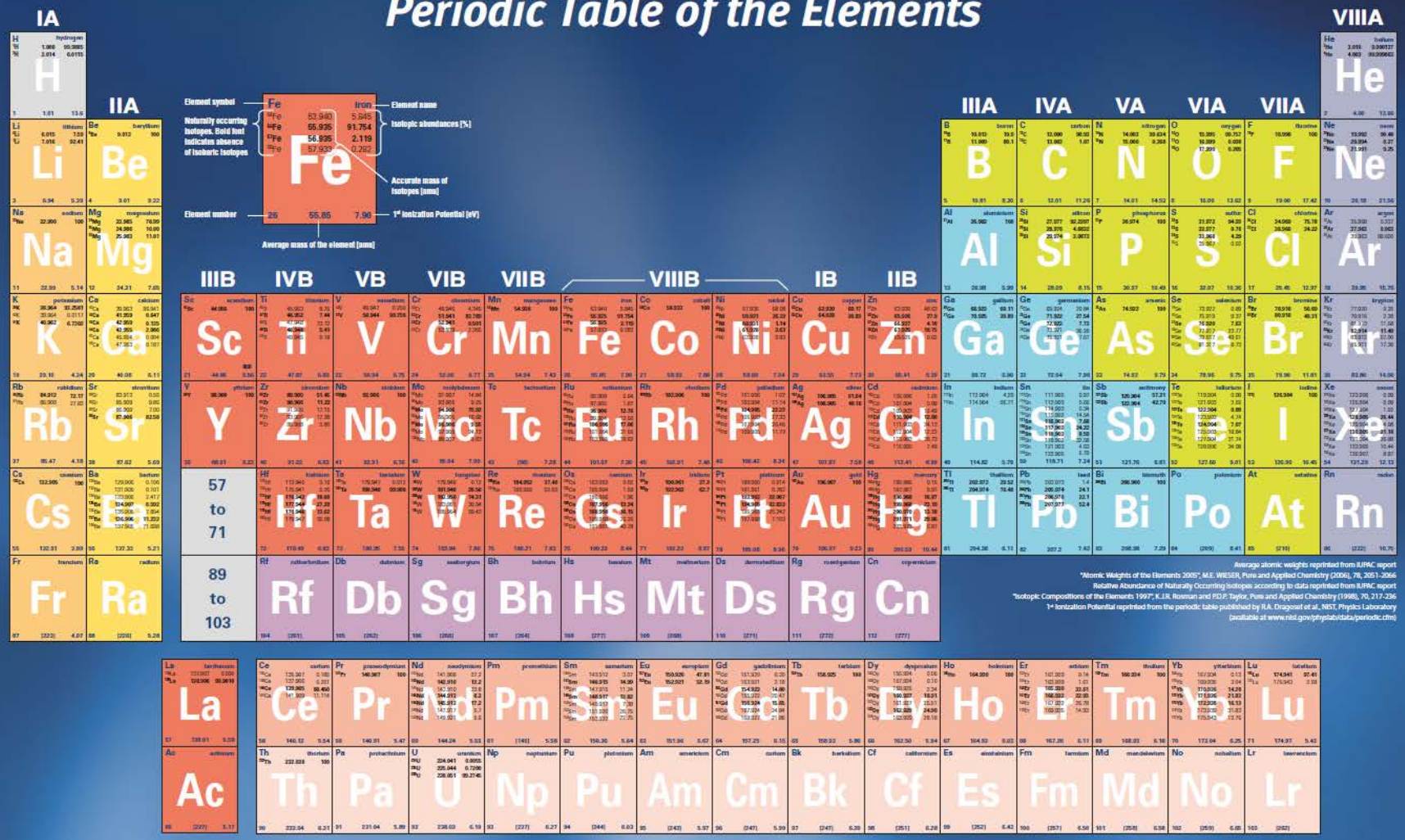
Micronutrients

Mikronährstoffe

Franz Hadacek

Periodic Table of the Elements



Average atomic weights reprinted from IUPAC report
"Atomic Weights of the Elements 2005", M.E. WIESER, Pure and Applied Chemistry (2006), 78, 2051-2066
Relative Abundance of Naturally Occurring Isotopes according to data reprinted from IUPAC report
"Isotopic Compositions of the Elements 1997", K.J.R. Rosman and P.D.P. Taylor, Pure and Applied Chemistry (1998), 70, 217-235
1st Ionization Potential reprinted from the periodic table published by R.A. Dragoset et al., NIST, Physics Laboratory
(available at www.nist.gov/physlab/data/periodic.cfm)

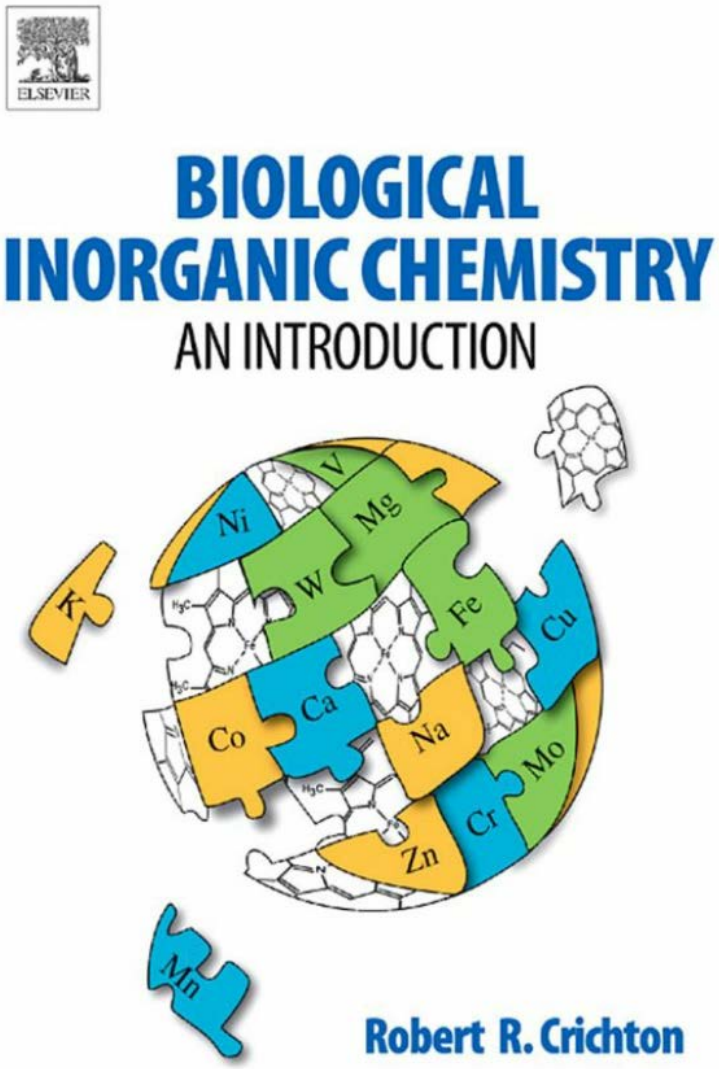
- Alkali metals
- Alkaline earth metals
- Transition metals
- Lanthanide series
- Actinide series
- Poor metals
- Nonmetals
- Noble gases

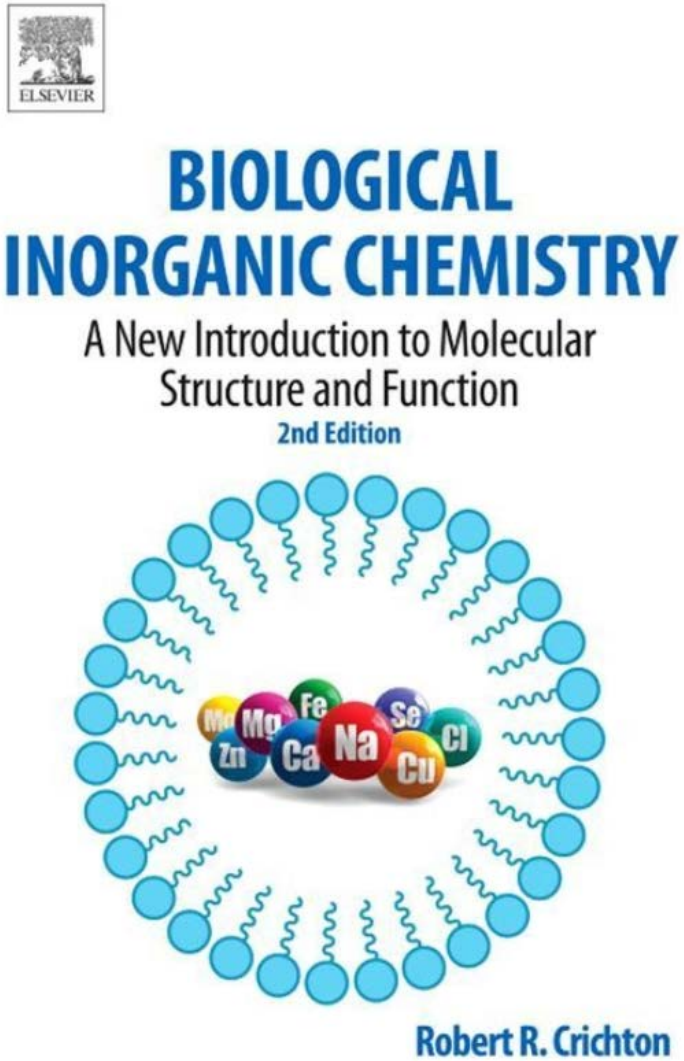
www.thermoscientific.com

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	CO2, HCO3$^-$, H_2O, O2, NO3$^-$, SO4^{2-}, SO2 (SeO4^{2-})	Essential elements involved in enzymatic reactions, low- and high-molecular-weight metabolites, polymers
	P	Phosphate esters	Phosphates	Energy transfer
Amorphous hard structures	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	Coordination complex	Ion,	Chlorophyll, phosphate metabolism
	Fe, Cu	Oxygen transport	Coordination complex	Proteins

3





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.

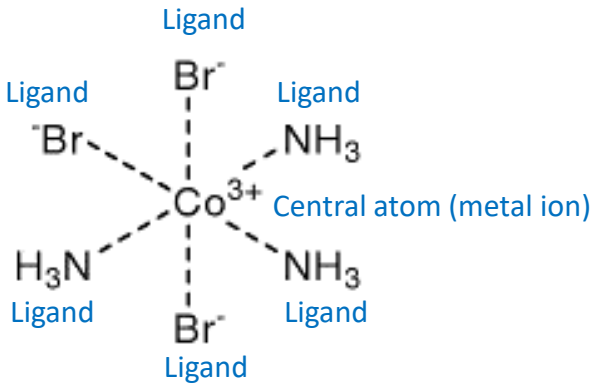
$$Na^{+}Cl^{-}$$

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 $\mathbf{H_2}$. 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**.



$CoBr_3 \cdot 3NH_3$ 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-}, $ROPO_3^{2-}$, $(RO)_2PO_2^-$, 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 informing 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.

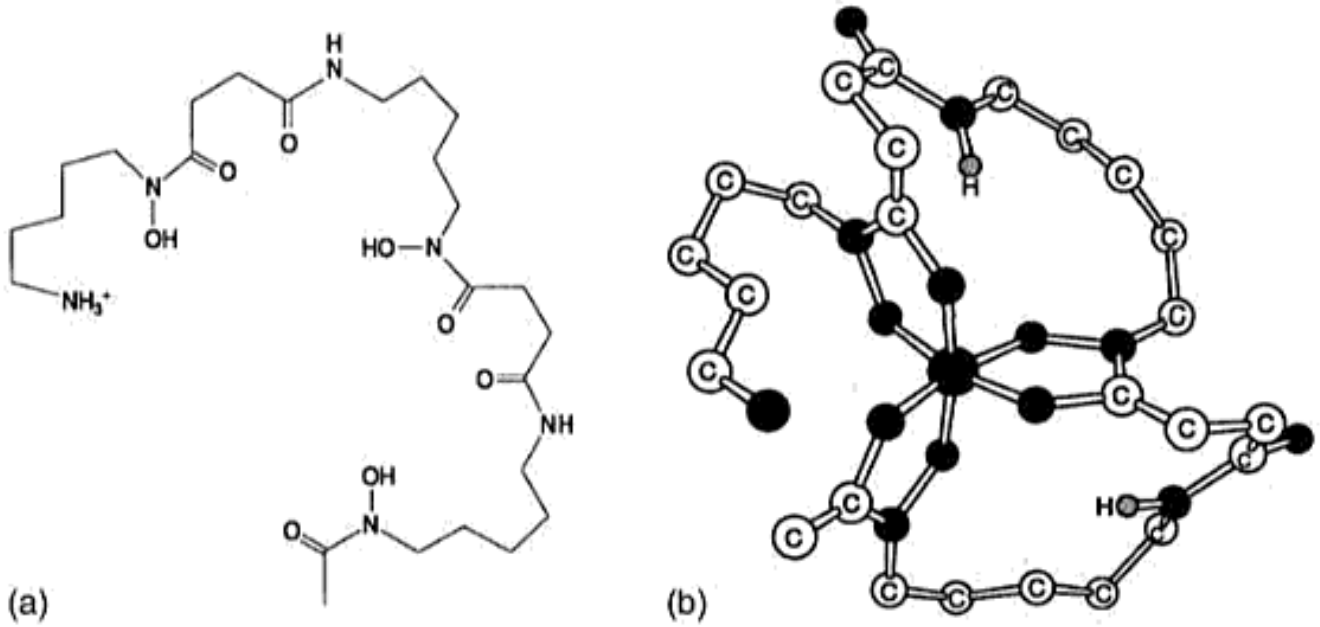


Figure 2.3 (a) The metal chelator desferrioxamine (DFO) and (b) its complex with iron.

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**.

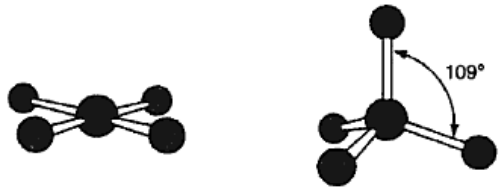
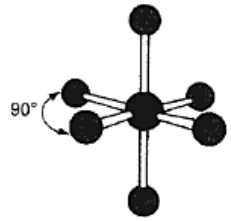
Table 2.2

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

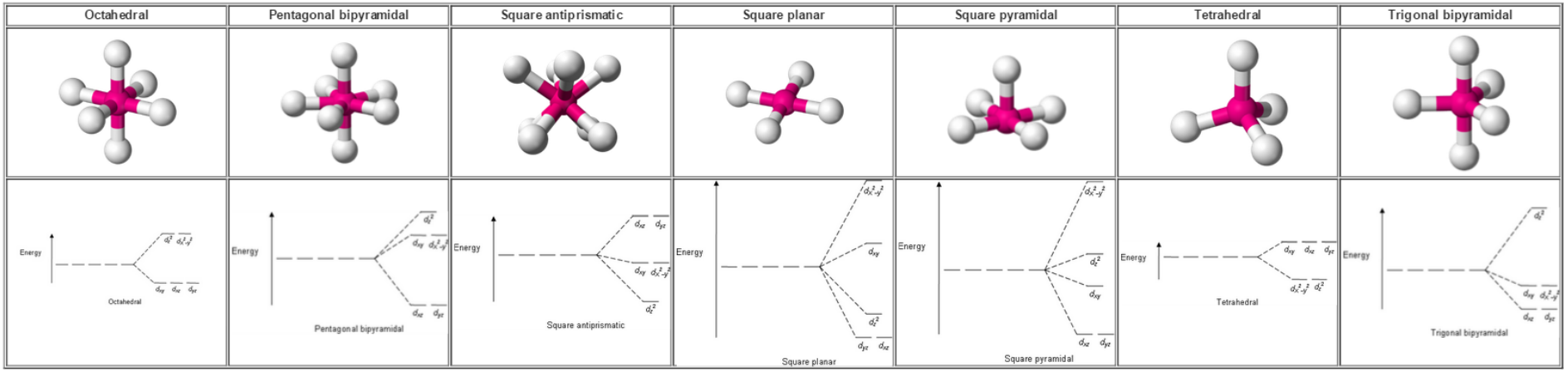
Table 2.4

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

Coordination number	Geometry of coordination compound	Example
4	 Square Tetrahedral	$[Cu(NH_3)_4]^{2+}$ (square planar) $CuCl_4$ (tetrahedral)
6	 Octahedron	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**.



$$I^- < Br^- < SCN^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- \sim RCOO^- < H_2O \sim RS^- < NH_3$$
$$\sim \text{Im (imidazole)} < \text{bpy (2,2′-bipyridine)} < CN^- < CO$$

Biological ligands:

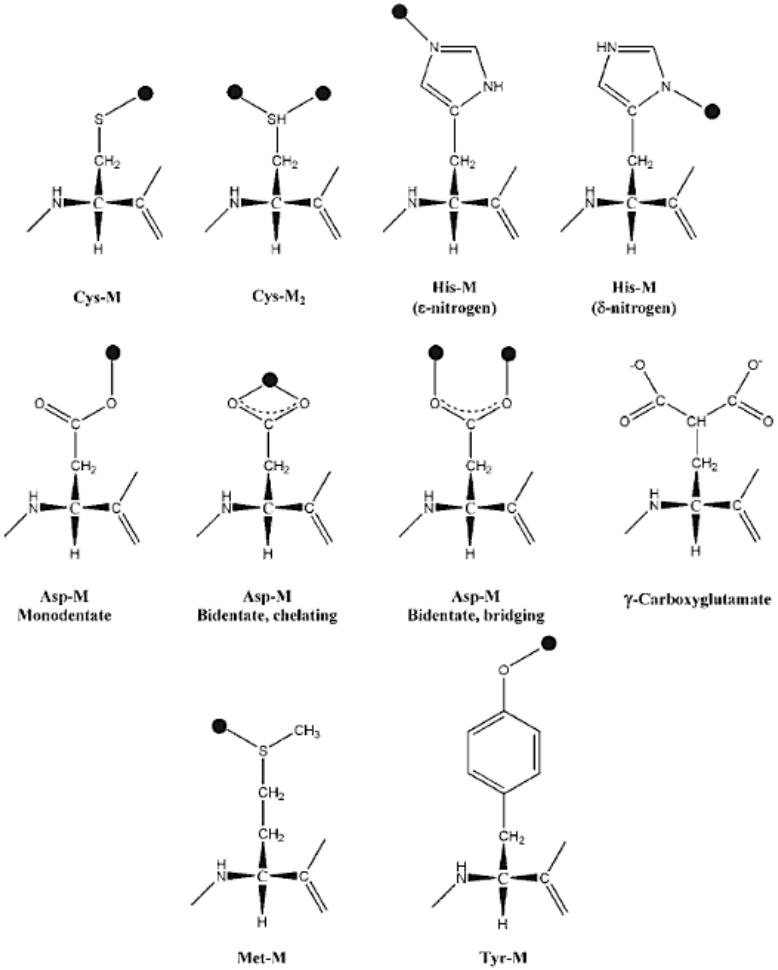


Figure 3.1 Principal protein amino acid side-chain metal–ion binding modes (the metal ion represented as a dark filled circle) and (right) the structure of the Ca^{2+}-binding γ-carboxyglutamate found in proteins of the blood-clotting cascade.

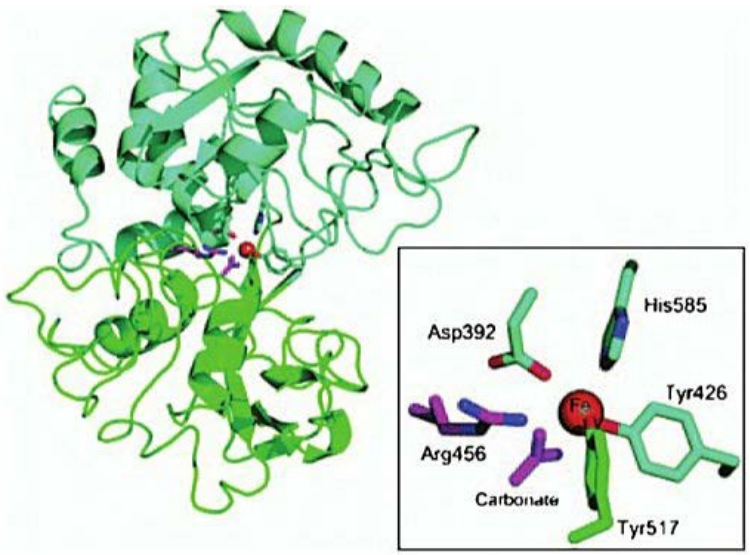


Figure 3.2 Ribbon diagram of the C-lobe of human transferrin with the two domains shown in different colours (cyan for C1 and green for C2). The inset shows the four protein ligand residues together with the arginine residue which stabilizes binding of the synergistic carbonate ion (both in magenta).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

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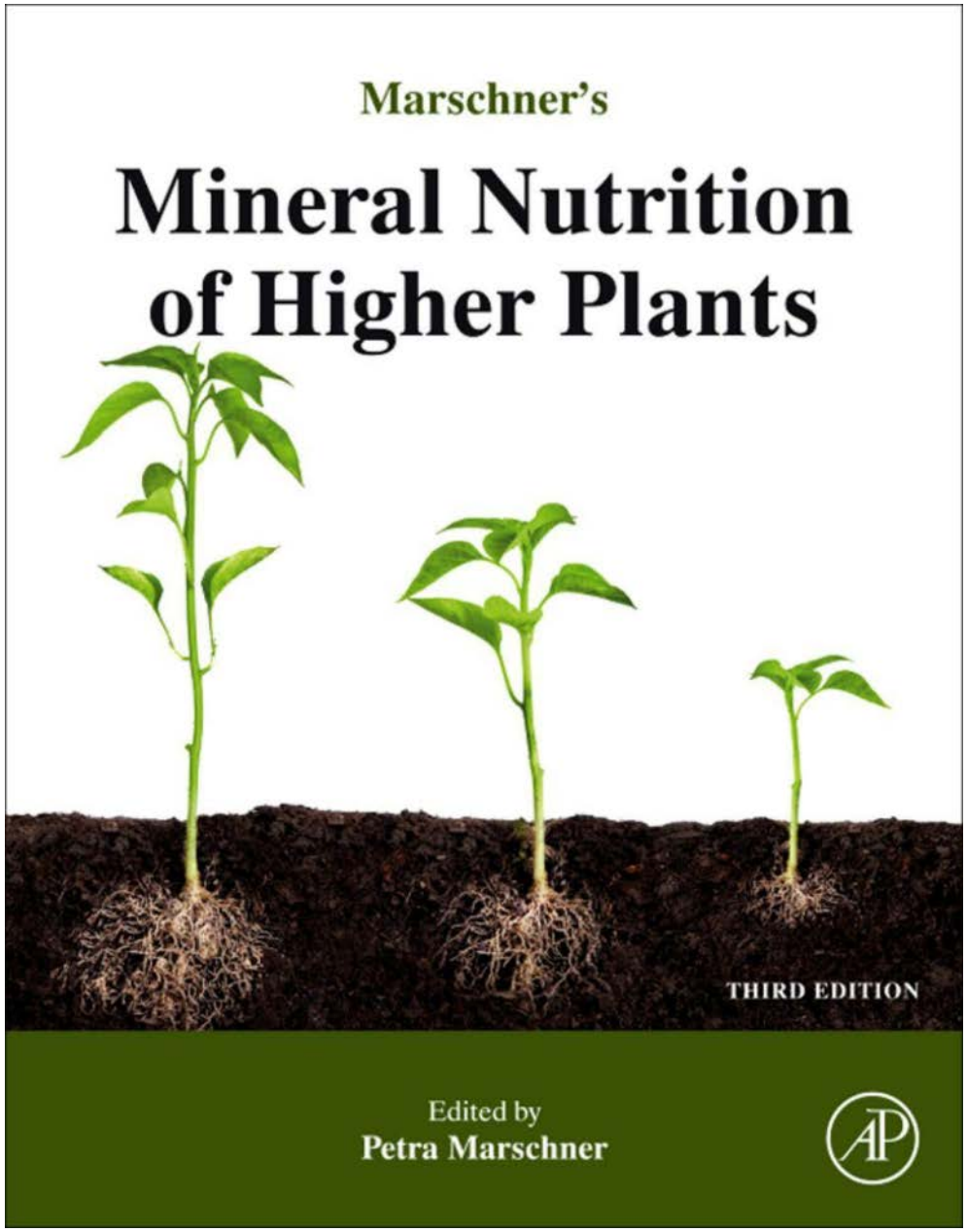
Marschner's
Mineral Nutrition of Higher Plants
THIRD EDITION
Edited by
Petra Marschner

Table 1
Element composition of the earth's crust by weight (%) and the typical relative proportion of minerals found in plant tissue assuming N levels at 100%

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Silicon	27.7	Potassium	50	Iron	0.03
Aluminium	8.1	Calcium	25	Boron	0.03
Iron	5.0	Magnesium	10	Manganese	0.02
Calcium	3.6	Phosphorous	8	Zinc	0.007
Sodium	2.8	Sulfur	5	Copper	0.002
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 *et al.*
Ni	1987	P.H. Brown *et al.*

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:

$$Cl^-$$

Monovalent anion

and
the most abundant in plants

and
an essential counter ion
for membrane potential stabilization

Cl

- Photosynthetic O_2 evolution PSII complex

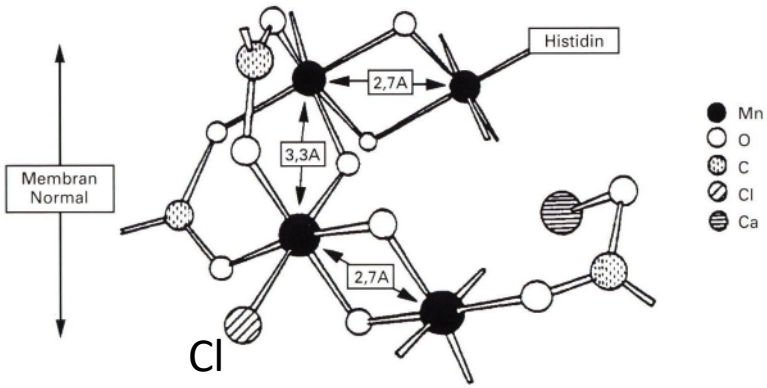
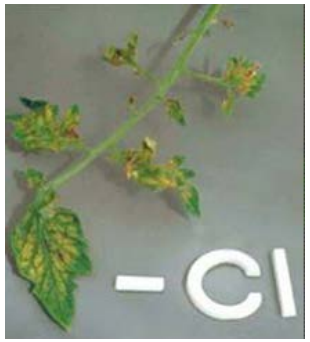


Abb. 64. Modell des wasseroxidierenden Mn-Komplexes innerhalb des Photosystems II auf der Basis von Messungen mit der Röntgenstrahl-Absorptions- sowie der e^--paramagnetischen Resonanz-Spektroskopie (entnommen aus BOWYER und LEEGOOD 1997).

Marschner's Mineral Nutrition of Higher Plants

- Stimulation of various membrane-bound phosphorylating enzymes, ATPases amongst others

- Stomatal regulation (together with K^+ and malate)



http://www.farmspeak.com/nutrient-deficiency.html

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All others	1.5				

Iron:

$$Fe^{II} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} Fe^{III}$$

Transition metal

Haber-Weiss (inkl. Fenton) Reaction:

Fe

$$O_2^{\bullet -} + Fe^{3+} \longrightarrow Fe^{2+} + O_2$$

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH$$

Superoxid Dismutase (SOD):

$$2\,O_2^{\bullet -} + 2\,H^+ \xrightarrow{SOD} O_2 + H_2O_2$$

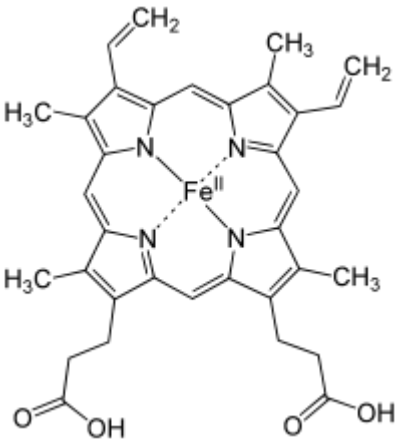
Reactive oxygen (nitrogen) species

Fe

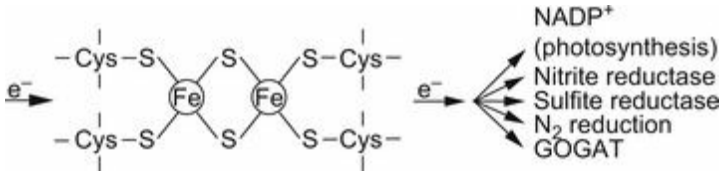
Dioxygen (molecular oxygen)	Superoxide anion radical	Hydrogen peroxide	Hydroxyl radical	Water
Singlet oxygen				
$\cdot\bar{\underline{O}} - \bar{\underline{O}}\cdot$	$\cdot\bar{\underline{O}} - \bar{\underline{O}}:$	$H:\bar{\underline{O}} - \bar{\underline{O}}:H$	$\cdot\bar{\underline{O}}:H$	$H:\bar{\underline{O}}:H$
$\bar{\underline{O}} - \bar{\underline{O}}:$				
O_2	$O_2^{\bullet -}$	H_2O_2	$^{\bullet}OH$	H_2O
$+ e^-$	$+ e^- + 2\,H^+$	$+ e^-$ OH^-	$+ e^- + H^+$	
	$O_2^{\bullet -} + H^+ \rightleftarrows HO_2^{\bullet}$	$:\bar{\underline{O}}:H$		
	$\cdot\bar{\underline{O}} - \bar{\underline{O}}:H$	$OH^- + H^+ \rightleftarrows H_2O$		Nitric oxide
	Hydroperoxyl radical			$\cdot\bar{N} = \bar{\underline{O}}$
				$^{\bullet}NO$

Fe

- Heme proteins
  (e.g. cytochromes)



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

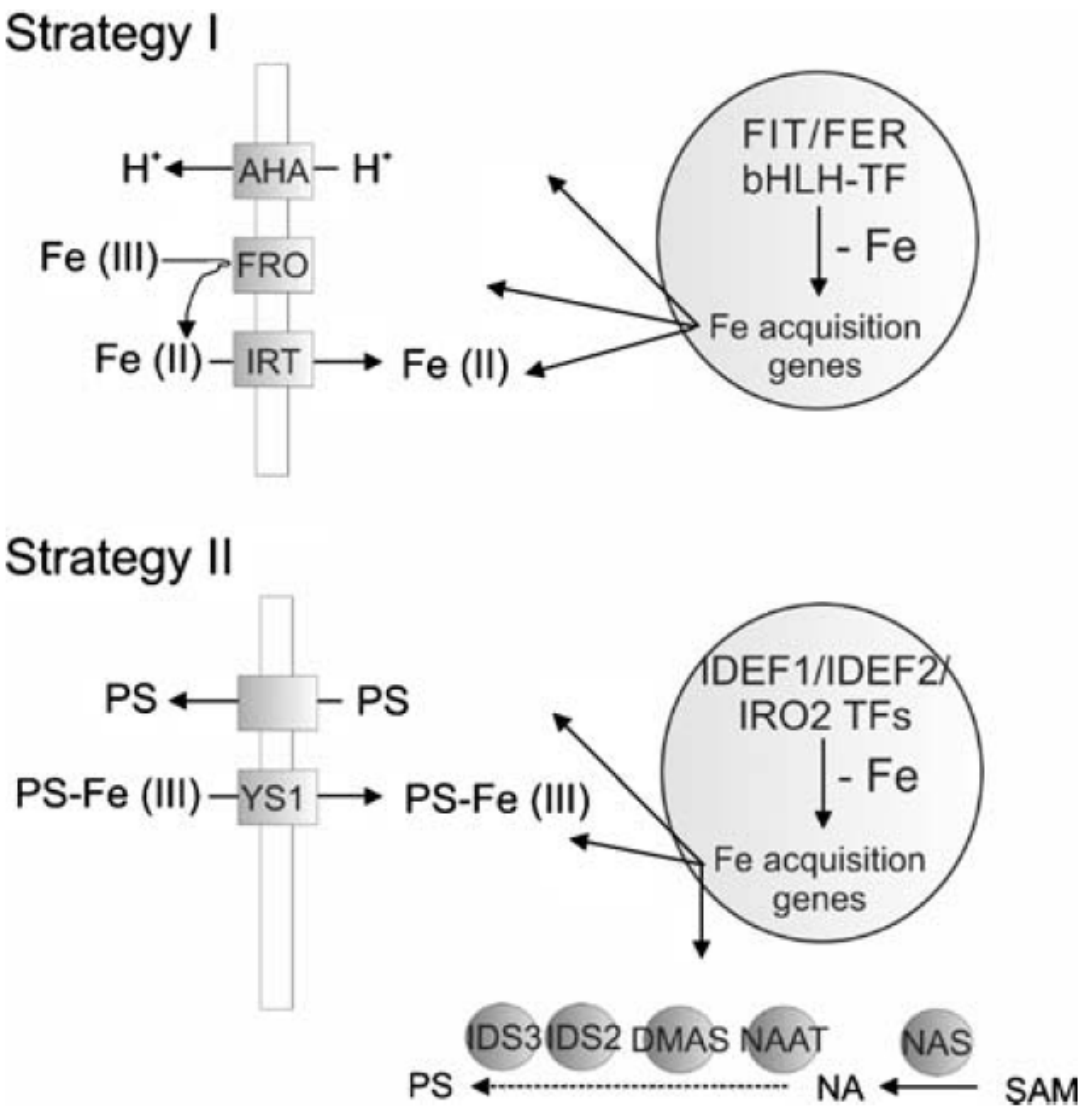


- Other enzymes
  (e.g. lipoxygenases)

http://www.farmspeak.com/nutrient-deficiency.html

Iron uptake mechanisms by plant roots:

Fe



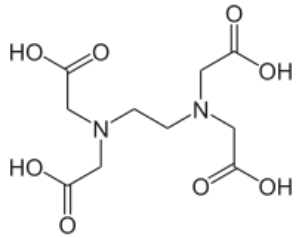
Dicots and nongramineous monocots

Gramineous monocots

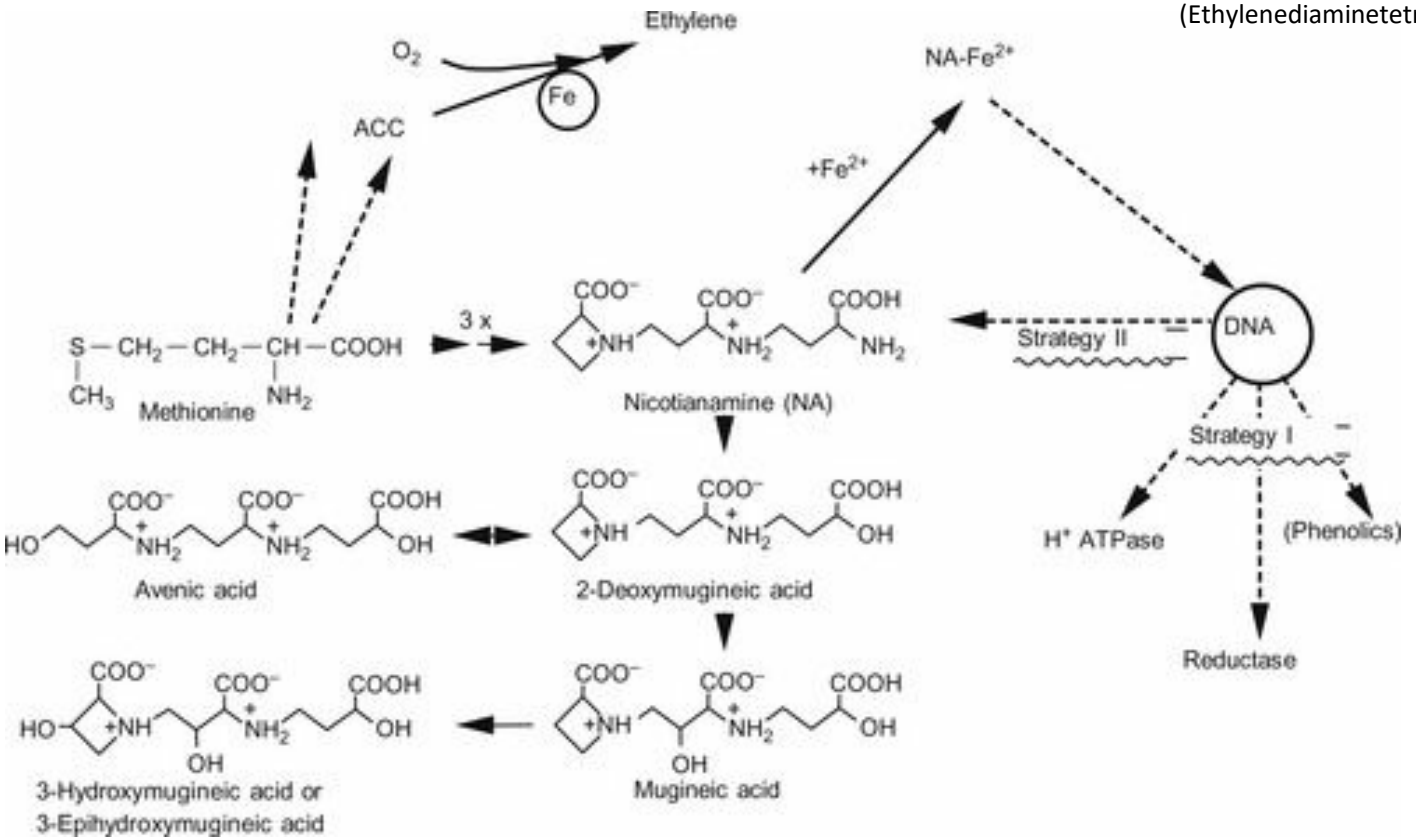
Lemanceau et al., 2009, Plant Soil 321: 513-35

Phytosiderophores:

Fe



EDTA
(Ethylenediaminetetraacetic acid)



Ferritin:

Fe

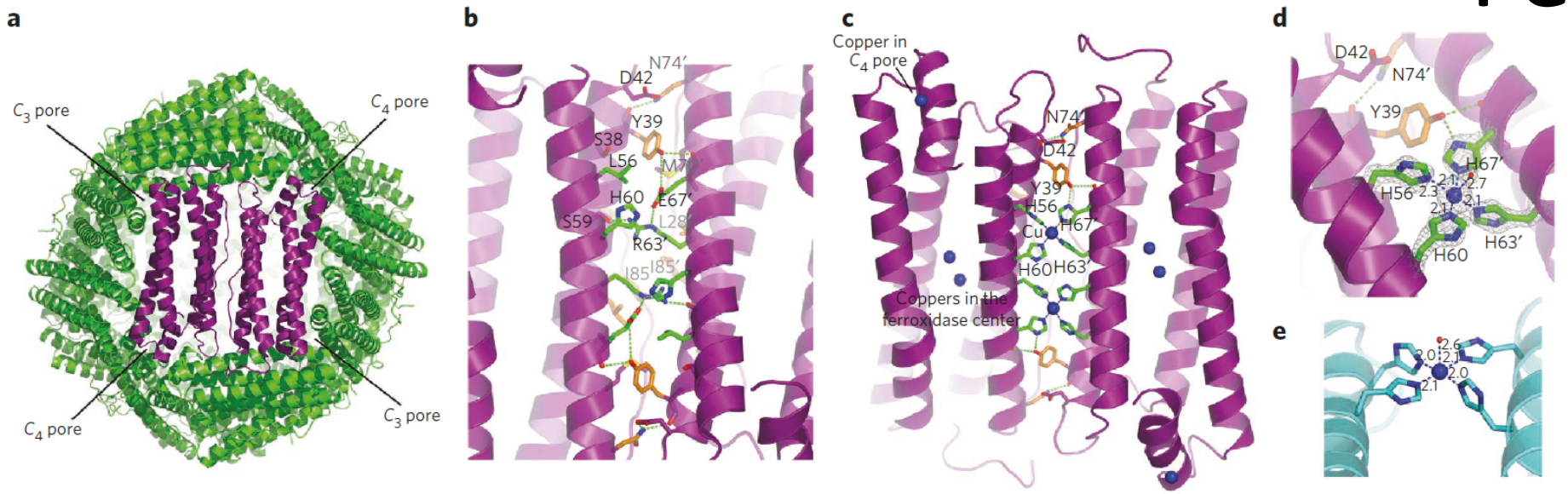
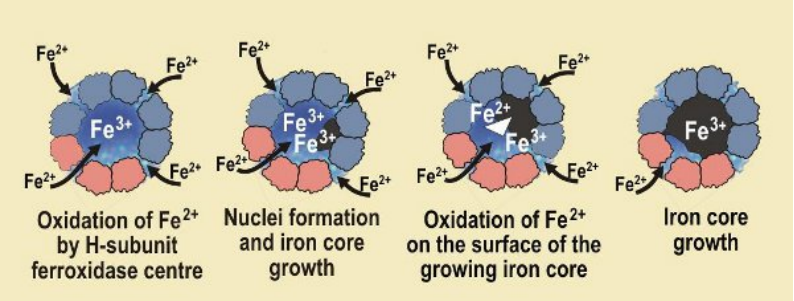


Figure 2 | The ferritin cage architecture and intersubunit interactions in the C_2 interface. (**a**) The 24-meric ferritin architecture viewed down the C_2 symmetry axis. Alternative views down the C_3 and C_4 axes are shown in **Supplementary Figure 5**. A C_2-symmetric dimeric component of ferritin 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_2:MBPC1$_2$ 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.

Koorts AM & Viljoen M, Ferritin and ferritin isoforms

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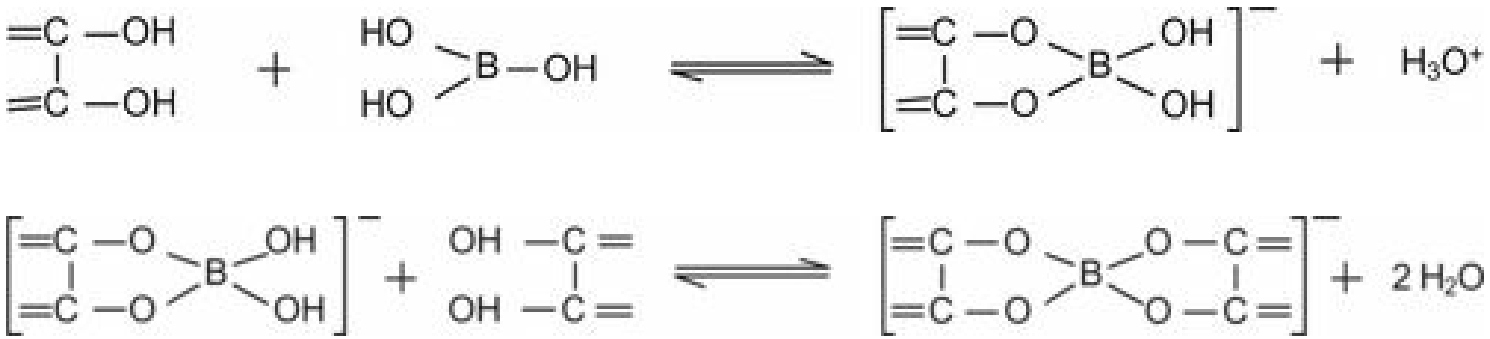
All others	1.5				

Boron:

Metalloid

$$B(OH)_3 + 2\ H_2O \leftrightarrow B(OH)_4^- + H_3O^+$$

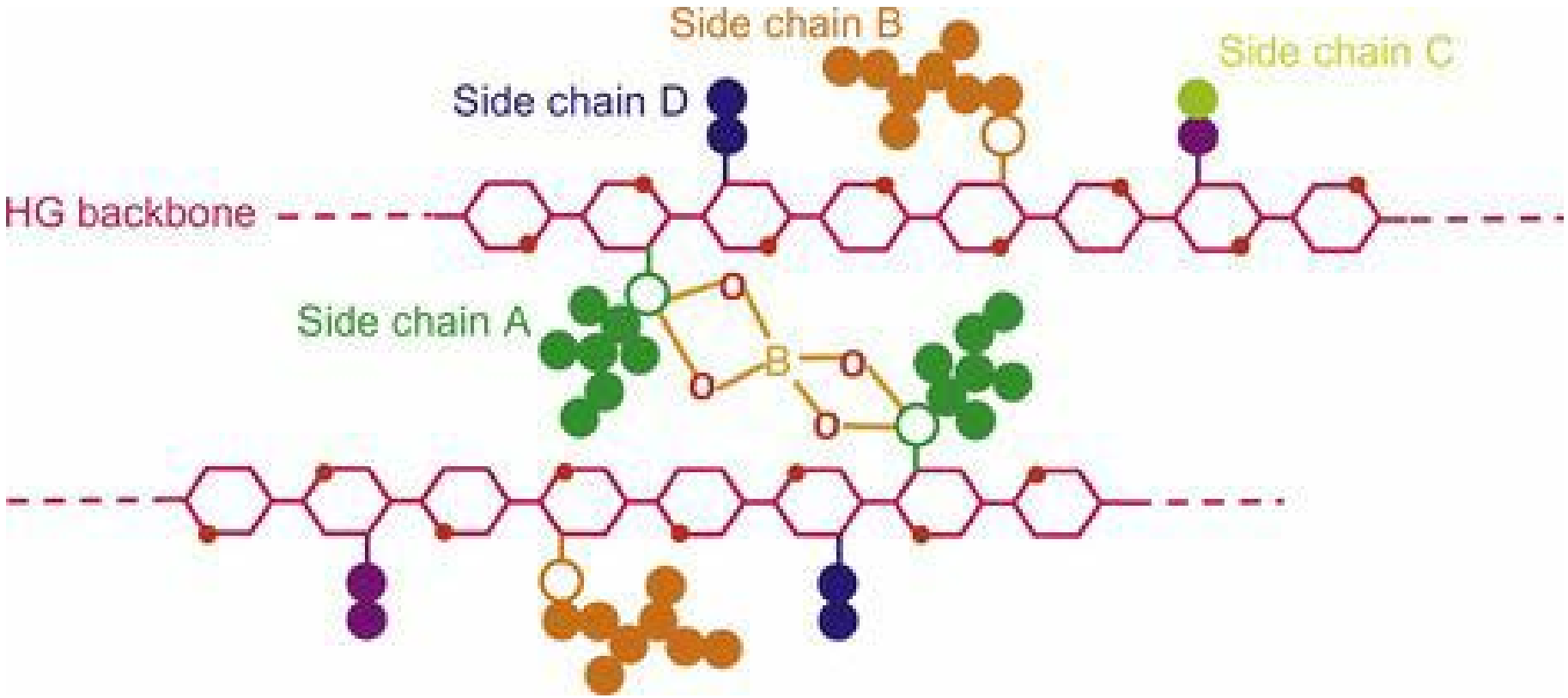
Boric acid Borate



Complexes with diols and polyols

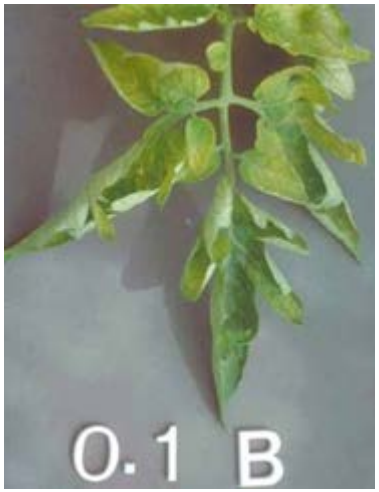
cis-diol configuration in
mannitol, mannan, polymannuronic acid,
pectin and hemicelluloses

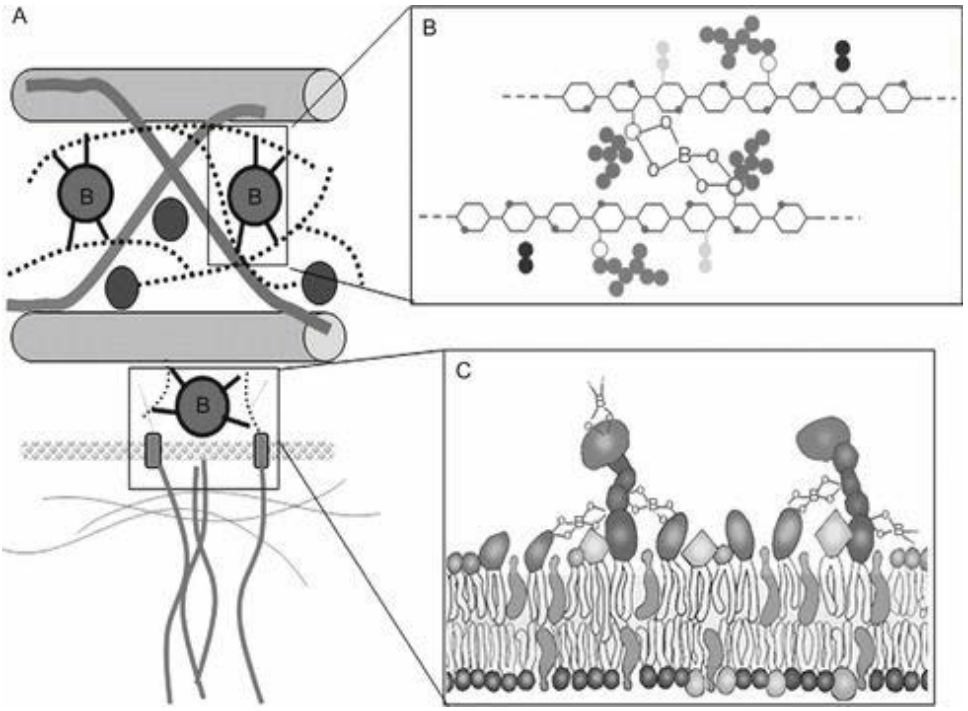
B



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.

Marschner‘s Mineral Nutrition of Higher Plants

Table 1
Element composition of the earth's crust by weight (%) and the typical relative proportion of minerals found in plant tissue assuming N levels at 100%

		Plant tissue levels			
Earth's crust composition		**Macronutrients**		**Micronutrients**	
Oxygen	46.6	Nitrogen	100	Chlorine	0.05
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Aluminium	8.1	Calcium	25	Boron	0.03
Iron	5.0	Magnesium	10	Manganese	0.02
Calcium	3.6	Phosphorous	8	Zinc	0.007
Sodium	2.8	Sulfur	5	Copper	0.002
Potassium	2.6			Nickel	0.0004
Magnesium	2.1			Molybdenum	0.0001
All others	1.5				

Manganese:

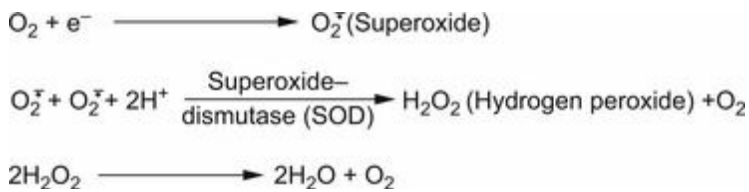
Mn

$$Mn^{II} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} Mn^{III} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} Mn^{IV}$$

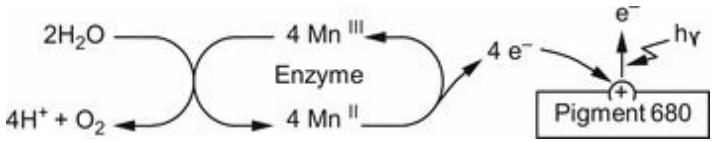
Transition metal

Mn

- Superoxide dismutase



- Mn protein in PSII



- Oxalate oxidase

- Mn^{2+} acts as cofactor for 35 different enzymes (shikimate pathway and aromatic amino acids, various peroxidases, terpenoid and lipid biosynthesis)

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Zinc:

Zn

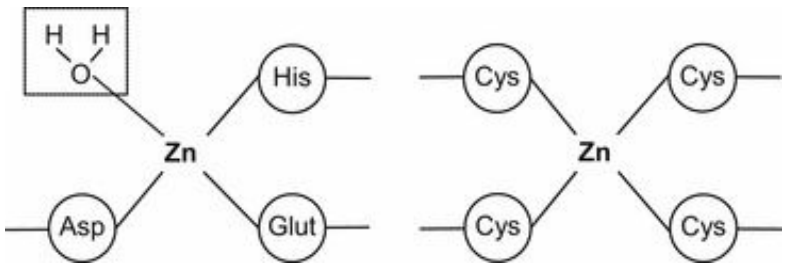
Zn^{II}

Transition metal

$ZnOH^{+}$

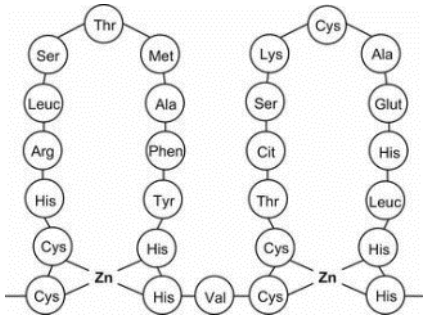
Zn

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



- Zn^{2+} is a cofactor for dehydrogeneases, aldolases, isomerases, trans-phosphorylases 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“

Marschner‘s Mineral Nutrition of Higher Plants

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All others	1.5				

Copper:

Cu

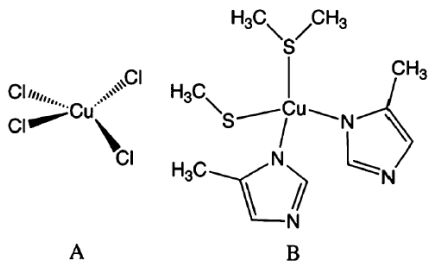
$$Cu^{I} \underset{+\,e^{-}}{\overset{-\,e^{-}}{\rightleftharpoons}} Cu^{II}$$

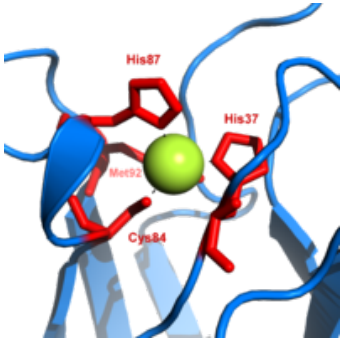
Transition metal

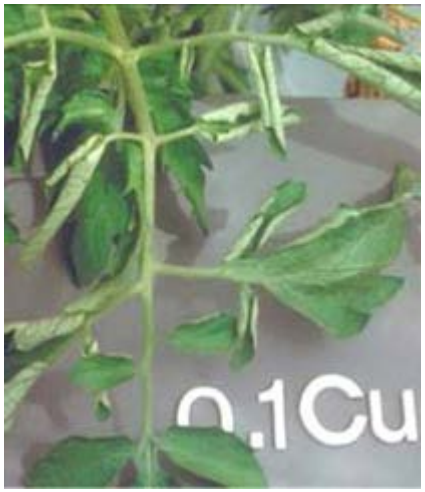
Cu

- Present in more than 100 different proteins

- More than 50 % in **plastocyanin** in electron transport chains of PSI

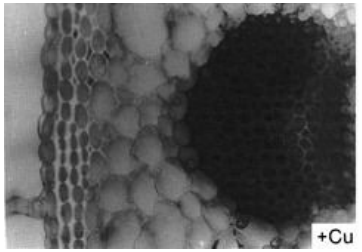


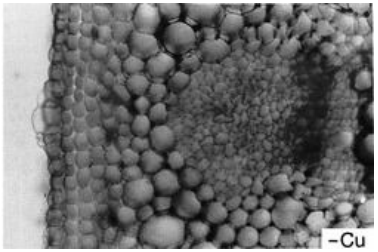




- Superoxide dismutase, ascorbate oxidase etc.

- Lignification





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All others	1.5				

Nickel:

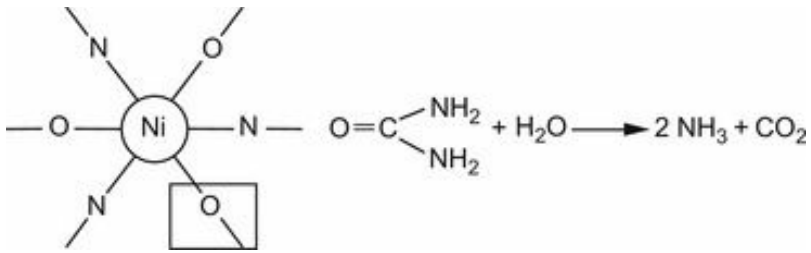
Ni

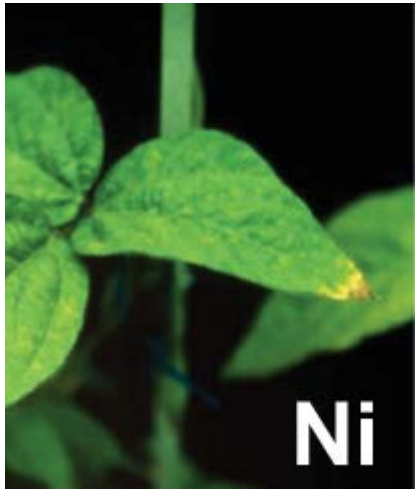
$$Ni^{I} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} Ni^{II} \underset{+\,e^-}{\overset{-\,e^-}{\rightleftharpoons}} Ni^{III}$$

Transition metal

Ni

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





Urea toxicity
(yellow leaf tips)

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Potassium	2.6			Nickel	0.0004
Magnesium	2.1			Molybdenum	0.0001
All others	1.5				

Molybdenum:

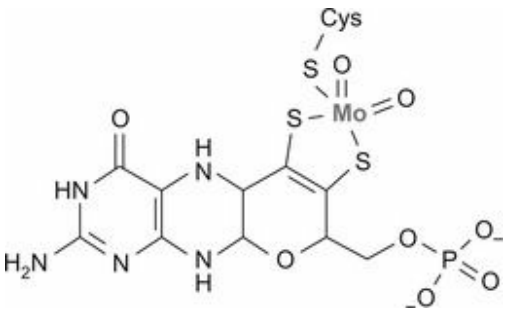
Mo

$$MoO_4^{2-}$$

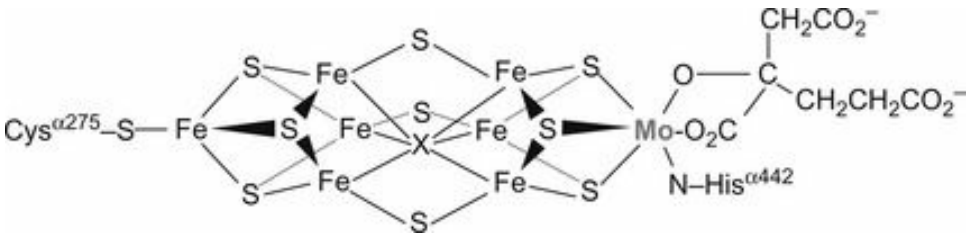
Transition element,
More present in the lithosphere than in soils

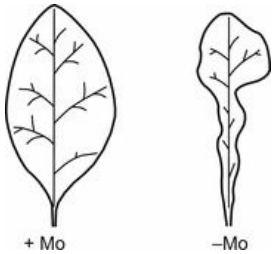
Mo

- Nitrate reductase cofactor Moco



- Nitrogenase (all N_2 fixing microorganisms)





"whiptail"

Marschner's Mineral Nutrition of Higher Plants

Oxidative stress

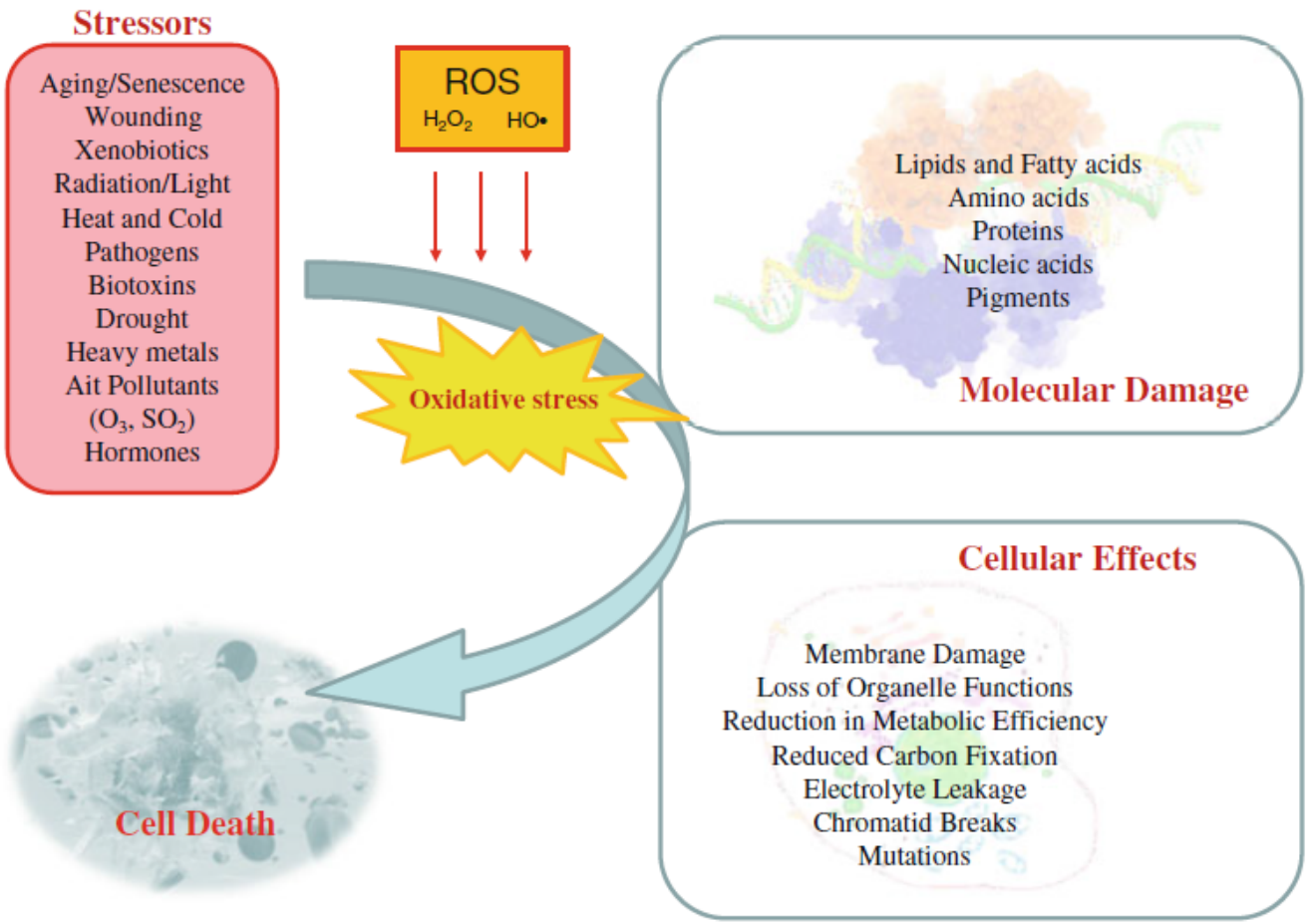
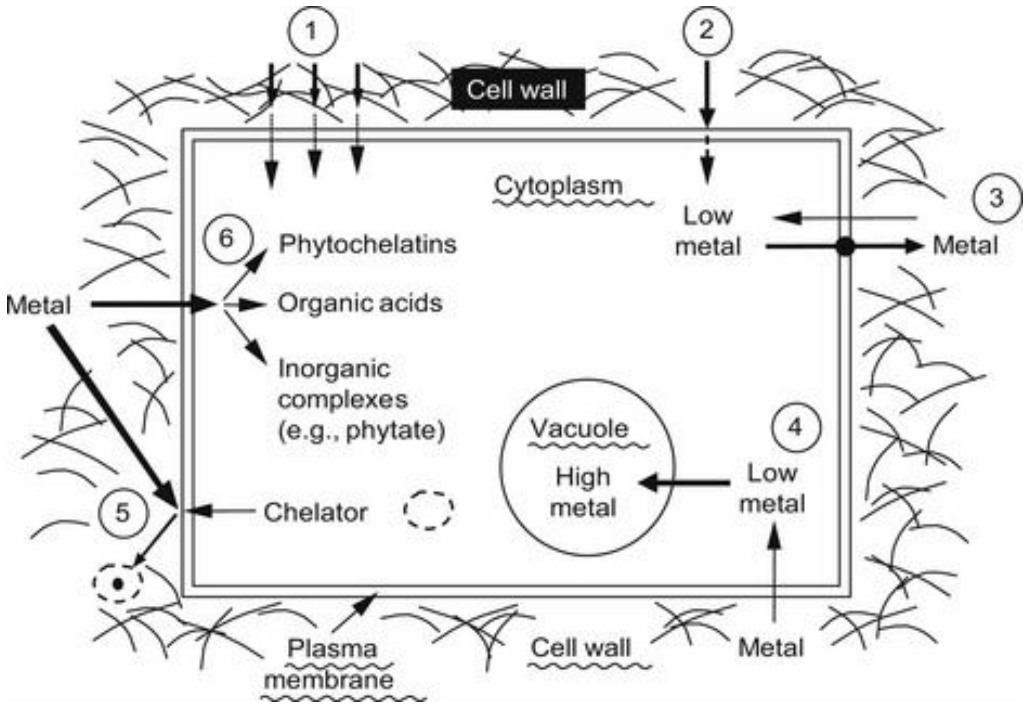


Fig. 1 Scheme showing some of the initiators (stressors) of reactive oxygen species (ROS) and the biological consequences leading to a variety of physiological dysfunctions that can lead to cell death

D. K. Gupta et al. (eds.), *Heavy Metal Stress in Plants*,
DOI: 10.1007/978-3-642-38469-1_2, © Springer-Verlag Berlin Heidelberg 2013

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.

Transpiration enhances nutrient uptake

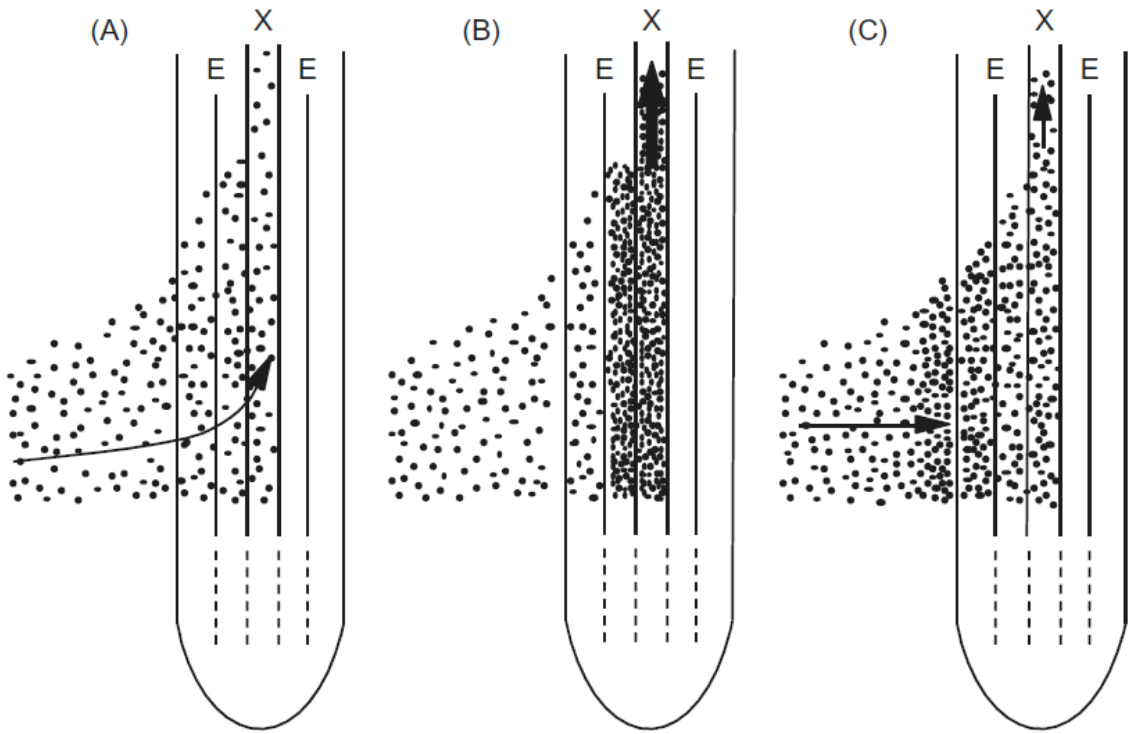


FIGURE 3.5 Models for the enhancement of uptake and translocation of elements by plant roots by increased transpiration. A. Drag of elements through the root apoplasm into the stele. B. Water flow-induced increase in the efflux of solutes from the root symplasm to the xylem vessels. C. Increased mass flow of the external solution to the rhizoplane and into the apparent free space, favouring greater uptake into the symplasm and delivery to the xylem. E, endodermis; X, xylem; arrow, water flux.

Xylem unloading

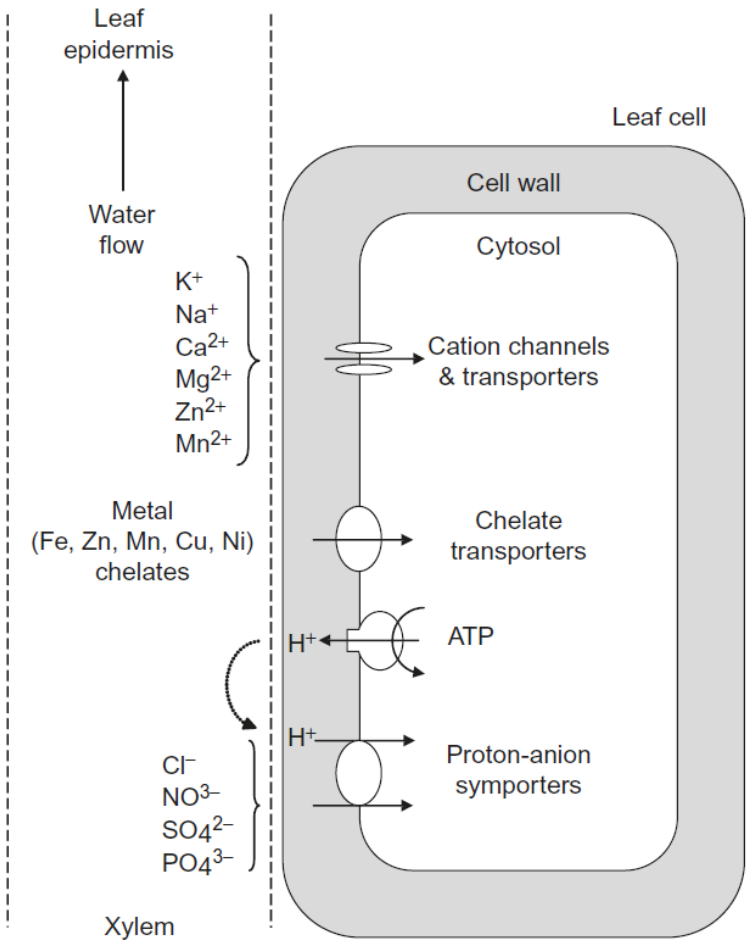
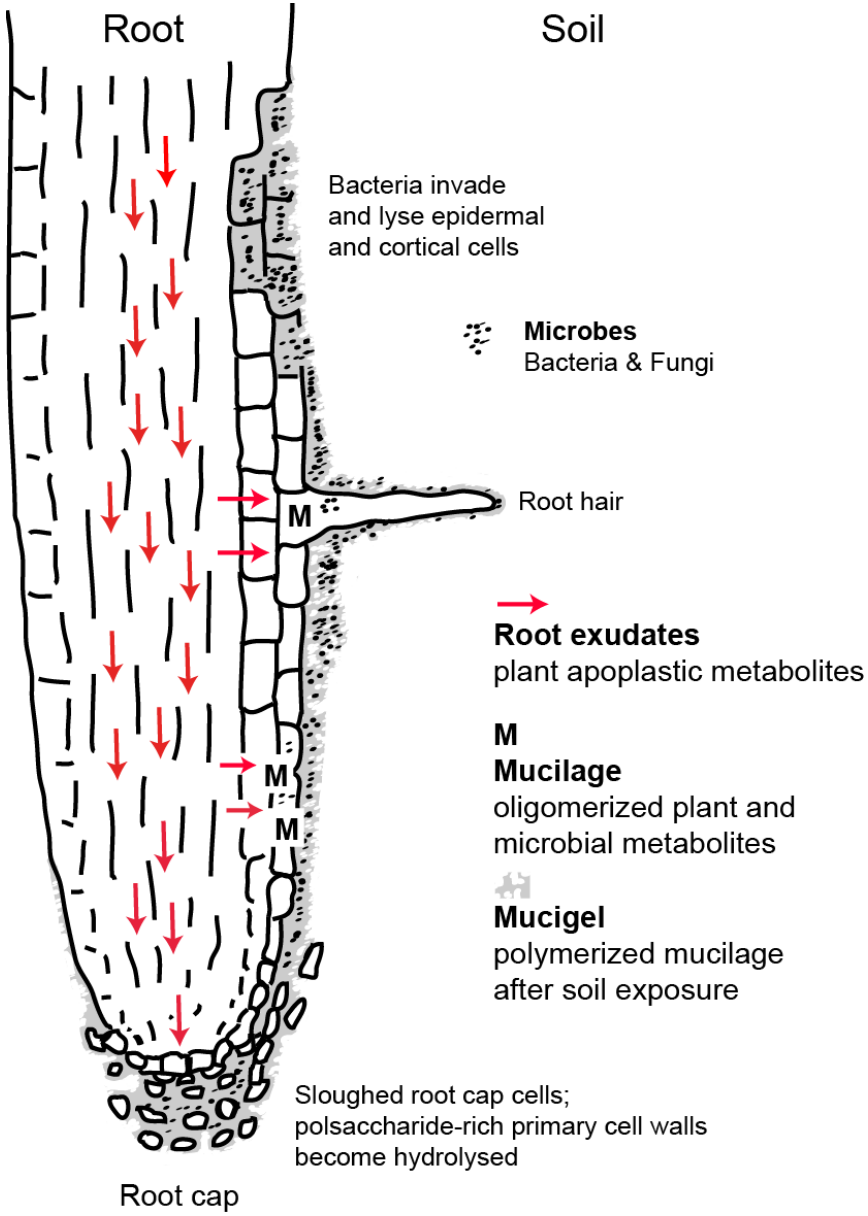


FIGURE 3.4 Model for the retrieval of major solutes from the xylem sap ('xylem unloading') in leaf cells.

Marschner's Mineral Nutrition of Higher Plants

Root exudation



Rovira AD, Bowen GD & Foster RC (1983) In: Inorganic Plant Nutrition (A. Läuchli, R.L. Bieleski, eds.), Springer.