PHOTOSYNTHESIS

THE LIGHT REACTION

Dept of Botany
PPES ACS College.

ATMOSPHERIC CO_2 IS "FIXED" BY PLANTS AND CYANOBACTERIA

- A LIGHT-DRIVEN PROCESS
- THE CARBON BECOMES AVAILABLE AS CARBO-HYDRATE (CH_2O)
- THE OVERALL REACTION IS:

$$CO_2 + H_2O \rightarrow (CH_2O) + O_2$$

- CO_2 IS REDUCED
- H_2O IS OXIDIZED

THERE ARE TWO PHASES IN PHOTOSYNTHESIS

- THE “LIGHT REACTION”
  - H_2O IS SPLIT
    - **2 H_2O □ O_2 + 4 [H·]**
  - NADPH AND ATP ARE GENERATED
- THE “DARK REACTION”
  - NADPH AND ATP FROM THE LIGHT REACTION DRIVES CH_2O PRODUCTION FROM CO_2 AND [H·] :
    - **4 [H·] + CO_2 □ (CH_2O) + H_2O**
  - IT’S REALLY A LIGHT-INDEPENDENT REACTION
  - YOU HAVE ALREADY STUDIED IT
    - **THE “CALVIN CYCLE”**

IN-CLASS QUESTION

- $H_2{}^{18}O$ IS ADDED TO A SUSPENSION OF CHLOROPLASTS CAPABLE OF PHOTOSYNTHESIS. WHERE DOES THE LABEL APPEAR?

PHOTOSYNTHESIS OCCURS IN CHLOROPLASTS

- CHLOROPLASTS CONTAIN:
  - AN OUTER MEMBRANE
    - **HIGH PERMEABILITY**
  - AN INNER MEMBRANE
    - **NEARLY IMPERMEABLE**
  - THE STROMA
    - **AQUEOUS**
    - **CONTAINS ENZYMES, DNA, RNA, RIBOSOMES**
  - THE “THYLAKOID”
    - **A MEMBRANEOUS COMPARTMENT**
      - **DERIVED FROM INVAGINATIONS OF INNER MEMBRANE**
    - **A SINGLE HIGHLY-FOLDED VESICLE**
    - **“GRANA” : DISK-LIKE SACS**
    - **GRANA ARE CONNECTED BY “STROMAL LAMELLAE”**

CHLOROPLASTS

- STRUCTURE IS VERY SIMILAR TO MITOCHONDRIA
  - PROBABLY EVOLVED FROM A CYANOBACTERIUM INCORPORATED INTO A NON-PHOTOSYNTHETIC EUKARYOTE (SYMBIOSIS)
- IN EUKARYOTES, THE LIGHT REACTION OCCURS IN THYLAKOID MEMBRANE
- IN PROKARYOTES, THE LIGHT REACTION OCCURS IN:
  - INNER (PLASMA) MEMBRANE
  - IN "CHROMATOPHORES"
    - INVAGINATIONS OF INNER MEMBRANE
- IN EUKARYOTES, THE DARK REACTION OCCURS IN THE STROMA

CHLOROPHYLL IS THE MAJOR PHOTORECEPTOR IN PHOTOSYNTHESIS

- A CYCLIC TETRAPYRROLE, LIKE HEME, BUT:
  - HAS A CENTRAL Mg^{2+} ION
  - A CYCLOPENTANONE RING (RING V) IS FUSED TO PYRROLE RING III
  - PARTIAL REDUCTION OF RING IV
    - IN EUKARYOTES AND CYANOBACTERIA
      - **CHLOROPHYLL a**
      - **CHLOROPHYLL b**
  - OR IN RINGS II AND IV
    - IN PHOTOSYNTHETIC BACTERIA
      - **BACTERIOCHLOROPHYLL a**
      - **BACTERIOCHLOROPHYLL b**

MOLECULAR EVENTS DURING LIGHT ABSORPTION

- PHOTONS (LIGHT “PARTICLES”)
  - ENERGY = hv
- PHOTORECEPTORS
  - HIGHLY CONJUGATED MOLECULES
    - STRONGLY ABSORB VISIBLE LIGHT
- ABSORPTION OF A PHOTON USUALLY PROMOTES A GROUND-STATE ELECTRON TO A MOLECULAR ORBITAL OF HIGHER ENERGY
  - LAW OF CONSERVATION OF ENERGY
- EACH ELECTRONIC ENERGY LEVEL HAS
  - VIBRATIONAL AND ROTATIONAL SUB-STATES

POSSIBLE FATES OF EXCITED ELECTRON

- INTERNAL CONVERSION (A FAST PROCESS)
  - ELECTRONIC ENERGY CONVERTED TO KINETIC (HEAT) ENERGY
    - SOMETIMES "RELAX" BACK TO GROUND STATE
    - IN CHLOROPHYLL, RELAXATION TO LOWEST EXCITED STATE
- FLUORESCENCE (A SLOWER PROCESS)
  - A PHOTON IS EMITTED, WITH DECAY TO GROUND ELECTRONIC STATE
- EXCITON TRANSFER ("RESONANCE TRANSFER")
  - EXCITATION ENERGY TRANSFERRED TO NEARBY UNEXCITED MOLECULES WITH SIMILAR ELECTRONIC PROPERTIES
- PHOTO-OXIDATION
  - THE EXCITED MOLECULE TRANSFERS ITS ELECTRON TO AN ACCEPTOR MOLECULE
    - A REDOX PAIR

EXCITON TRANSFER

- "COUPLING" OF MOLECULAR ORBITALS
  - ALLOWS FOR SERIAL TRANSFER OF EXCITATION
  - OR COUPLED MOLECULES ACT AS A "SUPERMOLECULE"
- THIS KIND OF TRANSFER IS SEEN AS LIGHT ENERGY IS "FUNNELED" TO "PHOTOSYNTHETIC REACTION CENTERS"

PHOTO-OXIDATION

- THE EXCITED ELECTRON IS TRANSFERRED TO THE "PHOTOSYNTHETIC REACTION CENTER"
- EXCITED CHLOROPHYLL IS THE DONOR IN PHOTOSYNTHESIS
- AFTER THE TRANSFER, CHLOROPHYLL IS OXIDIZED TO A CATIONIC FREE RADICAL
- RETURNS TO ITS GROUND STATE BY OXIDIZING ANOTHER MOLECULE

“ANTENNA” CHLOROPHYLLS

- THERE ARE ~ 300 CHLOROPHYLL MOLECULES PER REACTION CENTER
- THE FUNCTION OF MOST CHLOROPHYLLS IS TO GATHER LIGHT
- ACT LIKE ANTENNAS
  - “LIGHT-HARVESTING COMPLEXES (LHCs)
- LIGHT ENERGY IS PASSED BY EXCITON TRANSFER TO THE REACTION CENTER
  - THESE HAVE SLIGHTLY LOWER EXCITATION ENERGIES
  - >90% EFFICIENCY OF THE TRANSFER PROCESS!

THE REACTION CENTER CHLOROPHYLL

- ITS LOWEST EXCITED STATE IS AT A LOWER ENERGY LEVEL THAN EXCITED STATES OF ANTENNA CHLOROPHYLLS
  - THE EXCITATION IS “TRAPPED” THERE

LIGHT-HARVESTING COMPLEXES: ACCESSORY PIGMENTS

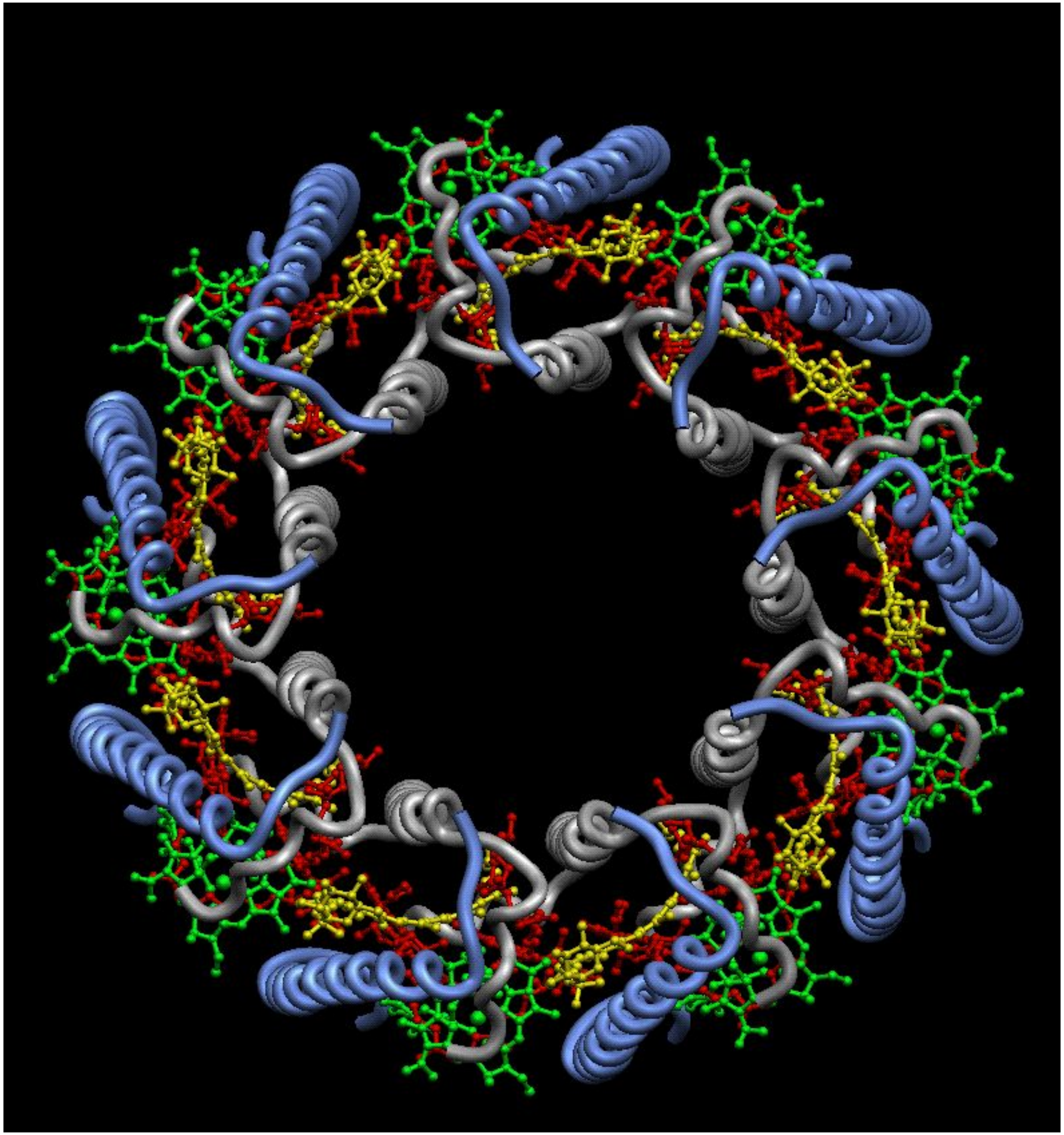
- DIFFERENT PHOTOSYNTHETIC PIGMENTS ABSORB LIGHT AT DIFFERENT FREQUENCIES
  - ALLOWS LIGHT TO BE ABSORBED AT ALL FREQUENCIES OF THE VISIBLE SPECTRUM
- LHCs CONTAIN
  - CHLOROPHYLL
    - EACH CHL. HAS A RED AND A BLUE ABSORPTION BAND
  - “ACCESSORY” PIGMENTS: “FILL IN” THE SPECTRUM
    - CAROTENOIDS (LIKE β-CAROTENE AND LYCOPENE)
    - FOUND IN ALL GREEN PLANTS
    - IN MANY PHOTOSYNTHETIC BACTERIA

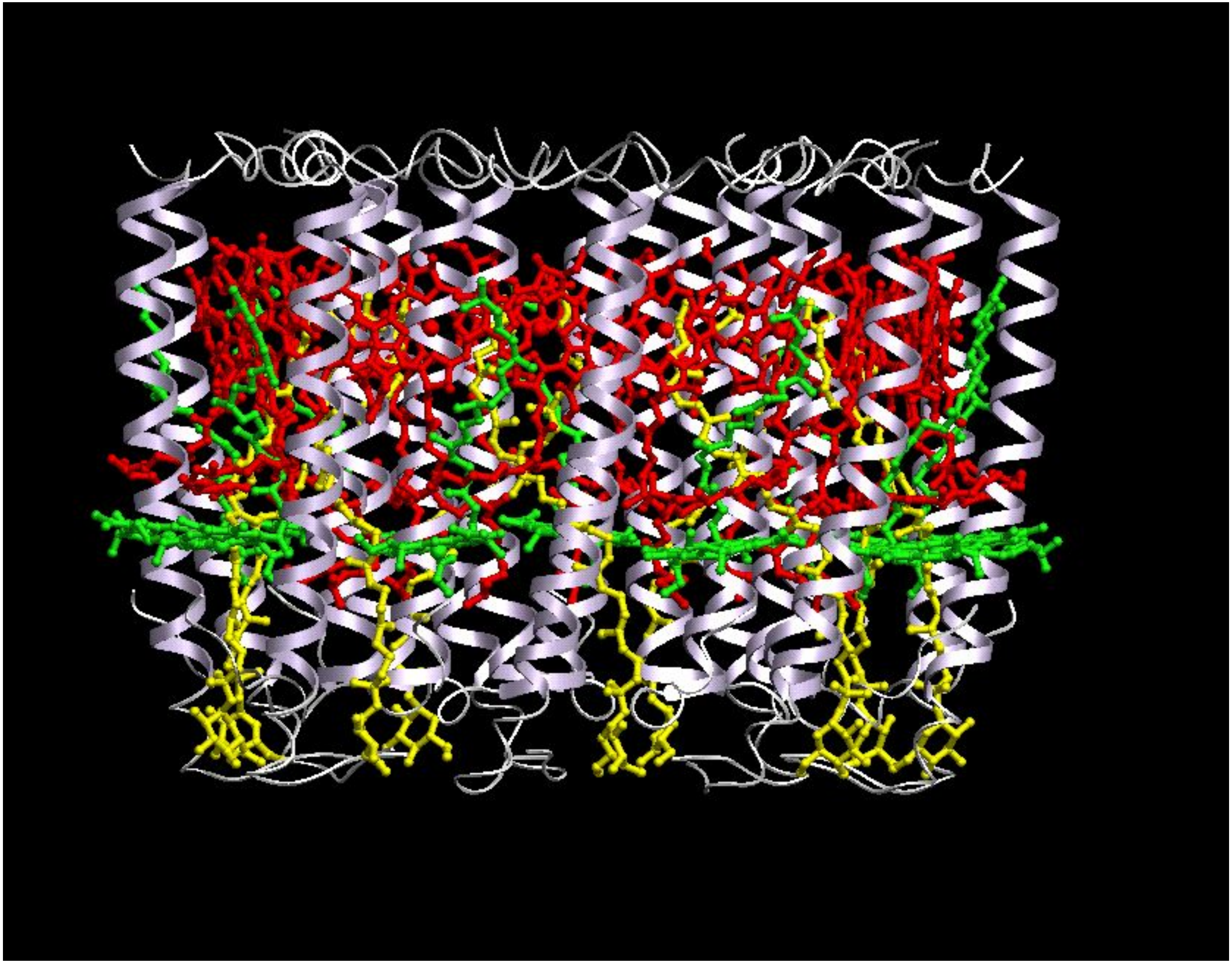
LHCs IN PURPLE PHOTOSYNTHETIC BACTERIA

- LH-2 FROM *Rhodospirillium molischianum*
  - TWO 8-FOLD SYMMETRIC CONCENTRIC RINGS
    - α-SUBUNITS ON INNER RING
    - β-SUBUNITS ON OUTER RING
  - 32 PIGMENT MOLECULES BETWEEN THE RINGS
    - 24 OF THESE ARE BACTERIOCHLOROPHYLL a
    - 8 ARE LYCOPENE MOLECULES
- IN-CLASS EXERCISE:
  - REVIEW THE STRUCTURE OF A SIMILAR LHC, *Rs. acidophilus* (1KZU)
    - LOCATE STRUCTURES DESCRIBED ABOVE

(ACCESSIBLE FROM www.RCSB.org

LH2 FROM *Rs. acidophhilus*





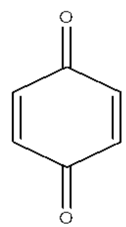
LHC-II

- MOST ABUNDANT MEMBRANE PROTEIN IN CHLOROPLASTS OF GREEN PLANTS
- A TRANSMEMBRANE PROTEIN
- BINDS
  - ~ 7 CHLOROPHYLL a MOLECULES
  - ~ 5 CHLOROPHYLL b MOLECULES
  - TWO CAROTENOIDS
- COMPRISES ABOUT 50% OF ALL CHLOROPHYLL IN BIOSPHERE

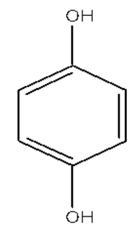
ONE-CENTER ELECTRON TRANSPORT IN PHOTOSYNTHETIC BACTERIA

- LOOK AT THE REACTION CENTER OF PURPLE PHOTOSYNTHETIC BACTERIA (PbRC)
- CONTAINS 3 HYDROPHOBIC SUBUNITS
  - H,L,M
  - INCLUDES 11 TRANSMEMBRANE HELICES
- THESE BIND THE FOLLOWING PROSTHETIC GPS:
  - 4 MOLECULES OF BACTERIOCHLOROPHYLL
  - 2 MOLECULES OF BACTERIOPHEOPHYTIN
- ALSO BIND
  - Fe(II) ION
  - 2 MOLECULES OF UBIQUINONE
    - OR ONE UBIQUINONE AND ONE MENAQUINONE

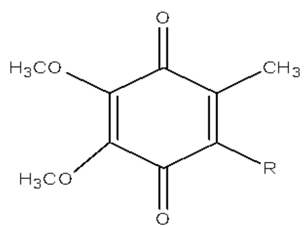
QUINONES CAN SERVE AS BIOLOGICAL REDOX REAGENTS



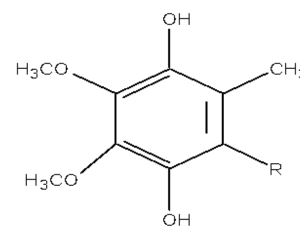
QUINONE



HYDROQUINONE



COENZYME Q
(UBIQUINONE)



REDUCED COENZYME Q

"R" IS:

$$-(-CH_2-CH{=}\underset{}{\overset{\displaystyle CH_3 \atop |}{C}}-CH_2-)_{10}-H$$

IN-CLASS EXERCISE

- EXPLORE THE STRUCTURE OF THE PHOTOSYNTHETIC REACTION CENTER FROM *Rb. sphaeroides*

  LOCATE ALL STRUCTURES DESCRIBED ON THE PREVIOUS SLIDE

  .

ACCESS THIS MOLECULE FROM THE WEB SITE PDBid 2RCR

GEOMETRY OF THE PROSTHETIC GROUPS IN PbRC OF *RHODOPSEUDOMONAS VIRIDIS*

- ALMOST PERFECT TWO-FOLD SYMMETRY
- A “SPECIAL PAIR” OF BACTERIOCHLOROPHYLL MOLECULES
  - CAN BE Bchl a : MAXIMUM ABSORBPTION AT 870 nm (P870)
  - OR Bchl b : MAX. ABS. AT 960 nm (P960)
- EACH MOLECULE OF SPECIAL PAIR CONTACTS, IN TURN:
  - AN ACCESSORY Bchl b MOLECULE
  - A BPheo b MOLECULE
- THE MENAQUINONE MOLECULE IS NEAR THE L-SUBUNIT’S BPheo b
- THE UBIQUINONE ASSOCIATES WITH THE M-SUBUNIT OF BPheo b
- THERE IS AN Fe (II) BETWEEN THE UBI- AND MENAQUINONE

IN-CLASS QUESTION

- PURPLE PHOTOSYNTHETIC BACTERIA HAVE DIFFERENT PIGMENTS THAN HIGHER PLANTS. WHY IS THIS AN ADVANTAGE FOR THESE BACTERIA?

THE TRANSPORT OF ELECTRONS IN PHOTOSYNTHETIC BACTERIA

- THE FOLLOWING EVENTS OCCUR IN THE L-SUBUNIT AFTER THE ABSORPTION THE FIRST PHOTON BY THE SPECIAL PAIR
  - AN EXCITED ELECTRON IS DELOCALIZED OVER THE SPECIAL PAIR: P960 $\rightarrow$ P960*
  - P960* TRANSFERS ELECTRON TO BPheo b
    - **NOW WE HAVE $P960^{+}$ BPheo b^{-}**
    - **THE ACCESSORY BChl b IS PART OF PATHWAY FOR ELECTRON FLOW; IT IS NOT REDUCED**
  - ELECTRON MIGRATES TO Q_A
    - **IS NOW REDUCED TO Q_A^-**
    - **NOTE: THIS IS THE <u>SEMIQUINONE</u> FORM OF Q_A**

THE FIRST PHOTON ABSORPTION EVENT

- P960* EXISTS FOR ONLY ~3 ps
- ELECTRON MUST BE REMOVED RAPIDLY FROM VICINITY OF $P960^+$
  - WHY?
- THE QUANTUM YIELD OF THE ELECTRON TRANSFER EVENT IN PbRC IS ALMOST 100% !

Q_A^- TRANSFERS ITS ELECTRON TO Q_B

- THE Fe(II) ATOM DOES IS NOT DIRECTLY INVOLVED DURING THE TRANSFER
- Q_A NEVER BECOMES FULLY REDUCED
- A SECOND PHOTON EVENT REDUCES Q_A AGAIN
  - SAME EVENTS AS FOR THE FIRST EVENT
  - REDUCED Q_A PASSES THE SECOND ELECTRON TO Q_B^-

FULLY REDUCED Q_B IS AN ANIONIC QUINOL (Q_B^{2-})

- Q_B^{2-} TAKES UP TWO H^+ FROM THE CYTOPLASM
- THE TWO ELECTRONS THAT HAVE BEEN TAKEN UP BY Q_BH_2 ARE RETURNED TO THE OXIDIZED SPECIAL PAIR
  - THE REDOX CARRIERS CAN INCLUDE
    - **A POOL OF MEMBRANE-BOUND UBIQUINONES**
    - **CYTOCHROME bc_1 COMPLEX**
    - **CYTOCHROME c_2**
  - AN “ELECTRON TRANSPORT CHAIN”
  - OCCURS WITHIN BACTERIAL PLASMA MEMBRANE
- WHEN QH_2 TRANSFERS ELECTRONS TO CYT bc_1, THE PROTONS ARE TRANSLOCATED ACROSS THE PLASMA MEMBRANE

ELECTRON TRANSFER FROM QH_2 TO CYT c_2 OCCURS VIA A TWO-STAGE "Q-CYCLE"

- QH_2 IS A TWO-ELECTRON CARRIER
- CYT c_2 IS A ONE-ELECTRON CARRIER
- FOR EVERY 2 ELECTRONS TRANSFERRED FROM QH_2 TO CYT c_2 , 4 H^+ ENTER THE PERIPLASMIC SPACE
- A TRANSMEMBRANE PROTON GRADIENT
- DISSIPATION OF THE GRADIENT DRIVES ATP PRODUCTION
  - "PHOTOPHOSPHORYLATION"

ELECTRON TRANSPORT IN PURPLE PHOTOSYNTHETIC BACTERIA IS A CYCLIC PROCESS

- THERE IS NO NET OXIDATION-REDUCTION
- OVERALL PROCESS IS IRREVERSIBLE
  - ELECTRONS ARE TRANSFERRED TO PROGRESSIVELY LOWER ENERGY STATES
    - STANDARD REDUCTION POTENTIALS ARE PROGRESSIVELY MORE POSITIVE

IN-CLASS QUESTION

- THE STANDARD REDUCTION POTENTIAL FOR THE OXIDATION OF WATER IS 0.815 V.

$O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O$

CAN THIS VALUE BE OBTAINED FROM PURPLE PHOTOSYNTHETIC BACTERIAL PHOTOSYNTHESIS?

(ASSUME THAT THE SPECIAL PAIR CONSISTS OF BChl a)

ANOTHER WAY OF ASKING THE SAME QUESTION: CAN $P870^+$ OXIDIZE WATER? (EXPLAIN YOUR ANSWER.)

WHERE DO THE REDUCING EQUIVALENTS COME FROM?

- IN PLANTS AND CYANOBACTERIA
  - FROM OXIDATION OF H_2O
    - NET RXN' OF PHOTOSYNTHESIS:
      $CO_2 + 2\ H_2O \rightarrow (CH_2O) + H_2O + O_2$
- IN PURPLE PHOTOSYNTHETIC BACT.
  - FROM OXIDATION OF
    - H_2S
    - S
    - $S_2O_3^{2-}$
    - H_2
    - ETHANOL
      - NET REACTION: $CO_2 + 2\ H_2A \rightarrow (CH_2O) + H_2O + 2\ A$

IN-CLASS PROBLEM

- SOME PHOTOSYNTHETIC BACTERIA USE H_2S AS A HYDROGEN DONOR AND PRODUCE ELEMENTAL SULFUR, WHILE OTHERS USE ETHANOL AND PRODUCE ACETALDEHYDE.
  - WRITE THE NET REACTIONS FOR PHOTO-SYNTHESIS CORRESPONDING TO THESE BACTERIA
  - WHY IS NO OXYGEN PRODUCED?

WHAT HAPPENED WHEN AVAILABLE REDUCTIVE RESOURCES WERE EXHAUSTED?

- A PHOTOSYNTHETIC SYSTEM EVOLVED THAT HAD ENOUGH EMF TO ABSTRACT ELECTRONS FROM WATER
- O_2 BUILT UP AS A “TOXIC WASTE PRODUCT”
- PHOTOSYNTH. BACTERIA ARE ANAEROBES, SO THEY NOW INHABIT NARROW ECOLOGICAL NICHES

PHOTOSYNTHESIS IN PLANTS AND CYANOBACTERIA IS NON-CYCLIC

- A MULTI-STEP PROCESS
- TWO PHOTOSYNTHETIC REACTION CENTERS
  - PSII AND PSI
- EACH CENTER IS INDEPENDENTLY ACTIVATED BY LIGHT
- ELECTRONS FLOW FROM PSII → PSI
- PSII OXIDIZES H_2O
- PSI REDUCES $NADP^+$

- H_2O OXIDATION IS COUPLED TO $NADP^+$ REDUCTION

ELECTRON TRANSFER OCCURS BETWEEN MEMBRANE-BOUND PARTICLES

- PSII
- CYTOCHROME b_6f COMPLEX
- PSI

- MOBILE ELECTRON CARRIERS SHUTTLE THE ELECTRONS BETWEEN THESE COMPLEXES
  - PLASTOQUINONE (Q) LINKS PSII TO CYTOCHROME b_6f COMPLEX
    - **Q IS REDUCED TO QH_2 BY PSII**
    - **THEN QH_2 REDUCES CYTOCHROME b_6f COMPLEX**
  - PLASTOCYANIN (PC) LINKS CYTOCHROME b_6f TO PSI

THE ELECTRONS ULTIMATELY REDUCE $NADP^+$

- THE ENZYME IS FERREDOXIN-$NADP^+$ REDUCTASE (FNR)
- DURING THE ENTIRE FOUR-ELECTRON PROCESS
  - WATER IS OXIDIZED
  - THE ELECTRONS PASS THROUGH A Q-CYCLE
  - A TRANSMEMBRANE PROTON GRADIENT IS GENERATED
    - THE pH IS LOWER IN THE THYLAKOID LUMEN
  - THE FREE ENERGY OF THIS GRADIENT DRIVES ATP SYNTHESIS

THE "Z-SCHEME"

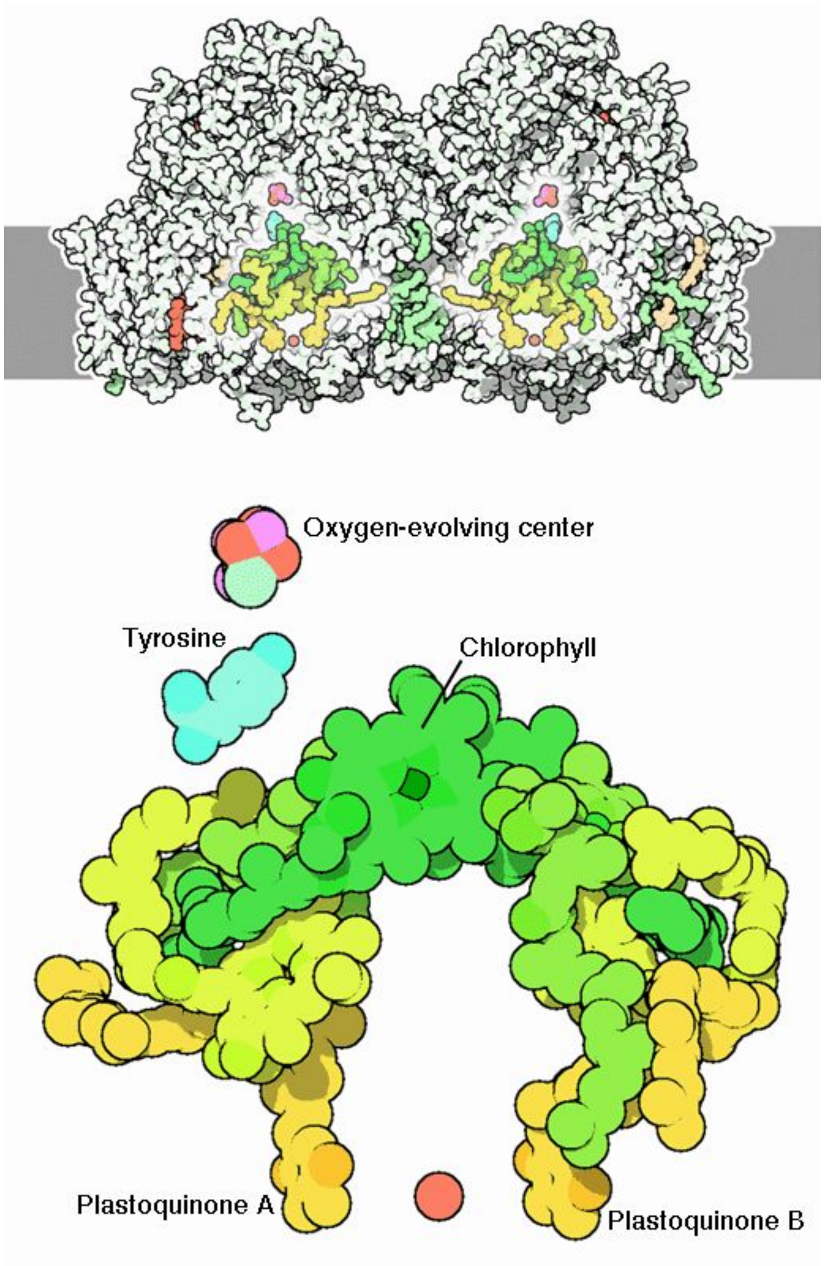
- A ZIG-ZAG DIAGRAM REPRESENTING PROSTHETIC GROUPS INVOLVED IN PHOTOSYNTHESIS
- TWO LOCI REPRESENT PSII AND PSI

- ELECTRONS FLOW FROM <u>LOW TO HIGH</u> REDUCTION POTENTIALS

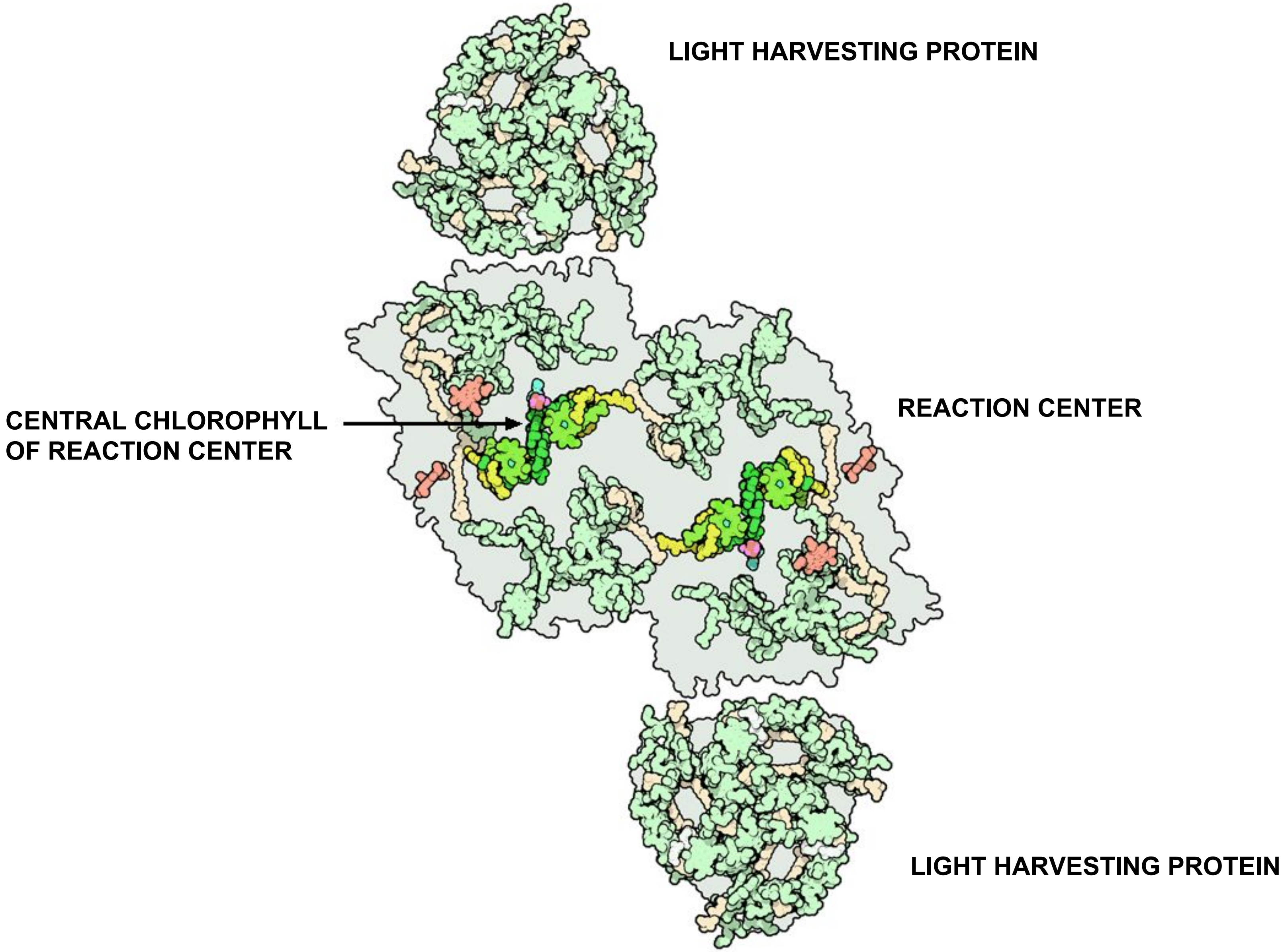
PSII

- CRYSTALLIZES AS A SYMMETRIC DIMER
- EACH PROTOMER WITH PSEUDO TWO-FOLD SYMMETRY
- REACTION CENTER COFACTORS ORGANIZED SIMILARLY TO PbRC
  - Chl a INSTEAD OF BChl b
  - Pheo a INSTEAD OF BPheo b
  - PLASTOQUINONE INSTEAD OF MENAQUINONE
- P680 : TWO Chl a RINGS SIMILAR TO “SPECIAL PAIR”

PHOTOSYSTEM II (PDB 1s5l) : "MOLECULE OF THE MONTH" NOVEMBER 2004



PSII (1s5I): TOP VIEW, SHOWING PIGMENT MOLECULES



EVENTS AT PSII

- FIRST PHOTON EVENT EJECTED ELECTRON
- TRANSFERRED THRU ACCESSORY Chl a TO Pheo a, AND THEN TO Q_A
- Q_A IS THE BOUND PLASTOQUINONE
- THEN THE ELECTRON IS TRANSFERRED TO Q_B

A SECOND PHOTON EVENT OCCURS

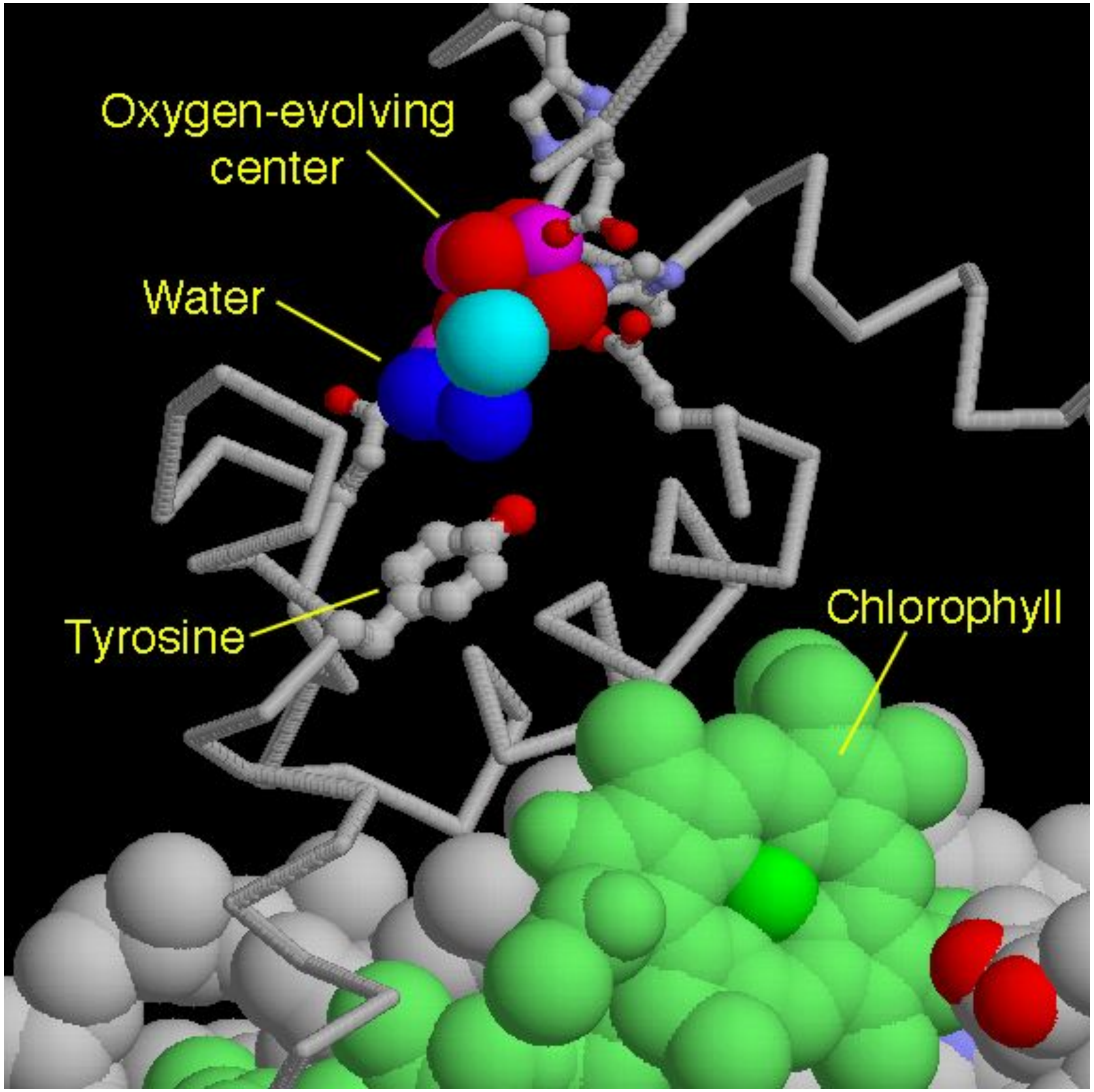
- THE SECOND ELECTRON IS TRANSFERRED TO Q_B
- Q_B (WITH 2 ELECTRONS) TAKES UP 2 PROTONS
  - AT STROMAL SURFACE
- Q_BH_2 (PLASTOQUINOL) EXCHANGES WITH MEMBRANE-BOUND POOL OF PLASTOQUINONE MOLECULES
- DCMU INHIBITS PHOTOSYNTHESIS
  - IT COMPETES WITH PLASTOQUINONE MOLECULES FOR THE Q_B-BINDING SITE ON PSII

THE OXYGEN EVOLVING CENTER (OEC)

- A “WATER-SPLITTING” ENZYME
- MUST UNDERGO 4 LIGHT-DEPENDENT REACTIONS BEFORE RELEASING O_2
- 4 PROTONS ARE RELEASED TO INNER THYLAKOID SPACE IN A STEPWISE MANNER
- REACTION DRIVEN BY EXCITATION OF PSII RC

- A Mn_4CaO_4 COMPLEX

THE OXYGEN EVOLVING CENTER



THE TYROSINE RADICAL BRIDGES THE WATER MOLECULE AND THE CHLOROPHYLL MOLECULE

MECHANISM OF OEC

- NOT CLEAR
- OEC PROGRESSES THROUGH 5 STATES
- Mn CHANGES ITS OXIDATION STATE AS THE OEC CYCLES THROUGH ITS STATES
- PROTONS, ELECTRONS ABSTRACTED AS Mn CYCLES THROUGH II,III,IV, AND V STATES
- EACH ELECTRON IS INDIVIDUALLY TRANSFERRED TO $P680^+$
- TyrO· , A TRANSIENT RADICAL, RELAYS THE e^-
  - WHERE ELSE HAVE YOU SEEN THE TYROSYL RADICAL?

PSII OEC

- RECENT REFERENCES:

  J. Ch. Ed. Vol. 82 (5) May 2005, pages 791 – 794

  Although this article describes experiments regarding this bioinorganic molecule, there is a good diagram of the proposed catalytic mechanism on page 792 for "complex 1", a synthesized molecule which is a functional model of the Mn_4 cluster.

A fully manipulable Chime version of the four-manganese center in PSII is available at the following web site:

http://www.jce.divched.org/JCEWWW/Features/MonthlyMolecules/2005/May/

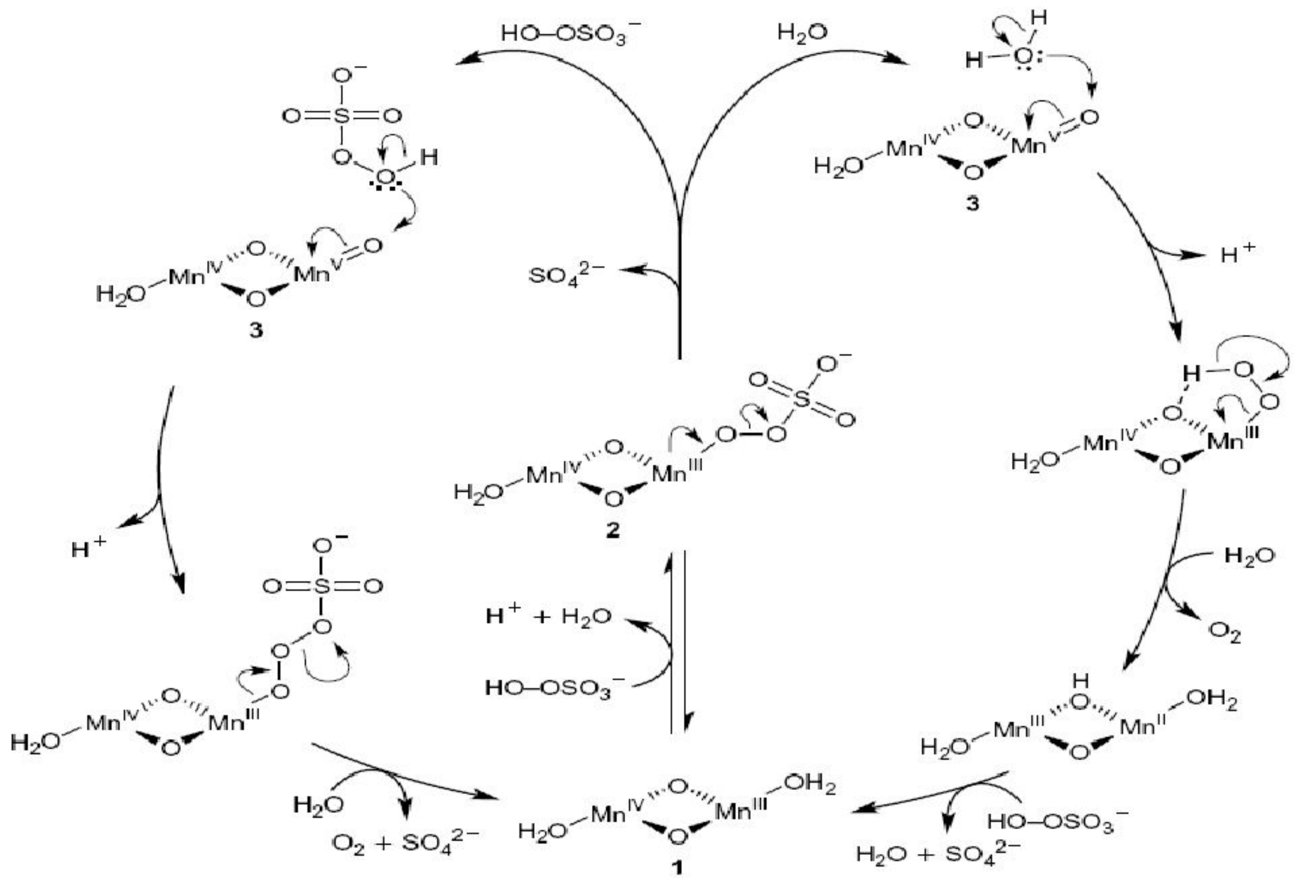


Figure 2. Proposed catalytic cycle for the oxidation of H_2O by **1**. The terpy ligands are not shown for clarity.

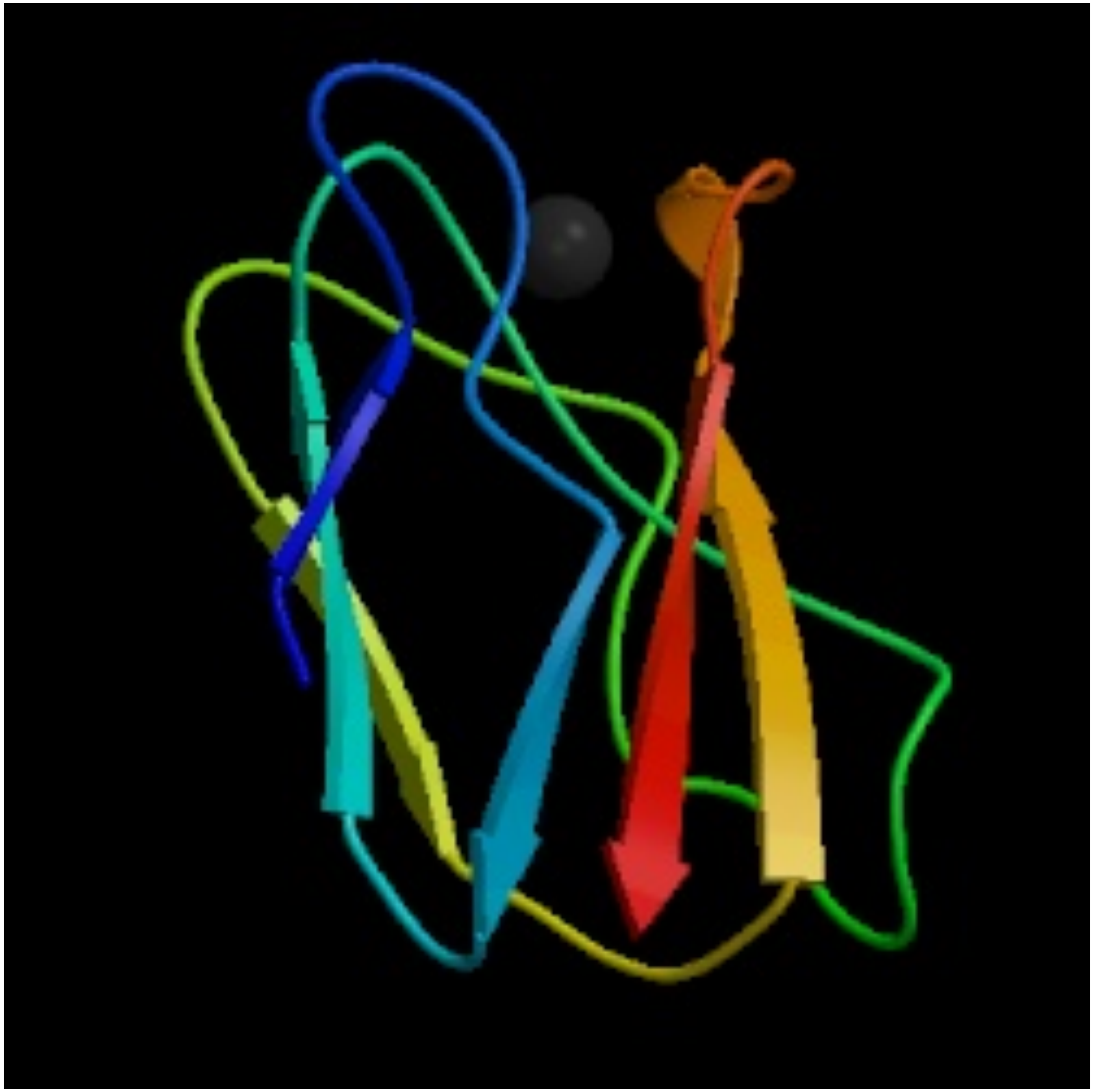
Journal of Chemical Education : Vol 82(5) May 2005 Pages 791-794

ELECTRONS ARE TRANSFERRED THROUGH Cyt b_6f COMPLEX

- VIA A Q POOL (PLASTOQUINONE)
- ELECTRON FLOW OCCURS THROUGH A "Q-CYCLE"
- FOR EACH e^- TRANSPORTED, 2 PROTONS ARE TRANSPORTED ACROSS THYLAKOID MEMBRANE
  - □ 8 H^+ ARE TRANSPORTED (THERE ARE 4 e^- FROM THE TWO WATER MOLECULES THAT ARE SPLIT
- THIS ELECTRON TRANSPORT IS RESPONSIBLE FOR GENERATING MOST OF THE ELECTROCHEM-ICAL PROTON GRADIENT

PLASTOCYANIN : A “BLUE COPPER” PROTEIN

- MEDIATES ELECTRON TRANSFER BETWEEN CYT f AND PSI
  - CYT f IS THE TERMINAL ELECTRON CARRIER OF THE CYT b_6f COMPLEX
  - ON THE THYLAKOID LUMENAL SURFACE
- ITS REDOX CENTER CONTAINS COPPER
  - CYCLES BETWEEN Cu(I) AND Cu(II) OXIDATION STATES



IN-CLASS CHIME EXERCISE

LOOK AT PDBid 1PLC

FIND:

THE “β-SANDWICH”

IDENTIFY THE COPPER ION

FIND THE 4 LIGANDS THAT TETRAHEDRALLY COORDINATE THE Cu ION

LOCATE THE 6 ASP AND GLU RESIDUES THAT FORM A (-) CHARGED PATCH ON THE SURFACE

CYT f HAS A LYS 187 SIDECHAIN THAT IS ONE OF 5 (+) CHARGED RESIDUES ON ITS SURFACE. IT CAN BE CROSS- LINKED (EXPERIMENTALLY) TO ASP 44 ON PC, WHICH IS ONE OF THE ASPs IN THE (-) CHARGED PATCH

SUGGEST AN INTERMOLECULAR MECHANISM BY WHICH CYT f AND PC ASSOCIATE

"TUNING" THE REDOX POTENTIAL

- PROTEINS CAN CHANGE THE STANDARD REDUCTION POTENTIALS OF THEIR REDOX CENTERS THROUGH A STRAIN MECHANISM

- FOR EXAMPLE:
  - $E^{O'}$ FOR THE NORMAL Cu(II)/Cu(I) HALF-REACTION IS 0.158 VOLTS
  - $E^{O'}$ FOR THE SAME HALF-REACTION IN PC IS 0.370 V

LIGAND GEOMETRY OF 4-COORDINATED COPPER ATOMS

- USUALLY SQUARE PLANAR FOR Cu(II)
- USUALLY TETRAHEDRAL FOR Cu(I)

- IN PC, THE Cu ATOM HAS A DISTORTED TETRAHEDRAL GEOMETRY
  - CYS
  - MET
  - TWO HIS RESIDUES
- THE PROTEIN IMPOSES THE TETRAHEDRAL GEOMETRY ON THE Cu(II) STRAIN
  - LOOKS MORE LIKE THE Cu(I) GEOMETRY

ELECTRON TRANSFER IS FACILITATED BY THE STRAIN

- THE ΔE^O IS GREATER FOR THE ELECTRON TRANSFER EVENT IN PLASTOCYANIN
- SINCE $\Delta G^O = -nF\ \Delta E^O$, THE REACTION IS MORE SPONTANEOUS UNDER STANDARD CONDITIONS

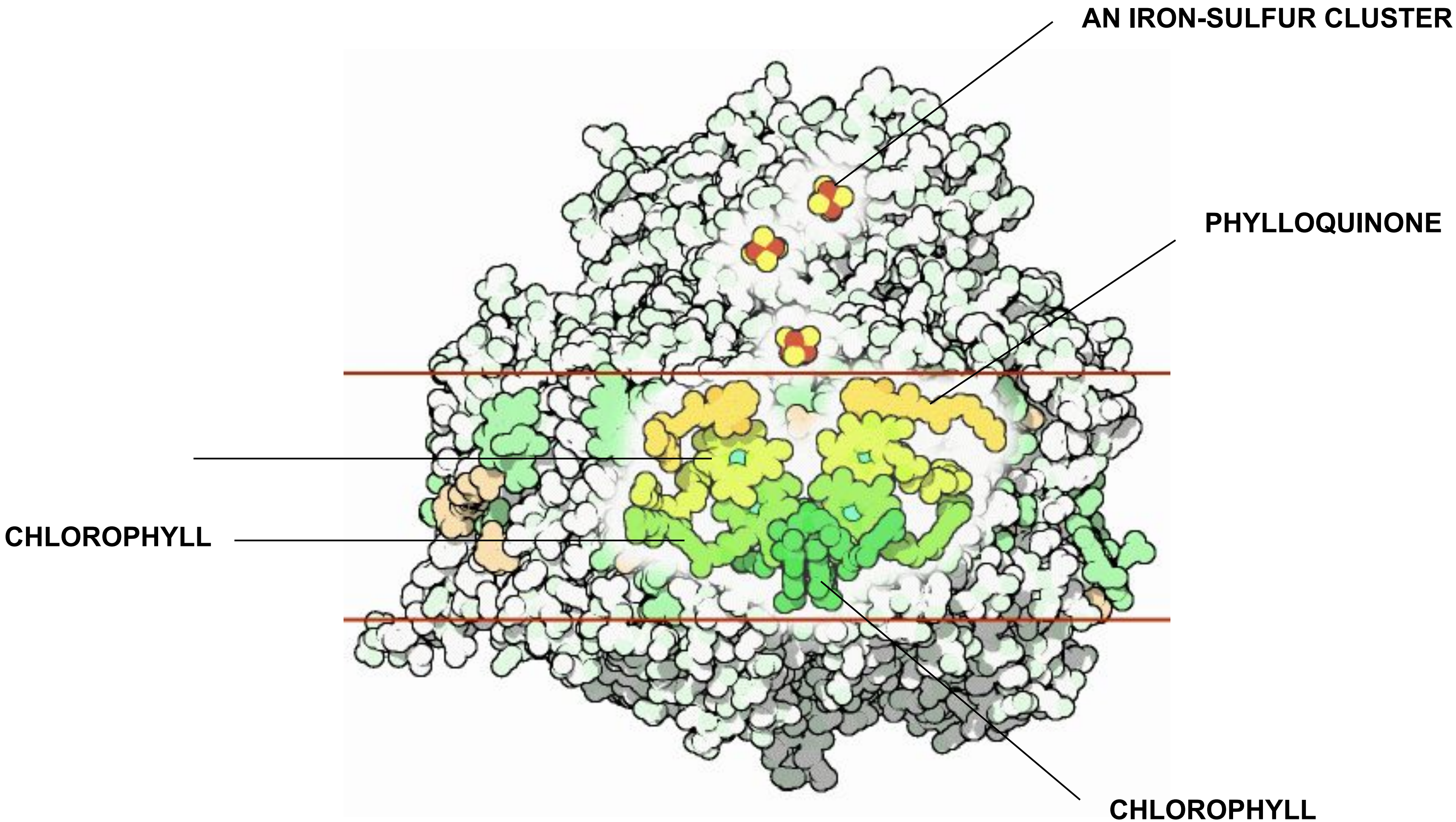
PSI

- IN CYANOBACTERIA, THESE ARE TRIMERS
  - **EACH PROTOMER HAS**
    - **31 TRANSMEMBRANE HELICES ANCHOR EACH MONOMER**
    - **96 CHLOROPHYLL MOLECULES**
    - **22 CAROTENOIDS**
- CHLOROPHYLLS AND CAROTENOIDS OPERATE AS A LIGHT-HARVESTING COMPLEX
- EACH MONOMER HAS AN ACTIVE CENTER
  - **ONE OR TWO CHLOROPHYLL MOLECULES (P700)**
- P700 IS EXCITED BY PHOTONS FUNNELED THROUGH ANTENNAE PIGMENTS
  - **EXCITON TRANSFER**

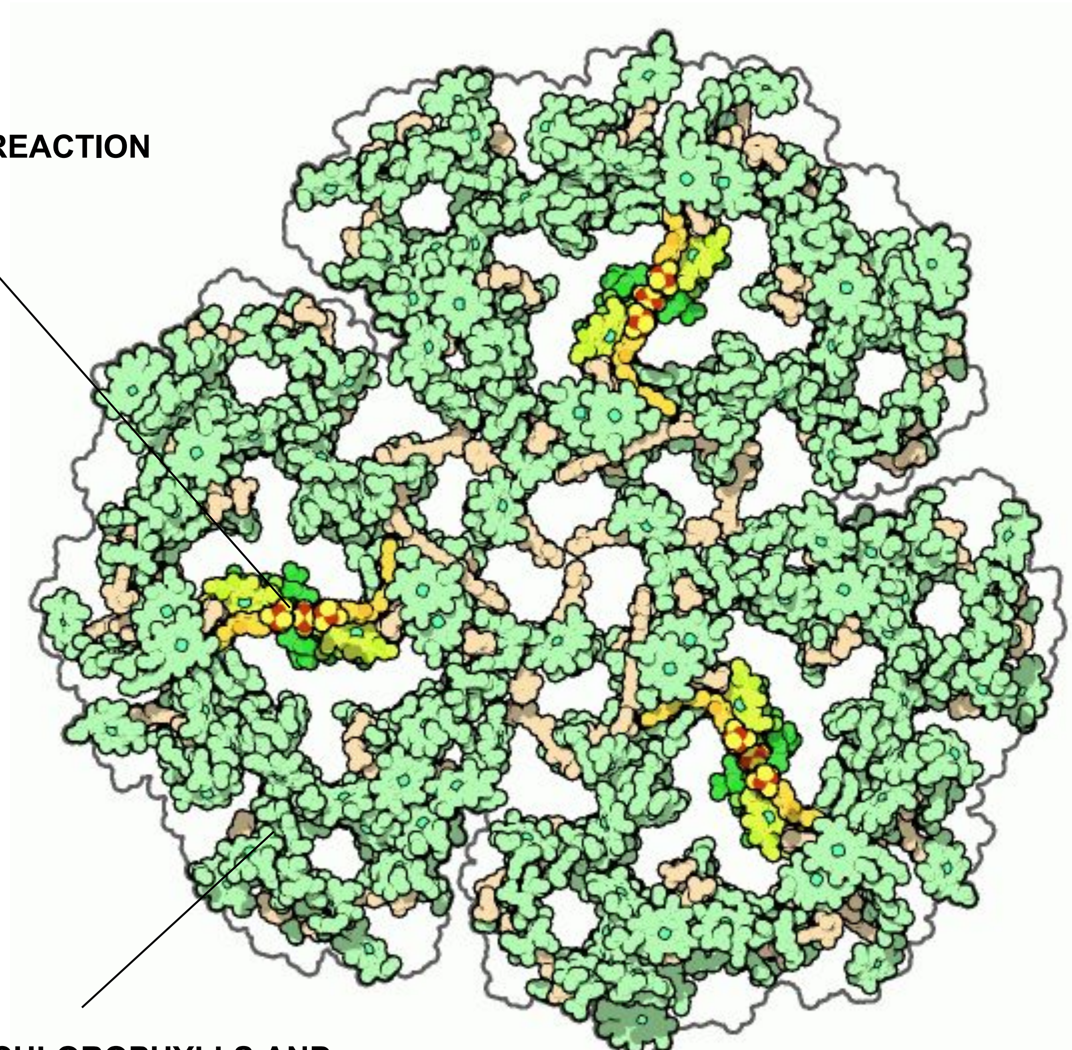
PSI

- P700 IS PHOTO-EXCITED TO P700*
- P700* PASSES ITS EXCITED ELECTRON ON THROUGH A CHAIN OF ELECTRON CARRIERS
  - **EACH ONE AT A LOWER REDUCTION POTENTIAL**
- THE CARRIERS INCLUDE
  - **Chl a**
  - **PHYLLOQUINONE**
  - **THREE [4Fe-4S] CLUSTERS**
- OXIDIZED P700 ($P700^+$) IS A WEAK OXIDANT
  - **$E^{o'}$ IS ABOUT 0.4 V**
- THE PROSTHETIC GROUPS HAVE AN APPROXIMATE 2-FOLD SYMMETRY

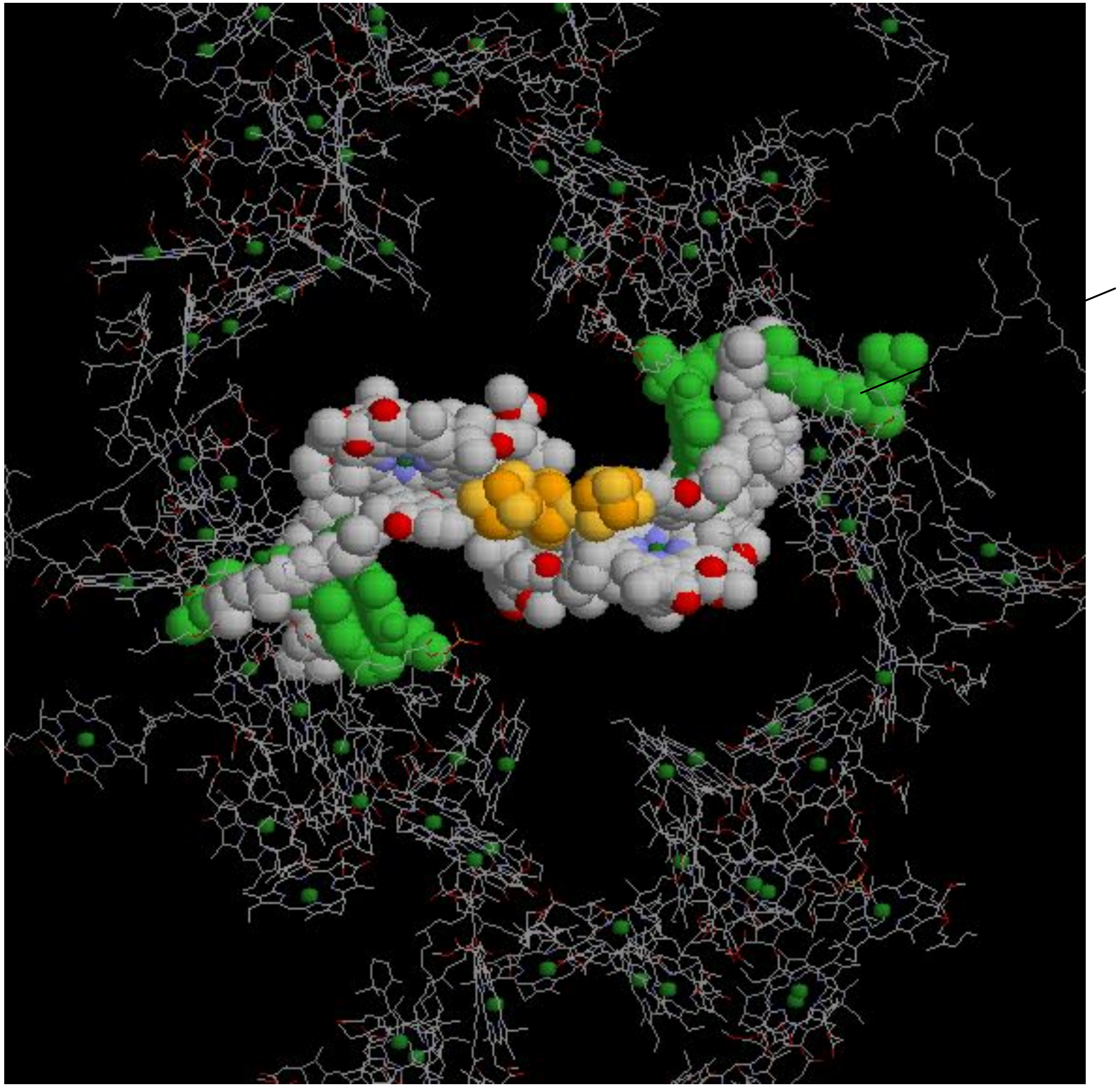
PHOTOSYSTEM I (   ) : MOLECULE OF THE MONTH



PS I AS VIEWED FROM THE TOP



PDB 1jbo : PHOTOSYSTEM I COFACTORS



THERE ARE 2 POSSIBLE PATHWAYS FOR ELECTRON FLOW IN PSI

- NON-CYCLIC
- CYCLIC

THE NON-CYCLIC PATHWAY

- THE NON-CYCLIC PATHWAY
  - **MOST ELECTRONS FOLLOW THIS PATHWAY**
  - **PASSED ON TO A SOLUBLE FERREDOXIN**
    - **LOCATED IN THE STROMA**
    - **CONTAINS A [2Fe-2S] CLUSTER**
  - **TWO REDUCED Fd MOLECULES EACH SEND AN ELECTRON ON TO THE ENZYME "FERREDOXIN-NADP$^+$ REDUCTASE (FNR)**
    - **CONTAINS FAD**
  - **FAD IS REDUCED TO $FADH_2$**
  - **$FADH_2$ REDUCES 2 NADP$^+$ MOLECULES**
- NADPH IS THE FINAL PRODUCT OF CHLOROPLAST LIGHT-REACTION

OVERALL RESULT OF NON-CYCLIC PATHWAY

- 4 ELECTRONS ARE TRANSFERRED FROM 2 WATER MOLECULES TO 2 $NADP^+$ s TO PRODUCE 2 NADPH MOLECULES
- A TRANSMEMBRANE H^+ GRADIENT IS ESTABLISHED
  - 12 H^+ TRANSLOCATED INTO THYLAKOID LUMEN
  - CAN DRIVE SYNTHESIS OF ~ 3 ATP MOLECULES
- NOTE: 2 H^+ ARE RELEASED INTO LUMEN FOR EACH H_2O SPLIT. 4 H^+ ARE USED UP IN STROMA WHEN 4 e^- REDUCE 2 $NADP^+$
- 1 O_2 MOLECULE IS FORMED
- A TOTAL OF 8 PHOTONS ARE ABSORBED

THE CYCLIC PATHWAY

- THE RETURN OF SOME ELECTRONS TO THE POOL OF PLASTOQUINONES (Q-POOL)
- OCCURS THROUGH CYT b_6
- PROTONS ARE TRANSLOCATED ACROSS THE THYLAKOID DURING THIS PROCESS
- BECAUSE IT'S A CYCLIC PROCESS:
  - INDEPENDENT OF PSII
  - NO O_2 EVOLVED

PROBABLE REASON FOR A CYCLIC ALTERNATIVE

- INCREASES LEVEL OF ATP RELATIVE TO THAT OF NADPH
- CELL PRODUCTION OF EACH OF THESE ACCORDING TO ITS NEEDS
- THE REGULATORY MECHANISM IS NOT YET KNOWN

IN-CLASS EXERCISE

- CALCULATE $\Delta G^{o\prime}$ AND $\Delta E^{O\prime}$ FOR THE LIGHT REACTION IN PLANTS
  - (IE, FOR THE 4 ELECTRON OXIDATION OF 2 H_2Os AND SUBSEQUENT REDUCTION OF 2 NADP+) .
- IS THIS PROCESS SPONTANEOUS UNDER PHYSIOLOGIC STANDARD CONDITIONS?
  - WHAT SUPPLIES THE ENERGY TO DRIVE THE REACTION?
- HERE ARE THE "HALF-REACTIONS"
  - $O_2 + 4\ e^- + 4\ H^+ \rightarrow 2\ H_2O \qquad E^{o\prime} = 0.815\ V$
  - $NADP^+ + H^+ + 2\ e^- \rightarrow NADPH \qquad E^{o\prime} = -0.324\ V$
- YOU WILL NEED TO USE : $\Delta G^{o\prime} = -nF\Delta E^{o\prime}$
  - $F = 96{,}485\ J\ V^{-1}\ MOL^{-1}$

STUDY QUESTION FOR EXAM #6

- I WILL GIVE YOU THE PICTURE OF TWO-CENTER PHOTOSYNTHESIS AS WELL AS THAT OF THE “Z-SCHEME”. THEY WILL NOT BE COMPLETE, THOUGH.
- I WILL ASK QUESTIONS ABOUT EACH OF THESE, AND THE ANSWERS WILL BE EASY TO DETERMINE, AS LONG AS YOU UNDERSTAND HOW THE PROCESS WORKS.