Vanadium in Live Aspects

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In Earth's regions accessible for living organisms (Earth's crust, crude oil, water sanctuaries and lower atmosphere), vanadium is present in the oxidation states +III and—essentially—+IV (cationic) and +V (cationic and anionic), with the redox interchange and biochemical recycling often monitored by bacteria. Organisms having available vanadium-containing (bio)molecules with essential functions for life include marine brown algae (haloperoxidases), ascidians and fan worms, as well as terrestrial organisms, viz., nitrogen-fixing bacteria (associated with the roots of legumes), and the fly agaric mushroom.

halide oxidation   dinitrogen reduction   marine organisms

1. Introduction

On Earth, the crustal abundance of vanadium (0.019%; 20th most abundant element) compares to that of zinc; however, vanadium is more dispersed than Zn. The common redox states in the minerals of the Earth's crust are +V, +IV and +III [1]. Crude oil (asphaltenes) can obtain up to 5 g V per litre; the high concentrations here originate from the coordinative incorporation of vanadium (VO^{2+}) into, essentially, porphinogens. The main sources of atmospheric vanadium are marine aerosols and continental dust originating from geological processes, and due to anthropogenic input, including emissions—VO_2, V_2O_5 and vanadium carbide—from combustion engines. In aqueous media, such as seawater, lakes and rivers, vanadium is present as $H_2VO_4^-$/HVO_4^{2-} (depending on the pH); common average concentrations in marine environments (pH~7; where the dominant species is $H_2VO_4^-$ (and $HV_2O_7^{3-}$ at higher concentrations)) amount to 1.8 µg/L, in rivers to 0.7 µg/L. The average amount of vanadium in sediments is 150 mg/kg [2]. In mining areas, vanadium concentrations in aqueous environments can go up by a factor of 10^6. In human blood plasma, vanadium concentrations are higher by a factor of ~10 with respect to seawater, pointing towards a (possibly essential) role of vanadium in life: In living organisms, vanadate $H_2VO_4^-$ acts as an antagonist/competitor/enhancer of phosphate but tends to be toxic at non-physiological concentrations. Vanadate also forms binary and ternary compounds with carbonate, viz., $HVO_3CO_3^{2-}$ and $VO_2(CO_3)_2^{3-}$, with $\log K$ values of 1.09 and 0.17, respectively. At higher concentrations, oligomers such as the dimeric $V_2O_7^{4-}$ can form; reducing conditions are responsible for the generation of $V^{IV}O^{2+}\cdot aq$ (which precipitates to form $VO(OH)_2$ or remains dissolved due to coordination to (organic) substrates) and $V^{III}\cdot aq$ (present in, e.g., ascidians). The redox interconversion of vanadium ($V^V \leftrightarrow V^{IV} \leftrightarrow V^{III}$) in a natural environment is often monitored or exerted by specialised bacteria, such as *Pseudomonas vanadiumreducens*.

Besides various strains of bacteria, several multicellular organisms resort to vanadium as an essential element, the latter occasionally also in cooperation with bacteria. Noteworthy among these higher organisms are ascidians,

marine brown algae and certain mosses, amavadin in *Amanita* mushrooms and the nodules in the roots of legumes.

2. Vanadium in Haloperoxidases, Nitrogenases, Amanita Mushrooms, Ascidians and Fan Worms

Along with the potentiality of vanadium in many catalytic applications carried out in the frame of industrial processes (examples are oxidation reactions, carbon–carbon bond formation, hydrogenation and dehydrogenation and cyanation [3]), the role of vanadium in naturally occurring catalytic processes is noteworthy. These functions include the oxidation of halides catalysed by haloperoxidases (particularly in seawater estuaries) on the one hand, and the reductive conversion of aerial dinitrogen into ammonia/ammonium ions (and hence nitrogen in a form utilisable in bio-physiological processes), catalysed by nitrogenases on the other hand. An additional naturally occurring vanadium compound is amavadin, present in the fly agaric mushroom.

Specific brown and red algae, fungi and bacteria—such as the marine brown alga *Ascophyllum nodosum*, the marine flavobacterium *Zobiella galactanivorans* [4] and the cyanobacterium *Synechocosccus* (associated with macroalgae and specialised in the oxidation of iodide)—can have available *vanadate*-dependent haloperoxidases, one of the six known families of halogenating enzymes [5]. Actually, the VHPOs apparently derive from a species closely related to bacterial acid phosphatase [4], well in agreement with the structural similarity between phosphate and vanadate, and the competitive/comparable behaviour of these two anions in life processes. Iodide, bromide, chloride and cyanide may be subject to oxidation to hypohalite/hypohalous acid and cyanate, respectively. The halide specificity essentially reflects differences in hydrogen-bonding interaction between the active centre and the extended (second) coordination sphere. The oxidising agent commonly is H_2O_2/peroxide. Hypohalite in turn is involved in the biosynthesis of halogenated organic compounds, such as bromoform, which is released into the atmosphere. **Figure 1** (left) shows the active centre of the vanadate-dependent iodo/bromoperoxidase of the marine brown alga *Ascophyllum nodosum* (**Figure 1**, right) from which this enzyme had been originally isolated [6] and characterised with respect to its reactivity [7]. The active centres of the enzyme present in other algal and bacterial species are essentially identical, i.e., they only differ in the second sphere amino acid surroundings of the central penta-coordinated {VO(OH)(O⁻)His} unit, and in H-bonding interaction between the first and the second coordination sphere. In summary, halogenases are involved in the oxidation of halides (to hypohalous acids) and, in such a way, in the halogenation of organic compounds and the oxidative elimination of (invasive) bacteria via the intermediate formation of reactive oxygen species [8].
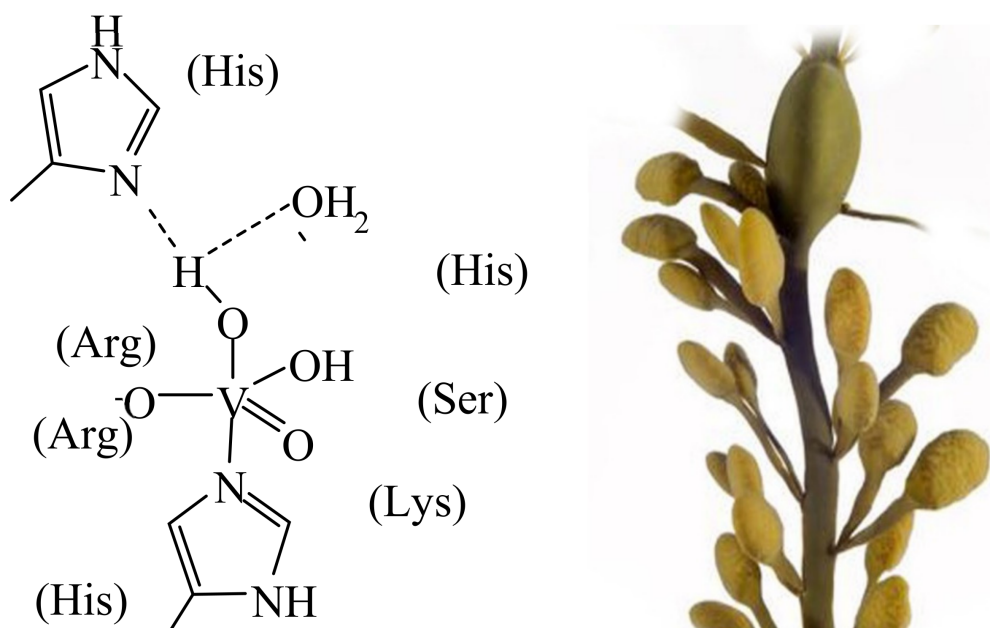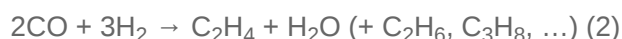
Figure 1. The active centre (schematised (**left**)) of vanadate-dependent, bromo/iodoperoxidases present in the brown alga *Ascophyllum nodosum* (**right**).

A second vanadium-based enzyme is the vanadium nitrogenase VNase (**Figure 2**), which—along with the more prominent molybdenum variant and an additional "alternative" nitrogenase based on iron only—is present in nitrogen-fixing (soil) bacteria, such as the obligate anaerobic *Azotobacter vinelandii* [9], facultative anaerobes (e.g., *Klebsiella oxytoca*) [9] and the cyanobacterium *Anabaena variabilis* [10]; VNase can also be expressed in, e.g., symbionts of lichens [11]. In all of these diazotrophic organisms, V-Nases are predominantly activated under conditions of Mo limitation. The bacterium *Rhodopseudomonas palustris*, present—inter alia—in marine coastal sediments, has available all three (Mo, V and Fe-only) nitrogenases. Most N_2-fixing bacteria are obligatory anaerobes. The dominant function of this enzyme is the reductive conversion of inert dinitrogen to ammonium ions, Equation (1), thus making nitrogen accessible for (alimentary) utilisation by plants. The energy afforded for this reductive process, required to overcome a high activation energy barrier, is provided by adenosine triphosphate, ATP. The reduction of N_2 progresses via HN=NH and H_2N-NH_2. In the absence of N_2, H_2 is generated. Other substrates, such as carbon monoxide, are equally reduced, eventually forming alkenes and alkanes, Equation (2) [12]. Furthermore, CO_2 can be reduced to CH_4, Equation (3) [13].

$$N_2 + 8H^+ + 6e^- \rightarrow 2NH_4^+ \text{ (1)}$$

$$\text{(powered by: MgATP} + H^+ \rightleftharpoons \text{MgADP} + HPO_4^{2-})$$

$$2CO + 3H_2 \rightarrow C_2H_4 + H_2O \text{ (+ } C_2H_6, C_3H_8, \ldots) \text{ (2)}$$

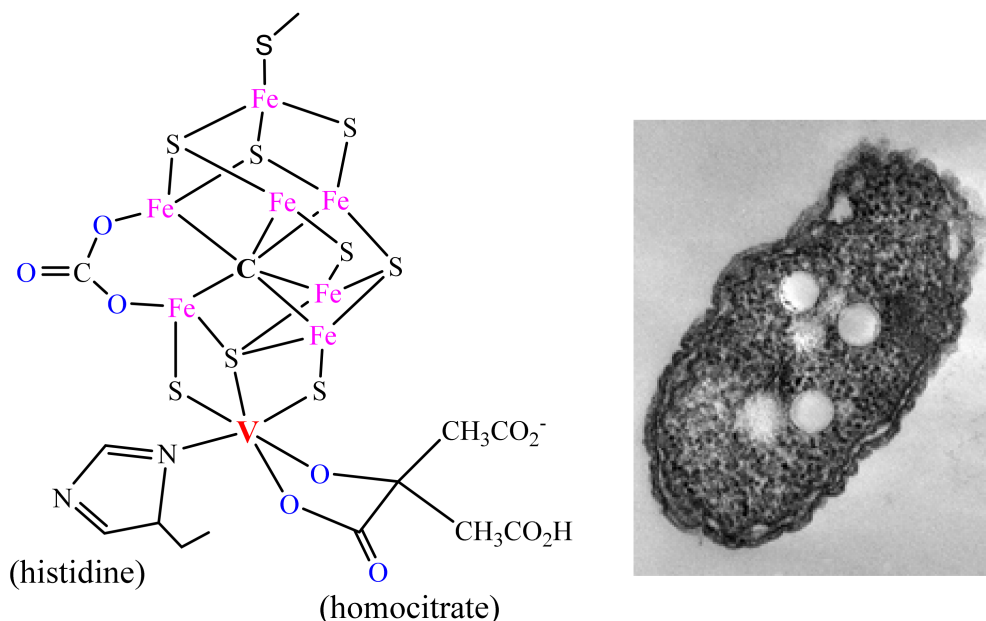$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \text{ (3)}$$

Figure 2. The active centre of vanadium nitrogenase and the soil bacterium *Azotobacter vinelandii*.

The fly agaric mushroom *Amanita muscaria* (**Figure 3**) accumulates vanadium at concentrations of up to several hundred mg kg^{-1} dry mass [14], with a maximum concentration found in the bulb. Other species of the genus *Amanita* can also store vanadium; examples are *A. regalis* and *A. velatipes*. Vanadium is present as the non-oxido V(IV) coordination compound amavadin (**Figure 3**) in the Λ and Δ isomeric forms. Its biological function has so far not yet been established with certainty. Due to the reversible oxidation/reduction ($V^{IV} \leftrightarrows V^{V} + e^{-}$), a role for amavadin as a redox catalyst is assumed: Amavadin homologues have been shown to mediate the reduction of NO_2^{-} to N_2O and the oxidation of water to O_2 [15].
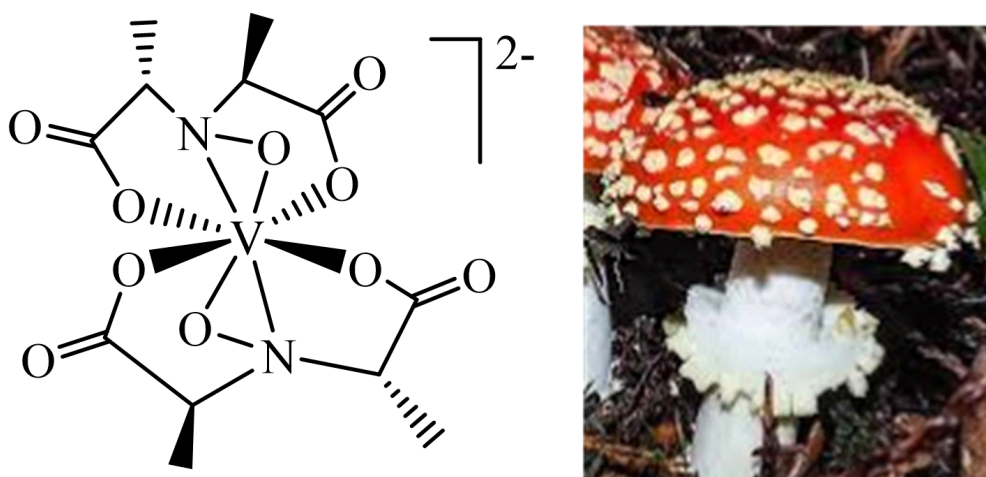

Figure 3. Amavadin present in the fly agaric (*Amanita muscaria*).

Sea dwellers such as ascidians (e.g., *Ascidia sydneiensis samea*) and polychaeta fan worms (*Pseudopotamilla* [16], *Perkinsiana* [17]) accumulate vanadium from seawater. The fan worm *P. occelata* (**Figure 4**, left) contains vanadium bound to a nucleoside diphosphate kinase homolog, located in the epidermis of the branchial crown. The function

of vanadium may be associated with the suppression of the activity of a kinase by V^{IV} (VO^{2+}); the kinase otherwise remains unaffected by V^V ($H_2VO_4^-$) [16].
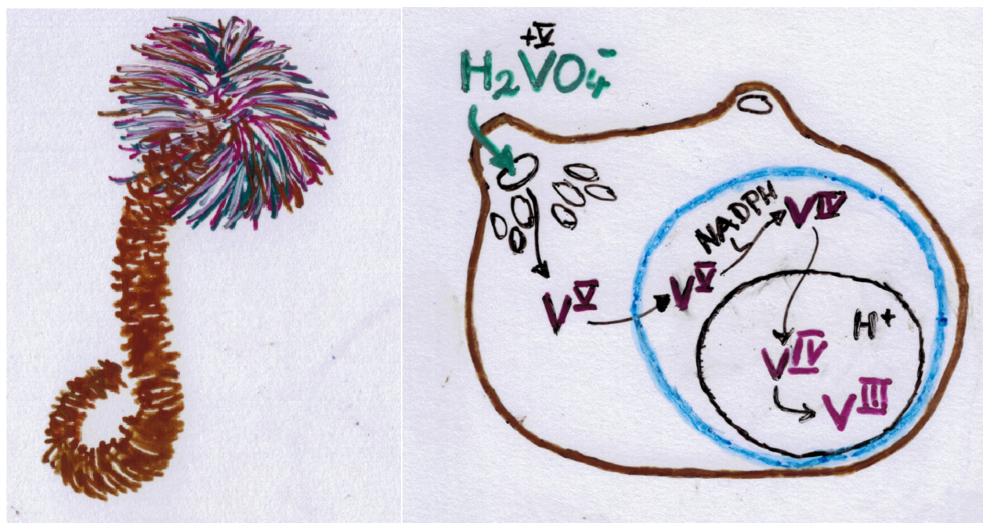

Figure 4. The fan worm *Pseudopotamilla occelata* (**left**) and the sea squirt *Ascidia sydneiensis* (**right**), the latter with the branchial crown at the upper left.

Ascidians (also known as tunicates or sea squirts) such as *Ascidia gemmata* [17] and *A. sydneiensis samea* [18] accumulate vanadium in blood cells (the so-called vanadocytes; **Figure 4**, right). The actual vanadium concentration amounts to 350 mM, hence 10^7 times that of vanadium ($H_2VO_4^-$) in seawater. Bacterial genera (*Pseudomonas* and *Ralstonia*) in the branchial sac of the ascidia, and *Treponema* and *Borelia* in the intestinal content, appear to contribute to vanadium accumulation by absorption of vanadium through the epithelium of the branchial sac and reduction of vanadate to oxidovanadium(IV) and V^{3+} [19], the latter being stored in the cytoplasm and vacuoles termed vanadocytes. Vanadium is thus also involved in the redox interconversion of disulphide/dithiolate. In its non-oxido +IV state, vanadium binds to proteins rich in cysteine residues, referred to as vanabins. Vanabins can differ in the number of amino acids. For a biomimetic system modelling the reduction of vanadate (V) and coordination of non-oxido-V^{IV} to vanabin, see ref. [20].

3. Bacterial Issues

Matters concerning bacteria have already briefly been mentioned in ch. 3 in the context of N_2 fixation (see also cyanobacteria in rice fields [21]), haloperoxidases, amanita mushrooms and ascidians. Other bacterial activities aiming at redox interconversion (essentially reduction of vanadium(V)) concern several strains of bacteria—belonging to the eucarya—that are able to reduce vanadate $H_2VO_4^-$ to oxidovanadium(IV) VO^{2+} (which commonly precipitates in the form of $VO(OH)_2$) and thus can contribute to the removal of vanadate(V) from drinking water. Vanadate—being a phosphate antagonist—is toxic at higher, non-physiological concentrations. Examples of these bacteria are *Pseudomonas vanadiumreductans*, *Shewanella oneidensis*, *Geobacter metallireducens* and *Saccharomyces cerevisiae* [22]. Reduction of vanadate to VO^{2+} can also be achieved by *mesophilic* bacteria (an archaeal bacterial strain) such as *Methanosarcina mazei*, which is active at 37 °C, and the thermophile

Methanothermobacter termautropicus, which is thriving at an optimum temperature of 65 °C [23] and further—at concentrations < 5 mM, by *Thiobacillus thiooxidans* [21]. This bio-reduction of V^V to V^{IV} ($VO(OH)_2\downarrow$) in a special anoxic growth medium inhibits methanogenesis (CO_2/acetate → → CH_4, the reductant usually is H_2), the otherwise common domain of activity for these bacteria.

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