Vanadium in Biology: Accumulation Mechamism in Ascidians

Hitoshi Michibata[1], Tatsuya Ueki[1], Nobuo Yamaguchi[2], Koichi Fukui[3], Toshiyuki Hamada[4], Miwako Asanuma[4] and Hiroshi Hirota[4]

[1]Department of Biological Science and [2]Marine Biological Laboratory, Graduate School of Science, Hiroshima University, Higashi-Hiroshima, [3]Department of Chemistry, Faculty of Science and Engineering, Waseda University,Tokyo and [4]RIKEN Genomic Sciences Center, Protein Research Group, Yokohama, Japan

Ascidians, so-called sea squirts, are well known to contain high levels of vanadium. In remarkable cases, the concentration of cellular vanadium reaches 350 mM, corresponding to about 10^7 times the concentration of seawater. Vanadium accumulated in the ascidians is reduced to the +3 oxidation state via the +4 oxidation state and stored in vacuoles of vanadocytes (1). From the vanadocytes of a vanadium-rich ascidian, *Ascidia sydneiensis samea*, we isolated some vanadium binding proteins, designated as Vanabin. Recently, we identified five types of Vanabin, Vanabin1, Vanabin2, Vanabin3, Vanabin4 and VanabinP that are likely to be involved in vanadium accumulation processes as so-called metallochaperone. Among them, recombinant proteins of Vanabin1 and Vanabin2 bound to 10 and 20 vanadium(IV) ions with dissociation constants of 2.1×10^{-5} M and 2.3×10^{-5} M, respectively (2). Multi-dimensional NMR experiments have revealed the first 3D structure of Vanabin2 in an aqueous solution which shows novel bow-shaped conformation, with four α-helices connected by nine disulfide bonds (3). There are no structural homologues reported so far. The ^{15}N HSQC perturbation experiments of Vanabin2 indicated that vanadyl cations, which are exclusively localized on the same face of the molecule, are coordinated by amine nitrogens derived from amino acid residues such as lysines, arginines, and histidines, as suggested by the EPR results (4). Recently, glutathione S-transferase (GST), known to protect organisms against oxidative stress induced by heavy metals, was extracted from digestive organs of a vanadium-rich ascidian. Recombinant protein of ascidian GST was found to bind with vanadium(IV). A significance of the vanadium-binding property is under investigation.

Ref.: (1) Michibata, H. *et al.*, (2003) Coord. Chem. Rev., 237, 41-51. (2) Ueki, T. *et al.*, (2003) Biochim. Biophys. Acta, 1626, 43-50. (3) Hamada, T. *et al.*, (2005) J. Am Chem. Soc., 127(12):4216-4222. (4) Fukui, K. *et al.*, (2003) J. Am Chem. Soc., 125, 6352-6353.