles in physiological environments, including the interaction with lipid structures [4]. The latter aspect will be retrieved in Section 5. The general role of (commonly simple) vanadium compounds, such as vanadium oxides and alkoxides, in redox and Lewis acid/base catalysis is well established [5], and the abundance and wide-spread availability of vanadium minerals in the Earth's crust, and vanadate in sea water, is suggestive of a general role of this element in enabling – i.e. catalyzing – processes which have contributed to furnishing the versatility of basic and perhaps even complex molecules that are important precursors and/or building blocks in the process of evolution of molecules of life. Amavadin, though its role in the *Amanita* mushrooms remains illusive, has been shown to be an effective catalyst in oxidation, oxo-transfer and oxidative C–C coupling reactions [6], while vanadate-dependent haloperoxidases are examples for the potential of V^V in Lewis acid catalysis.

In the light of this potential of vanadium on our planet, the question arises whether simple vanadium compounds such as vanadium oxides (including low-valent vanadium, in particular vanadium(II)) and vanadium nitride can have contributed, and still contribute, to the inventory of more or less complex organic molecules present in regions beyond our home system, such as interstellar clouds, circumstellar envelopes of late AGB (asymptotic giant branch) stars and preplanetary nebulae, pro-planetary nebulae (from which planetary systems evolve), the comae of comets, and the atmospheres of dwarf stars and exoplanets, as well as on Earth in matter originating from interplanetary dust and other celestial bodies in our solar system, viz. meteorites of, essentially, asteroidal origin [7]. Table 1 provides an overview of vanadium abundances.

I will review here the – still sparse – present extent of knowledge of extraterrestrial vanadium species on the molecular and nano scale, and their potential in (i) catalyzing reactions which provide basic molecules necessary for assembling structures of higher complexity, and (ii) host and thus protect and further process "life molecules". I will further delineate the potential of specific vanadium-based systems to act as transport vehicles across hydrophilic–hydrophobic interfaces.

2. Vanadium in meteorites

Meteorites of asteroidal origin are of particular interest, because they represent material which has remained essentially unprocessed since our solar system formed by accretion out of a protoplanetary nebula 4.6 billion years ago. The protoplanetary nebula in turn did represent the remains of a collapsing interstellar gas and dust cloud, with dust particles of about the same composition as the inner planets (Mercury, Venus, Earth and Mars) and the asteroids, the larger ones of which are differentiated in a similar way as the inner planets, i.e. they have an iron (or iron–nickel) core, a rocky mantle dominated by silicate-based minerals, and a crust consisting of silicateous material or water ice, or a mixture of both. The main type of meteorites, about 94%, are stony meteorites (chondrites: 85%, achondrites: 9%) with a mineral composition reminiscent of terrestrial minerals. Overall vanadium contents in stony meteorites are of about the same order of magnitude as in Earth's crust (Table 1).

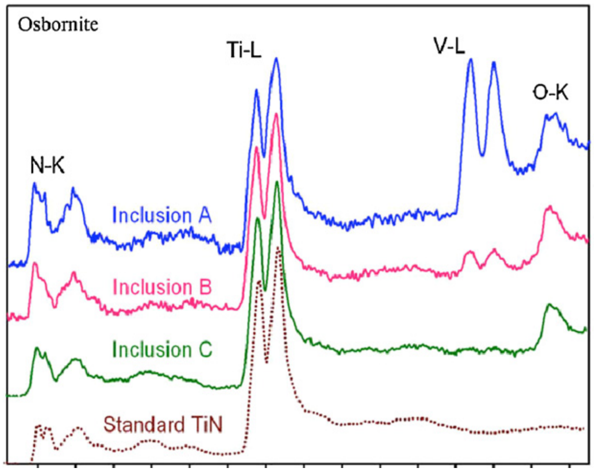


Fig. 1. Electron energy loss spectra (EELS) of 2–40 nm diameter vanadium-bearing osbornite inclusions in Inti. The titanium and vanadium L-edges exhibit two peaks (L_2 and L_3) due to spin-orbit coupling of the 3*p* levels. N–K and O–K are the nitrogen and oxygen K-edges, respectively. ©Elsevier; Fig. 3 in Ref. [12].

Examples for a vanadium bearing minerals in meteorites are pyroxenes. Pyroxenes have the general composition $M1M2T_2O_6$, where M1 is, e.g., Mg^{2+}, Ca^{2+}, Fe^{2+}, Mn^{2+} (in an octahedral environment), and T refers to Si^{IV} and Al^{III} in a tetrahedral environment. M2 can be represented by Ti^{4+} and V^{3+} in terrestrial (and lunar) pyroxenes. In refractory Ca- and Al-rich inclusions (CAI) present in carbonaceous chondrites (chondrites with up to 2–3% carbon-based compounds), up to two thirds of titanium and vanadium is present in the *low*-valent oxidation states Ti^{III} and V^{II} (with V^{2+} possibly at the M1 sites), indicating very reducing conditions accompanied by particularly low oxygen fugacities in the early solar nebula out of which these minerals accreted [8], and thus conditions which are comparable to a gas of solar composition. Divalent vanadium has also been detected, through X-ray absorption near edge structure spectroscopy (XANES) in meteoritic diopside ($CaMgSi_2O_6$), forsterite (Mg_2SiO_4) and enstatite ($MgSiO_3$), with Ca/Mg sites partially replaced by V^{2+} [9]. In contrast, vanadium in basaltic glasses in Martian meteorites is mainly in the oxidation states +III and +IV, while comparable lunar melts are dominated by V^{III}, and terrestrial melts by V^{IV} [10], reflecting the differing oxygen fugacities of the moon (no oxygen), Mars (very low oxygen) and Earth (high oxygen).

3. Vanadium in the coma of comet Wild 2

Comet Wild 2 [pronounce "vilt"] is a short period comet belonging to the Jupiter family which, as other comets, is believed to have been displaced from the Oort cloud some time ago. The Oort cloud represents the outer halo of our solar system at a distance of 1–2 light years, and is thought to be home of millions of chunks, objects consisting of ice and dust. Wild 2 became encountered by the Stardust mission, which started in 1999, picked up dust particles from the comet's coma in 2004, and shuttled back these samples to Earth in 2006. The last mission of Stardust – now termed NExT (for New Exploration of Temple) – a mission to the comet Temple 1. In a refractory CAI termed "Inti" (the god of the Sun and rainbows. in Incan mythology), the non-terrestrial mineral osbornite, has been terminated in March 2011. [11]. Osbornite, which also occurs in meteorites, is titanium nitride TiN. The osbornite in Inti contains varying amounts of vanadium, with compositions up to $Ti_{0.36}V_{0.63}N$, Fig. 1. The condensation of osbornite out of the nebular gas requires high temperatures and highly reducing conditions, suggesting the formation of this mineral relatively close to the protosun, followed by its transport, together with other refractory minerals, outward towards the comet-forming regions [12].

In interstellar clouds, vanadium nitride VN can form from (silica embedded) vanadium oxides and ammonia according to Eq. (1). VN in turn is active in ammonia decomposition [13]. Interstellar ammonia is readily available and forms in interstellar clouds in a cascade of ion-neutral reactions from N^+ and H_2 via NH_3^+ Eq. (2a), terminated by electron transfer to NH_3^+ from magnesium atoms, Eq. (2b). Vanadium oxide VO is a constituent in the atmospheres of, e.g., type M stars (vide infra), and can be generated, in interstellar gas media, in various ways by reaction between vanadium atoms and cationic oxygen species, Eq. (3a), or vanadium cations and oxygenic radicals, Eq. (3b). Contrasting the oxides of more abundant elements (FeO, AlO), molecular VO has not (yet) been detected in interstellar clouds, also because the main part of metal oxides becomes absorbed on dust particles. Further, water alteration of VN in dust grains can generate vanadium oxides, Eq. (4). Water ice is an integral constituent of comets, asteroids and sufficiently large (ca. 100 nm) interstellar dust grains, and can become “activated” (i.e. liquefied) as a comet or asteroidal fragment approaches the temperate, “habitable” zone around the sun, or – in interstellar dust grains – locally by bombardment with highly energetic cosmic rays. Vanadium nitride catalyzes the dehydrogenation of propane to propene, Eq. (5), and butane to C_4 olefins, and thus promotes the formation of building blocks for unsaturated fatty acids. Note that Eqs. (1) and (4) have been formulated non-stoichiometrically.

$$\{SiO_2{\cdot}VO_x\} + NH_3 \rightarrow \{SiO_2{\cdot}VN\} \tag{1}$$

$$N^+ + H_2 \rightarrow NH^+ + H;\ NH^+ + 2H_2 \rightarrow\rightarrow NH_3{}^+ + 2H \tag{2a}$$

$$NH_3{}^+ + Mg \rightarrow NH_3 + Mg^+ \tag{2b}$$

$$V + OH^+ \rightarrow VO^+ + H \tag{3a}$$

$$V^+ + HCO \rightarrow VO + CH^+ \tag{3b}$$

$$\{SiO_2{\cdot}VN\} + H_2O \rightarrow \{SiO_2{\cdot}VO_x\} + NH_3 \tag{4}$$

$$CH_3{-}CH_2{-}CH_3 \rightarrow CH_3{-}CH{=}CH_2 + H_2 \tag{5}$$

4. Vanadium oxide in dwarf stars and exoplanets

Dwarf stars of the early M category (also called red dwarfs) have a mass of less than 0.45 solar masses, and surface temperatures typically somewhat above 2000 K. In the atmosphere of these stars, TiO and VO are major constituents [14–16], detected by their optical spectra, Fig. 2. As temperatures drop below 1960 K, calcium titanates begin to condense out, and vanadium becomes absorbed to these condensates. Consequently, the less massive and hence cooler late M dwarfs and the L dwarfs (categories which are subsumed as brown dwarfs) do not show distinct atmospheric spectral features of VO.

Vanadium (and titanium) oxides have also been detected in the atmospheres of exoplanets belonging to the category “hot Jupiters” (pM exoplanets). Exoplanets, i.e. planets orbiting other suns than ours, are being discovered in increasing numbers. “Hot Jupiter” refers to an exoplanet which is about the size of Jupiter, but orbits its sun in a very narrow orbit and thus attains a pretty hot atmosphere. An example is the exoplanet “Osiris” (officially cataloged as HD 209458-b) in the constellation of Pegasus, with a mixing ratio for VO of 3×10^{-2} in the hot ($T > 1600$ K) stratospheric region ($\approx 10^3$ Pa) [17]. Below 1600 K, vanadium condenses into solid VO and then into V_2O_3. In addition, mixed oxides of composition $(Ti,V)O_2$ and $(V,Fe)O(OH)$, the equivalent of the terrestrial mineral montroseite, are responsible for the high optical opacities of these planets [18].

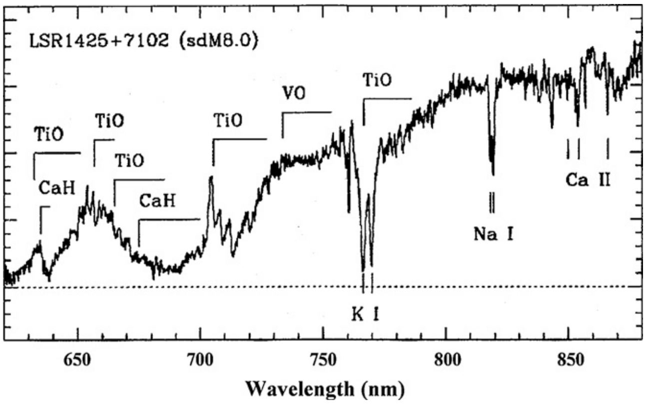


Fig. 2. Optical spectrum of the atmosphere of the M8 subdwarf (sd) of designation LSR1425 + 7102, showing, along with bands due to TiO and VO, those for CaH, K atoms (KI), Na atoms (NaI) and Ca^+ (CaII). ©American Astronomical Society; Fig. 2 in Ref. [14].

Vanadium oxides and oxidic vanadium ores, of whatever provenience, are redox catalysts for a variety of reactions also, under ambient conditions, for the genesis of molecules of potential biological relevance. Examples include the oxidation of butane to acetic acid, Eq. (6); ethanol formation by carbon dioxide fixation, Eq. (7); denitrification by symproportionation, Eq. (8); and ammonification of NO_x with concomitant formation of isocyanic acid which, in the presence of water, isomerizes and forms urea, Eq. (9).

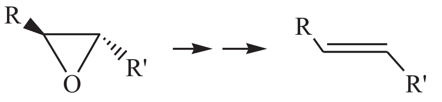
$$CH_3{-}CH_2{-}CH_2{-}CH_3 \rightarrow\rightarrow CH_3{-}CO_2H \tag{6}$$

$$CO_2 + H_2O \rightarrow\rightarrow CH_3{-}CH_2OH \tag{7}$$

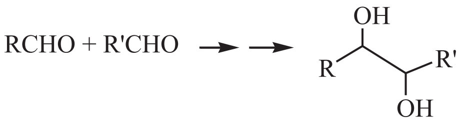
$$NO_x + NH_3 \rightarrow\rightarrow N_2 \tag{8}$$

$$NO_x + CO + H_2 \rightarrow\rightarrow NH_3 + HNCO[\leftrightarrows HOCN \rightarrow\rightarrow O{=}C(NH_2)_2] \tag{9}$$

Other reactions catalyzed by low-valent vanadium compounds include the deoxygenation of epoxides to olefins, Eq. (10) [19], and reductive coupling of, e.g., aldehydes, Eq. (11) [20]. An epoxide, viz. ethylene oxide, has been detected in interstellar clouds; and the simplest aldehyde, formaldehyde, is a major interstellar molecular species.



(10)



(11)

5. Vanadium oxide based protective and transport systems

Further aggregation of vanadium oxides can yield cage structures such as realized in the mixed polyoxidovanadate–molybdate, constituting a $\{V_{30}Mo_{72}O_{547}\}^{n-}$ hollow cluster [21], or VO_x nano tubes [22], or structures reminiscent of honey combs [23], which may be referred to as protocells or pseudo-cells, because they provide a large and reactive surface area as well as protective pockets, protective for molecules synthesized and assembled on the reactive surface. To what extent these structure elements, based on oligomeric and polymeric $(VO_x)_n$ units, are actually available as reactive species (in the sense of Reactions (6)–(11)) in extraterrestrial specimens and terrestrial objects of extraterrestrial origin remains to be explored.

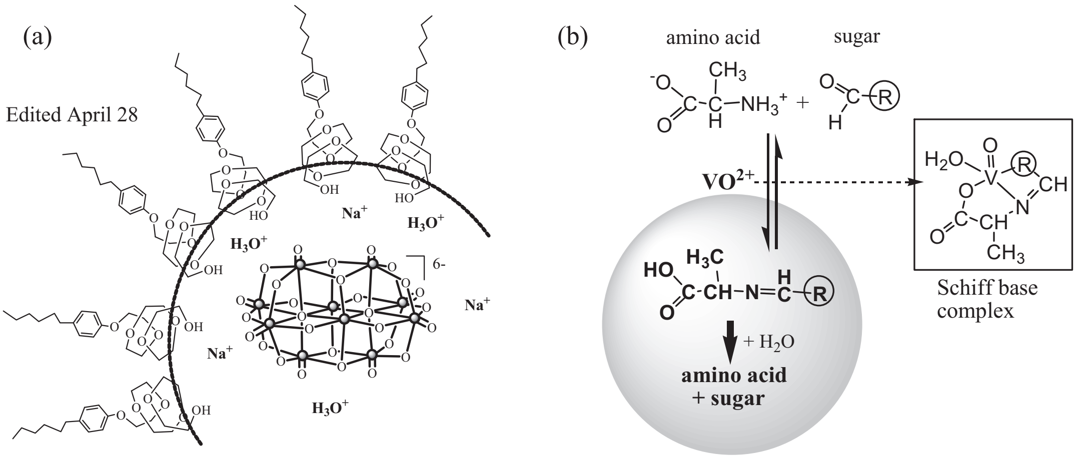
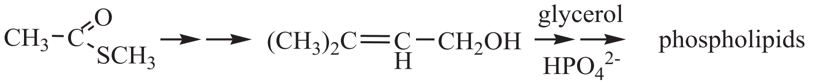


Fig. 3. (a) A section of a reverse micelle as a model of a protocell, having incorporated $V_{10}O_{28}{}^{6-}$ in a nano-sized water droplet within the micelle. The micellar membrane consists of alkylbenzene moieties linked to polyglycol via ester bonds. Modified from Ref. [27]. (b) Mediation of the transport of biomolecules by VO^{2+} into a lipid vesicle. Modified from Ref. [28]. Ms. no. CCR-D-11-00027R1 (D. Rehder).

The formation of fatty acids and alcohols, and the glycerol esters and ethers thereof, hence lipids, in primordial scenarios affords, as an initiating step, the formation of “activated acetic acid”, i.e. the methyl ester of thioacetic acid, $CH_3C(O)SCH_3$. This molecule can form by reductive coupling of CH_3SH and CO_2 [24], Eq. (12). Both molecules have been available in the primordial soup, and their reductive coupling can be promoted, at least on principal, in VO_x matrices with vanadium in a low valent state, acting both as a catalyst and electron source and, in addition, as a scavenger for sulfide. Condensation, reduction and decarboxylation of active acetic acid provides dimethylallyl alcohol which, by condensation with glycerol (which on its part is generated by condensation of formaldehyde) and in the presence of phosphate yields phospholipids (see, e.g. ch. 7.4 in Ref. [7]), Eq. (13), and hence one of the life molecules employed in the membrane of archaea. For a feasible role of VN as a catalyst in the formation of precursor compounds for unsaturated fatty acids see Eq. (5) in Section 3.

$$2CH_3SH + CO_2 + 2e^- + H^+ \rightarrow CH_3C(O)SCH_3 + HS^- + H_2O \qquad (12)$$



$$CH_3{-}C{\overset{O}{\underset{SCH_3}{}}} \longrightarrow\longrightarrow (CH_3)_2C{=}\underset{H}{C}{-}CH_2OH \xrightarrow[HPO_4^{2-}]{glycerol} \text{phospholipids} \qquad (13)$$

The reaction represented by Eq. (12) can be powered by troilite FeS, which provides the reduction equivalents ($2S^{2-} \rightarrow S_2{}^{2-} + 2e^-$) to form pyrite FeS_2. A similar role may be taken over by vanadium sulfides: vanadium becomes enriched in meteoritic sulfide phases such as troilite [25], and may end up as patronite $V(S_2)_2$. The recently demonstrated ability of vanadium nitrogenase, which contains the sulfidic cofactor cluster $\{VFe_7S_9\}$ at its reactive center, to reduce carbon monoxide to ethene and ethane [26] (and thus mimicking Fischer–Tropsch syntheses) points into the same direction.

Cellular membranes can be modelled, to some extent, by micelles and reverse micelles. Once micelles and/or reverse micelles are available, they can interact with “particulate vanadium oxide”, such as the polyoxidovanadate clusters and cages mentioned above, or anionic decavanadate $H_nV_{10}O_{28}{}^{(6-n)-}$ ($n = 0$–3) [4,27], Fig. 3(a). Also of interest in this context is a potential primordial transport system for sugars and amino acids, based on oxidovanadium(IV) (vanadyl, VO^{2+}) as transport system, and a lipid vesicle as protocell. These systems have already been proposed by Stillwell and Rau thirty years ago [28]. The transport process is based on the vanadyl ion acting as a template for the formation of a Schiff base from an amine (such as an amino acid) and an aldehyde (such as an aldose sugar). Schiff base complexes of VO^{2+} are very common, see Ref. [29] for recent examples, and there are many examples where Schiff bases form *in situ* in the present of VO^{2+}. Contrasting the three single components of the Schiff base complex, viz. VO^{2+}, the amine, and the aldehyde, the complex entity itself is sufficiently lipophilic to overcome the membrane of the lipid vesicle. Once inside the protocell, the Schiff base can be taken apart by hydrolysis, and the components – sugar and amino acid – may subsequently undergo polymerization (catalyzed by a primitive polymerase) or consecutive chemistry promoted by, inter alia, VO^{2+}.

6. Conclusion

Certain prokarya can employ vanadium, as a constituent of a vanadium–iron–sulfur cluster, in nitrogen fixation or, in the form of vanadate(V), as an electron acceptor in respiration. Histidyl-vanadate(V) is an essential cofactor (of haloperoxidases) for several genera of phylogenetically early organisms such as algae, fungi and lichen. Vanadium is further present, in the form of hydrated V^{3+} and protein-bound VO^{2+}, in many ascidians, hence in highly developed marine organisms, classified as protochordata (or urochordata). Finally, trace amounts of vanadate $H_2VO_4{}^-$ likely intervene with the phosphate metabolism in all living beings, including humans. This global bio-presence of vanadium leads over to questions such as: (i) to what extent is vanadium essential for life on a whole, and (ii) has vanadium been involved in the generation of pre-life forms, and in the development of early life forms, either directly (incorporation of vanadium as a bio-metal) or indirectly by resorting to (mineralized) vanadium. In the latter case, vanadium compounds have presumably been involved in the catalytically conducted generation of bio-molecules, and/or as transport vehicles, and/or as reaction vessels and shelters for reactants and further processing of reactants. The two latter aspects have been extemporized in Section 5.

If vanadium took over a role in the development of primitive life on our planet (and, perhaps, in extraterrestrial habitats as well), it should be kept in mind that the specific conditions were primarily reducing on the primordial Earth (and other potentially suitable celestial bodies), i.e. about 4 billion years ago, and up the to "Great Oxygen Event" 2.4 billion years ago. Consequently, low-valent vanadium compounds – sulfides, oxides and nitrides – will have triggered chemical processes. These simple compounds will have been available on our planet. They are still being supplied from extraterrestrial sources, mainly by meteorites and interplanetary dust, and hence from the essentially unaltered remains of a time, 4.6 billion years ago, when our solar system formed by accretion after the collapse of an interstellar gas and dust cloud, furnishing VN, VO and VS. VN and VO have been detected as constituents in meteoritic minerals and cometary dust particles; Sections 2 and 3. However their presence is not restricted, at least as far as vanadium oxide is concerned, to our planetary system: as outlined in Section 4, VO and V_2O_3 are also common in the atmospheres of exoplanets.

So far, information on vanadium species in extraterrestrial material is still sparse, but hopefully will increasingly enter into the focus of research as the knowledge on vanadium's role in the generation of life molecules, and Life on the whole, spreads and progresses.

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