Metal ions present in biological systems

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 (Mg^{2+}) for living organisms can be found in the hydrosphere. The concentration of Mg^{2+} in seawater is around 55 mM. Mg^{2+} is readily available to cells during early evolution due to its high solubility in water. Other transition metals like calcium precipitate from aqueous solutions at much lower concentrations than the corresponding Mg^{2+} salts.

Since magnesium was readily available in early evolution, it can be found in every cell type living organism. Magnesium in anaerobic prokaryotes can be found in MgATP. Magnesium also has many functions in prokaryotes such as glycolysis, all kinases, NTP reaction, signaling, DNA/RNA structures, and light capture. In aerobic eukaryotes, magnesium can be found in cytoplasm and chloroplasts. The reactions in these cell compartments are glycolysis, photophosphorylation , and carbon assimilation.

ATP, the main source of energy in almost all living organisms, must bind with metal ions such as Mg^{2+} or Ca^{2+} to function. Examination of cells with limited magnesium supply has shown that a lack of magnesium can cause a decrease in ATP.[9] Magnesium in ATP hydrolysis acts as a co-factor to stabilize the high negative charge transition state.[10] 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 Ca^{2+}. Therefore, the dominant ATP in living organisms is MgATP. A greater binding constant also gives magnesium the advantage as a better catalyst over other competing transition metals.

Manganese

Evidence suggests that manganese (Mn) was first incorporated into biological systems roughly 3.2–2.8 billion years ago, during the Archean Period. Together with calcium, it formed the manganese-calcium oxide complex (determined by X-ray diffraction) which consisted of a manganese cluster, essentially an inorganic cubane (cubical) structure. The incorporation of a manganese center in photosystem II was highly significant, as it allowed for the photosynthetic oxygen evolution of plants. The oxygen-evolving complex (OEC) is a

critical component of photosystem II contained in the thylakoid membranes of chloroplasts; it is responsible for terminal photooxidation of water during light reactions.

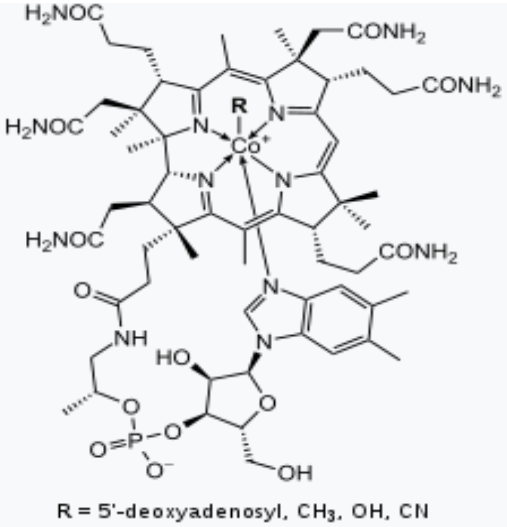
The incorporation of Mn in proteins allowed the complexes the ability to reduce reactive oxygen species in Mn-superoxide dismutase (MnSOD) and catalase, in electron transfer-dependent catalysis (for instance in certain class I ribonucleotide reductases) and in the oxidation of water by photosystem II (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.

Iron

Iron (Fe) is the most abundant element in the Earth and the fourth most abundant element in the crust, approximately 5 percent by mass. Due to the abundance of iron and its role in biological systems, the transition and mineralogical stages of iron have played a key role in Earth surface systems. It played a larger role in the geological past in marine geochemistry, as evidenced by the deposits of Precambrian iron-rich sediments. 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 H_2S to SO_4^{-2}), which is a central process in marine sediments. Many of the first metalloproteins consisted of iron-sulphur complexes formed during photosynthesis.[13] 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.

The prevalence of iron is apparently due to the large availability of Fe(II) in the initial evolution of living organisms, before the rise of photosynthesis and an increase in atmospheric oxygen levels which resulted in the precipitation of iron in the environment as $Fe(OH)_3$. It has flexible redox properties because such properties are sensitive to ligand coordination, including geometry. Iron can be also used in enzymes due to its Lewis acid properties, for example in nitrile hydratase. Iron is frequently found in mononuclear sites in the reduced Fe(II) form, and functions in dioxygen activation; this function is used as a major mechanism adopted by living organisms to avoid the kinetic barrier hindering the transformation of organic compounds by O_2. Iron can be taken up selectively as ferredoxins, Fe-O-Fe (hemerythrin and ribonucleotide reductase), Fe (many oxidases), apart from iron porphyrin. Variation in the related proteins with any one of these chemical forms of iron has produced a wide range of enzymes. All of these arrangements are modified to function both in the sense of reactivity and the positioning of the protein in the cell. Iron can have various redox and spin states, and it can be held in many stereochemistries.

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 centers 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.

Copper

Before the Great Oxygenation Event, copper was not readily available for living organisms. Most early copper was Cu^{+} and Cu. This oxidation state of copper is not very soluble in water. One billion years ago, after the great oxidation event, the oxygen pressure rose sufficiently to oxidize Cu^{+} to Cu^{2+}, increasing its solubility in water. As a result, copper became much more available for living organisms.

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. Mn-SOD and Fe-SOD are found in most prokaryotes and mitochondria of the eukaryotic cell. Cu-SOD can be found in the cytoplasmic fraction of the eukaryotic cells. The

three elements, copper, iron, and manganese, can all catalyze superoxide to ordinary molecular oxygen or hydrogen peroxide. However, Cu-SOD is more efficient than Fe-SOD and Mn-SOD. Most prokaryotes only utilize Fe-SOD or Mn-SOD due to the lack of copper in the environment. Some organisms did not develop Cu-SOD due to the lack of a gene pool for Cu-SOD adoption.

Zinc

Zinc (Zn) was incorporated into living cells in two waves. Four to three Ga, anaerobic prokaryotes arose, and the atmosphere was full of H_2S 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.

During the second wave, once the Great Oxygenation Event occurred, more Zn(II) ions were available in the seawater. This allowed its incorporation in the single-cell eukaryotes as they arose at this time. It is believed that the later addition of ions such as zinc and copper allowed them to displace iron and manganese from the enzyme superoxide dismutase (SOD). Fe and Mn complexes dissociate readily (Irving–Williams series) while Zn and Cu do not. This is why eukaryotic SOD contains Cu or Zn and its prokaryotic counterpart contains Fe or Mn.[7]

Zn (II) doesn't pose an oxidation threat to the cytoplasm. This allowed it to become a major cytoplasmic element in the eukaryotes. It became associated with a new group of transcription proteins, zinc fingers. This could only have occurred due to the long life of eukaryotes, which allowed time for zinc to exchange and hence become an internal messenger coordinating the action of other transcription factors during growth.