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Transition metal related redox processes in the metabolic reactions of living system

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Abstract: Natural development of chemicals and elements challenged organisms to adapt or die. Current organisms require redox reactions to induce metabolism and other life processes. Metals have a tendency to lose electrons and are important for redox reactions. Metals have become so central to cellular function that the collection of metal-binding proteins (referred to as the metallomes) accounts for over 30% of all proteins in the cell. Metals are known to be involved in over 40% of enzymatic reactions, and metal-binding proteins carry out at least one step in almost all biological pathways.¹

Key words: Transition metal, molybdenum, metalloproteins, superoxide dismutase (SOD) enzyme.

INTRODUCTION

Metals are also toxic so a balance must be acquired to regulate where the metals are in an organism as well as in what quantities.² Many organisms have flexible systems in which they can exchange one metal for another if one is scarce. Metals in this discussion are naturally occurring elements that have a tendency to undergo oxidation. Vanadium, molybdenum, cobalt, copper, chromium, iron, manganese, nickel, and zinc are deemed essential because without them biological function is impaired.

Tungsten

Tungsten is one of the oldest metal ions to be incorporated in biological systems, preceding The Great Oxygenation Event. Before the abundance of oxygen in Earth's atmosphere, oceans teemed with sulfur and tungsten, while molybdenum, a metal that is highly similar chemically, was inaccessible in solid form. The abundance of tungsten and lack of free molybdenum likely explains

why early marine organisms incorporated the former instead of the latter. However, as cyanobacteria began to fill the atmosphere with oxygen, molybdenum became available (molybdenum becomes soluble when exposed to oxygen) and molybdenum began to replace tungsten in the majority of metabolic processes, which is seen today, as tungsten is only present in the biological complexes of prokaryotes (methanogens, gram-positive bacteria, gram-negative aerobes and anaerobes), and is only obligated in hyperthermophilic archaea such as *P. furiosus*. Tungsten's extremely high melting point (3,422°C), partially explains its necessity in these archaea, found in extremely hot areas.³

Molybdenum

Molybdenum (Mo) is the most abundant transition element in solution in the sea (mostly as dianionic molybdate ion) and in living organisms, its abundance in the Earth's crust is quite low. Therefore, the use of Mo by living organisms seems surprising at first glance. Archaea, bacteria, fungi, plants, and animals, including

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humans, require molybdenum. It is also found in over 50 different enzymes.

Copper

Most copper-containing proteins and enzymes can be found in eukaryotes. Only a handful of prokaryotes such as aerobic bacteria and cyanobacteria contain copper enzymes or proteins. Copper can be found in both prokaryotes and eukaryotes superoxide dismutase (SOD) enzyme. There are three distinct types of SOD, containing Mn, Fe and Cu respectively.

Magnesium

Magnesium is the eighth most abundant element on earth. It is the fourth most abundant element in vertebrates and the most abundant divalent cation within cells. The most available form of magnesium (Mg²⁺) for living organisms can be found in the hydrosphere.

ATP, the main source of energy in almost all living organisms, must bind with metal ions such as Mg²⁺ or Ca²⁺ to function. Examination of cells with limited magnesium supply has shown that a lack of magnesium can cause a decrease in ATP. Magnesium in ATP hydrolysis acts as a co-factor to stabilize the high negative charge transition state.⁴ MgATP can be found in both prokaryotes and eukaryotes cells. However, most of the ATP in cells is MgATP. Following the Irving–Williams series, magnesium has a higher binding constant than the Ca²⁺. Therefore, the dominant ATP in living organisms is MgATP. A greater binding constant also give magnesium the advantage as a better catalyst over other competing transition metals.

Manganese

The incorporation of Mn in proteins allowed the complexes the ability to reduce reactive oxygen species in Mn-superoxide dismutase (MnSOD) and catalase, in electron transfer-dependent catalysis (for instance in certain class I ribonucleotide reductases) and in the oxidation of water by photosystem II (PSII), where the production of thiobarbituric acid-reactive substances is decreased. This is due to manganese's ability to reduce superoxide anion and hydroxyl radicals as well as its chain-breaking capacity.⁵

Nickel and cobalt

Coenzyme B12- Theorized as the first occurrence of cobalt in a biological system. Around 4-3 Ga, anaerobic prokaryotes began developing metal and organic cofactors

for light absorption. They ultimately ended up making chlorophyll from Mg(II), as is found in cyanobacteria and plants, leading to modern photosynthesis. However, chlorophyll synthesis requires numerous steps. The process starts with uroporphyrin, a primitive precursor to the porphyrin ring which may be biotic or abiotic in origin, which is then modified in cells differently to make Mg, Fe, nickel (Ni), and cobalt (Co) complexes. The centres of these rings are not selective, thus allowing the variety of metal ions to be incorporated. Mg porphyrin gives rise to chlorophyll, Fe porphyrin to heme proteins, Ni porphyrin yields factor F-430, and Co porphyrin Coenzyme B12.^{6,7}

Iron

The redox transformation of Fe(II) to Fe(III), or vice versa, is vital to a number of biological and element cycling processes. The reduction of Fe(III) is seen to oxidize sulfur (from H₂S to SO₄²⁻), which is a central process in marine sediments. Many of the first metalloproteins consisted of iron-sulphur complexes formed during photosynthesis. Iron is the main redox metal in biological systems. In proteins, it is found in a variety of sites and cofactors, including, for instance, haem groups, Fe–O–Fe sites, and iron–sulfur clusters.

Zinc

Zinc (Zn) was incorporated into living cells in two waves. Four to three Ga, anaerobic prokaryotes arose, and the atmosphere was full of H₂S and highly reductive. Thus most zinc was in the form of insoluble ZnS. However, because seawater at the time was slightly acidic, some Zn(II) was available in its ionic form and became part of early anaerobic prokaryotes' external proteases, external nucleases, internal synthetases and dehydrogenases.

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