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<http://arrive.at/thermosynthesis>

# Thermosynthesis Niches in the Solar System



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Biomedical Sciences**

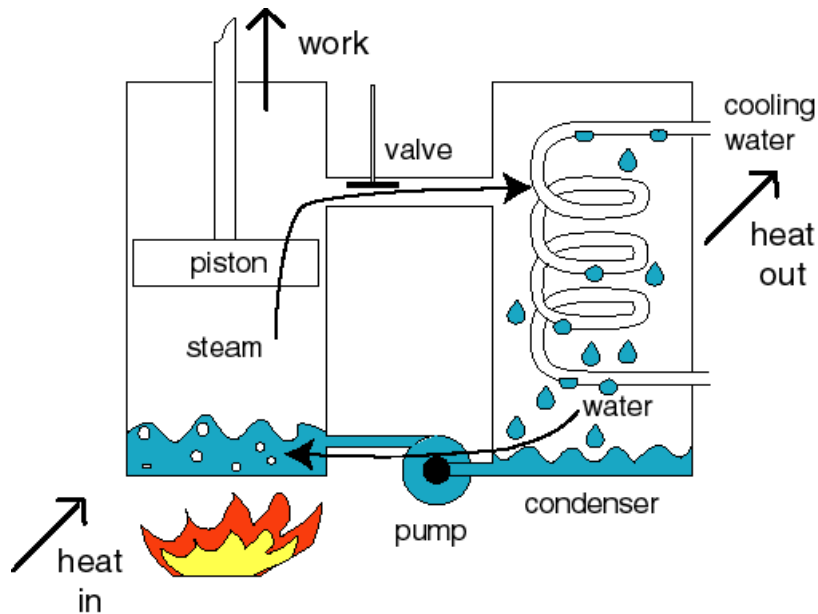
## **Introduction**

Present-day biological energy conversion is a complex process. Bacterial photosynthesis (BPS), for instance, uses many components: light-harvesting proteins, reaction centers, charged biomembranes, ATPsynthases driven by protons that move across the membrane. How can such a complex system have emerged during evolution?

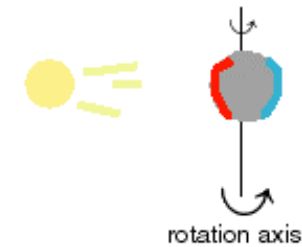
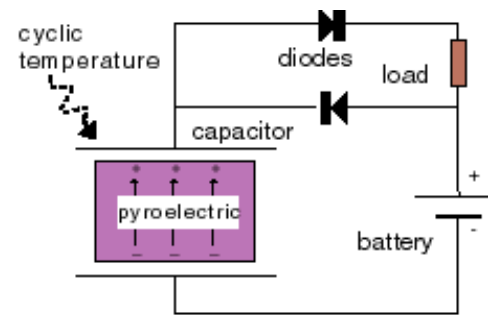
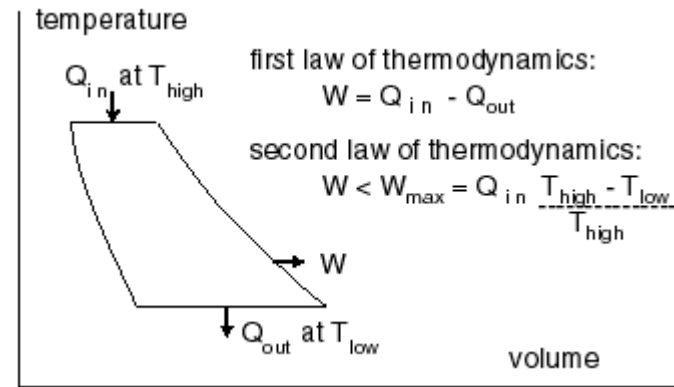
The [thermosynthesis](#) theory shows that BPS could have evolved from biological heat engines working on the thermal cycling occurring in convecting volcanic hot springs ([Part 1](#)). The earliest energy generating system is a direct progenitor of the contemporary ATPsynthase enzyme. In a simple origin of life model, this first system condenses not only phosphates but also peptides ([Part 2](#)). In the resulting polypeptides library a very small fraction of these peptides has itself peptides-condensing capabilities during thermal cycling—the first system propagates. [Part 3](#) correlates the [thermosynthesis](#) model with other origin of life studies. The power of [thermosynthesis](#) is much smaller than the power of photosynthesis, fermentation or respiration, and it may be difficult to detect. Terrestrial ([Part 4](#)) and extraterrestrial ([Part 5](#)) environments containing a thermal gradient that could permit [thermosynthesis](#) are pointed out.

## What is a heat engine?

The steam engine is an example of a heat engine. In the boiler the water becomes steam, which pushes a piston, and external work is done. In the condenser the steam becomes a liquid again. This water is returned to the boiler by pumping. The water is thermally cycled.



Several types of heat engines are known. In all of them heat enters at a high temperature and leaves at a low temperature.



Thermodielectric device: a heat engine based on a capacitor that contains as dielectric a pyroelectric substance (in pyroelectrics the polarization depends strongly on the temperature). The cyclic temperature results in an alternating current through the load.

During its rotation in the sunlight the surface of a satellite is thermally cycled. Application of the thermodielectric device to artificial satellites was proposed in the 60s (Margosian).

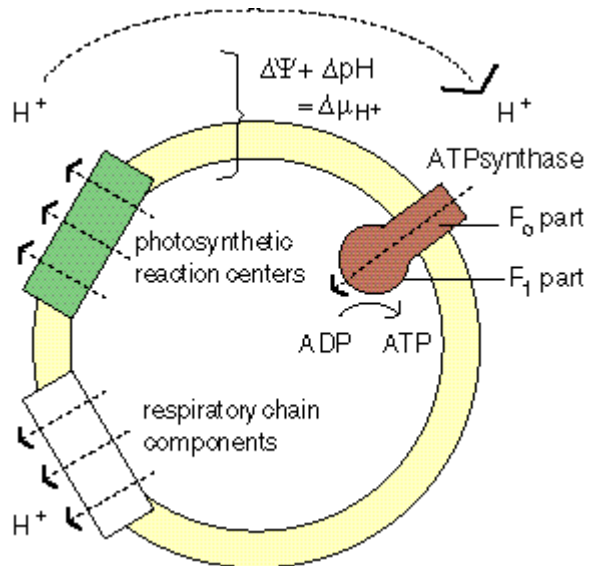
## part 1. the thermosynthesis model for the evolution of photosynthesis

- bacterial photosynthesis (BPS)
- photosystem 0 (PS0)
- membrane-associated thermosynthesis (MTS)
- protein-associated thermosynthesis (PTS)

- **the chemiosmotic mechanism and bacterial photosynthesis**

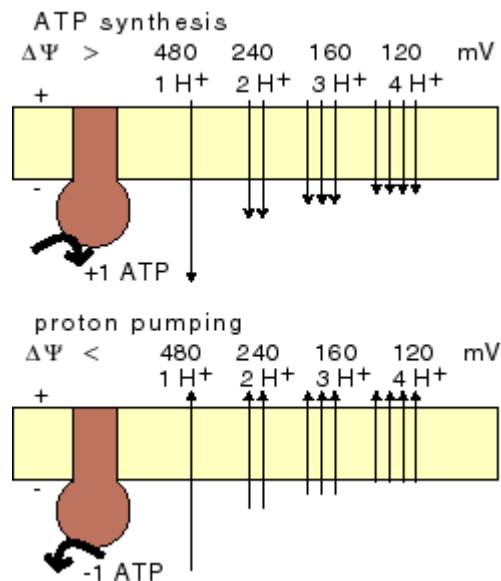
In all organisms free energy is carried by the ATP molecule. Almost all ATP is synthesized by the chemiosmotic mechanism.

## the chemiosmotic mechanism



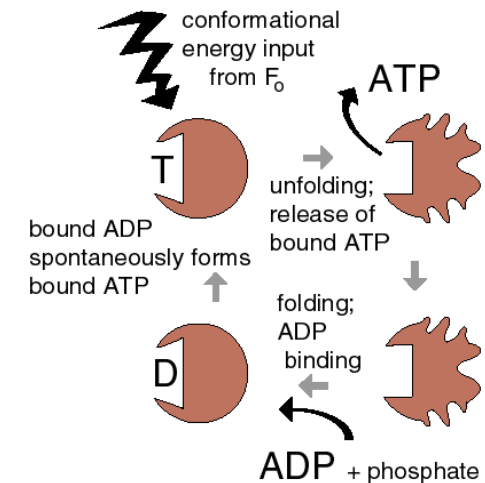
During photosynthesis and respiration protons are pumped across a membrane. The voltage across the membrane increases. The protons fall back through the ATPsynthase enzyme, which transduces their energy in the free energy of ATP.

## membrane voltage and proton/ATP ratio



ATPsynthase can synthesize ATP, but it can also perform the reverse process, proton pumping across the membrane. Whether—at a given membrane voltage—the enzyme functions as an ATP synthesizer or as a proton pump depends on the enzyme's  $H^+/ATP$  ratio.

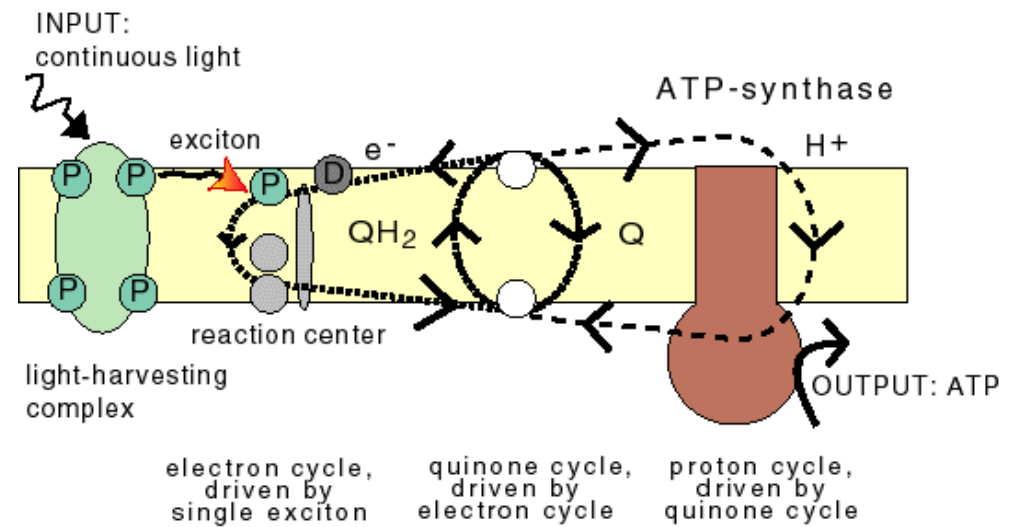
## binding change mechanism



ATPsynthase consists of two parts:  $F_0$  and  $F_1$ . The  $F_1$  part binds ADP and phosphate. Upon closing of the enzyme — and in the local absence of water—ATP forms spontaneously. The  $F_0$  part transduces the energy of the returning protons by opening  $F_1$  (the ‘binding change’) and forcing the ATP release.

## bacterial photosynthesis

Proton pumping is a simple process in BPS. Upon photon capture by a light-harvesting complex, the resulting excitations ('excitons') diffuse towards a reaction center. Here the exciton energy is transferred to electrons, which then move along an array of charge carriers to the other side of the membrane, where they reduce a quinone, which also

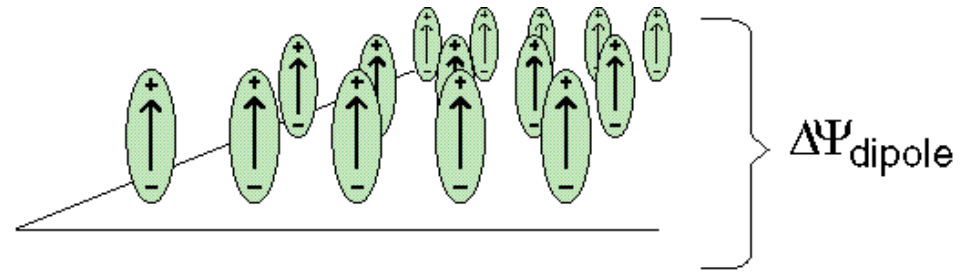


picks up protons from the medium. The resulting quinol (QH<sub>2</sub>) diffuses back across the membrane. The electrons return to the reaction center and the protons are released.

In the proposed evolution model for photosynthesis the BPS components are removed stepwise: firstly the light-harvesting complex and the quinones (resulting in the PS0 mechanism), next the reaction center (resulting in MTS), and finally the F<sub>o</sub> part of ATPsynthase (resulting in the PTS mechanism).

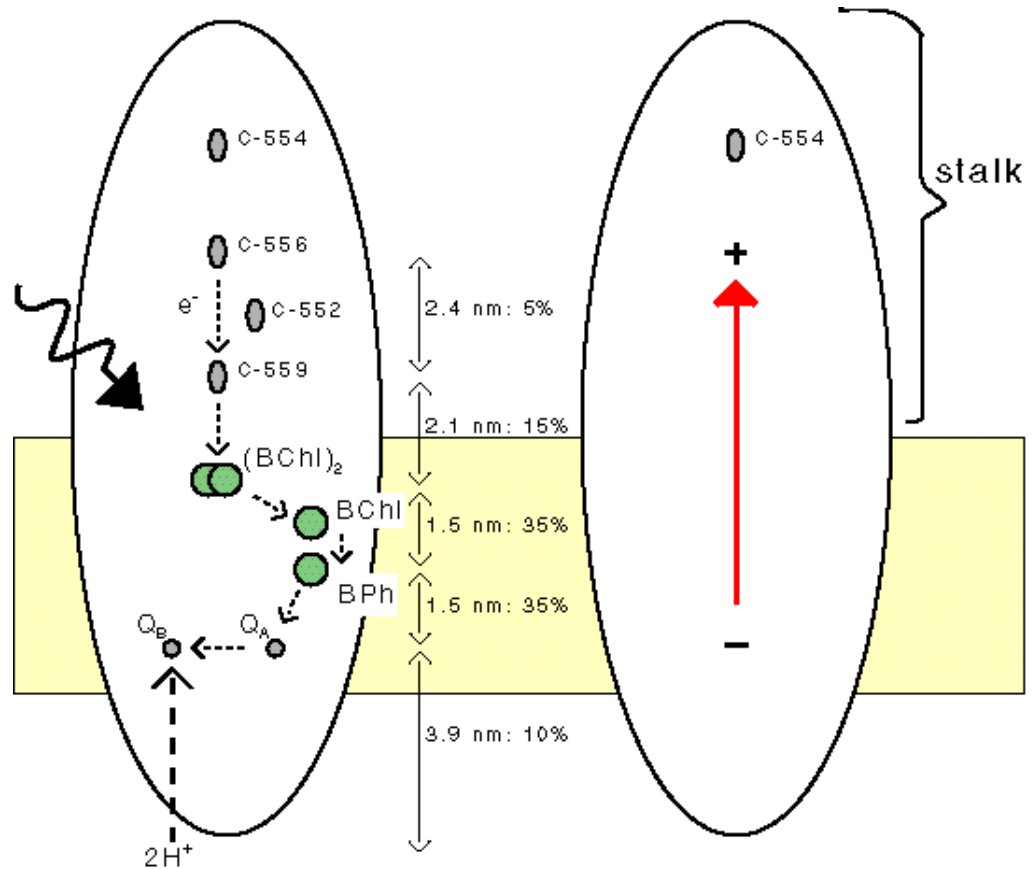
- **photosystem 0 (PS0)**

Instead of generating a membrane voltage by a charge transfer across the membrane, a membrane potential can also be generated by changing its polarization. A voltage difference is present across a dipole layer.



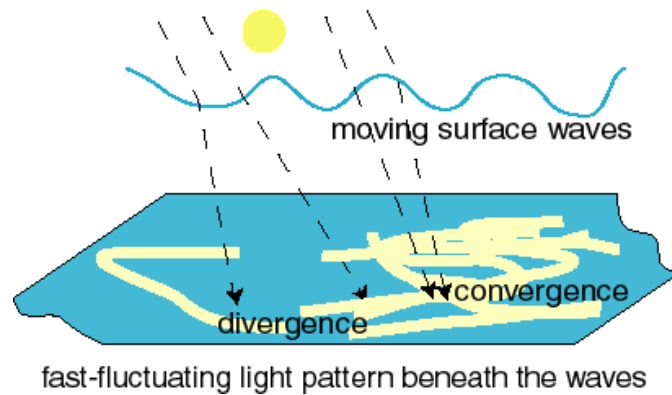
In the photosynthetic reaction center a large dipole is formed when the excited electron moves to the other side of the membrane. The PS0 mechanism uses the voltage difference caused by the light-induced dipoles in these reaction centers.

In some bacterial reaction centers the dipole is especially large, as these centers contain a charged stalk that extends far into the medium. In PS0 this stalk has a function, i.e. permitting a large dipole, while in standard photosynthesis this stalk has no function.

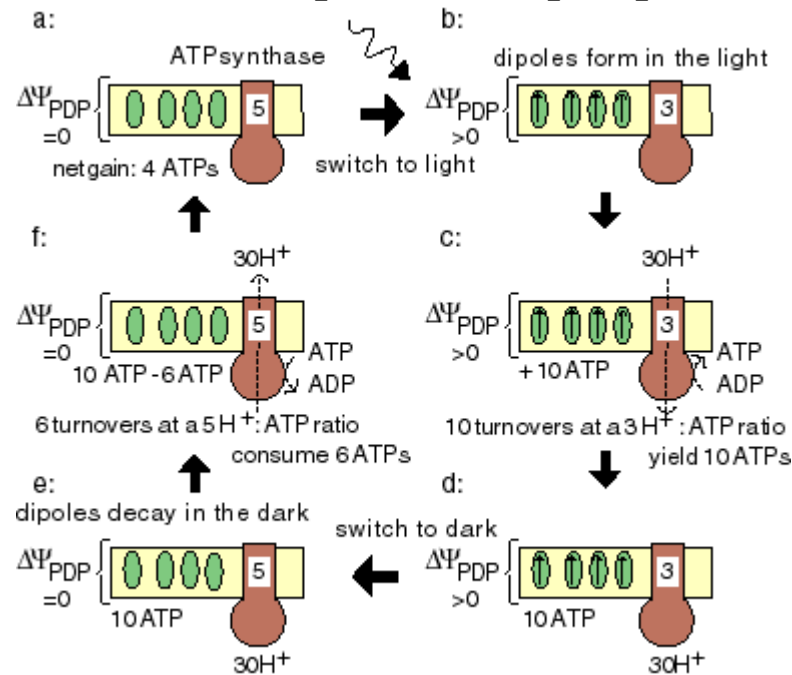


The PS0 mechanism makes use of light/dark cycling. In the BPS machinery the quinones have been removed. The ATPsynthase functions both forwards and backwards during the PS0 cycle.

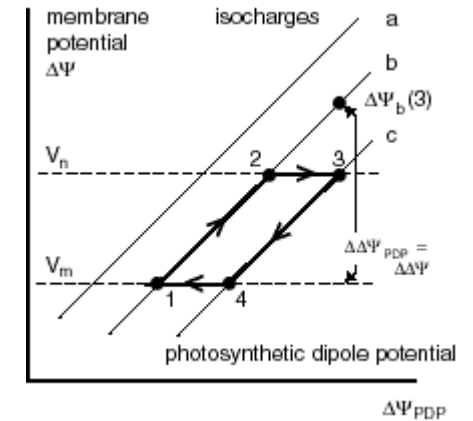
All organisms beneath the surface of natural waters are subject to cyclic changes in light intensity due to the focussing and defocussing of the incoming sunlight by surface waves.



The PS0 cycle. In the light the excited electrons can move within the reaction center, but after having reached the other side of the membrane, they can only fall back in the dark. The dipoles result in a dipole potential that drives ATP synthesis. In the dark the protons are pumped back.



The PS0 cycle on a membrane-potential vs photosynthetic dipole potential plot.

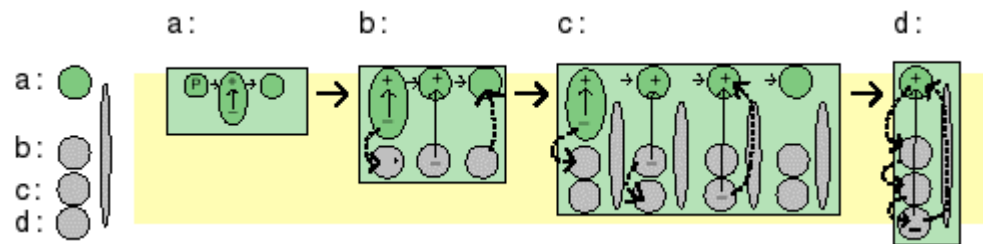




The stepwise evolution of the photosynthetic reaction center is easily pictured in terms of PS0.

In the very first PS0 photosynthesizer only an *intramolecular* dipole was

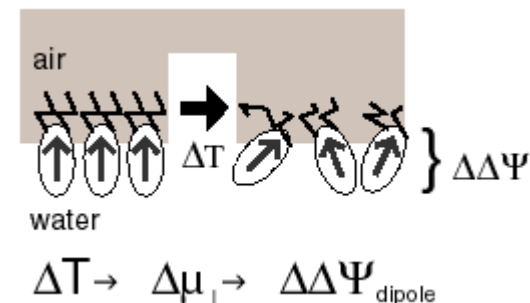
present (a), later added charge carriers permitted temporary *intermolecular* charge separation (b and c), and in (d) the added charge carrier results in charge transfer across the membrane.



- **membrane-associated thermosynthesis (MTS)**

Lipids can form a monolayer at the water/air interface. Just like liquids and solids, such a monolayer can undergo a phase transition, the ‘thermotropic phase transition’.

The oriented molecules of the monolayer constitute a dipole layer; the associated dipole potential is easily measured. During the phase transition this dipole potential can change strongly, e.g. can decrease with  $\sim 100$  mV upon a change in temperature of  $5^\circ\text{C}$ .

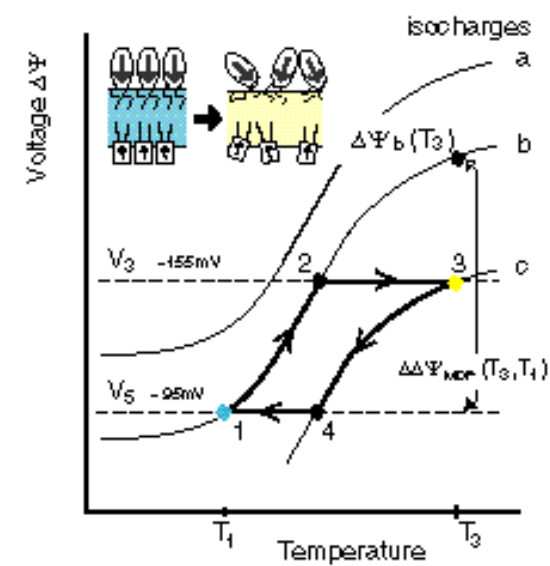
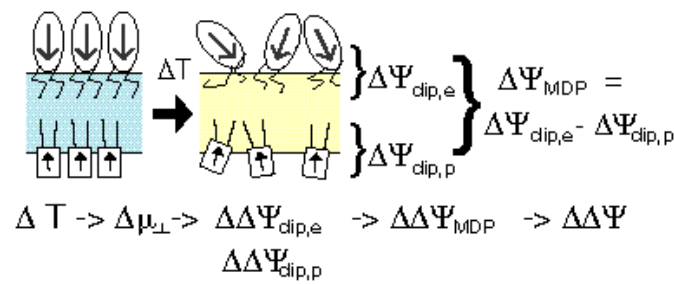
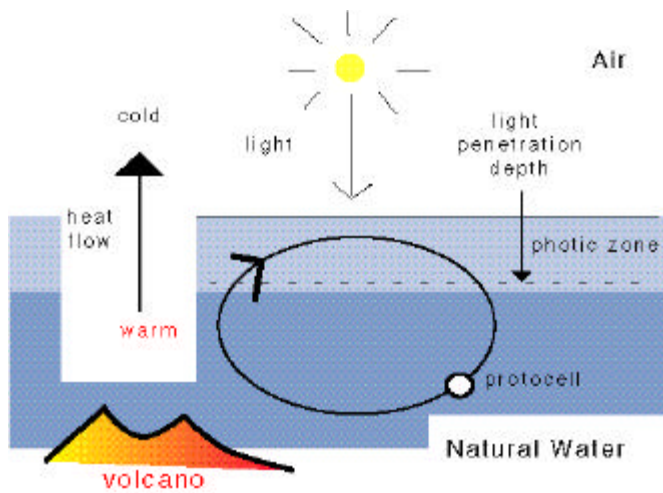


A biomembrane can be imagined as consisting of two different monolayers placed back-to-back. Their difference in dipole potentials results in a membrane dipole potential that will change during a thermotropic phase transition. MTS makes use of this change. During thermal cycling the membrane potential varies just as during light/dark cycling in PS0, and ATP can be gained similarly to PS0, using the same ATPsynthase. MTS requires no photosynthetic reaction centers.

Thermal cycling occurs in convecting volcanic hot springs.

The net dipole potential and its change during a thermotropic phase transition.

The MTS cycle on a membrane-potential vs temperature plot.



- **protein-associated thermosynthesis (PTS)**

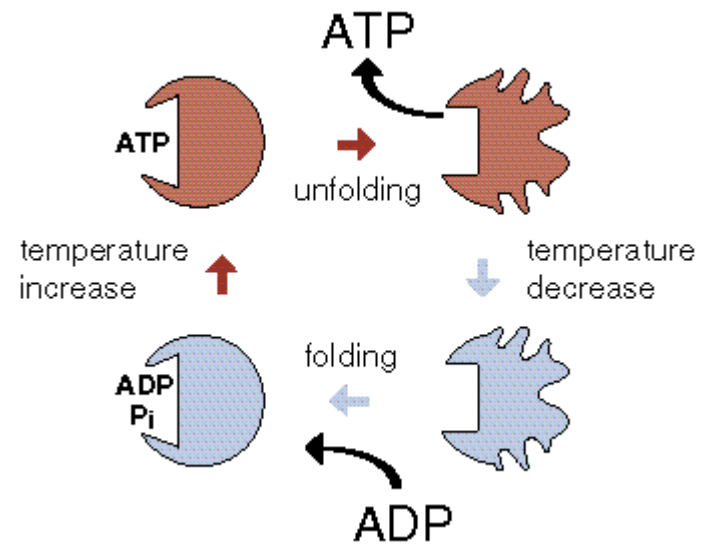
One can easily imagine ATP synthesis during thermal cycling by  $F_1$  *only*, without involvement of a membrane or  $F_0$ , using a variation of the binding change mechanism. Since in the local absence of water ATP is spontaneously formed from ADP and phosphate, all that is needed is a thermal unfolding of  $F_1$ . This is called the ‘temperature-induced binding change mechanism’, and the enzyme a ‘ $pF_1$ ’.

The PTS cycle consists of a binding of ADP and phosphate at a low temperature by an unfolded enzyme, followed by its folding, and a spontaneous formation of bound ATP. At a high

temperature the enzyme unfolds again, and the ATP is released. The unfolded enzyme is then ready for another thermal cycle.

Do the numbers permit this mechanism? The  $\Delta H$  for the unfolding of an  $F_1$  subunit is  $\sim 660$  kJ/mol.

Assuming a temperature difference  $\Delta T$  of  $7,5^{\circ}\text{C}$ , the available free energy according to Carnot equals  $660 (7,5/330) = 15 \text{ kJ/mol}$ , which is a reasonable value for a phosphate bond (and a peptide bond).



## part 2. thermosynthesis applied to the origin of life

- **generalization of PTS and  $\text{pF}_1$  activity**

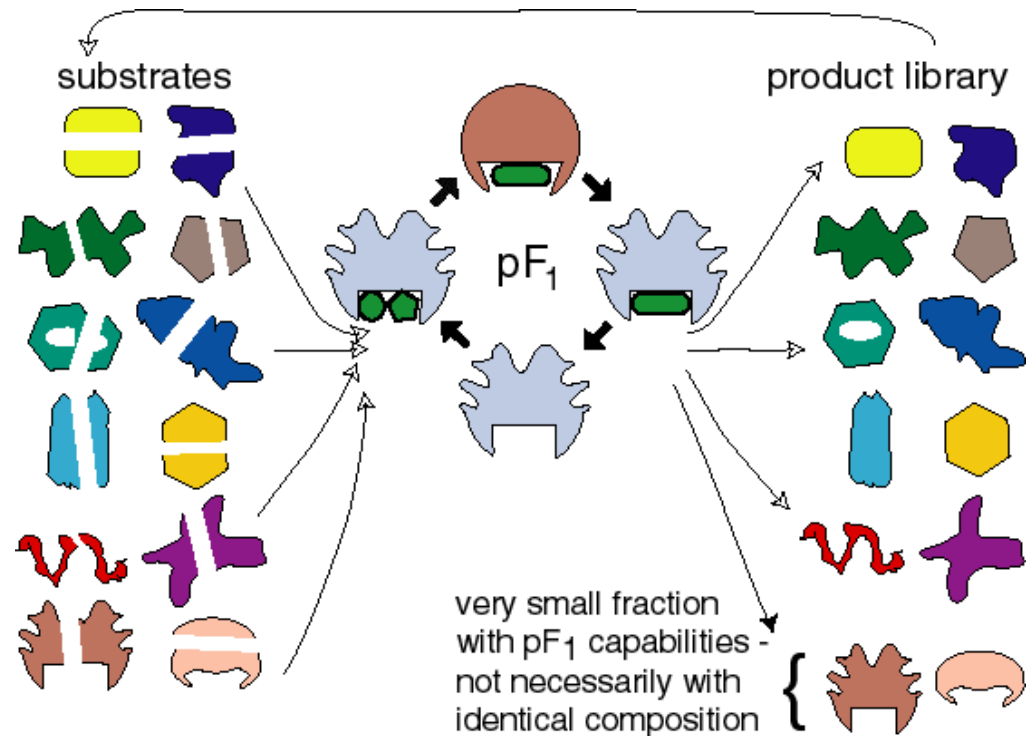
During the origin of life, an energy source must have been present before information processing could become possible.

The first living organism arose around an energy conversion system (Granick), which may have been a heat engine (VanHolde).

In a generalization of PTS it is assumed that during thermal cycling  $\text{pF}_1$  could not only synthesize a phosphate bond, but a peptide bond as well. Just like a phosphate bond, a peptide bond does not require free energy in the absence of water: this absence may be global, but also local, i.e. in an enzymatic cleft. Since  $\text{pF}_1$  is itself a polypeptide,  $\text{pF}_1$  could propagate. In the [thermosynthesis](#) theory,  $\text{pF}_1$  is the very first enzyme.

Life starts with an enzyme that resembles the  $F_1$  moiety of ATP synthase,  $pF_1$ . During thermal cycling  $pF_1$  performs dehydration reactions such as peptide bond formation or phosphorylation. After many cycles the resulting daughter protein library contains many different proteins.

A very small fraction of these proteins can itself function as a  $pF_1$ .  $pF_1$  thus propagates in a functional sense—yielding daughters with the same capability—but not in a compositional sense: the composition of the daughters may differ. The availability of an energy source makes this very inefficient process possible.



- **Convection**

In the beginning, a convection current carries the first cell. The contents of a convection cell is thermally cycled, therefore permitting PTS.

The origin of life requires both self-organization and a dissipative structure. A convection cell is one of the few **self-organizing dissipative structures** known to physics.

*self-organizing*: convection organizes itself: a thermal gradient suffices.

*dissipative structure*: in the universe structures are either

- (a) equilibrium structures, i.e. at or near thermodynamic equilibrium; they are at rest, or 'dead', or
- (b) dissipative structures, i.e. far from thermodynamic equilibrium; these structures can perform external work. Examples are machines and organisms.

- **primordial combinatorial chemistry by pF<sub>1</sub>**

Is the chance formation of a pF<sub>1</sub> by a pF<sub>1</sub> probable?

Assume a target sequence of 30 amino acid residues: only one in all possible combinations of peptides with 30 residues can function as a pF<sub>1</sub>.

Note that Avogadro's number  $N_A = 6 \cdot 10^{23}$ , and  $2^{10} = 1024 \sim 10^3$

20 different residues: chance  $1 : 20^{30} = 2^{30} 10^{30} = (2^{10})^3 10^{30} \sim (10^3)^3 10^{30} = 10^{39} \gg N_A \rightarrow$  improbable, **but**

4 different residues: chance  $1 : 4^{30} = 2^{60} = (2^{10})^6 \sim (10^3)^6 = 10^{18} \ll N_A \rightarrow$  **probable!**

- **nucleic acids and the genetic code**

Some protein-nucleic-acids (PNA, a progenitor of RNA) enhance the efficiency of pF<sub>1</sub> propagation. The very first PNAs may have been purely parasitic, having only the ability of quick reproduction, similar to a virus (Dyson), but later some PNAs were formed that enhanced the pF<sub>1</sub> propagation efficiency by functioning as ribosomal PNA, transfer PNA and messenger PNA.

Gradually, pF<sub>1</sub> propagation evolved from functional towards compositional, guided by information-carrying PNA molecules. The genetic code evolved until a system with accurate translation capability had been obtained. During or after this process the PNA was replaced by RNA.

## part 3. a comprehensive model for the origin of life

- **amino acids**

Amino acids have been detected in meteorites and have also been observed in Miller's experiments.

- **proteinoids**

Amino acids can form polypeptides when heated:

- proposed condensations in lagoons at low tide at mild temperatures (~50°C) (Bernal);
- demonstrated condensations just above the boiling water of water (~120°C) (Fox);
- demonstrated condensations (which also involved diketopiperazines) at hydrothermal vent conditions (Matsuno).

- **proteinoid microspheres**

Upon the addition of proteinoids membranes are formed, 'proteinoid microspheres', with the shape and size of bacteria (Fox)

- **convection in volcanic hot springs**

Convection is a self-organizing dissipative structure (Haken).

[In the thermosynthesis theory life emerges upon the addition of proteinoid microspheres to a volcanic hot spring.](#)

Archaeobacteria are the last common ancestor of all organisms; they live in volcanic hot springs (Woese).

- **PTS: protein-associated thermosynthesis**

The chemiosmotic mechanism (Mitchell);

The binding change mechanism for  $F_1$  (Boyer; Penefsky);

$F_1$  progenitor  $pF_1$ ; thermal cycling requirement; temperature induced binding change mechanism;

Substrate ambiguity for the first enzyme has been proposed (Black), only one first enzyme may be required: therefore  $pF_1$  condenses amino acids, phosphates.

*First biogenesis* involved a primitive metabolism (Dyson): in the thermosynthesis theory identified as PTS.

PTS capability selects microspheres, as phosphorylation of membrane components stabilizes the membrane—a selective advantage.

- **$pF_1$  propagation**

Randomly constituted protein synthesis; a minor fraction has itself  $pF_1$  capability.

- **nucleic acids**

The first nucleic acids may have been parasites that did not give an advantage (Dyson); later some become beneficial, the advantage being guidance of  $pF_1$  synthesis.

Ribose problem: where did the ribose in RNA come from? (Shapiro).

Peptide Nucleic Acids (PNAs) have been proposed as RNA progenitors (Nielsen).

- **genetic code**

The emergence of the system using a genetic code constituted the *second biogenesis* (Dyson);

The second biogenesis occurs during the gradual increase in accuracy of  $pF_1$  synthesis;

The code starts with a codon coding for one amino acid—glycine (Hartman)—with other codons coding for random amino acid insertion;

$pF_1$ , first expressed enzyme, ‘mother of all enzymes’;

proteins → cells → enzymes → genes (Fox);

reverse transcription yields DNA;

## genetic apparatus obtained

- **lipids / lipid membrane**

A lipid, insulating biomembrane is acquired. In general the two constituting monolayers have a different composition: in an asymmetric biomembrane a net surface dipole potential results.

During thermal cycling around the thermotropic phase transition temperature the membrane potential fluctuates.

The emergence of MTS is related to the emergence of ATPsynthase.

- **F<sub>0</sub> carrier / MTS**

In a proton translocator the membrane phase transition partially shields proton carrying groups.

This result in a heat engine that pumps protons during thermal cycling (but does not synthesize ATP) (the pump is not shown: see Muller, 1995).

- **F<sub>0</sub>F<sub>1</sub> ATPsynthase / MTS**

Upon combination of F<sub>0</sub> and F<sub>1</sub>: variable proton translocation and a variable H<sup>+</sup>/ATP stoichiometry (VanWalraven); net ATP synthesis during thermal cycling.

- **photosystem 0**

Photosynthesis in fluctuating light only; light-induced dipoles; increase in dipole size during evolution; physiological function of the stalk in the reaction center.

Upon membrane spanning: reducing power has been obtained.



- **quinones**

quinones and quinols; ability of transmembrane diffusion: photosynthesis in constant light; combined MTS/PS0/PS capability and their association with State 1 - State 2 transitions (not shown);

- **bc<sub>1</sub> complex**

the Q-cycle (not shown); descendancy from RC; BPS

### **present day bacterial photosynthesis obtained**

- **the evolution of biochemical control processes**

Urry (1992): free energy transduction by protein phosphorylation can be explained by a change in the protein folding temperature upon phosphorylation. The effect of Ca<sup>2+</sup> upon biomembranes can similarly be interpreted as an effect upon the thermotropic phase transition temperature of the membranes.

If the first organisms lived on thermal cycling, their metabolic processes must have depended on it. The prevalent biochemical processes of regulation by protein-phosphorylation and by Ca<sup>2+</sup> can be explained as ways to mimic primordially required thermal cycling isothermally.

This leads to the conjecture:

**ATP mimics primordial thermal cycling**

which answers the question, 'Why ATP?'

## part 4. potential terrestrial niches for thermosynthesizers

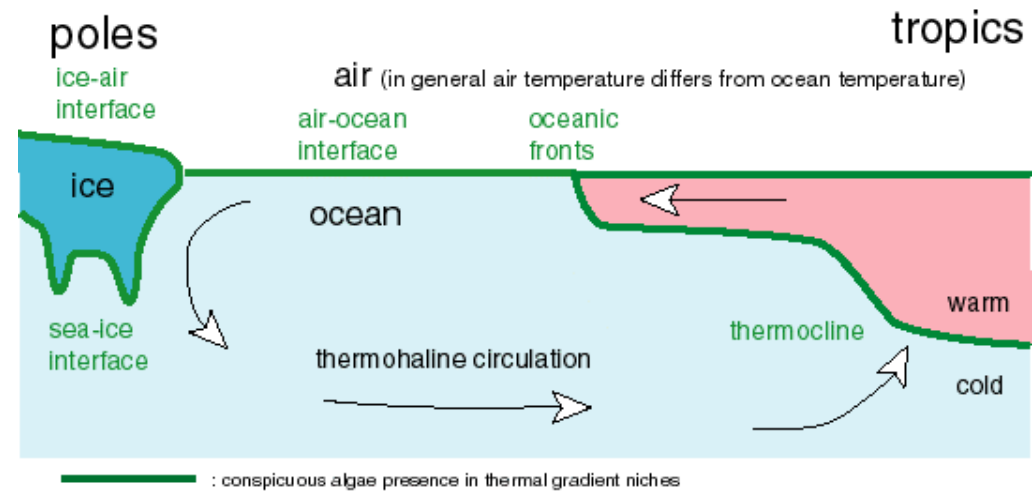
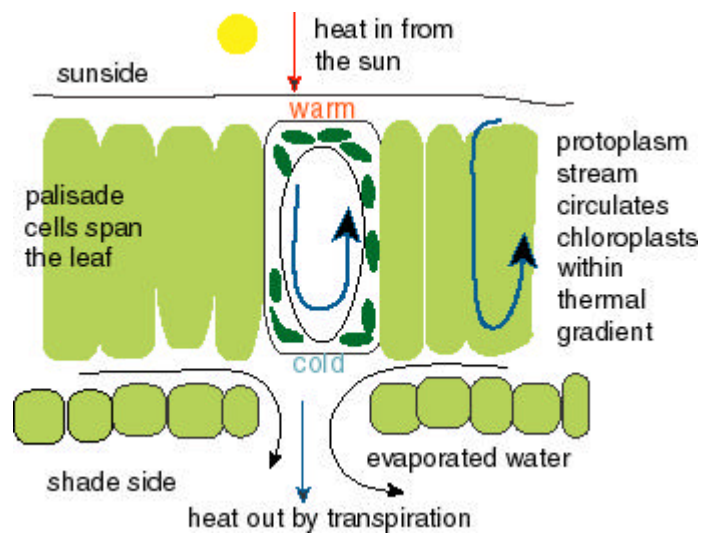
The driving force for the evolution from PTS/MTS by PS0 to BPS is increasing power, the free energy generated per unit time. This power is inversely proportional to the characteristic cycle time, which is for

PTS/MTS: the cycle time of the convection current: estimated lower limit, a few seconds, but in general much larger,  $\sim 10^2$  s;

PS0: the cycle time of light fluctuations beneath surface waves: 0.1 - 10 s;

BPS: the diffusion time of the quinone across the membrane:  $\sim 10$  ms

The power of BPS will therefore be  $\sim 100$  times the power of PS0, which in turn will be  $\sim 100$  times the power of PTS/MTS. One expects any BPS organism to outcompete any PS0 or PTS/MTS organism. PTS/MTS can, however, work in dark niches: at night, during the polar night, and in subsurface conditions or at great depths in natural waters. It can occur in convection cells, as well as in thermal gradients where an organism can thermally cycle its membranes. An illustrative example is given by chloroplasts in a leaf (which is of course **not** in the dark!). Leaves contain a thermal gradient, as the leaf is warmed at the sunny side and cooled at the shadow side by transpiration. The palissade cells span the leaf—and the thermal gradient—and the protoplasm stream circulates all cell organelles such as chloroplasts and mitochondria in this thermal gradient, which would permit thermosynthesis in these organelles.



More generally, the protoplasm stream can thermally cycle the cell organelles in any organism/cell placed in a thermal gradient. The world around us contains many thermal gradients, with a conspicuous organism presence:

- thermal cycling by passive movement: hot springs, convecting natural waters, Langmuir circulations in the ocean, meteoric waters, industrial cooling water systems (where 'biofouling' is a nuisance), hot water tanks, air conditioning systems;
- thermal cycling by active movement: many natural waters contain thermoclines: the ocean, lakes, saline ponds, hot springs, and migrate through these thermoclines. Many organisms are found at interfaces: algae at ground/air, snow/air, sea/air, sea/sea-ice interfaces, interfaces at industrial heat transfer systems.

## **part 5. potential niches for thermosynthesizers in the Solar System**

See the Figure.

### **Summary**

Thermosynthesis is not life as we know it — but thermosynthesis life is not that much different.

It provides a simple model for the origin of life,  
and the process can occur almost everywhere on Earth and in the Solar System.

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Photosystem 0 makes use of the fast changes in light intensity that occur beneath the surface of natural waters due to focussing/defocussing of sunlight by waves at the water surface. Such changes cause the complex, fast-moving patterns on the bottom of swimming pools that are shown here.