A Role for Vanadium in Ascidians and in Marine Algae

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INTRODUCTION

Vanadium is – next to molybdenum – the second-to-most abundant transition metal in sea water. Oxygenated sea water commonly contains 24-45 µM of vanadate H$_2$VO$_4^-$ (and is thus – next to molybdenum - the second-to-most abundant transition metal in sea water) with the levels mainly fluctuating with the season. Depletion by about 60% can occur as reduction to VO$^2+$ takes place which forms a sparingly soluble hydroxide, VO(OH)$_2$, that is readily absorbed by particulate organic matter [1]. Consequently, the factors influencing the occurrence of vanadium are redox conditions (such as dissolved O$_2$ and Fe$^{2+}$, the presence of NH$_3$ and S$^{2-}$), and – of course – its uptake by marine organisms. Vanadate is mainly taken up by marine algae, the most prominent one being knotted wrack (also known as rockweed) Asphodelium nodosum, (Figure 1), by ascidians and, to some extent, also by some Polychaeta fan worms [2]. The significance of vanadium as an essential element in these organisms will be addressed.

VANADIUM IN ASCIDIANS

In 1911, Henze discovered vanadium in the blood cells (the coelomic cells; singlet ring cells and vacuolated amoebocytes) of the Mediterranean sea-squirt (ascidian) Phallusia mammillata [3]. The vanadium compound present in these cells actually is hydrated vanadium in the oxidation states of (predominantly) high-spin +III, such as V$^{n+}$(H$_2$O)$_n$; the counter ion commonly is H$_2$SO$_4^-$ (Scheme 1) [4]. In addition, vanadium accumulating ascidians dispose of an enhanced capacity to metabolize glucose-6 phosphate (G6P); the activity of G6P-dehydrogenase is markedly elevated when compared to ascidians with low accumulation rates [5]. The intermittently formed VO$^2+$ binds to the lysine NH$_2$ residues of the vanabins. Vanabins are lysine-rich polypeptides of about 10 thousand kDa, attaining a bow-shaped conformation, with four α-helices connected by nine disulfide bonds [6-8].

Figure 1: Examples for algae that produce hypohalous acids: Left Corallina officinalis, right Asphodelium nodosum, the alga where the vanadate-dependent haloperoxidase was originally characterized by Vilter in 1983.

Scheme 1: (a) The step-wise reduction of vanadate (V) to vanadium (III). Cysteine-rich proteins (associated with the oligopeptide vanabin2) are involved in this process. (b) Section of vanabin2, illustrating the binding of VO$^2+$ to a lysine residue.

The amount of vanadium accumulated by ascidians strongly differs. An extraordinary degree of vanadium – up to 350 mM and hence the about 10$^7$ fold of vanadate in sea water (~35 nM) - can be absorbed. In the intestinal lumen, the concentration can reach 0.7 mM. This particularly effective accumulation of vanadium, occurring in the greater part of the ascidians, apparently is supported by bacterial genera such as Pseudomonas and Ralstonia (in the tissues of the branchial sacs of the ascidians), and Treponema and Borellia (in the intestines) [9-12] – a fact which is in line with the general ability of certain strains of bacteria from deep-sea hydrothermal vents (such as Pseudomonas vanadium-reductans) that reduce vanadate to vanadium in the +IV (and +III) state, using lactate as electron donor [13].
VANADIUM IN MARINE ALGAE

Several species of macro-algae in the marine environment (Figure 2) are able to catalyze the oxidation of the halide X⁻ (X⁻ = I⁻, Br⁻, Cl⁻) to hypohalous acid [14-17], as exemplified for the bromide oxidation in eqn. (1). The oxidant employed by these algae is hydroperoxide (H₂O₂, HO₂⁻); the oxidation is supported by heme-oxidation in eqn. (1). The oxidant employed by these algae is hydroperoxide (H₂O₂, HO₂⁻); the oxidation is supported by heme-oxidation in eqn. (1).

The several steps of this sequence are shown in Figure 4.

During turnover, the VHPOs are self-supporting in the sense that they only marginally change their coordination environment. In the course of the reaction, a peroxido intermediate is formed, in which the trigonal-bipyramidal arrangement at the vanadium centre is essentially retained. H₂O docks to the vanadium centre as hydroperoxide in a monodentate fashion, followed by the releases of one or two proton to form a η²-peroxido and/or -hydro-peroxido intermediate. This intermediate undergoes a nucleophilic attack by the substrate, such as bromide, and finally releases hypobromous acid. The several steps of this sequence are shown in Figure 4.

REFERENCES

1. Wang D, Wilhelmy SSA. Vanadium speciation and cycling in coastal waters. Marine Chem. 2009;117(1-4):52-58.
2. Fattorini D, Notti A, Nigro M, Regoli F. Hyperaccumulation of vanadium in the Antarctic Polychaeta Perkinsiana littoralis as a natural chemical defense against predation. Environ Sci Pollut Res Int. 2010;17(1):220-228.
3. Henze M. Untersuchungen über das Blut der Ascidien. I. Mitteilung. Die Vanadiumverbindung der Blutkörperchen. J Physiol Chem. 2011;72:494-450.
4. Hamada T, Asanuma M, Ueki T, Hayashi F, Kobayashi N. Solution Structure of Vanabin2, a Vanadium(IV)-Binding Protein from the Vanadium-Rich Ascidian Ascidia sydneiensis samea. J Am Chem Soc. 2005;127:4216-4222.
5. Treberg JR, Stacey JE, Driedzic WR. Vanadium accumulation in ascidian coelomic cells is associated with enhanced pentose phosphate pathway capacity but not overall aerobic or anaerobic metabolism. Comp Biochem Physiol B Biochem Mol Biol. 2012;161:323-330.
6. Yamamoto S, Matsuo K, Michibata M, Ueki T. The role of cystein residues in the V(V)-reductase of Vanabin2. Inorg Chim Acta. 2014;420:47-52.
7. Triveda S, Ueki T, Yamaguchi N, Michibata H. Novel vanadium binding proteins (vanabins) identified in c-DNA libraries and the genome of the ascidia Ciona intestinalis. Biochim Biophys Acta. 2003;1630(2-3):64-70.
8. Fukuzuki K, Ueki T, Ohyama H, Michibata H. Vanadium-Binding Protein in a Vanadium-Rich Ascidian Ascidia sydneiensis samea: CW and Pulsed EPR Studies. J Am Chem Soc. 2003;125:6352-6353.
9. Michibata H. The mechanism of accumulation of vanadium by ascidians: some progress towards an understanding of this unusual phenomenon. Zool Sci. 1996;13:489-502.
10. Michibata H, Ueki T. Advances in research on the accumulation, redox behavior, and the function of vanadium in ascidians. BioMol Concepts. 2010;1:97-107.

11. Carpentier W, DeSmet L, Van Beeumen J, Brigé A. Respiration and growth of Shewanella oneidensis MR.1 using vanadate as the sole electron acceptor. J Bacteriol. 2005;187:3293-3301.

12. Ueki T, Fujie M, Romaidi, Satoh N. Symbiotic bacteria associated with ascidian vanadium accumulation identified by 16S rRNA amplicon sequencing. Mar Genom. 2019;43:33-42.

13. Csotonyi JT, Stackebrandt E, Yurkov V. Anaerobic respiration on tellurate and other metalloids in bacteria from hydrothermal vent fields in the Eastern Pacific Ocean. Appl Environ Microbiol. 2006;72(7):4950-4956.

14. Weyand M, Hecht HJ, Kiess M, Liaud MF, Vilter H. X-ray structure determination of a vanadium-dependent haloperoxidase from Ascophyllum nodosum at 2.0 Å resolution. J Mol Biol. 1999;293(3):595-611.

15. Leblanc C, Vilter H, Fournier J, Delage L, Potin P. Vanadium haloperoxidases: From the discovery 30 years ago to X-ray crystallographic and V K-edge absorption spectroscopic studies. Coord Chem Rev. 2015;301-302:134-146.

16. Wever R, Krenn, BE, Renirie R. Marine vanadium-dependent haloperoxidases, their isolation, characterization and application. Methods Enzymolog. 2018;605:141-201.

17. McLauchlan CC, Murakami HA, Wallace CA, Crans DC. Coordination environment changes of the vanadium-dependent haloperoxidase enzymes. J Inorg Biochem. 2018;186:267-279.

18. Diethelm S, Teufel R, Kaysser L, Moore BS. One-pot enzymatic synthesis of merochlorin A and B - NCBI - NIH Angew. Chem Int Ed. 2014;53:11203-11206.

19. Johnson TL, Brahamsha B, Palenik B, Mühle J. Global biochemical cycle of vanadium Limnol. Oceanogr. 2015;60:1823-1835.

20. Vilter H, Glombitza KW, Grave A. Peroxidases from phaeophyceae: A vanadium(V)-dependent peroxidase from Ascophyllum nodosum. Bot Mar. 1983;26:331-340.

21. Wever R, Barnett P. Vanadium chloroperoxidases: The missing link in the formation of chlorinated compounds and chloroform in the terrestrial environment? Chem Asian J. 2017;12:1997-2007.