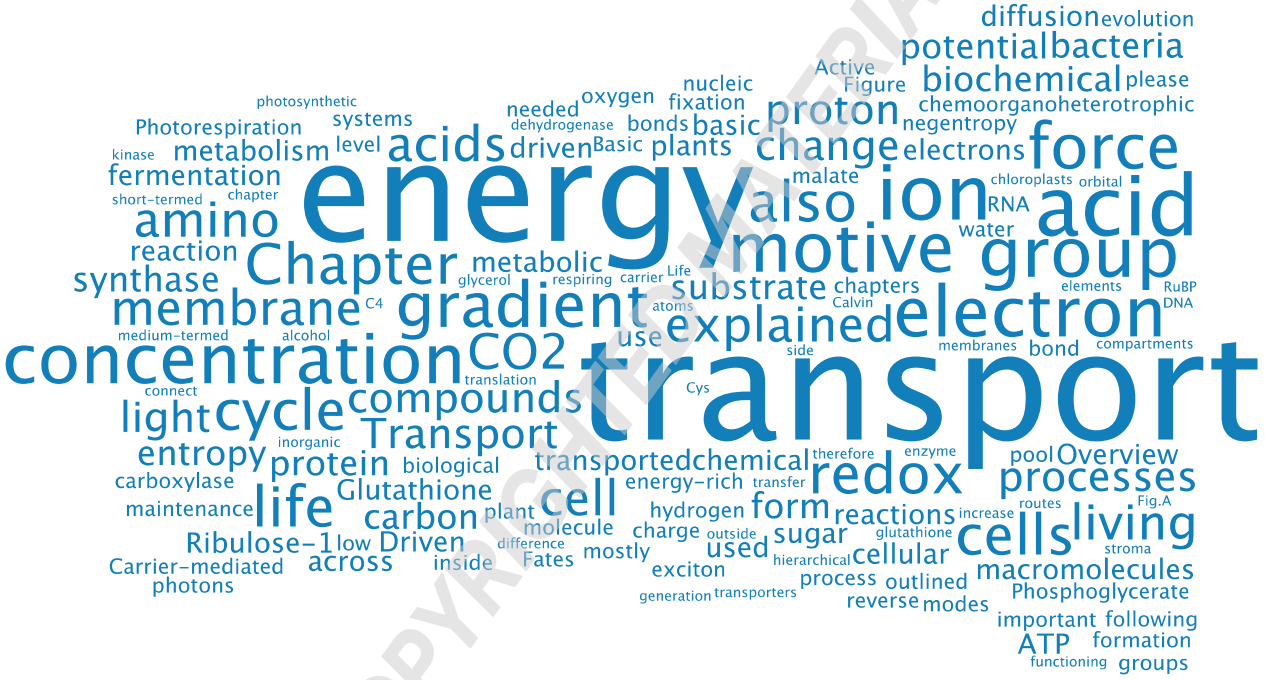

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1
Basic Biochemical Roots

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See extended version S1 of this chapter on companion website: http://www.wiley.com/go/Krauss/Nies/EcologicalBiochemistry

Overview

A thorough presentation of the basics needed to access "Ecological Biochemistry" can be found on the companion website (see URL above). The following pages give you an idea of what exactly can be looked up on this website and at the same time reproduce the most important basics-summarizing figures often referred to in the rest of the book.

1.1
Chemistry and Physics of Life

How does life function? Chapter S1 defines "life" as a thermodynamic process, following Erwin Schrödingers' famous lecture "what is life?" delivered at Trinity College, Dublin, in February 1943. Thermodynamics, entropy, and negentropy (= order) and how a living cell manages to form "order" despite the three basic laws of thermodynamics are explained. This chapter defines life as an energy-transducing process exerted by enclosed reaction compartments (= cells). From this, maintenance energy, the allochthonous and autochthonous modes of microbial life, and the processes evolution, mutation, and selection are derived. Generating negentropy in living cells means formation of macromolecules, and the four major groups of cellular macromolecules are introduced. Major and minor bioelements are listed and their bioavailability connected to the generation of elements in stars. This leads also to water as the optimum solvent for the cellular biochemistry (See also Chapter 10) and to the necessity of a semipermeable membrane surrounding living cells (Figure 1.1).

Important terms explained: allochthonous, autochthonous, carbohydrate, carbon, cell, DNA, dry mass, dry weight, maintenance energy, entropy, evolution, element generation, information, lipid, macromolecule, semipermeable membrane, mutation, nucleic acid, maintenance power, protein, RNA, selection, thermodynamics, transport, wet mass, wet weight.

1.2
Energy and Transport

The second section of Chapter S1 introduces how a living cell functions in general. In the liquid phase of a solvent, most likely water, a cell represents a separated system that continuously uses energy from the outside to increase its negentropy inside by the synthesis of carbon-based macromolecules, thereby overcompensating the decrease in entropy inside by a higher increase in entropy outside. Further sections of this chapter show how this can be accomplished.

The chapter starts with the explanation of the lowest systems level of interest for biologists, the atoms, electrons, and photons and continues with the basic modes of energy conservation. Atoms, orbitals, and the consequences of the structure of the electron shells for the chemical features of the elements, redox energy, and electronegativity are explained in depth. Atoms form molecules at the next systems level and new features emerge by this process, which can nevertheless be deduced from the electron structure of the involved atoms. This is also true for the most important functional groups of the building blocks of the macromolecules. Which energy sources can be used by cells and how the energy from photons can be harvested and ultimately converted to an ion gradient across a biological membrane, leading to the phototrophic life style are explained (Figure 1.2).

Transport processes change chemical gradients across biological membranes and these processes are categorized in a strict hierarchical manner (Figure 1.3), which leads also to the introduction of ion motive forces such as the proton motive force, and to the chemolithoautrophic and respiring chemoorganoheterotrophic life styles (Figure 1.2).

The important F_1F_0-ATPase is needed to connect the short-termed energy pool of the proton motive force to the medium-termed energy pool of ATP and related compounds, and consequently the structure and function of this ATPase is outlined (Figure 1.4). The fourth and last life style explained here is chemoorganoheterotrophic fermentation.

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In total, the basic modes of energy transformation in living beings are outlined and transport processes across biological membranes are explained in a thorough hierarchical scheme.

Important terms explained: acid anhydride group, acidocalcisomes, active transport, alcohol group, aldose, amide group, amine group, amino acid, amino sugar, antiport, *Archaea,* atom, atomic number, autotroph, bacteriorhodopsin, carbohydrate, carbonyl group, carboxyl group, charge transfer complex, chemotrophs, *Chlorobiaceae, Chloroflexaceae,* chlorophyll, chloroplast, *Chromatiaceae,* color, conjugated double bonds, cyanobacteria, diffusion (facilitated, simple), DNA, electron, pair, electron acceptor, electron donor, electronegativity, electrons (delocalized, valence), energy (concentration, conformational, light, redox), energy pool (short-termed, long-termed, medium-termed), entropy, ester group, exciton, fatty acid, fermentation, frontier orbital gap, γ-rays, glutathione, glycerol, halobacteria, heterotroph, hybridization, orbitals, hydrogen bond, ionizing radiation, isotope, ketose, methyl group, methylene group, mixed acid anhydrite, mixotroph, monosaccharide, motive force (ion, proton, sodium), neutron, nucleic acid, orbital, peptide bond, phospholipid, photon, phototroph, phycobilin, *Prochlorales,* proton, proton pump, radicals, replication, respiration, reverse electron flow, reverse electron transport, *Rhodospirillaceae,* RNA, spin, substrate-saturation, sugar acid, sugar alcohol, symport, syntrophy, thioester group, thioesters, transcription, translation, transport (carrier-mediated, membrane, primary, secondary), ultraviolet light, uniport, X-rays.

1.3 Basic Biochemistry

Starting from the physical and chemical constraints for cellular biochemistry as outlined in the first and second sections of this chapter, this part of the chapter is a concise overview of the basic biochemical pathways in living organisms including fermenting bacteria. This is a comprehensive biochemical text that covers this field in 12 sections.

1) Organization of the overall metabolism
2) Enzymes and Coenzymes
3) The backbone: fructose-1,6-bP pathway: Overview, Glucose, Hexosephosphate-isomerase, Phosphofructokinase, fructose-diphosphate-aldolase, Triosephosphate isomerase, Glyceryldehyde phosphate dehydrogenase, Phosphoglycerate kinase, Phosphoglycerate mutase, Phosphoglycerate enolase, Pyruvate kinase and phosphotransferase systems (PTS)
4) Cycles and shunts attached to the F1,6bP-pathway: Overview, 2-keto-3-desoxy-6-phosphogluconate (KDPG) pathway, Heterofermentative lactic acid fermentation and phosphoketolase, Pentosephosphate cycle (PPC), Calvin cycle, Ribulose-monophosphate cycle
5) Fates of pyruvate
6) Fates of acetyl-*S*-CoA: Overview, Tricarbonic acid cycle (TCA), Inverse TCA, Propionate fermentations, Butyric acid and butanol/acetone fermentation, Fatty acid and Polyhydroxyburyric acid (PHB) metabolism
7) Putting it together: anaerobic ecosystems
8) Assimilation of the 10 macrobioelements: Carbon, hydrogen, and oxygen, Nitrogen, Sulfur, Phosphate, Metals
9) Building blocks: Overview, E, D, Q, N, acidic amino acids and their amides, Sulfur-containing amino acids C, M, "alcohols" S and T, "conformation determinants" G and P, hydrophobic nonaromatic amino acids A, I, V, and L, Amino acids with long positively charged side chains, R and K, Aromatic amino acids, Y, F and W, Histidine and purine bases, Pyrimidine bases and pyrrol rings
10) Macromolecules in bacteria: nucleic acids and transcription, RNA and translation, Protein sorting, cellular metabolic network
11) DNA-replication and cell division in prokaryots
12) Genomes and evolution: genomes and their organization, epigenetics, phylogeny and Tree of Life.

Maps (Figures 1.5–1.13) shown on the following pages summarize fundamental metabolic routes needed to understand the consecutive chapters of this book, and to connect them to the subsequent chapters.

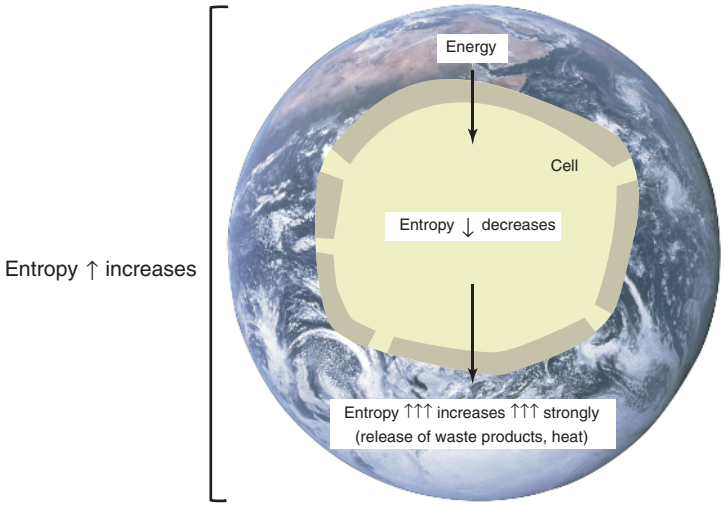


Figure 1.1 **What is Life?** To built order inside, cells continuously use energy to decrease the intracellular entropy (or increase the intracellular negentropy = order) and overcompensate this by increasing the entropy in the environment by release of waste products and heat. Thus, in the total system composed of a cell and its environment, the entropy increases steadily during the chemical reactions in a cell, and the second law of thermodynamics is kept. Energy can be light energy or chemical energy (see Section 1.2). Intracellular order means macromolecules. (Earth photo: Courtesy of NASA.)

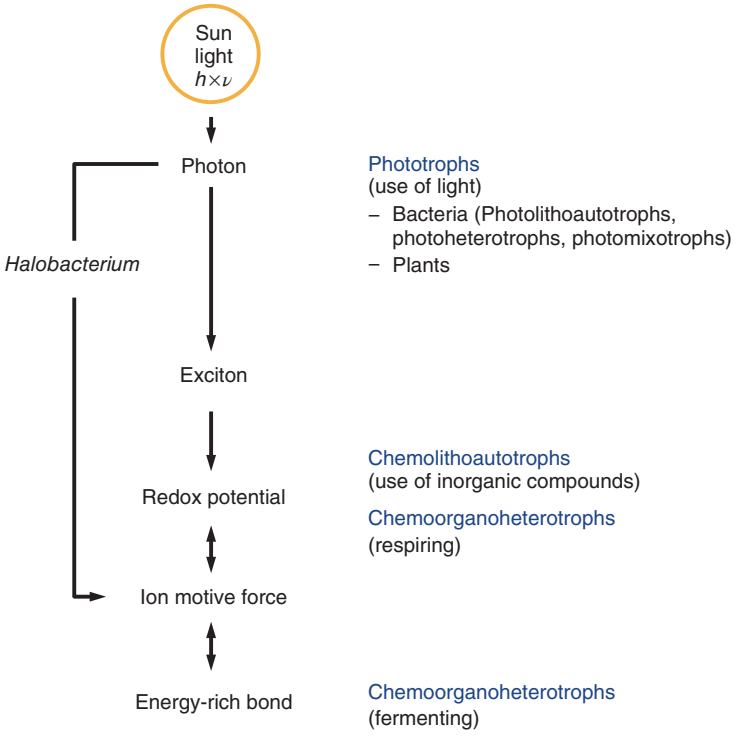
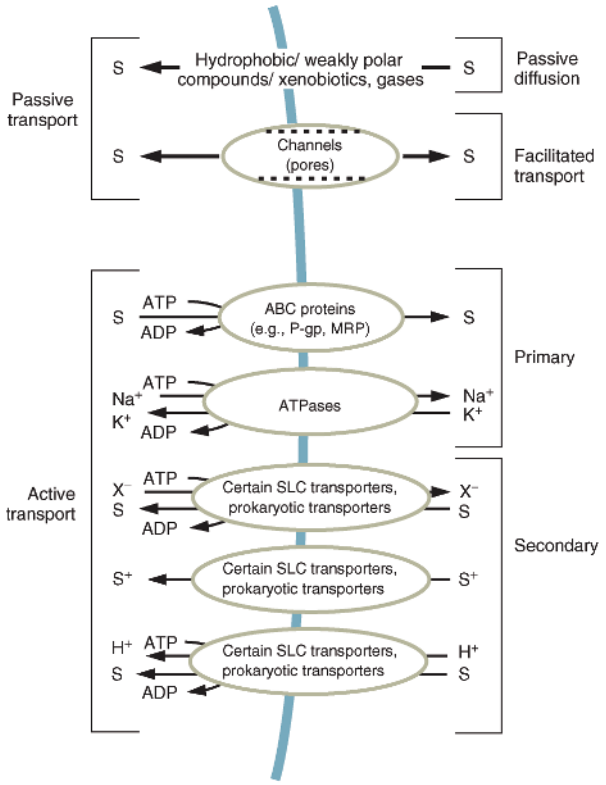


Figure 1.2 **The universal roadmap of energy conservation.** Phototrophs use light energy (photons) to create an exciton that is subsequently used to change the redox potential of a redox carrier to a lower potential (= higher energy). Electron transport from the resulting low redox potential to a more positive one drives ion transport to form an ion motive force, mostly in form of a proton motive force pmf. Finally, the ion motive force is used to generate compounds containing an energy-rich bond such as ATP. In a short cut, some archaea such as *Halobacterium* use a protein named bacteriorhodopsin to create an ion motive force directly from an exciton. Chemolithoautotrophic (cla) bacteria use the difference in redox potential of inorganic compounds to conserve energy, respiring chemoorganoheterotrophic (coh) bacteria transfer electrons from organic compounds to external electron acceptors that are mostly also inorganic compounds. Fermenting organism are also chemoorganoheterotrophs that use biochemical reactions for a direct formation of energy-rich bonds. Some phototrophs can grow photolithoautotrophically (pla), other photoheterotrophically (ph) or photomixotrophically (pm). Please note that energy-rich bonds can also be used to build an ion motive force, for example, for transport processes, and an ion motive force to drive electrons toward a low redox potential (reverse electron transport.)



I. **Simple diffusion**. Driven only by a concentration gradient. Transport rate depends on the concentration difference according to Fick's Law. *Transport of molecular hydrogen and oxygen across the cytoplasmic membrane.*

II. **Carrier-mediated transport.** Catalyzed by a carrier, mostly a trans-membrane protein. Faster than simple diffusion but showing **substrate-saturation**.

   A. **Facilitated diffusion**. Carrier-mediated transport driven exclusively by the concentration gradient of the substrate. No accumulation. *Transport through outer membrane porins, glucose and glycerol facilitators.*

   B. **Active transport.** Carrier-mediated transport driven by energy different from the concentration gradient of the substrate. **Accumulation** possible on either side of the membrane, which may lead to **concentration gradients.**

   1. **Primary transport.** Active transport driven by an energy form that is not another gradient, therefore a **gradient-forming** transport.
      a. Driven by light energy: Photons are harvested as exitons. Their energy is used to change the conformation of a transporter and the resulting conformational tension is relaxed by a transport event. Alternatively, the redox potential of a compound is decreased by the exiton energy, leading to electron transport, consecutively resulting in a transport event. *Bacteriorhodopsin, photosynthetic light reaction.*
      b. Driven by redox energy: electrons transfer from an electron donor to an electron acceptor drives the transport event. *Respiratory electron transport chain.*
      c. Driven by a chemical reaction such as ATP-hydrolysis. *Families of transport ATPases (ABC, P-type, F_1F_0), gradient-forming decarboxylases.*
   2. **Secondary transport.** Active transport driven by a concentration gradient, therefore **gradient-using** transport.
      a. **Uniport:** a **charge gradient** drives the transport reaction. Only the substrate is transported propelled by its charge. *Uptake of Mg^{2+} by CorA-like transporters, export of arsenite by ArsB- and chromate by ChrA-like transporters.*
      b. **Symport:** the substrate is transported into the **same direction** as a second ion or molecule, which forms the driving concentration gradient. *Lactose:proton symporter LacY.*
      c. **Antiport:** the substrate is transported into the **opposite direction** of the second ion or molecule, which forms the driving concentration gradient. *Sodium:proton-antiporter NhaA.*

Figure 1.3 **Hierarchy of transport processes and examples.**

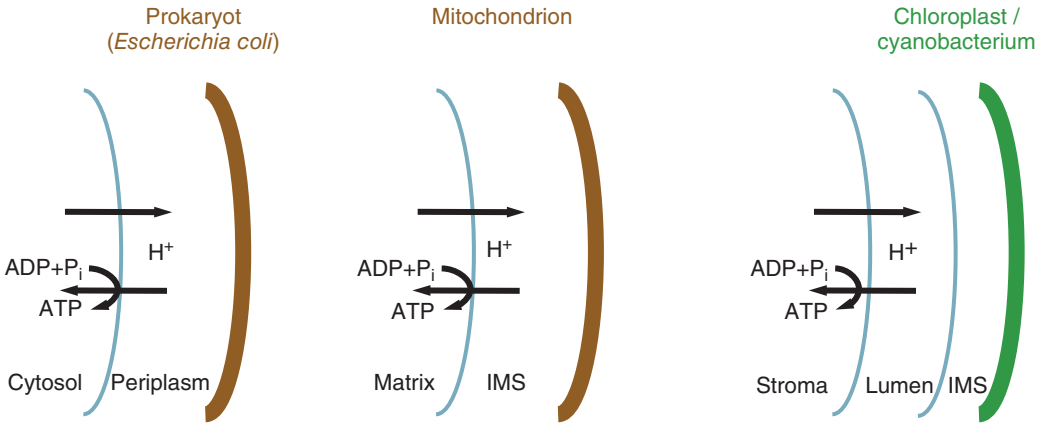


Figure 1.4 **Topology of ATP synthesis in bacteria and plant cell organelles (IMS – Intermembrane space; Lumen – Thylakoid lumen). (Graphics: D.Dobritzsch, G.-J. Krauss.)**

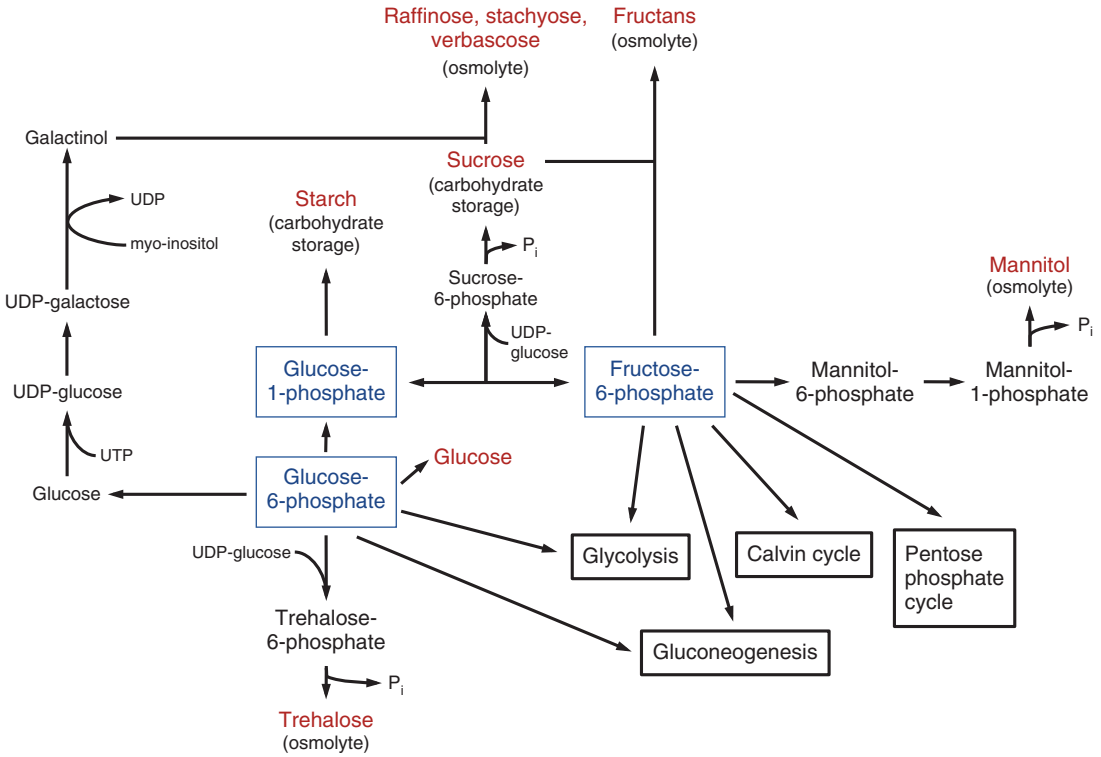


Figure 1.5 Primary sugar routes in plants. (Graphics: D. Dobritzsch, G.-J. Krauss.)

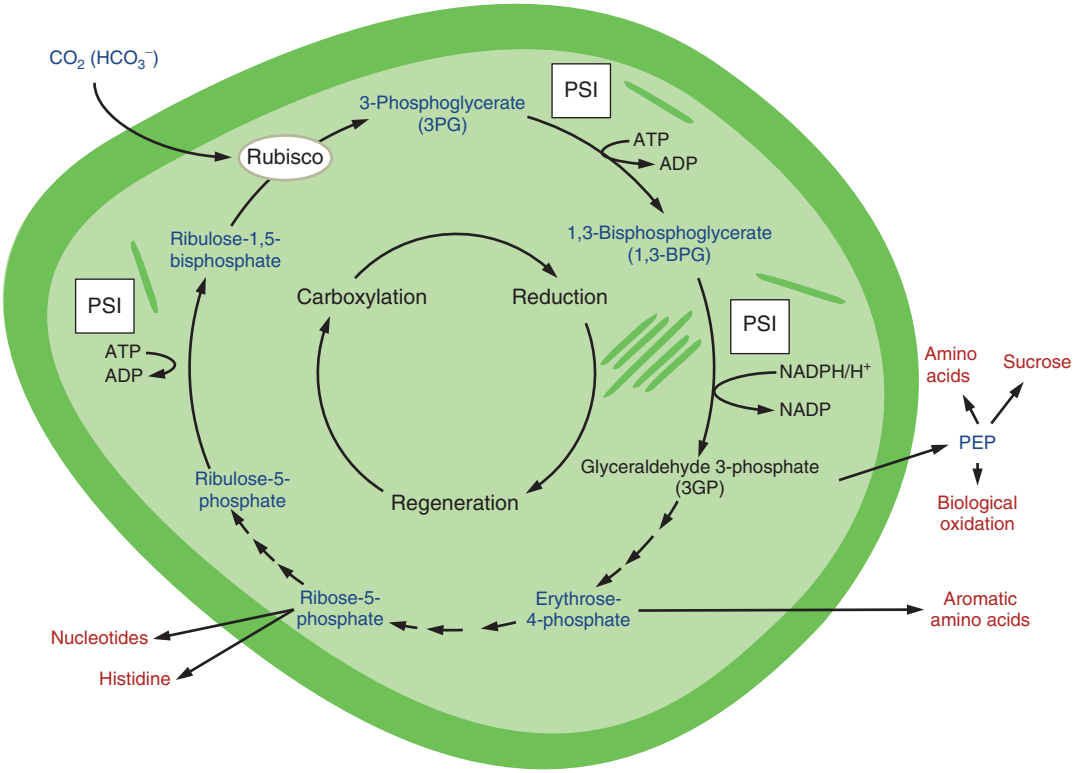


Figure 1.6 Calvin cycle in the stroma of the chloroplasts: A series of light-independent enzymatic reactions in the stroma of chloroplasts convert CO_2 and H_2O into organic compounds, using ATP and NADPH from the photosynthetic light reactions. The key enzyme for carbon fixation in this cycle is the ribulose-1,5-bisphosphate carboxylase: (Rubisco) (PSI – photosystem I). (Graphics: G.-J. Krauss, D. Dobritzsch.)

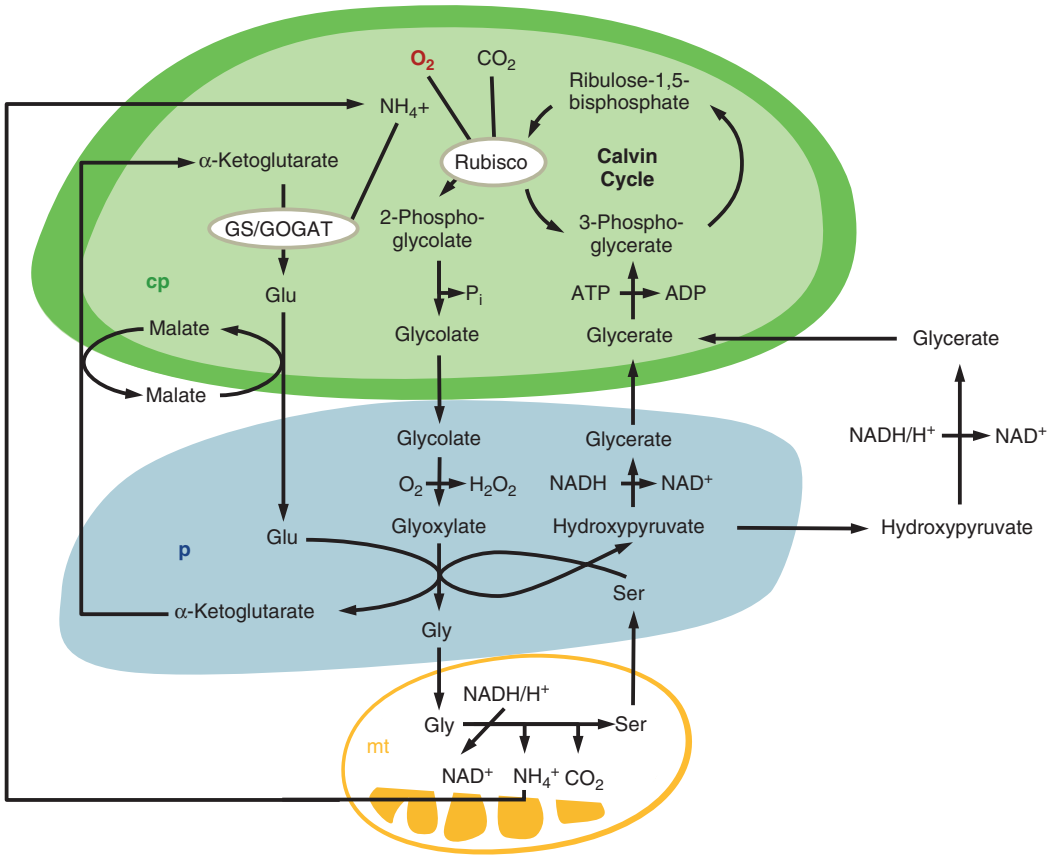


Figure 1.7 Photorespiration: Ribulose-1,5-bisphosphatecarboxylase can also oxygenate ribulose-1,5-bisphosphate (RuBP) which results in the incorporation of oxygen into the carboxyl groups of 3-phosphoglycerate and 2-phosphoglycolate. The two carbon molecule is metabolised back to RuBP via reactions in different cell compartments. Photorespiration happens when the CO_2 level inside the leaf become low and the O_2 ratio is increased relative to CO_2 concentration. Photorespiration is crucial for carbon salvage and adjustment of various metabolic functions. (GS – glutamine synthetase; GOGAT – glutamate α-ketoglutarate (oxoglutarate) aminotransferase; rubisco – ribulose 1,5,bisphosphate carboxylase-oxygenase). (Graphics: G.-J. Krauss, D. Dobritzsch.)

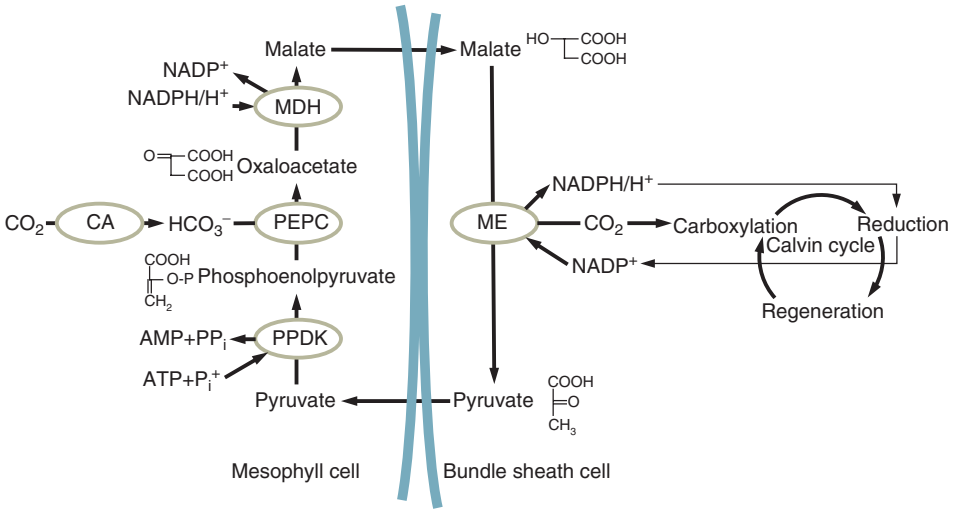


Figure 1.8 C4 photosynthesis (NADP + malic enzyme type): C4-carbon fixation: C4-plants evolved a special of CO_2 fixation in mesophyll cells via phosphoenolpyruvate (PEP) carboxylase, formation of C4 compound, usually malate, which is transported to the bundle sheet cells, where after its decarboxylation CO_2 finally is fixed by ribulose-1,5-bisphophate carboxylase. C4 carbon fixation: $NADP^+$-malic enzyme type. (CA – carboanhydrase, MDH – $NADP^+$-malate dehydrogenase, ME – NADP - malic enzyme, PEPC – phosphoenolpyruvate decarboxylase, PPDK – pyruvate orthophosphate dikinase (Graphics: D. Dobritzsch.)

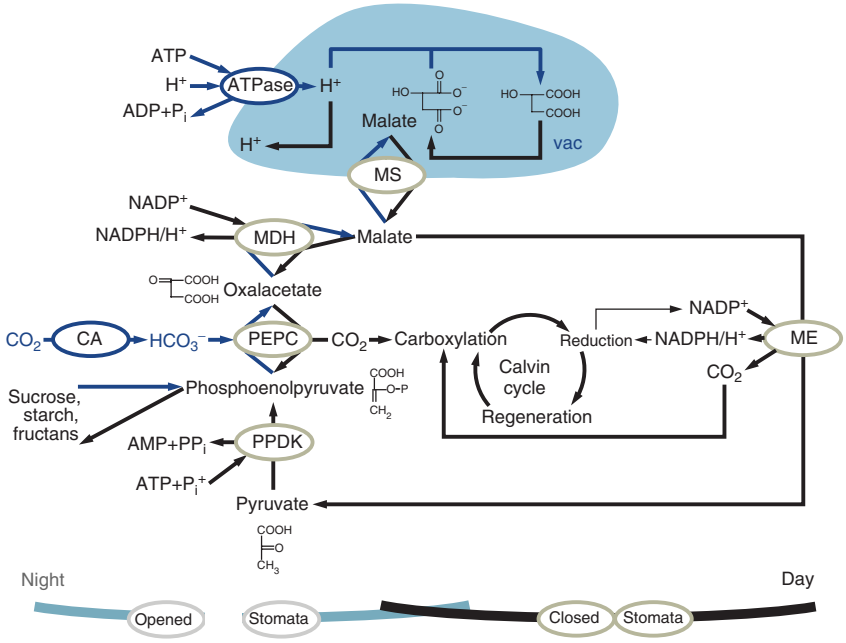


Figure 1.9 Crassulacean acid metabolism (CAM) in CAM-plants:CAM is functioning in some plants living in arid conditions. In these plants stomata open during night. Then CO_2 is transformed to malate and stored. During daytime stomata are closed to avoid loss of water and CO_2 is liberated from malate and fed into the calvin cycle.), blue arrows – reactions in the night; black arrows – reactions during day light (MDH – $NADP^+$-malate dehydrogenase; MS – malate shuttle; PEPC – phosphoenolpyruvate carboxylase; PPDK – pyruvate orthophosphate dikinase (Graphics: D. Dobritzsch.)

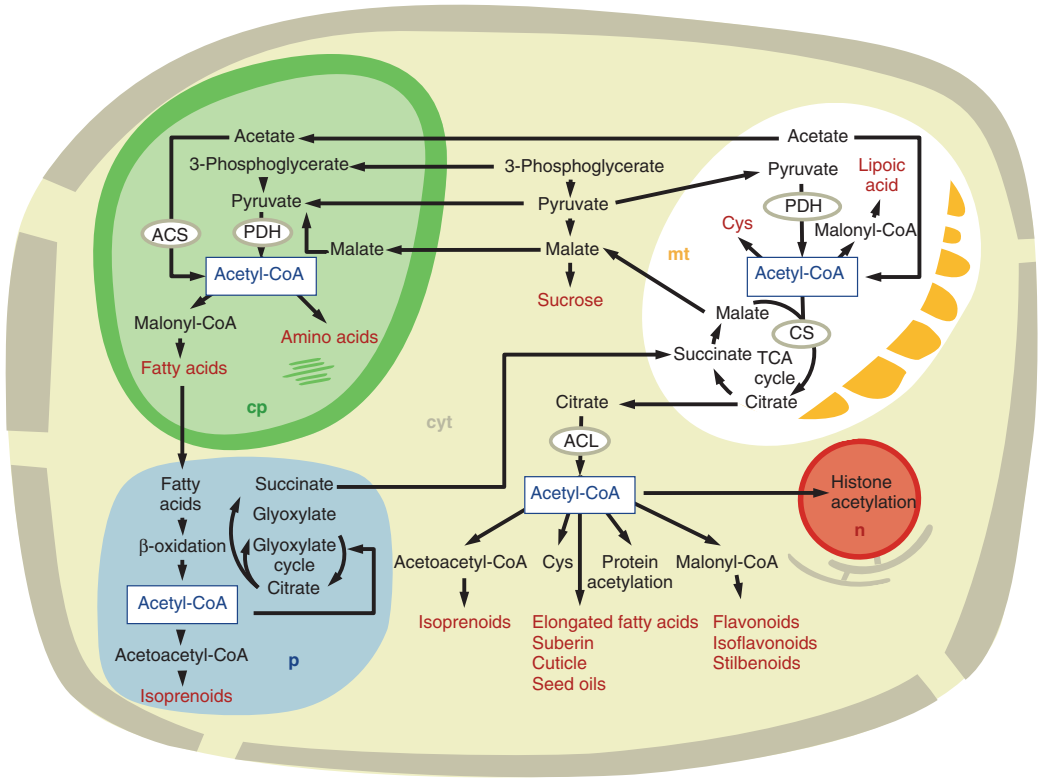


Figure 1.10 Fates of acetyl CoA in plant cells: ACS – acetyl-CoA synthase; ACL – ATP : citrate lyase; CS – citrate synthase; TCA cycle – tricarbonic acid cycle; PDH – pyruvate dehydrogenase; Leu – leucine; Cys – cysteine; Arg – arginine.) (Graphics D. Dobritzsch.)

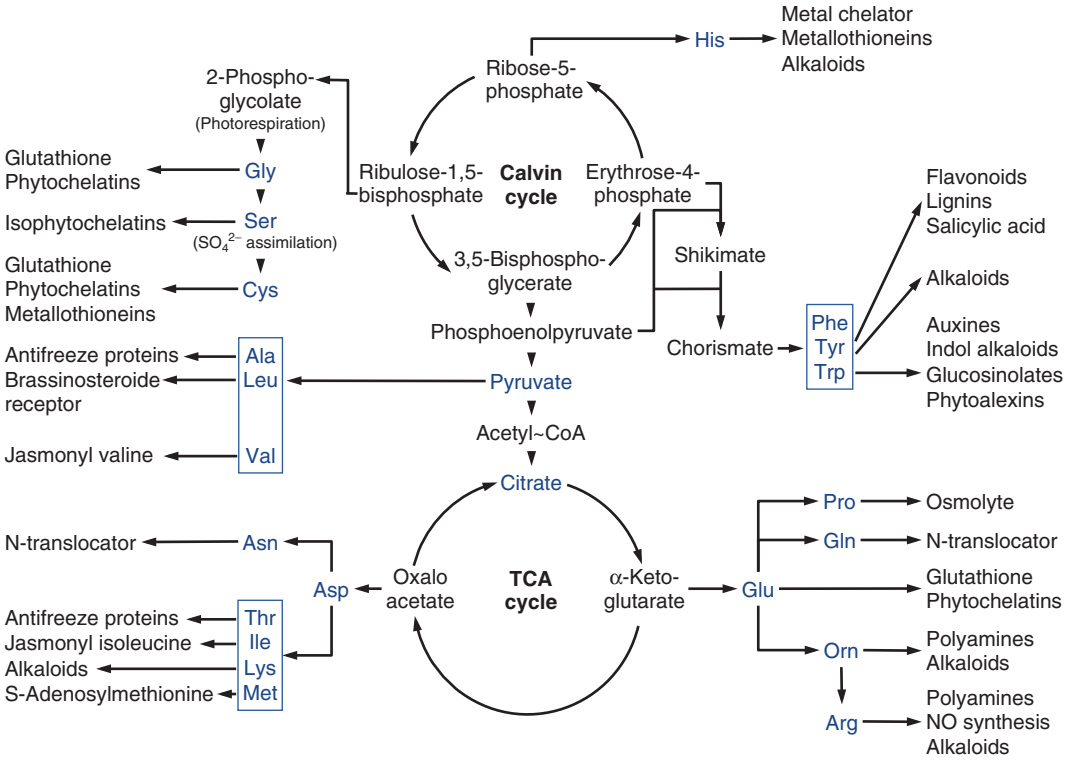


Figure 1.11 Biosynthetic origin of amino acids and their derivatives in plants. (Graphics: G-J. Krauss, D.Dobritzsch.)

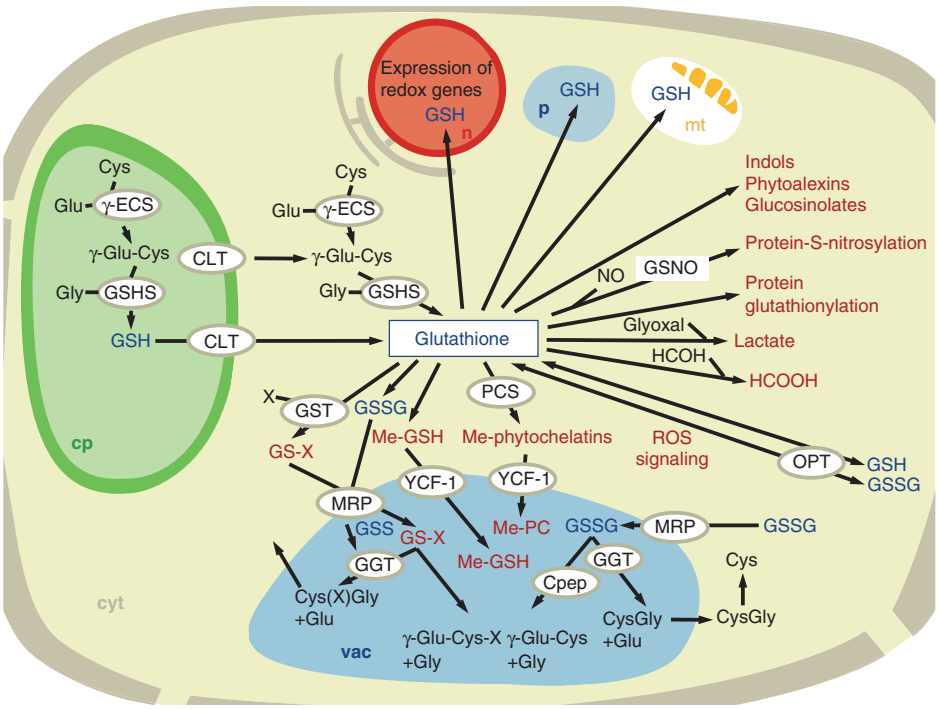


Figure 1.12 Compartmentation of glutathione metabolism in plant cells: GSSG – glutathione disulfide; GSNO – *S*-nitrosoglutathione; γ-EC – γ-glutamyl-cysteine; Glu – glutamate; Gly – glycine; Me – metal; PCS – phytochelatin synthase; GSH – glutathione; X – xenobiotic; GSX – glutathione conjugate; MRP – multridrug resistance-associated protein; Cpep – carboxypeptidase; GGT– γ-glutamyltranspeptidase; (YCF1 – yeast cadmium factor protein; CLT – chloroquinone resistance transporter; OPT – oligopeptide transporter; GST – glutathione-*S*-transferase; γ-ECS – γ-glutamyl-cysteinyl synthase; GSHS – glutathione synthase; Cys – cysteine. (Graphics: G-J. Krauss, D. Dobritzsch.)

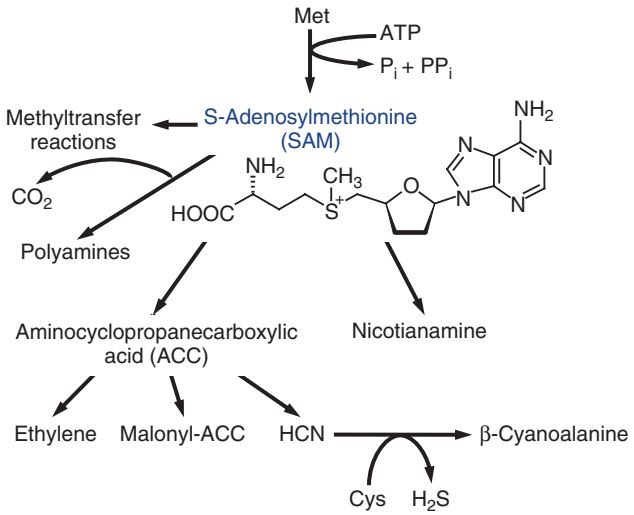


Figure 1.13 The central metabolic role of S-adenosylmethionine.