

Micronutrients

Mikronährstoffe

Periodic Table of the Elements

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3	Li lithium 6.941 6939	4	Be beryllium 9.012 182															5	B boron 10.811 704																																																																						
6	C carbon 12.011 15	7	N nitrogen 14.007 44	8	O oxygen 15.999 4	9	F fluorine 18.998 4032	10	Ne neon 20.179 7											11	Na sodium 22.989 76928																																																																				
12	Mg magnesium 24.304 0	13	Al aluminum 26.981 5386	14	Si silicon 28.085 579	15	P phosphorus 30.973 762	16	S sulfur 32.06 5	17	Cl chlorine 35.453	18	Ar argon 39.948 1634			19	K potassium 39.098 31																																																																								
20	Ca calcium 40.078 4	21	Sc scandium 44.955 912	22	Ti titanium 47.88 7	23	V vanadium 50.941 5	24	Cr chromium 51.996 1	25	Mn manganese 54.938 0443	26	Fe iron 55.845 2	27	Co cobalt 58.933 195	28	Ni nickel 58.693 4	29	Cu copper 63.546 3	30	Zn zinc 65.38 2	31	Ga gallium 69.723 17																																																																		
32	Ge germanium 72.64 1	33	As arsenic 74.921 60	34	Se selenium 78.96 2	35	Br bromine 79.904 1	36	Kr krypton 83.80 1	37	Rb rubidium 85.467 8	38	Sr strontium 87.62 4	39	Y yttrium 88.905 84	40	Zr zirconium 91.224 2	41	Nb niobium 92.906 38	42	Mo molybdenum 95.94 1	43	Tc technetium 98.906 254	44	Ru ruthenium 101.07 4	45	Rh rhodium 102.905 50	46	Pd palladium 106.363 5	47	Ag silver 107.868 2	48	Cd cadmium 112.411 8	49	In indium 114.818 1	50	Sn tin 118.710 7	51	Sb antimony 121.757 1	52	Te tellurium 127.603	53	I iodine 126.905 47	54	Xe xenon 131.29 4	55	Ba barium 137.327	56	La lanthanum 138.905 47	57	Ce cerium 140.12 1																																						
58	Pr praseodymium 140.907 68	59	Nd neodymium 144.242 8	60	Pm promethium 144.912 88	61	Sm samarium 150.36 8	62	Eu europium 151.964 1	63	Gd gadolinium 157.25 3	64	Tb terbium 158.925 32	65	Dy dysprosium 162.500 52	66	Ho holmium 164.930 32	67	Er erbium 167.259 4	68	Tm thulium 168.930 28	69	Yb ytterbium 173.054 68	70	Lu lutetium 174.967 06	71	Hf hafnium 178.49 1	72	Ta tantalum 180.947 88	73	W tungsten 183.84 1	74	Re rhenium 186.207 4	75	Os osmium 190.23 4	76	Ir iridium 192.222 76	77	Pt platinum 195.083 93	78	Au gold 196.966 57	79	Hg mercury 200.59 6	80	Tl thallium 204.38 3	81	Pb lead 207.2 1	82	Bi bismuth 208.980 4	83	Po polonium 209	84	At astatine 210	85	Rn radon 222	86	Fr francium 223	87	Ra radium 226	88	Ac actinium 227	89	Th thorium 232.037 7	90	Pa protactinium 231.036 88	91	U uranium 238.028 91	92	Np neptunium 237.048 17	93	Pu plutonium 244.064 2	94	Am americium 243.061 36	95	Cm curium 247.070 35	96	Bk berkelium 247.070 35	97	Cf californium 251.083 2	98	Es einsteinium 252.083 2	99	Fm fermium 257.105 28	100	Md mendelevium 258.105 28	101	No nobelium 259.105 28	102	Lr lawrencium 262.105 28
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Alkali metals
Alkaline earth metals

Transition metals
Lanthanide series

Actinide series
Poor metals

Nonmetals
Noble gases

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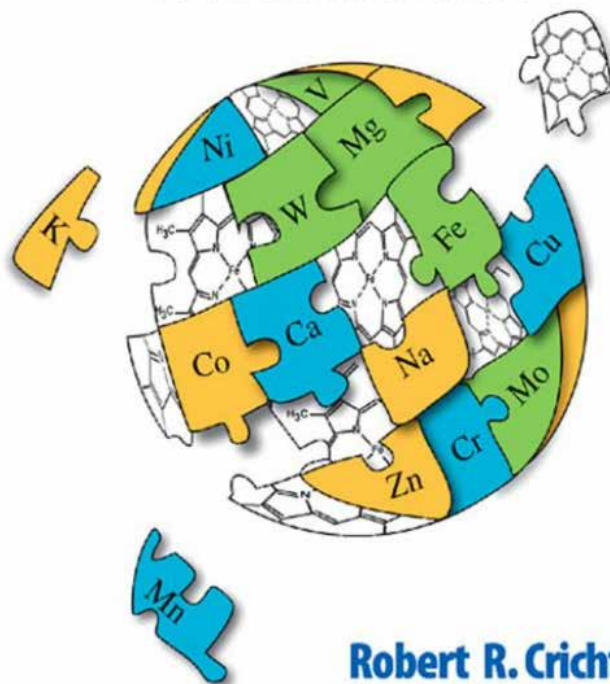
Table 1 | Main biochemical functions of elements (Fraústo da Silva and Williams, 2001; Crichton, 2008; Marschner, 2012; Williams and Rickaby, 2012).

General	Elements	Chemical form	Uptake	Specific functions (examples)
NON-METALS				
Major cell constituents, LMWMs and proteins	C, H, O, N, S (Se)	Lipo- and hydrophylic molecules	CO ₂ , HCO ₃ ⁻ , H ₂ O, O ₂ , NO ₃ ⁻ , SO ₄ ²⁻ , SO ₂ (SeO ₄ ²⁻)	Essential elements involved in enzymatic reactions, low- and high-molecular-weight metabolites, polymers
Amorphous hard structures	P	Phosphate esters	Phosphates	Energy transfer
	B	Esters with polyhydroxy compounds	Boric acid	Cell wall component, essential for plants but not animals
	Si	Coordination complex	Silicic acid	Major element in plants, minor in animals (shells of lower animals)
Non-specific	Cl	Anion	Cl ⁻	Ionic messenger, ion balance
METALS				
Structural	Ca, Mg	Sparingly soluble inorganic compounds	As ions	Skeleton, shells, teeth, membranes, muscles
Electrochemistry	K, Na (Ca, Mg)	Free cations	As ions	Nerves, metabolic energy Electrolytic equilibria and currents
Acid-base catalysis	Zn (Ni, Mn)	Coordination complex	Predominantly as coordination complex	Food digestion (Zn), Urea hydrolysis (Ni) Water splitting (Mn)
Redox catalysis	Fe, Cu, Mn, Mo, (Co, Ni, V)	Coordination complex	Predominantly as coordination complex	Oxygen reaction (Fe, Cu, Mn), Oxygen production (Mn), Oxidation outside cytoplasm (Cu), Nitrogen fixation (Mo), Nucleotide reduction (Co)
Signaling to DNA	Ca, Cu, Fe, Mg, Zn	Coordination complex	Ca as ion; all others as coordination complexes	Binding to transcription factors (Zn)
Various specific functions	Mg Fe, Cu	Coordination complex Oxygen transport	Ion, Coordination complex	Chlorophyll, phosphate metabolism Proteins



BIOLOGICAL INORGANIC CHEMISTRY

AN INTRODUCTION



Robert R. Crichton

BASIC COORDINATION CHEMISTRY FOR BIOLOGISTS

BASIC COORDINATION CHEMISTRY FOR BIOLOGISTS

Biological inorganic chemistry is by its nature an interdisciplinary subject with linguistic and conceptual problems that render it difficult for students who have a unique background in either biology or chemistry.

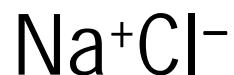
The major problem for the student with a background in biology is the understanding of the concepts inherent in the interactions of chemical species (charged or uncharged) with each other.

Such concepts involve electronic structure and considerations of symmetry, which in turn affect the bonding between them.

In this chapter we will lay out the basics of such concepts with particular reference to the interactions of **metal ions** with **organic molecules**.

Ionic bonds:

Large differences in electronegativity between atoms in a given molecule often cause the **complete transfer of an electron from the unfilled outer shell of one atom to the unfilled shell of another**. The resulting charged species (ions) are held together by electrostatic forces.

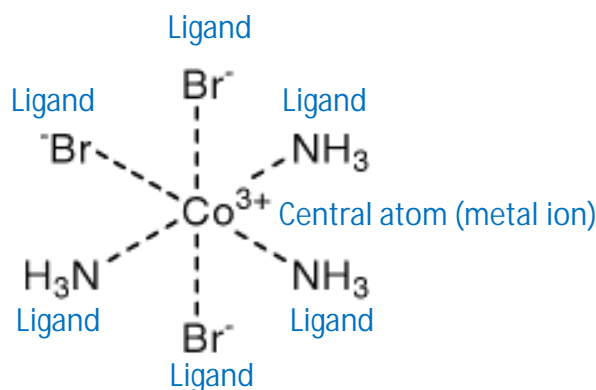


Covalent bonds:

Orbital overlap, i.e. **mutual sharing of one or more electrons**, can occur when two atoms are in close proximity to each other. The bonding resulting from such overlap is referred to as covalent bonding. Most frequently for a significant overlap and hence a more stable bond, either both atoms have half-filled valency orbitals, as in the H_2 molecule, or one atom has a filled valency orbital not used for bonding and the other one a vacant valency orbital. Pure covalent bonding occurs in compounds containing **atoms of the same element** such as H_2 . Most compounds however contain atoms of **different elements**, which have different electronegativities, and hence the commonest type of bonding lies somewhere between purely ionic and purely covalent as in HCl .

Coordination bonds:

Coordinate bonds are a special case of covalent bonds where the **electrons for sharing are supplied by one atom**. There is often a **fractional positive charge** on the **donor atom** and a **fractional negative charge** on the **acceptor atom**.



$\text{CoBr}_3 \cdot 3\text{NH}_3$ exhibits such type of bonding and hence traditionally is referred to as a coordination compound.

Lewis acids and bases:

In 1923 the American chemist G.N. Lewis provided a broad definition of acids and bases, which covered acid–base reactions not involving the traditional proton transfer: an **acid** is an **electron-pair acceptor** (Lewis acid) and a **base** is an **electron-pair donor** (Lewis base). The concept was extended to metal–ligand interactions with the **ligand** acting as donor, or **Lewis base**, and the **metal ion** as acceptor, or **Lewis acid**.

Classification of biologically important metal ions and ligands according to the 'hard–soft acid–base' concept and their general characteristics

Acid/acceptor (metal ions)		Base/donor (ligands)
Hard	High charge density Small ionic radius No easily excited outer shell electrons Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cr^{3+} , Fe^{3+} , Co^{3+}	Low polarizability High electronegativity Vacant, high-energy orbitals Hard to oxidize H_2O , OH^- , CO_2^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , ROPO_3^{2-} , PO_4^{3-} , ROPO_3^{2-} , $(\text{RO})_2\text{PO}_2^-$, ROH , RO^- , R_2O , NH_3 , RNH_2 , Cl^-
Intermediate	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}	NO_2^- , SO_3^{2-} , Br^- , N_3^- , imidazole
Soft	Low-charge density Large ionic radius Easily excited outer shell electrons Cu^+	High polarizability Low electronegativity Low-energy vacant orbitals Easily oxidized RSH , RS^- , CN^- , CO

The chelate effect:

Metal ions dissolved in water are effectively complexed to **water molecules**. Displacing the set of water ligands, partially or entirely by another set, in such aqua metal ions results in forming what is more conventionally known as **complexes**. Displacement of water molecules by **multi-dentate ligands** results in more stable complexes than similar systems with none or fewer chelates.

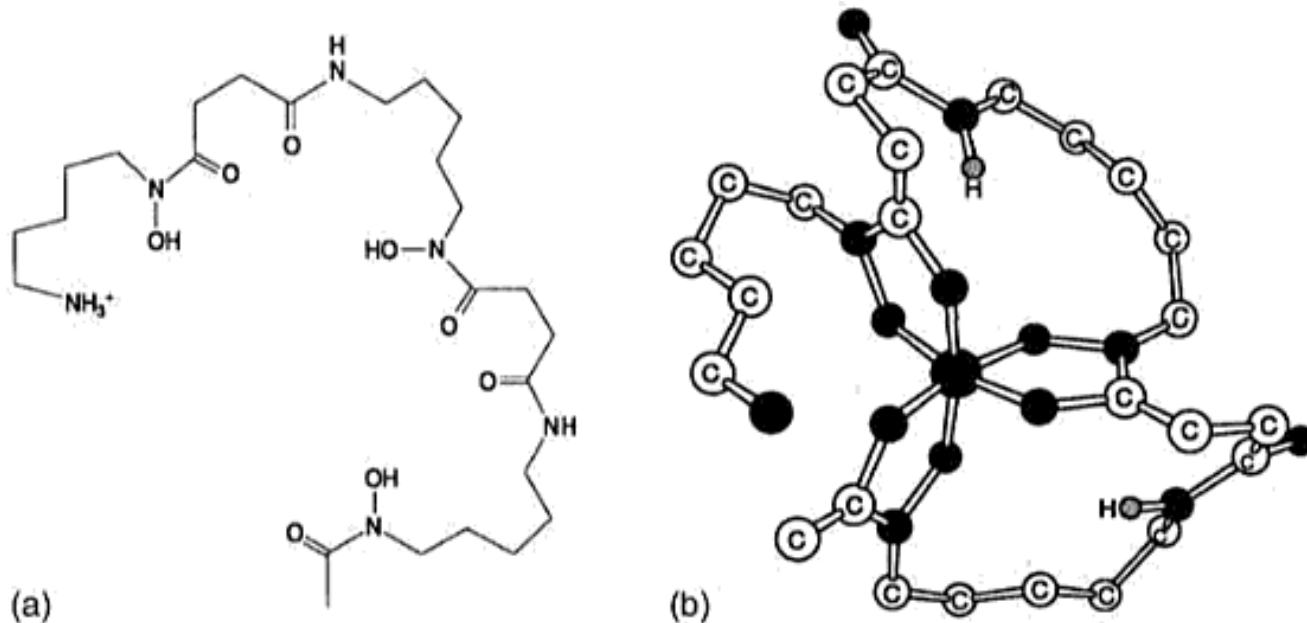


Figure 2.3 (a) The metal chelator desferrioxamine (DFO) and (b) its complex with iron.

Coordination geometry:

The shape of a molecule, i.e. its geometry, is generally defined by the bonds within the molecule, which are disposed in a 3-D array. The different pairs of electrons involved in bonding are attracted by two nuclei and they will tend to stay as far from each other as possible to minimize electrostatic repulsions. The **shape of a molecule** can be predicted on the basis of the **number of electron pairs in the valence shell of the central atom**.


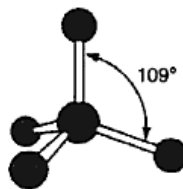
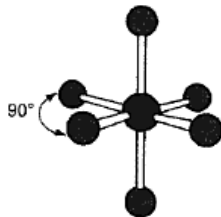
Table 2.2

Predicted arrangements of electron pairs in the valence shell of the central atom

Number of pairs	Predicted stable geometry
2	Linear
3	Equilateral triangle
4	Tetrahedron
5	Trigonal bipyramid square pyramid (less stable)
6	Octahedron

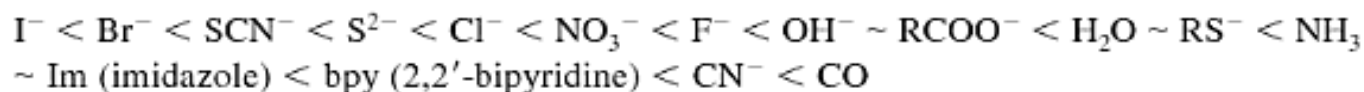
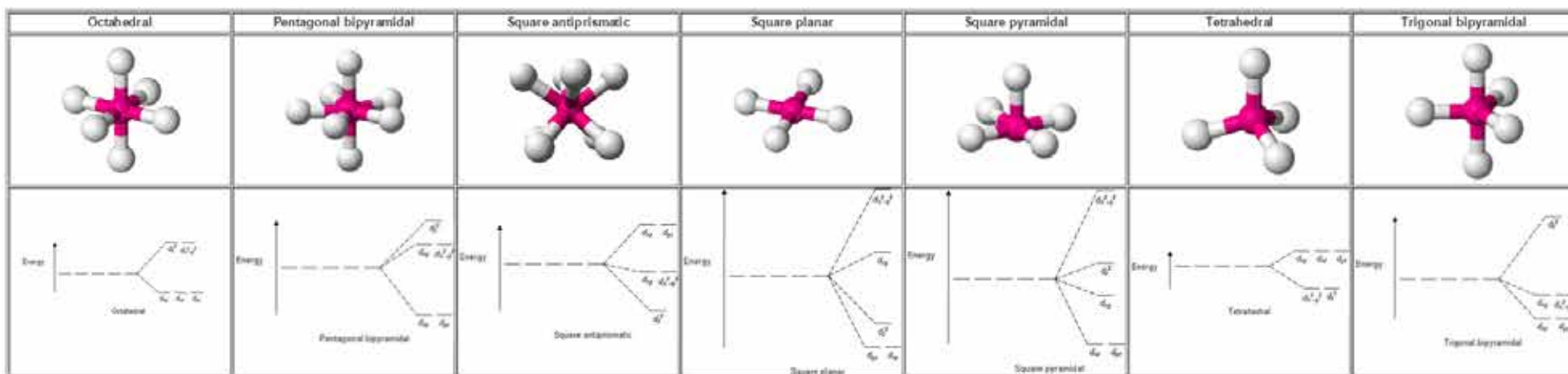
Table 2.4

Common geometries for 4- and 6-coordinate metal ions with examples for each case

Coordination number	Geometry of coordination compound	Example
4	 <p>Square</p>  <p>Tetrahedral</p>	<p>$[\text{Cu}(\text{NH}_3)_4]^{2+}$ (square planar) CuCl_4 (tetrahedral)</p>
6	 <p>Octahedron</p>	Fe^{3+} -DFO

Coordination geometry:

The **crystal field theory (CFT)** was developed for crystalline solids by the physicist Hans Bethe in 1929. The model takes into account the **distance separating the positively and negatively charged ions** and treats the ions simply as point charges with the attractive and repulsive interactions between them as purely electrostatic/ionic ones. The central point in this theory is the **effect of the symmetry of the arrangement of ligands on the energy of the *d* orbitals** of a central metal atom.



Biological ligands:

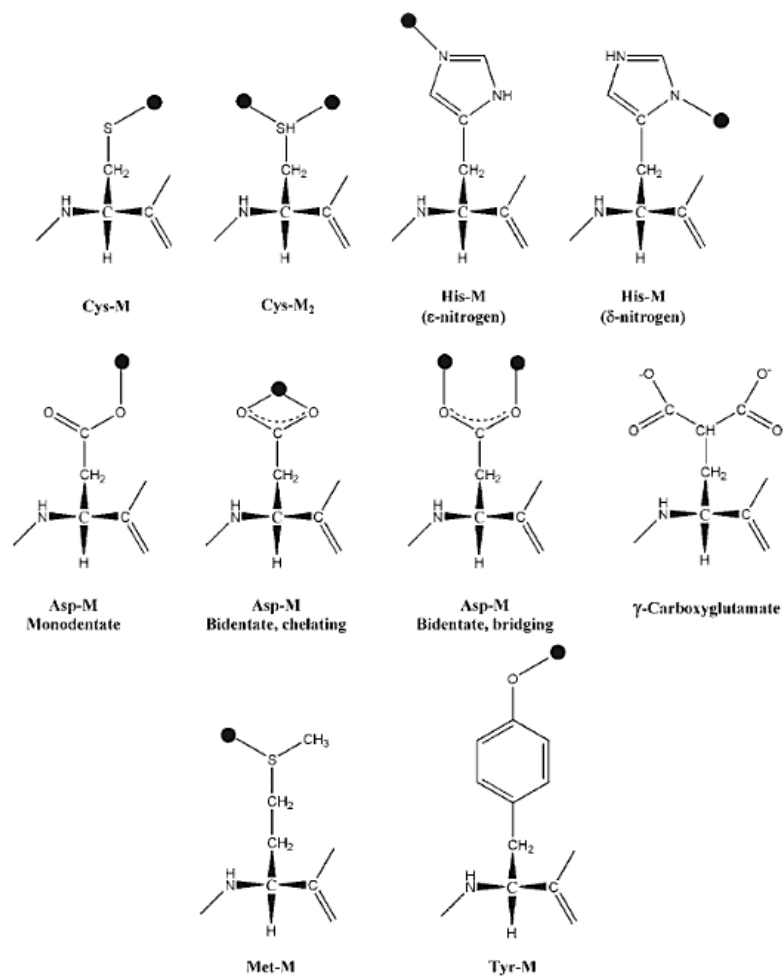


Figure 3.1 Principal protein amino acid side-chain metal-ion binding modes (the metal ion represented as a dark filled circle) and (right) the structure of the Ca²⁺-binding γ-carboxyglutamate found in proteins of the blood-clotting cascade.

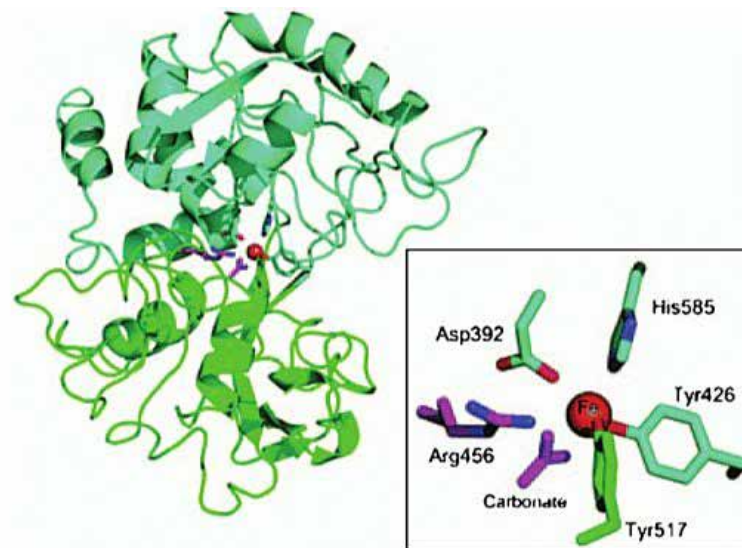


Figure 3.2 Ribbon diagram of the C-lobe of human transferrin with the two domains shown in different colours (cyan for C1 and green for C2). The inset shows the four protein ligand residues together with the arginine residue which stabilizes binding of the synergistic carbonate ion (both in magenta). (Reprinted with permission from Mason et al., 2005. Copyright (2005) American Chemical Society.)

Table 1 | Main biochemical functions of elements (Fraústo da Silva and Williams, 2001; Crichton, 2008; Marschner, 2012; Williams and Rickaby, 2012).

General	Elements	Chemical form	Uptake	Specific functions (examples)
NON-METALS				
Major cell constituents, LMWMs and proteins	C, H, O, N, S (Se)	Lipo- and hydrophylic molecules	CO ₂ , HCO ₃ ⁻ , H ₂ O, O ₂ , NO ₃ ⁻ , SO ₄ ²⁻ , SO ₂ (SeO ₄ ²⁻)	Essential elements involved in enzymatic reactions, low- and high-molecular-weight metabolites, polymers
Amorphous hard structures	P	Phosphate esters	Phosphates	Energy transfer
	B	Esters with polyhydroxy compounds	Boric acid	Cell wall component, essential for plants but not animals
	Si	Coordination complex	Silicic acid	Major element in plants, minor in animals (shells of lower animals)
Non-specific	Cl	Anion	Cl ⁻	Ionic messenger, ion balance
METALS				
Structural	Ca, Mg	Sparingly soluble inorganic compounds	As ions	Skeleton, shells, teeth, membranes, muscles
Electrochemistry	K, Na (Ca, Mg)	Free cations	As ions	Nerves, metabolic energy Electrolytic equilibria and currents
Acid-base catalysis	Zn (Ni, Mn)	Coordination complex	Predominantly as coordination complex	Food digestion (Zn), Urea hydrolysis (Ni) Water splitting (Mn)
Redox catalysis	Fe, Cu, Mn, Mo, (Co, Ni, V)	Coordination complex	Predominantly as coordination complex	Oxygen reaction (Fe, Cu, Mn), Oxygen production (Mn), Oxidation outside cytoplasm (Cu), Nitrogen fixation (Mo), Nucleotide reduction (Co)
Signaling to DNA	Ca, Cu, Fe, Mg, Zn	Coordination complex	Ca as ion; all others as coordination complexes	Binding to transcription factors (Zn)
Various specific functions	Mg Fe, Cu	Coordination complex Oxygen transport	Ion, Coordination complex	Chlorophyll, phosphate metabolism Proteins

Marschner's

Mineral Nutrition of Higher Plants



THIRD EDITION

Edited by
Petra Marschner



Table 1

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Potassium	2.6			Nickel	0.0004
Magnesium	2.1			Molybdenum	0.0001
All others	1.5				

Discovery of the essentiality of micronutrients for higher plants		
Element	Year	Discovered by
Fe	1860	J. Sachs
Mn	1922	J.S. McHargue
B	1923	K. Warington
Zn	1926	A.L. Sommer and C.B. Lipman
Cu	1931	C.B. Lipman and G. MacKinney
Mo	1938	D.I. Arnon and P.R. Stout
Cl	1954	T.C. Broyer <i>et al.</i>
Ni	1987	P.H. Brown <i>et al.</i>

Arnon, D.I.; Stout, P.R.,
The essentiality of certain elements in minute quantity for plants
with special reference to copper,
Plant Physiol. **14** (1939), 371–375.

Chlorine:



Monovalent anion

and

the most abundant in plants

and

an essential counter ion
for membrane potential stabilization

- Photosynthetic O₂ evolution PSII complex

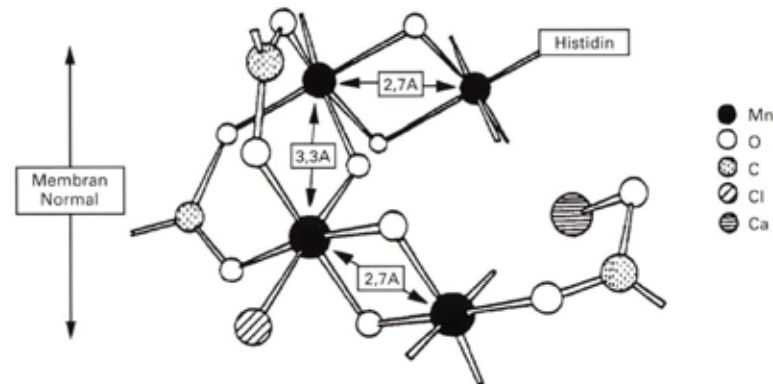


Abb. 64. Modell des wasseroxidierenden Mn-Komplexes innerhalb des Photosystems II auf der Basis von Messungen mit der Röntgenstrahl-Absorptions- sowie der e^- -paramagnetischen Resonanz-Spektroskopie (entnommen aus BOWYER und LEEGOOD 1997).

Marschner's Mineral Nutrition of Higher Plants

- Stimulation of various membrane-bound phosphorylating enzymes, ATPases amongst others
- Stomatal regulation (together with K⁺ and malate)

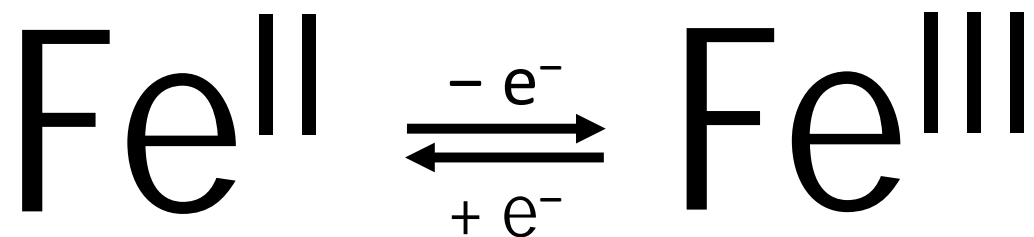


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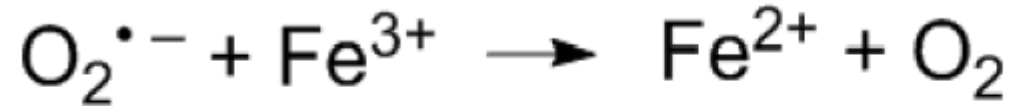
Iron:



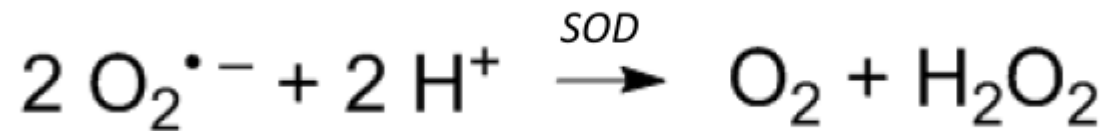
Transition metal

Haber-Weiss (inkl. Fenton) Reaction:

Fe



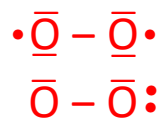
Superoxid Dismutase (SOD):



Reactive oxygen (nitrogen) species

Fe

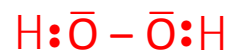
Dioxygen
(molecular oxygen)
Singlet oxygen



Superoxide
anion radical



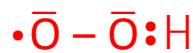
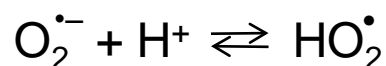
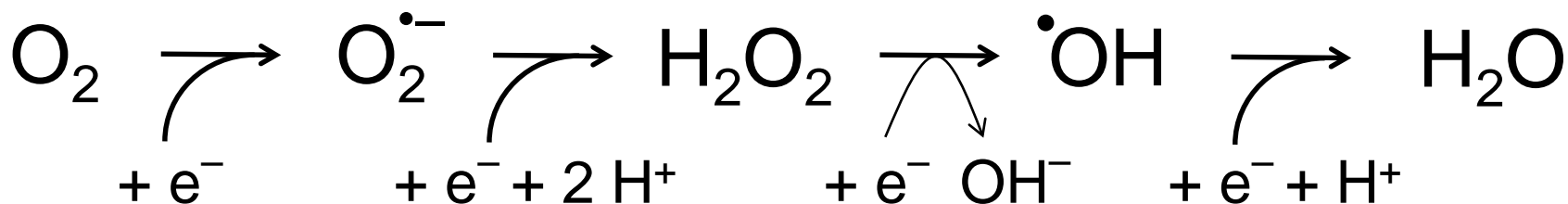
Hydrogen
peroxide



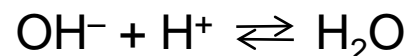
Hydroxyl
radical



Water



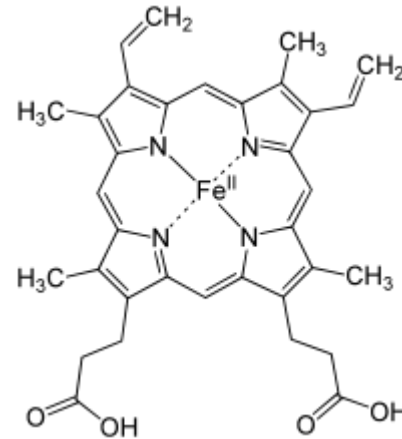
Hydroperoxyl
radical



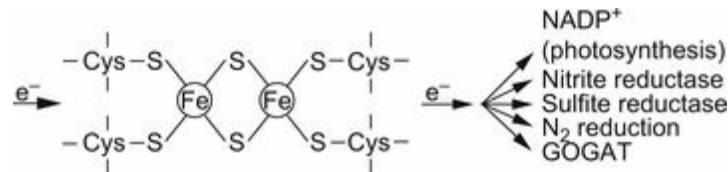
Nitric oxide



- Heme proteins
(e.g. cytochromes)



- Fe-S proteins
(e.g. ferredoxin)



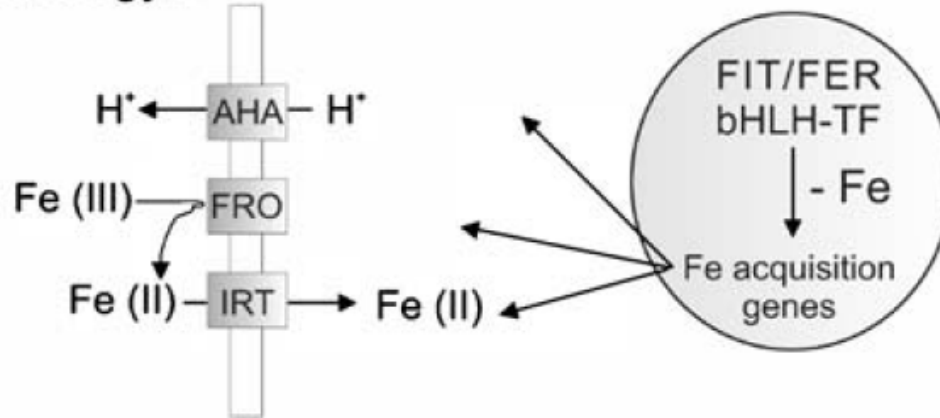
- Other enzymes
(e.g. lipoxygenases)



Iron uptake mechanisms by plant roots:

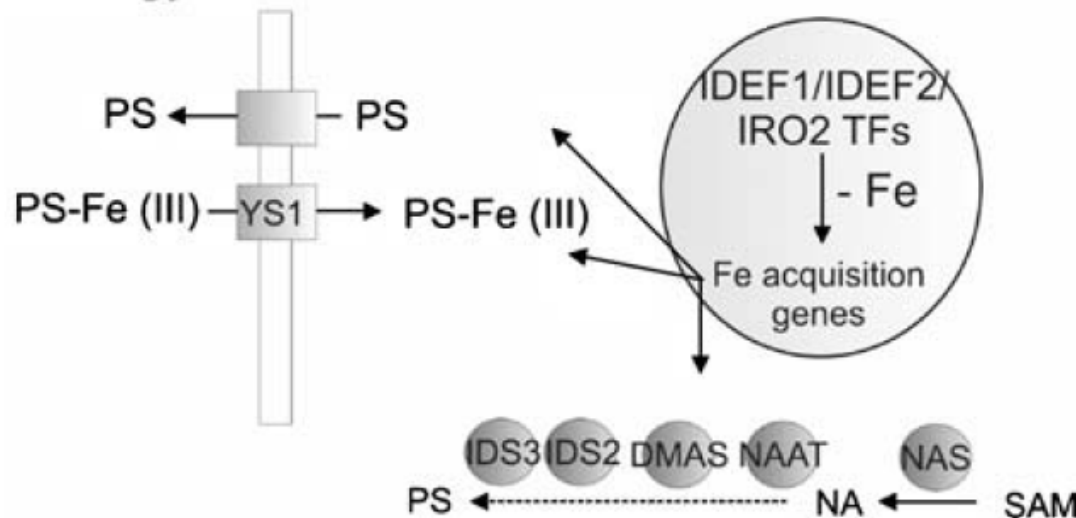
Fe

Strategy I



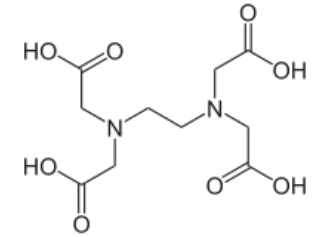
Dicots and nongramineous monocots

Strategy II

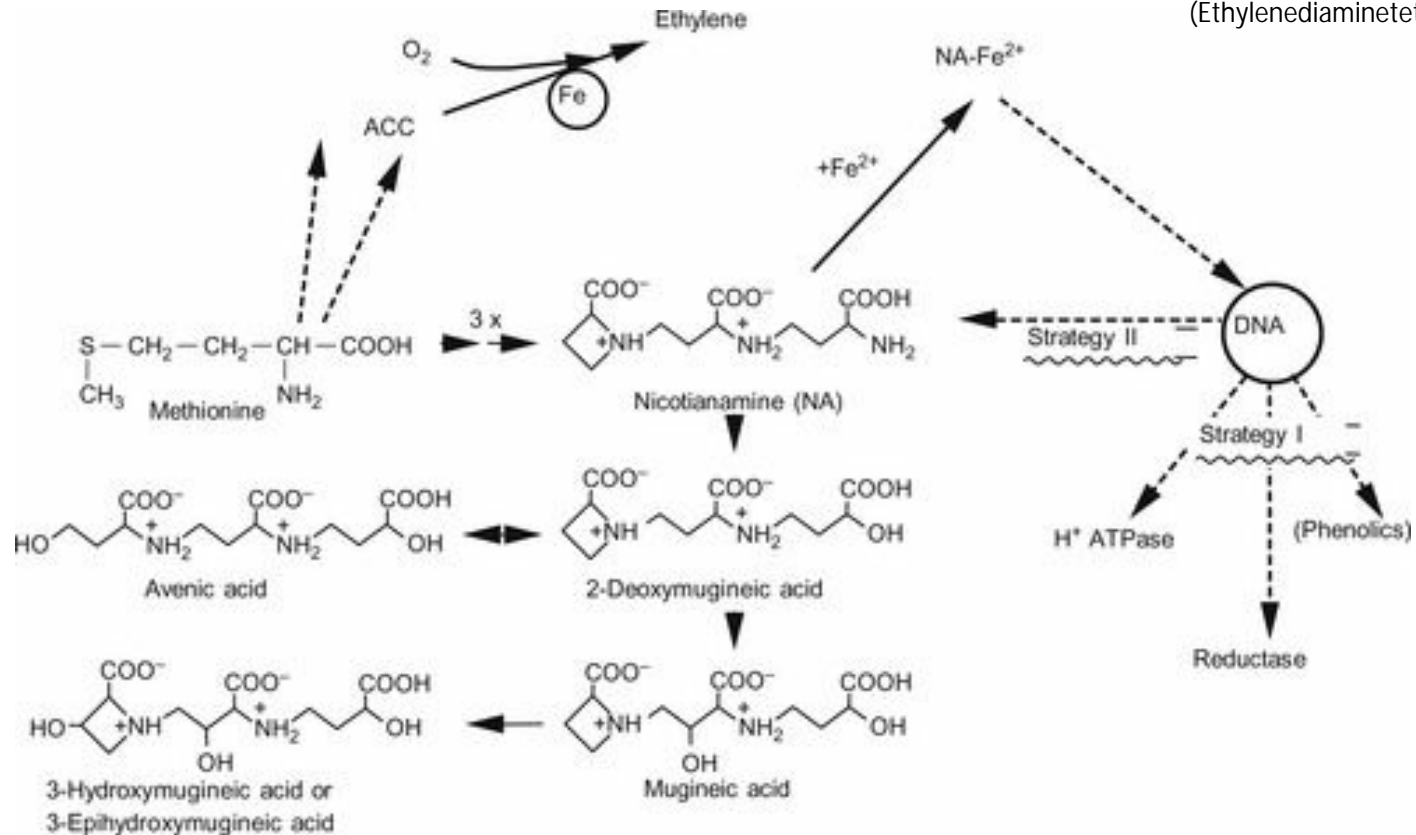


Gramineous monocots

Phytosiderophores:



EDTA
(Ethylenediaminetetraacetic acid)



Fe

Ferritin:

Fe

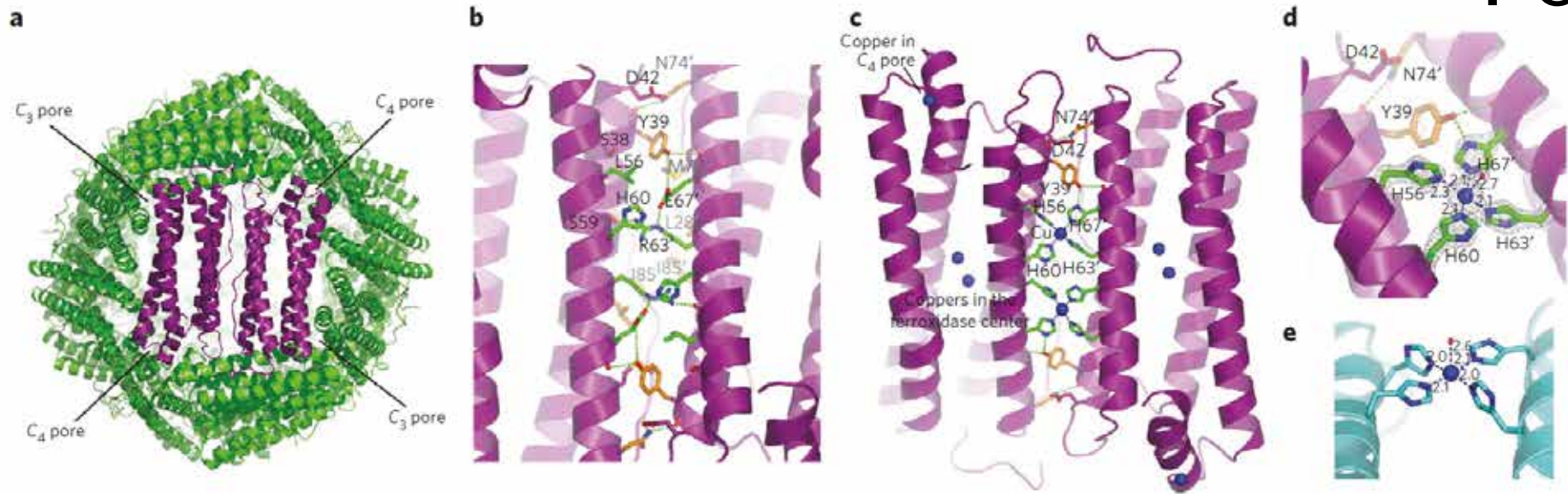
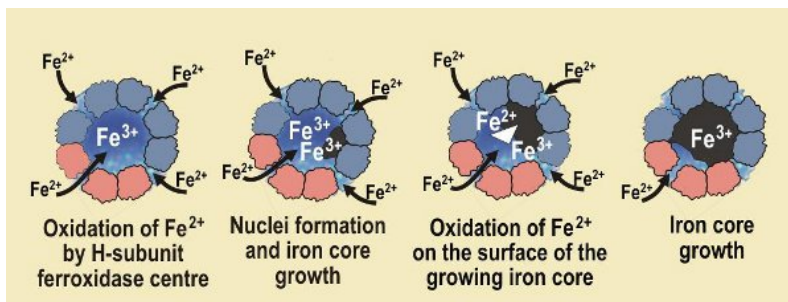


Figure 2 | The ferritin cage architecture and intersubunit interactions in the C_2 interface. (a) The 24-meric ferritin architecture viewed down the C_2 symmetry axis. Alternative views down the C_3 and C_4 axes are shown in **Supplementary Figure 5**. A C_2 -symmetric dimeric component of ferritin is highlighted in violet. (b) Intersubunit interactions in the C_2 interface of ferritin as viewed from the interior of the cage. Residues mutated for the construction of Cu(II)-coordination motifs and for the destabilization of the C_2 interface are highlighted as green and orange sticks, respectively. Other key side chains involved in contacts with the mutated residues are shown as violet sticks. (c) The C_2 dimer of the Cu-4His- ΔC^* cage viewed down the C_2 symmetry axis. (d) Close-up view of one of the two symmetrically related 4His-Cu(II) coordination motifs in the C_2 interface of Cu-4His- ΔC^* . The hydrogen bonds involving Tyr39 and Asn74 are shown as dashed green lines. The $2F_o - F_c$ electron density map associated with the square pyramidal Cu(II) coordination site is shown as a gray mesh contoured at 2σ . The bond distances (in Å) are indicated. (e) The square pyramidal Cu(II) coordination motif in the Cu-MBPC1 structure that served as a model for the construction of 4His- ΔC^* .

Huard DJE et al., 2013, *Nature Chemical Biology* 9:169-176



An animated presentation of ferritin molecules with eight subunits – five L-subunits in blue, and three H-subunits in red to show the mineralization process of iron by the ferritin protein shell. Oxidation of Fe^{2+} is performed by the ferroxidase centre of the H-subunit. This is followed by nuclei formation and iron core growth facilitated by L-subunits. Once the iron core reaches a sufficient size oxidation of Fe^{2+} can take place on the surface of the iron core.

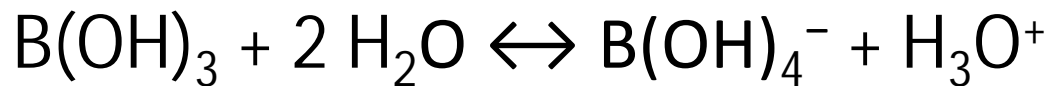
Table 1

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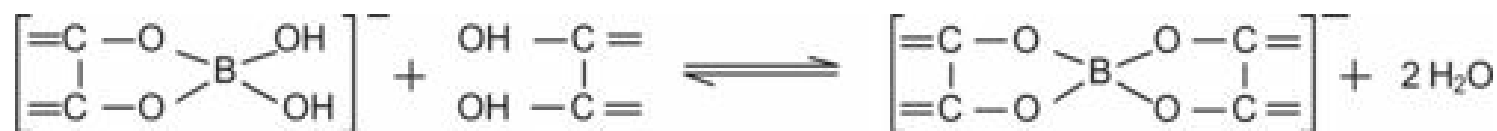
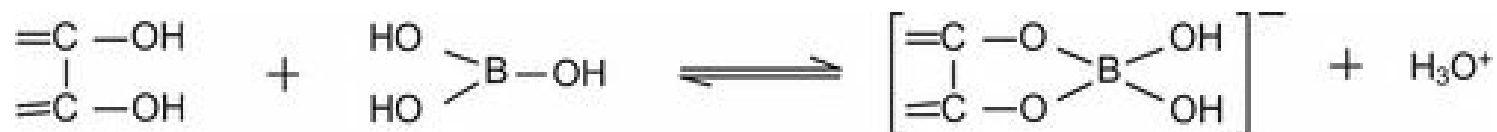
Boron:

Metalloid



Boric acid

Borate

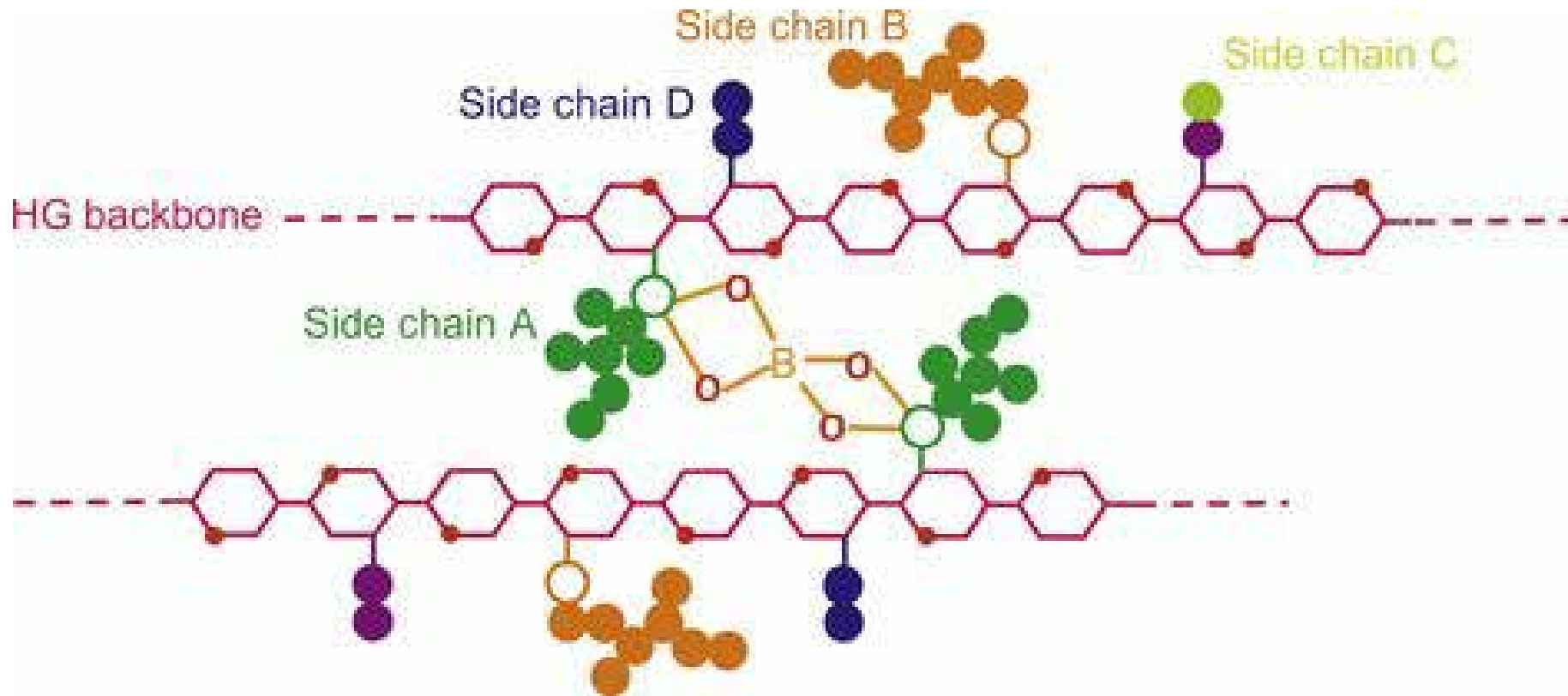


Complexes with diols and polyols

cis-diol configuration in

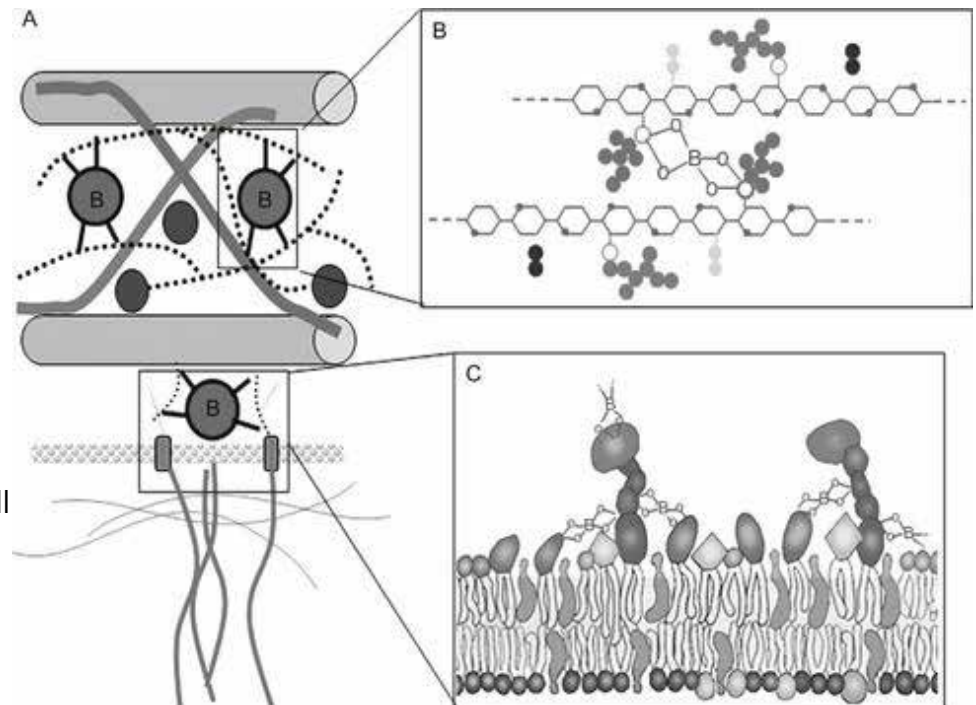
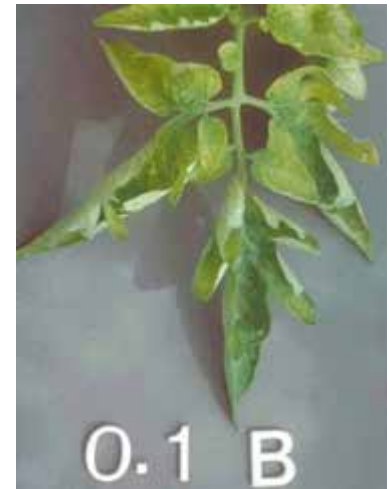
mannitol, mannan, polymannuronic acid,

pectin and hemicelluloses



Marschner's Mineral Nutrition of Higher Plants

- Cell wall structure
- Cell adhesion processes
- Nodule formation in symbiotic interactions
- Membrane integrity and function (also associated enzymes)
- Root and shoot meristems
- Mechanisms still unclear



- A. Network of cellulose fibrils, hemicelluloses, pectins and cell wall proteins. Plasma membrane with attachment sites of actin and tubulin
- B. Galacturonic and backbone with various side chains linked by B
- C. Membrane bilayer showing glycosphingolipids, sphingomyelins, glycosylphosphatidyl-inositol anchored proteins and other membrane components.

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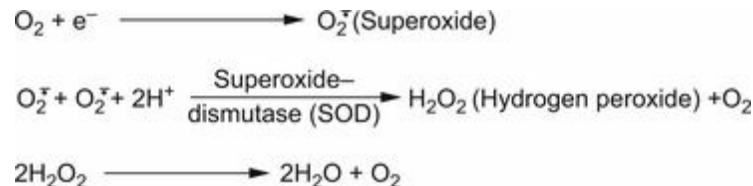
Manganese:

Mn

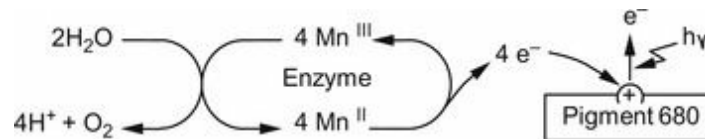


Transition metal

- Superoxide dismutase



- Mn protein in PSII



- Oxalate oxidase
- Mn²⁺ acts as cofactor for 35 different enzymes (shikimate pathway and aromatic amino acids, various peroxidases, terpenoid and lipid biosynthesis)

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Magnesium	2.1			Molybdenum	0.0001
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Zinc:

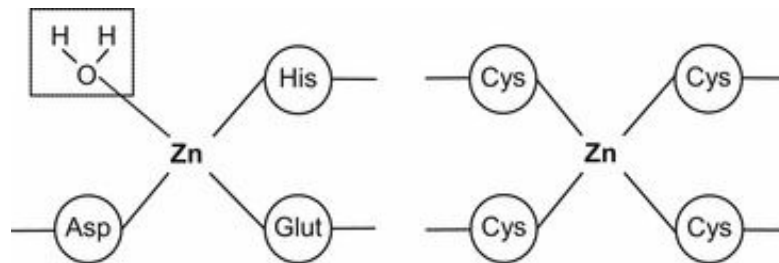
Zn

Zn^{II}

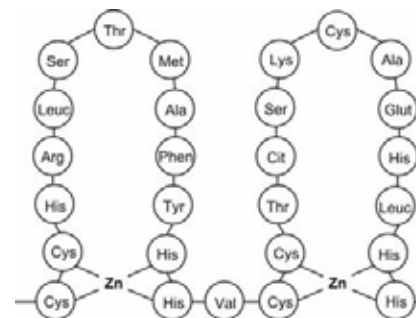
Transition metal

ZnOH^+

- Only metal that is present in all 6 enzyme classes, including oxidoreductases, transferases, hydrolases lyases, isomerases and ligases



- Zn^{2+} is a cofactor for dehydrogenases, aldolases, isomerases, transphosphorylases and RNA and DNA polymerases, amongst others
- Tertiary structure of peptide chains
- Protein synthesis in ribosomes
- Membrane integrity and protection against lipid peroxidation



"Zinc finger"

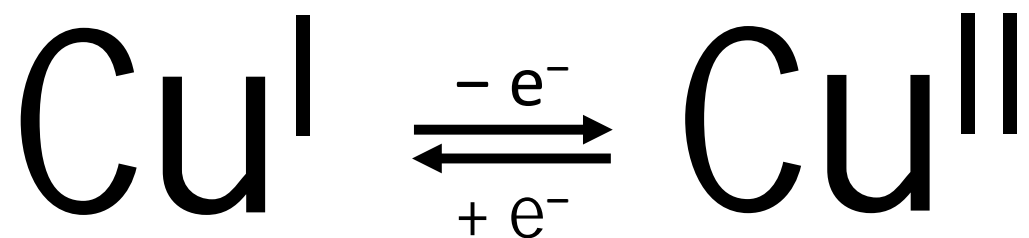
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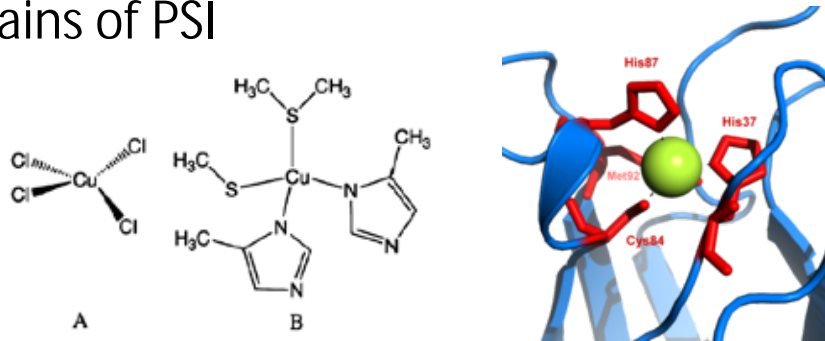
Copper:

Cu



Transition metal

- Present in more than 100 different proteins
- More than 50 % in **plastocyanin** in electron transport chains of PSI



- Superoxide dismutase, ascorbate oxidase etc.
- Lignification

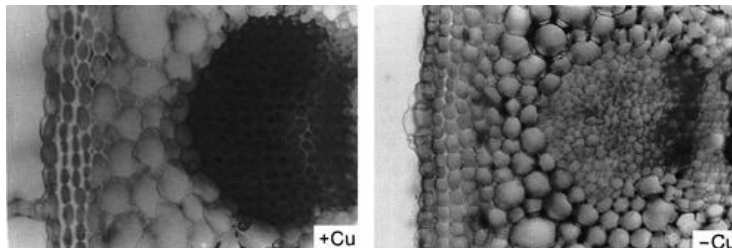


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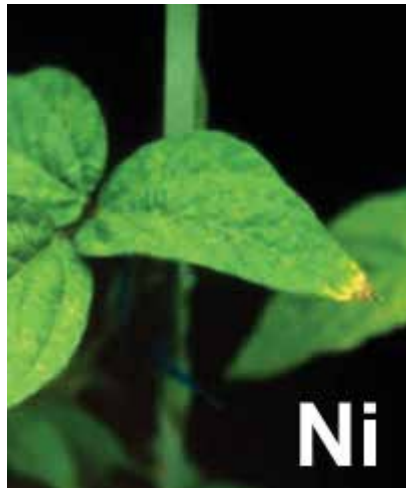
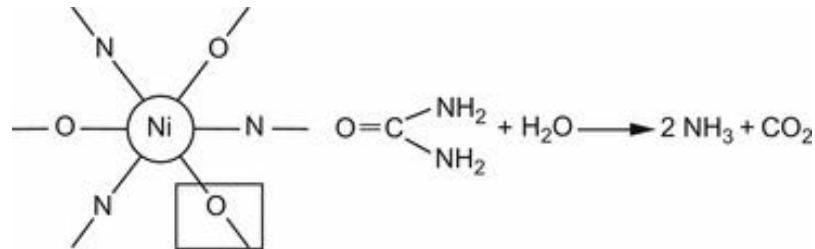
Nickel:

Ni



Transition metal

- Present in at least 9 proteins, in plants Ni Urease and Ni Urease associated protein



Urea toxicity
(yellow leaf tips)

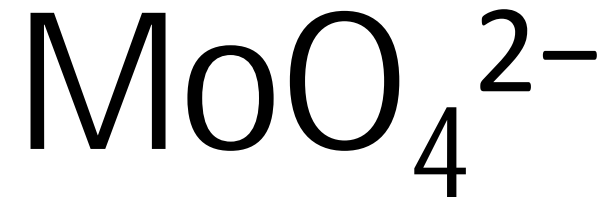
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All others	1.5				

Molybdenum:

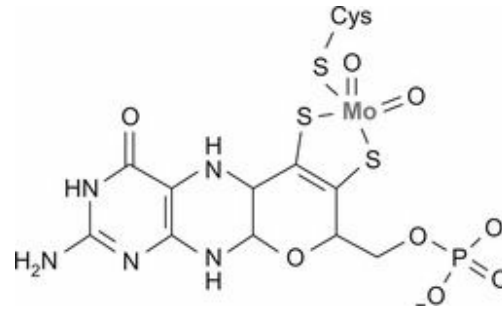
Mo



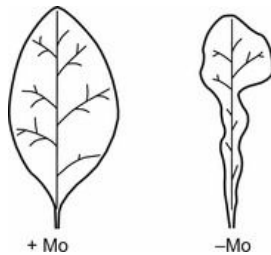
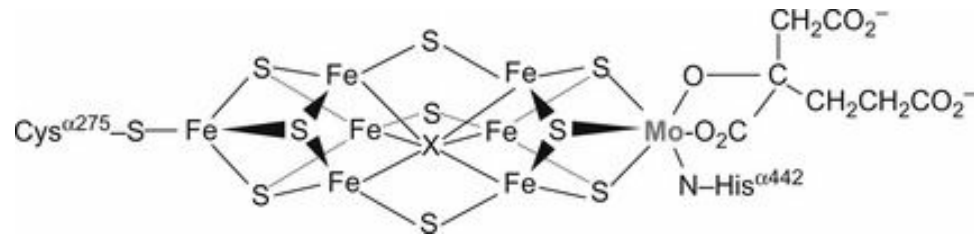
Transition element,
More present in the lithosphere than in soils

Mo

- Nitrate reductase cofactor Moco



- Nitrogenase (all N_2 fixing microorganisms)



"whiptail"



Oxidative stress

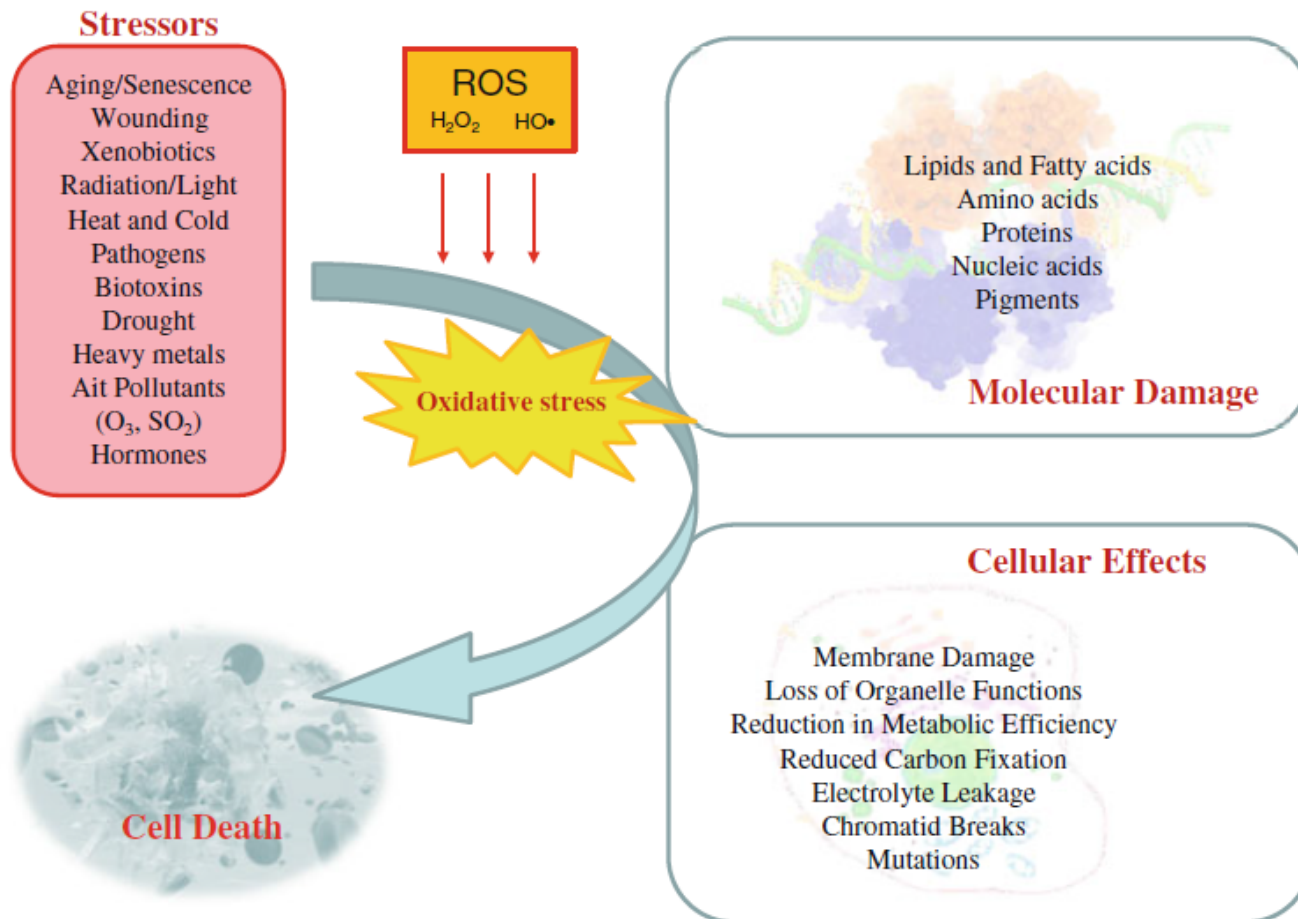
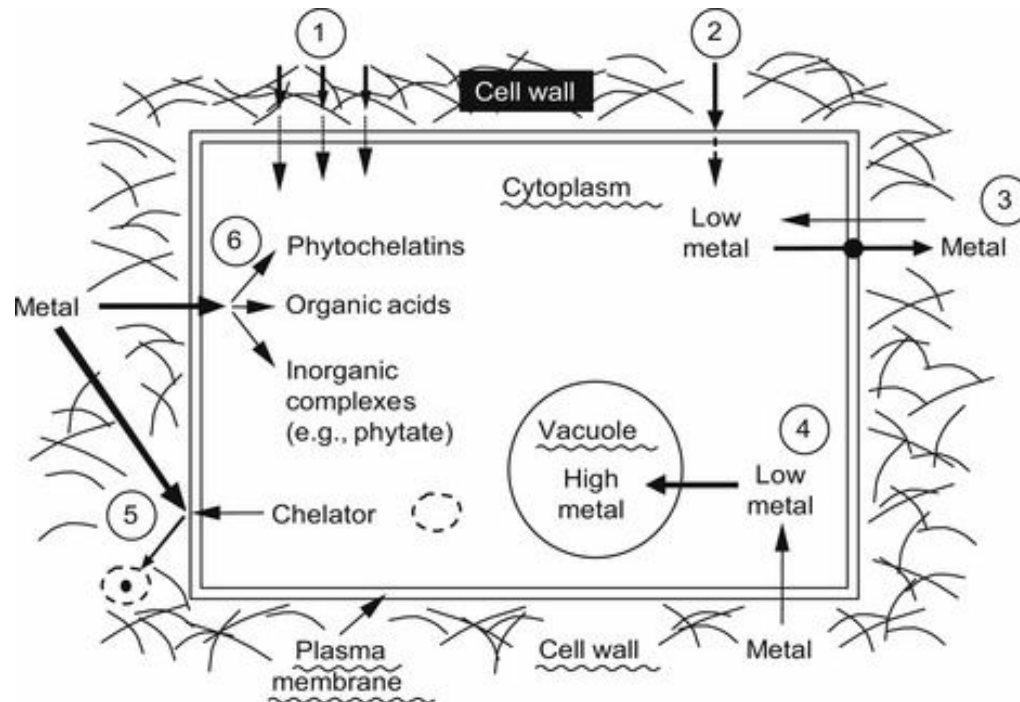


Fig. 1 Scheme showing some of the initiators (stressors) of reactive oxygen species (ROS) and the biological consequences leading to a variety of physiological dysfunctions that can lead to cell death

Heavy metal tolerance in plants: possible mechanisms



- (1) Binding to cell wall;
- (2) restricted influx through plasma membrane;
- (3) active flux;
- (4) compartmentation in vacuole;
- (5) chelation at the cell wall–plasma membrane interface;
- (6) chelation in the cytoplasm.