# The origin of sulfur in shale oils, gases and spent matter as decoded by $\delta^{34}S$ monitoring and better knowledge gained on various pyrolysis driven processes

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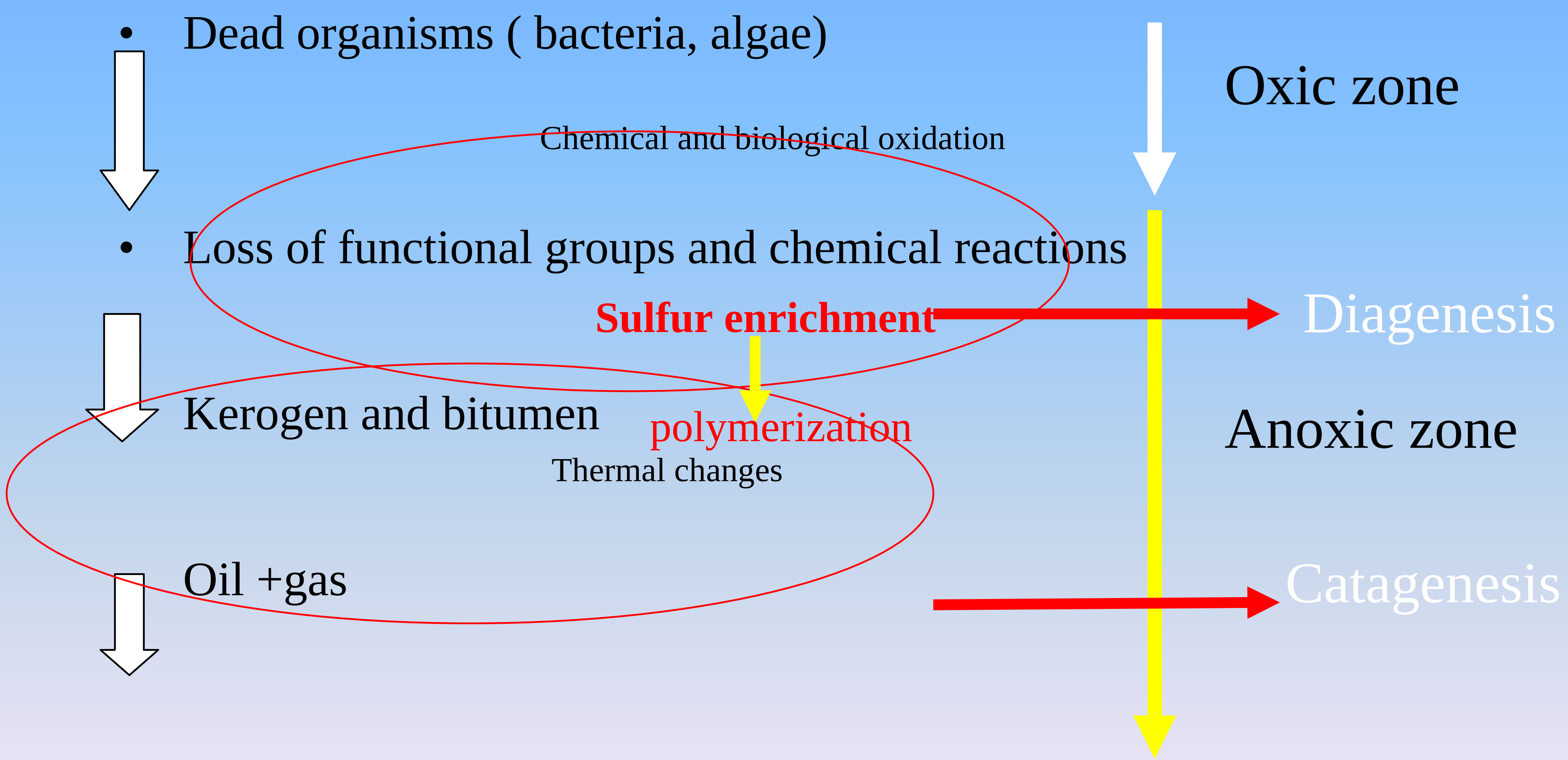
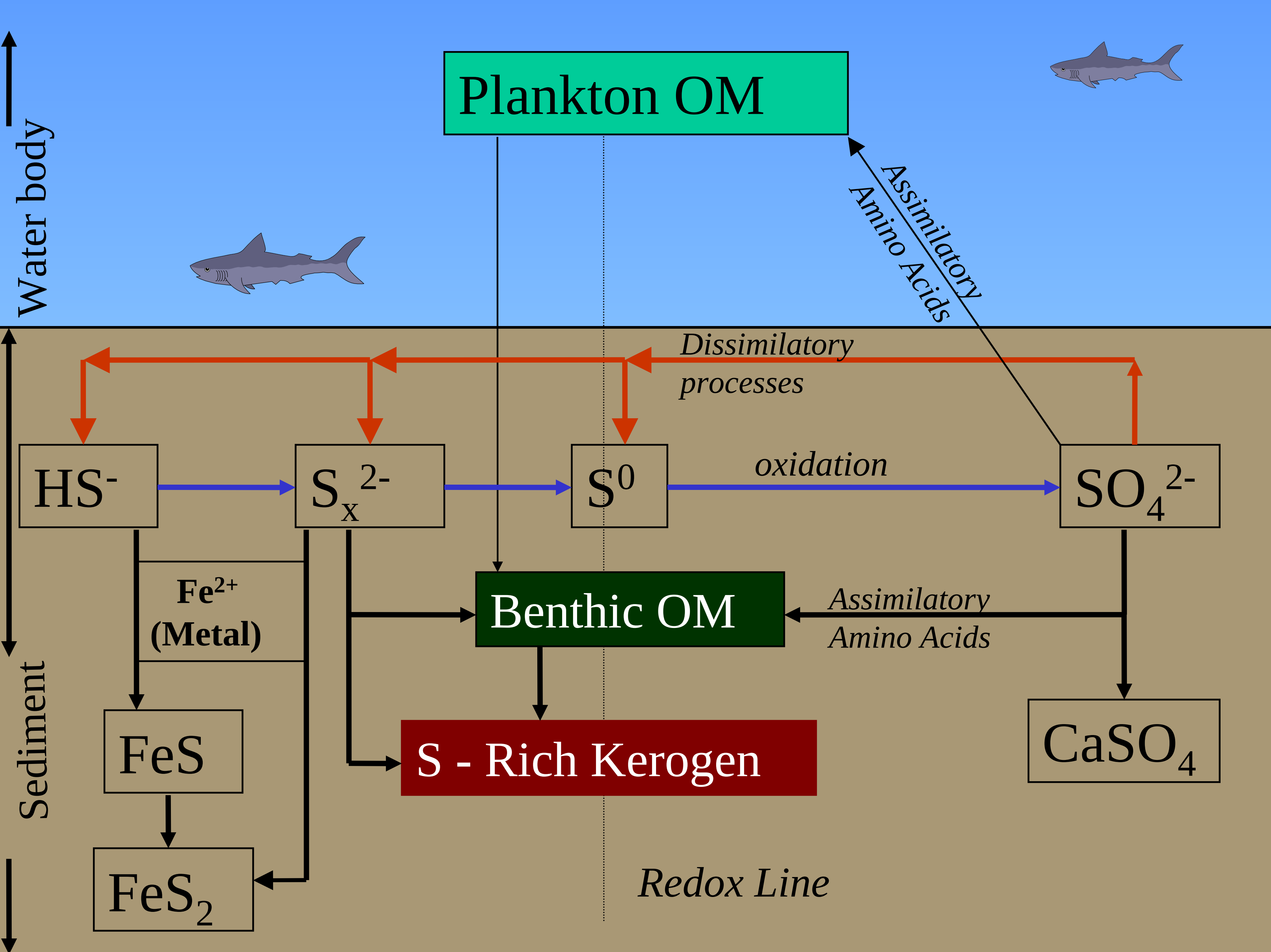
# Main points

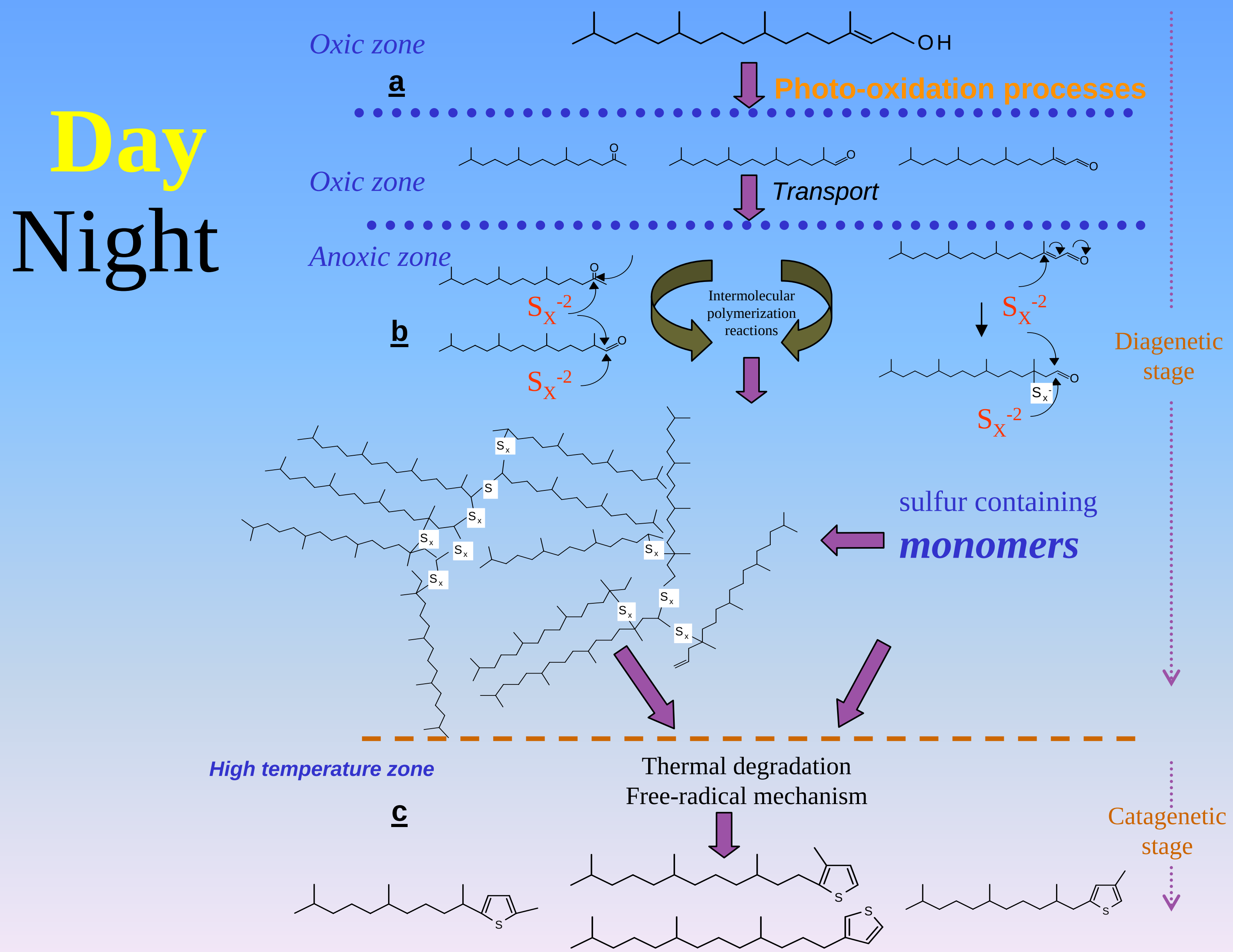
- The use of sulfur stable isotopes for recognition of sedimentation conditions and Diagenetic processes.
- Assimilatory and dissimilatory sources of organically bonded sulfur isotope imprint.

# The formation of oil in marine sediments



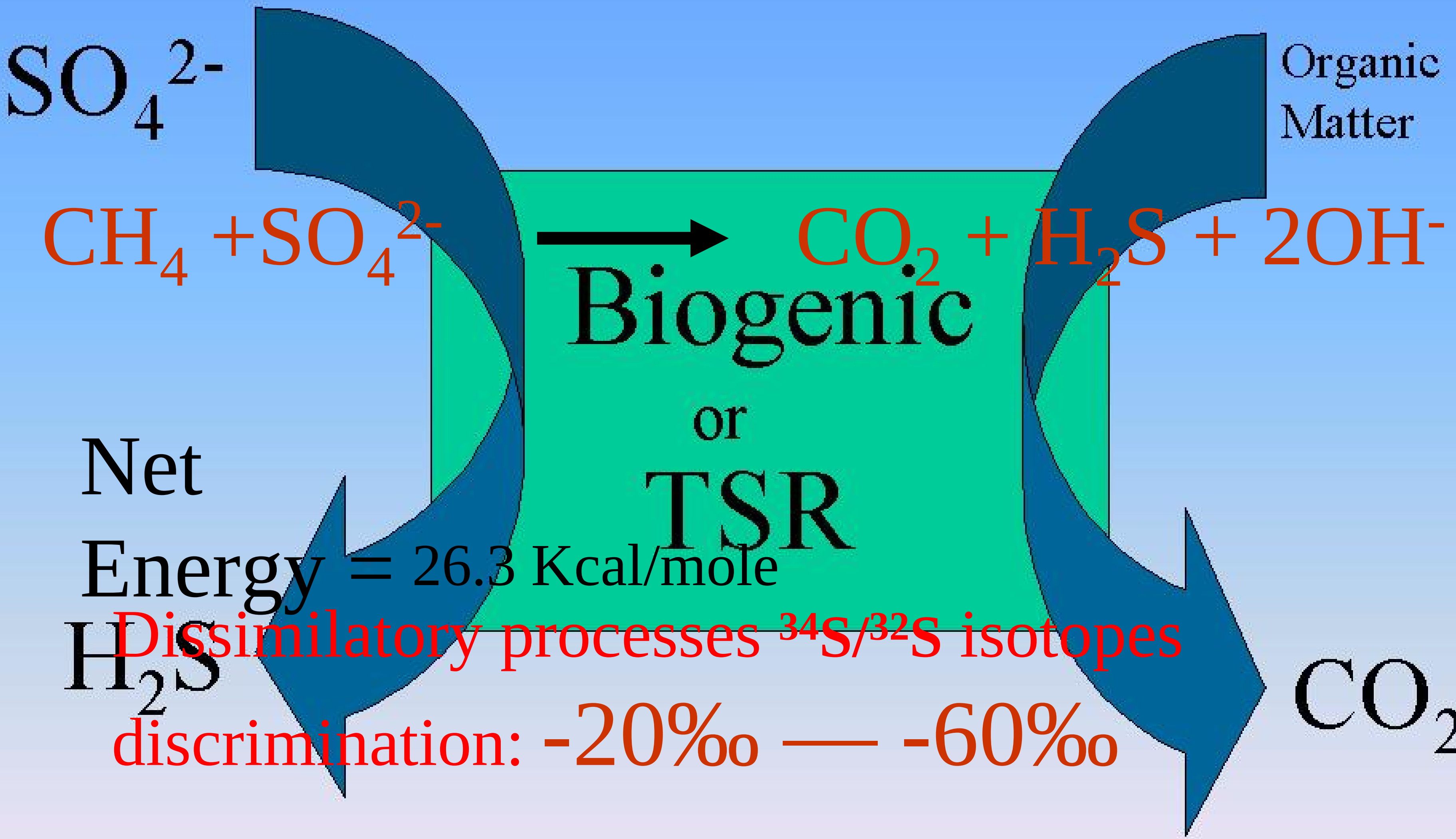


Plankton OM
Water body
Assimilatory
Amino Acids
Dissimilatory
processes
HS-
Sx 2-
S0
oxidation
SO4 2-
Sediment
Fe2+
(Metal)
Benthic OM
Assimilatory
Amino Acids
FeS
S - Rich Kerogen
CaSO4
FeS2
Redox Line



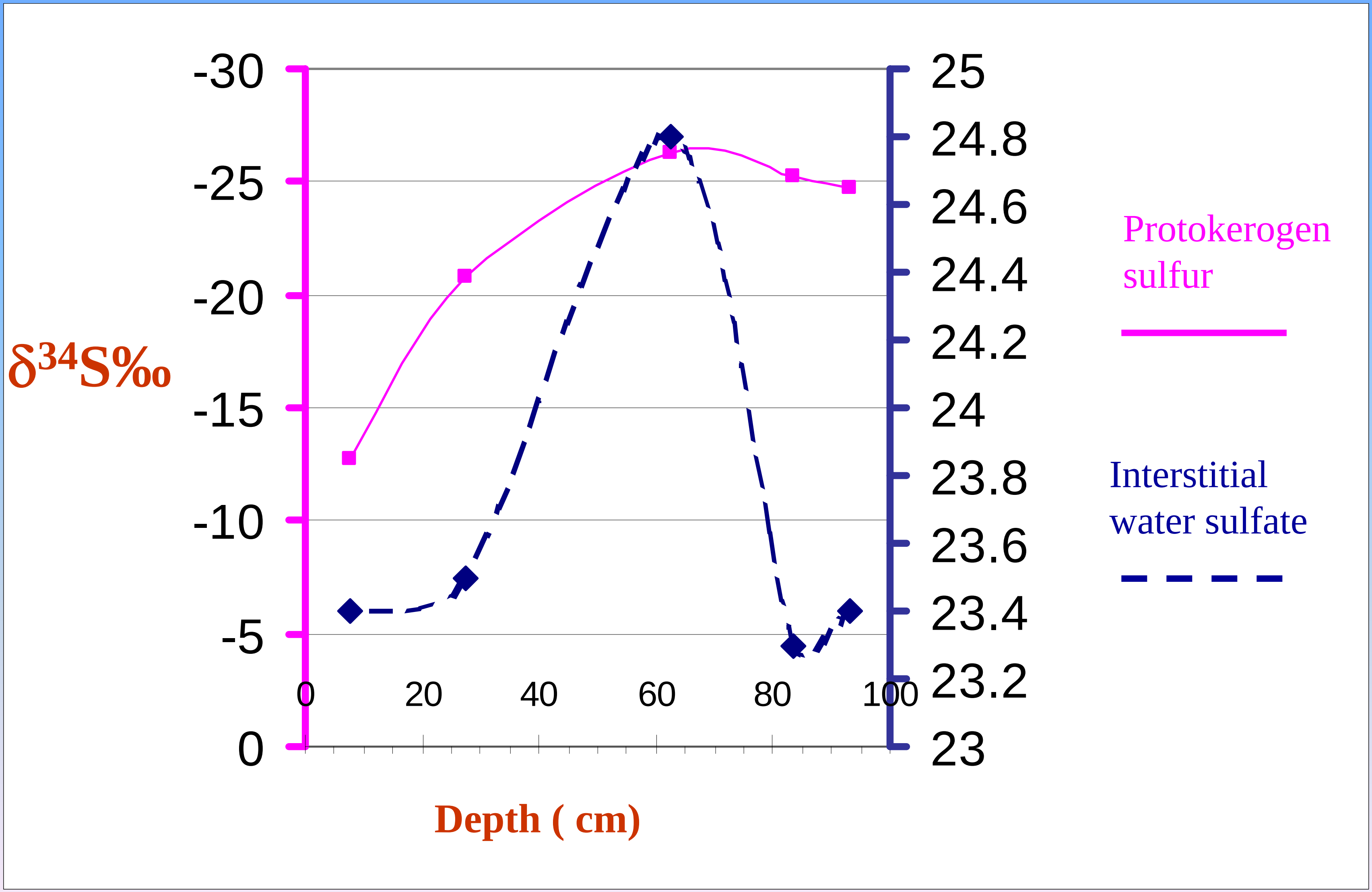
Day
Night
Oxic zone
OH
a
Photo-oxidation processes
Oxic zone
Transport
Anoxic zone
b
Intermolecular polymerization reactions
sulfur containing
monomers
Diagenetic stage
High temperature zone
Thermal degradation
Free-radical mechanism
c
Catagenetic stage

$CH_4 + SO_4^{2-} \rightarrow CO_2 + H_2S + 2OH^-$




Net Energy = 26.3 Kcal/mole

Dissimilatory processes $^{34}S/^{32}S$ isotopes discrimination: -20‰ — -60‰



δ34S‰
-30
-25
-20
-15
-10
-5
0
25
24.8
24.6
24.4
24.2
24
23.8
23.6
23.4
23.2
23
0
20
40
60
80
100
Depth ( cm)
Protokerogen sulfur
Interstitial water sulfate

# $\delta^{34}S$ Changes during Catagenetic processes, thermally induced

- Thermal maturation and influence of Open *versus* Closed systems.
- The possible role of mineral matrix.
- Application to evaluation of sulfur role In utilization of *in-situ /ex-situ* designed Processes.

Theoretic chemical $^{34}S/^{32}S$ isotopes discrimination: -25‰

Assimilatory processes $^{34}S/^{32}S$ isotopes

kinetics isotopes effect :

discrimination: up to -3‰

Open system

Dissimilatory processes $^{34}S/^{32}S$ isotopes

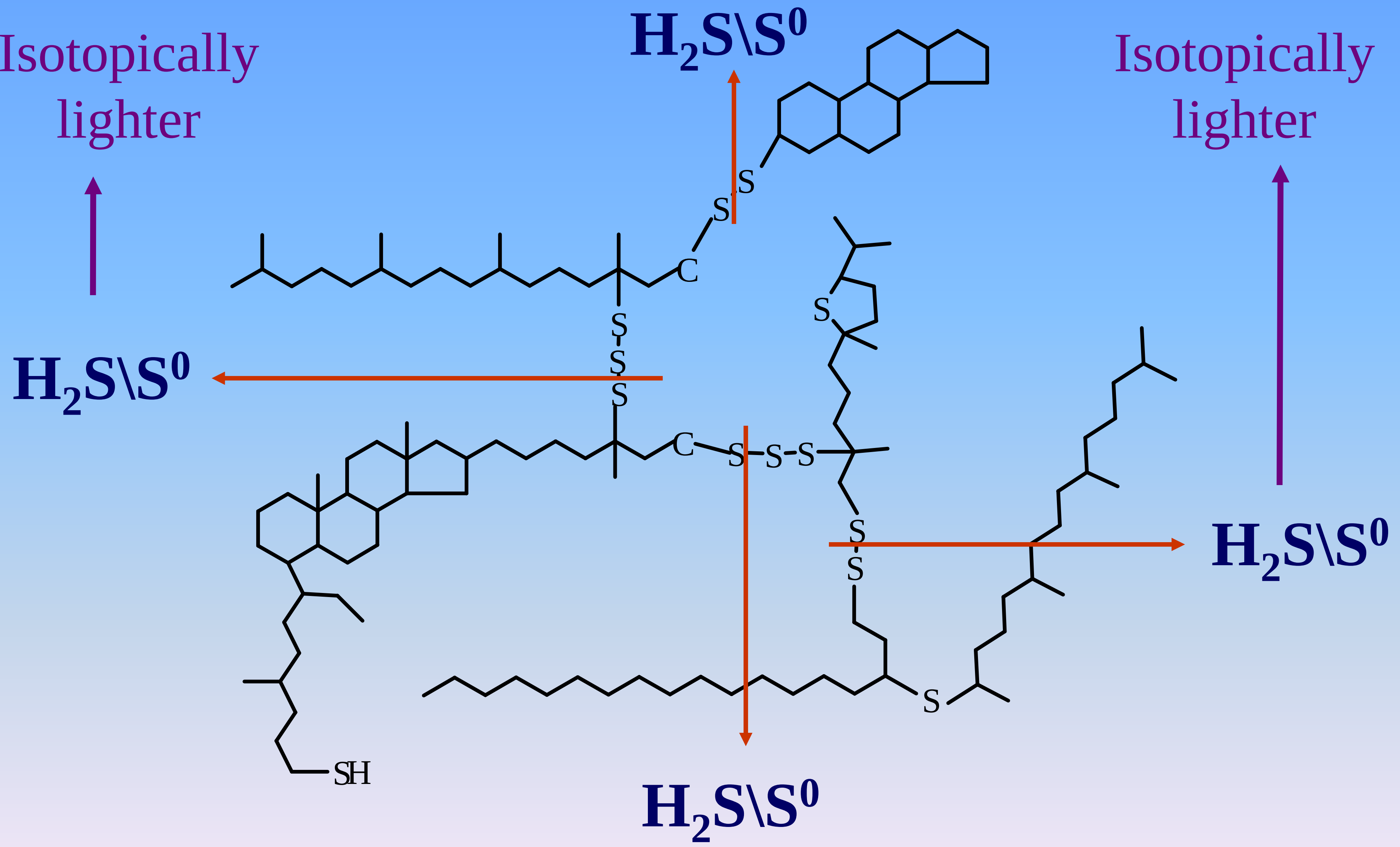
discrimination: -20‰ — -50‰

Closed system

# TSR

Data TRS discrimination

# Open system- Isotopes discrimination

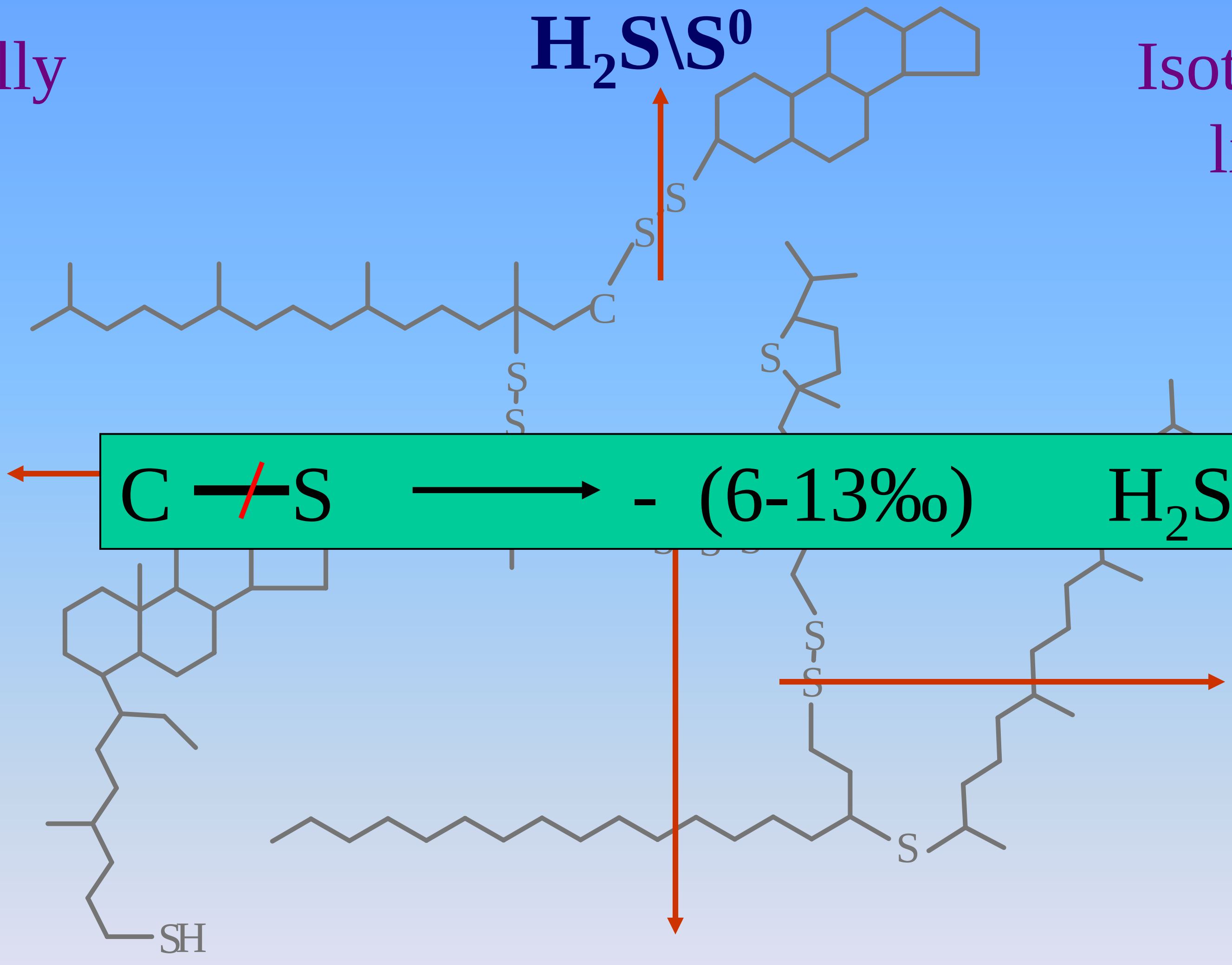


# Open system- Isotopes discrimination

$H_2S\backslash S^0$

Isotopically lighter

Isotopically lighter



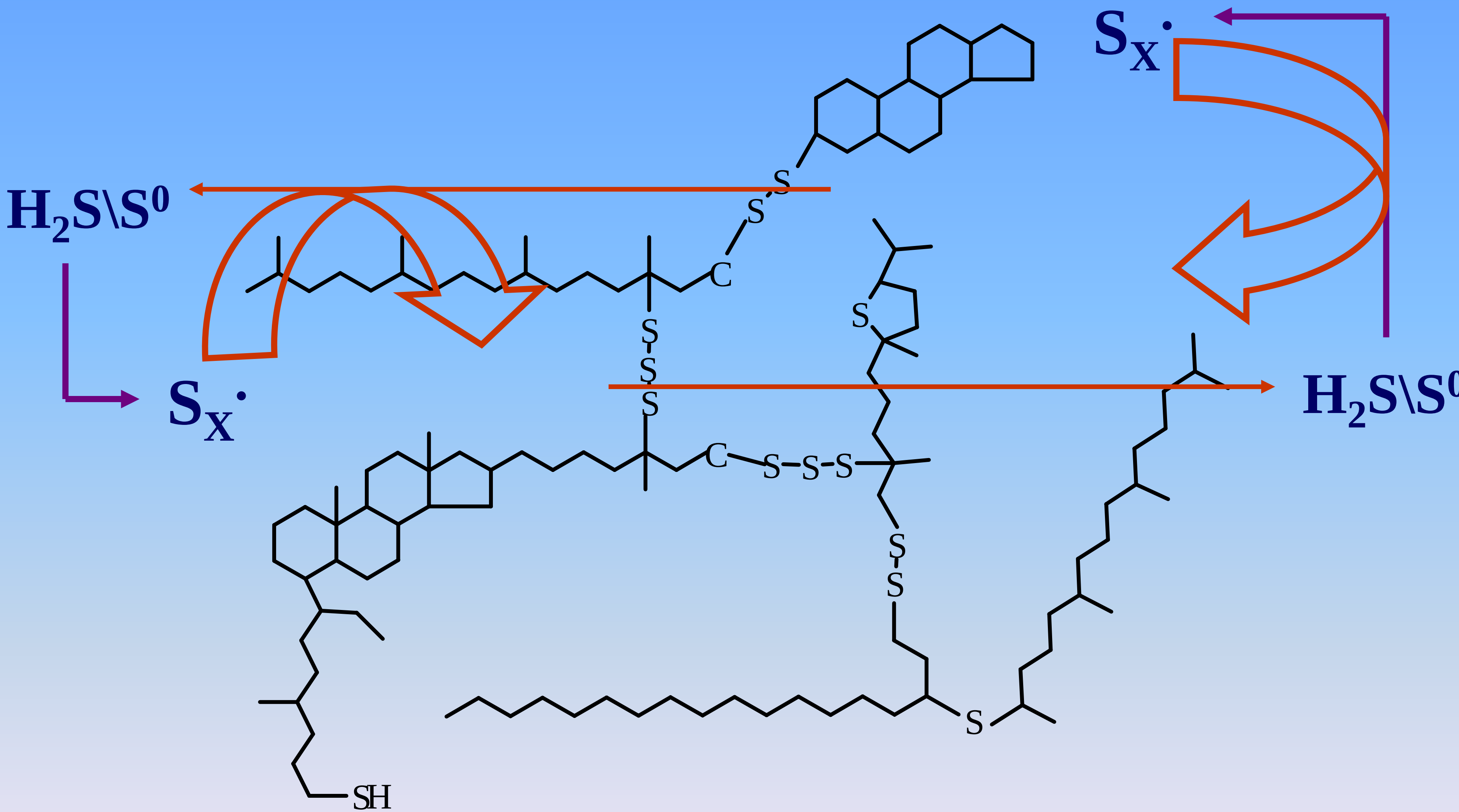

$H_2S\backslash S^0$

C –/– S ⟶ - (6-13‰) $H_2S$

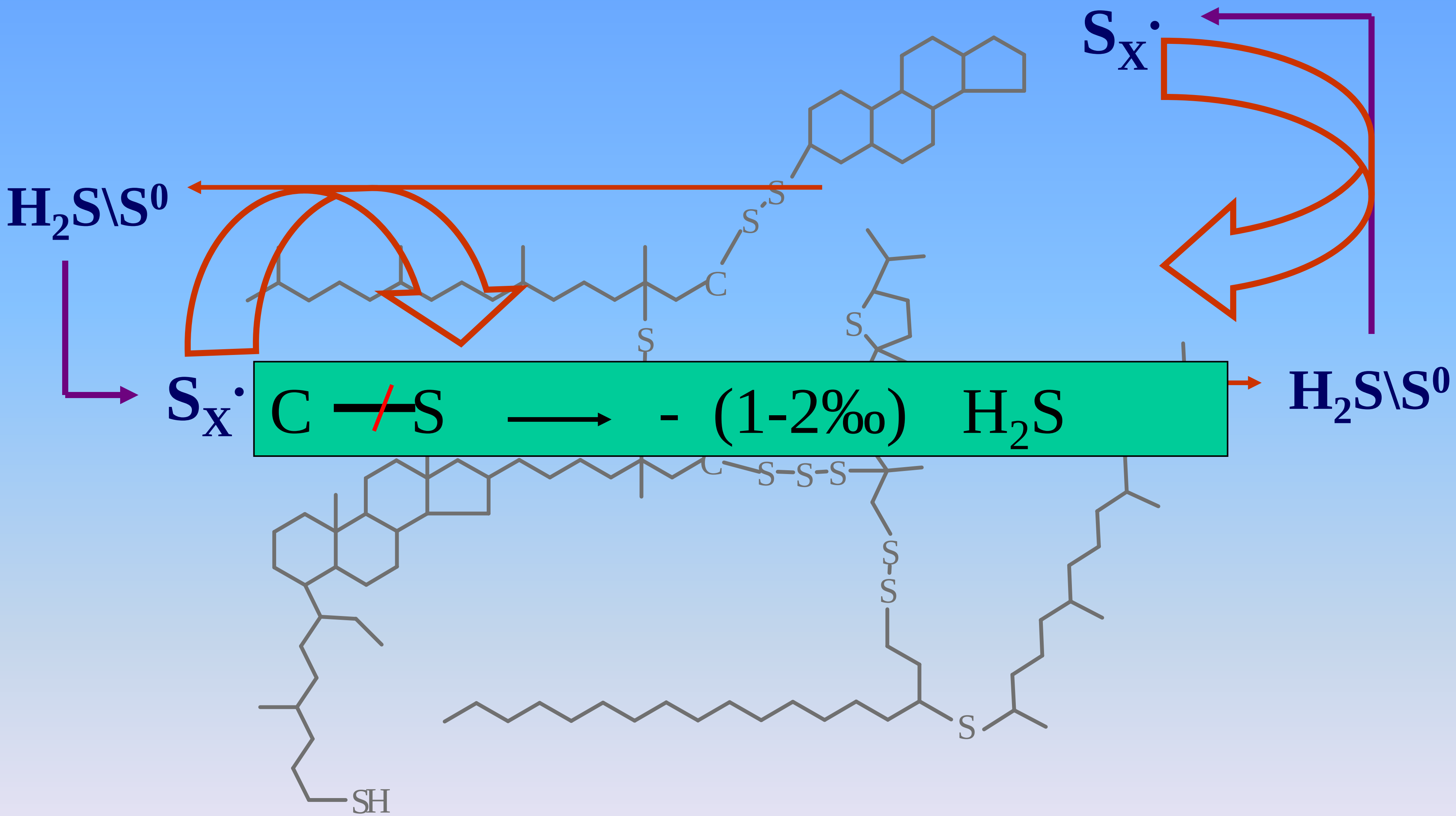
$H_2S\backslash S^0$

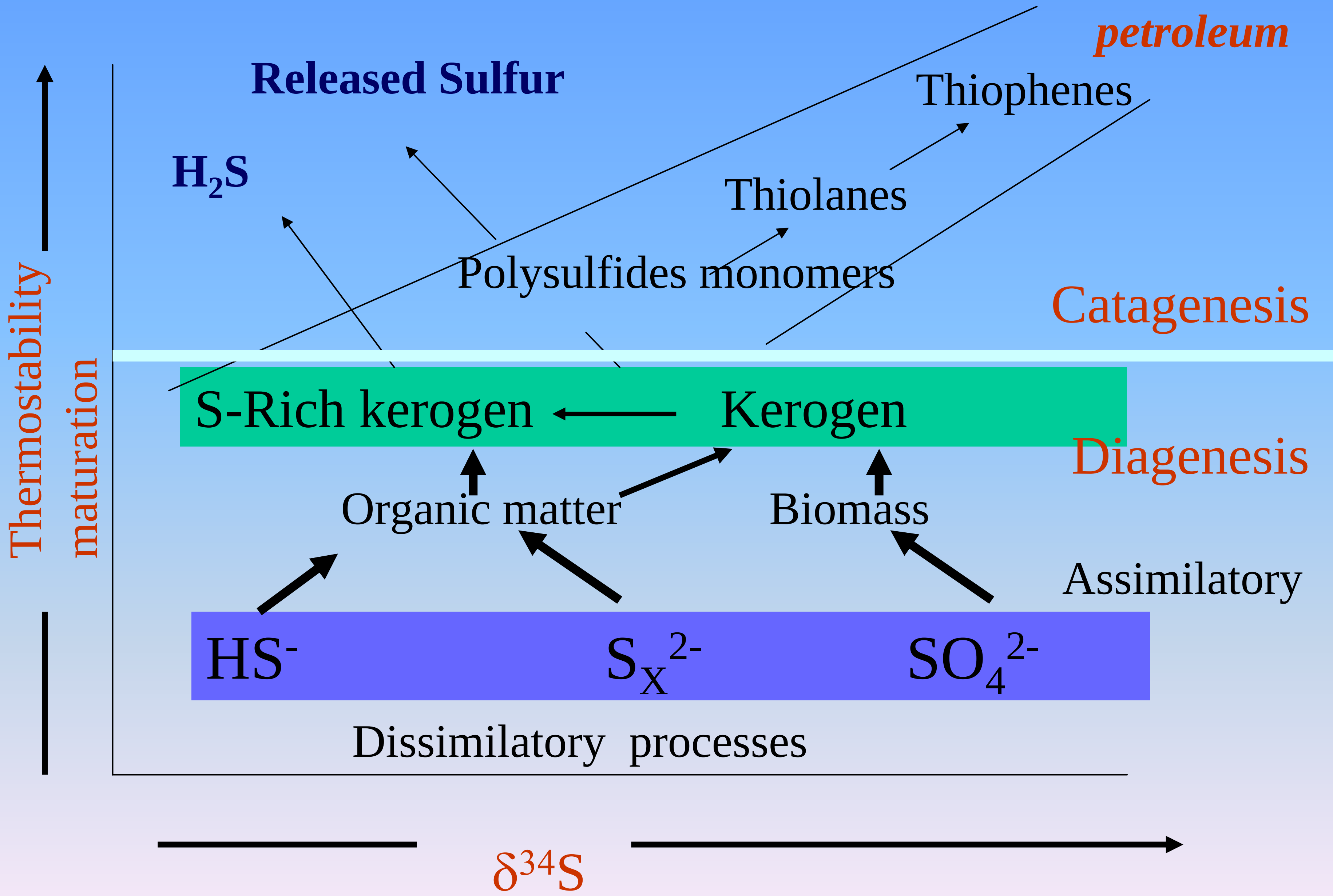
$H_2S\backslash S^0$

# Closed system - isotopes mixing



# Closed system - isotopes mixing



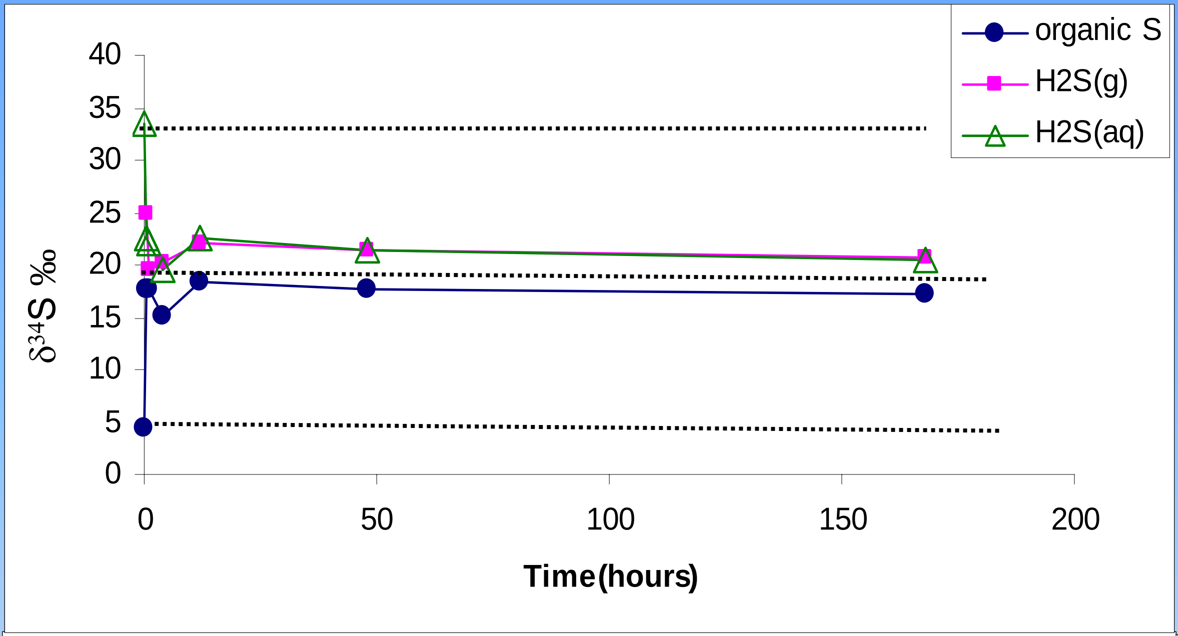


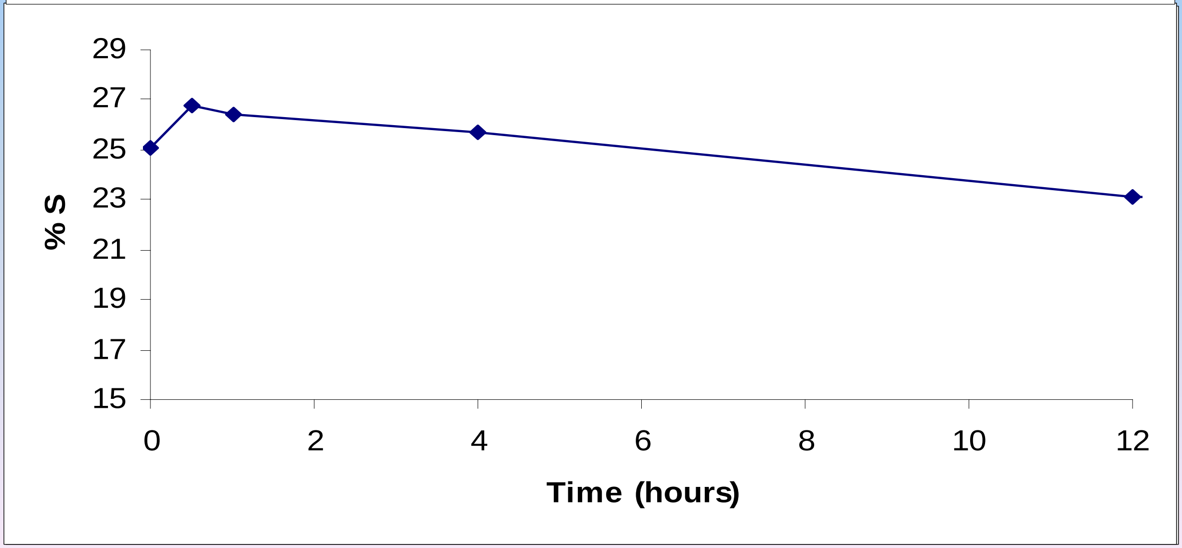
petroleum
Released Sulfur
Thiophenes
H2S
Thiolanes
Polysulfides monomers
Catagenesis
Thermostability
maturation
S-Rich kerogen
Kerogen
Diagenesis
Organic matter
Biomass
Assimilatory
HS-
Sx2-
SO42-
Dissimilatory processes
δ34S

# Isotopic Mixing

Graphic picture of our experiments

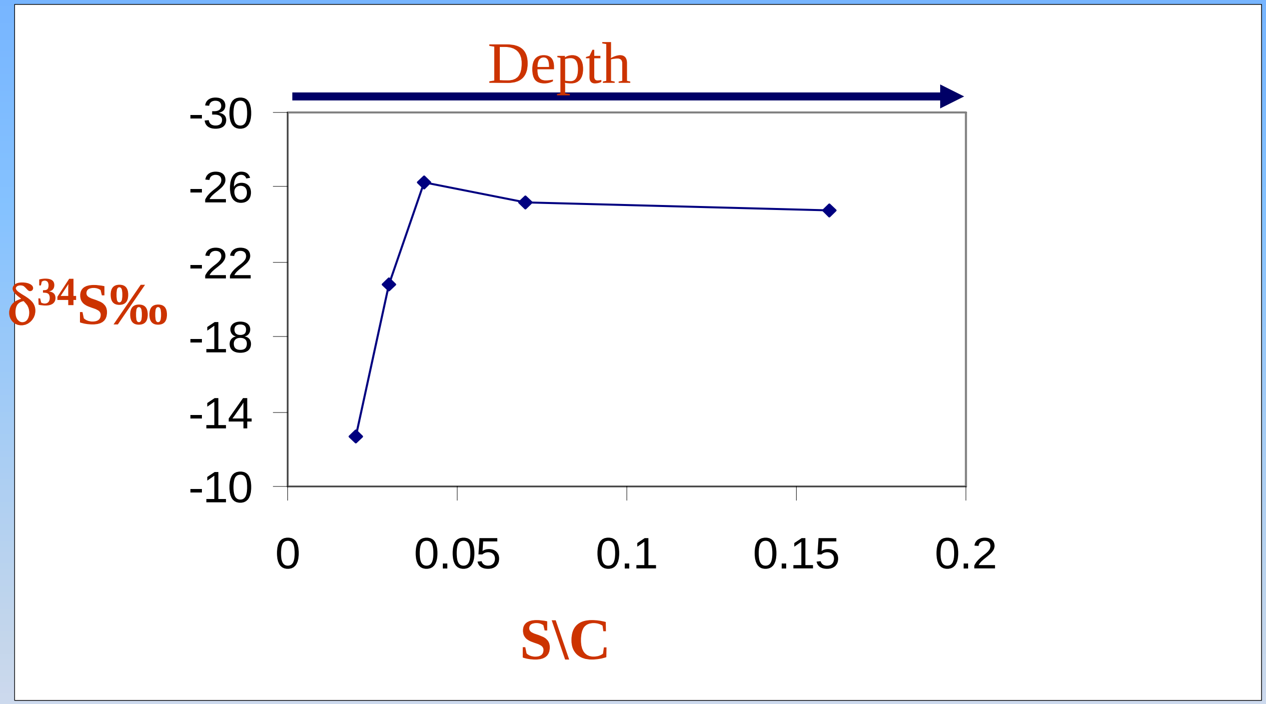
Polymer-S + $S_{(aq)}$ $\xrightarrow{200^oC}$

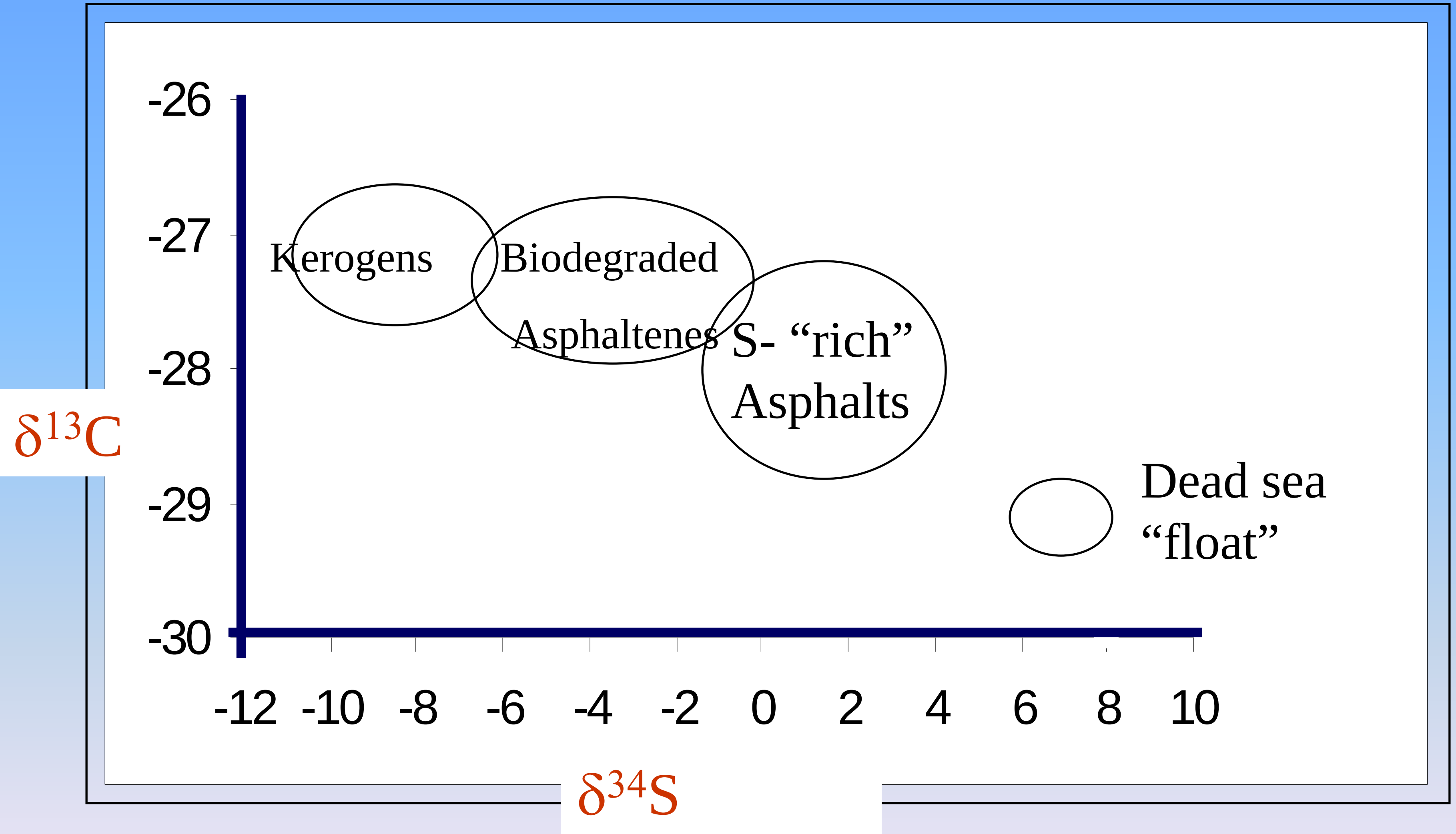


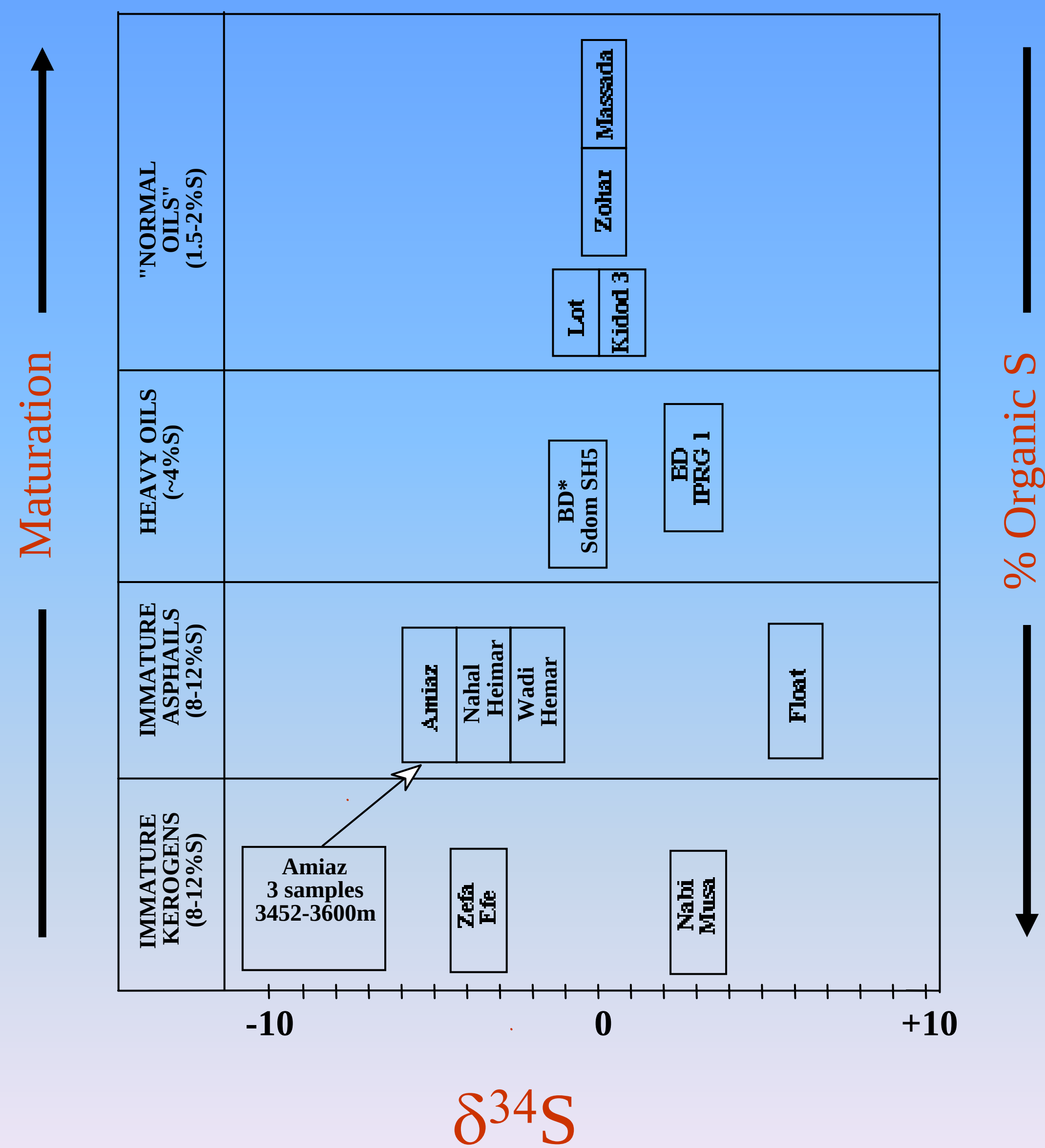



| Reactant | Sulfur mole ratio reactant/organic S mole | Initial reactant □$^{34}$S(‰) | Initial organic S □$^{34}$S(‰) | Residual organic S □$^{34}$S(‰) | $H_2S_{(g)}$ □$^{34}$S(‰) | Binary isotope mass balance □$^{34}$S(‰) | Residual organic sulfur content % |
|---|---|---|---|---|---|---|---|
| $H_2S_{(g)}$ | 1:3 | 36 | 19 | 32.1 | 34 | 32 | 38.5 |
| $H_2S_{(g)}$ | 1:1 | 60 | 4 | 30.4 | 29.1 | 32 | 34.3 |
| $S_8$ | 1:1 | -1.7 | 19 | 8.1 | 8.8 | 8.7 | 30±2 |

$\delta^{34}S$ values (error<0.4‰ ) and wt% for isotopes mixing experiments between polysulfide cross-linked polymer (25.1 wt% S) and $H_2S_{(g)}$ or $S_8$ at 200ºC for 48h


Depth
δ34S‰
-30
-26
-22
-18
-14
-10
0
0.05
0.1
0.15
0.2
S\C


-26
-27
-28
-29
-30
Kerogens
Biodegraded
Asphaltenes
S- “rich”
Asphalts
Dead sea
“float”
-12 -10 -8 -6 -4 -2 0 2 4 6 8 10
δ13C
δ34S



Maturation
% Organic S
"NORMAL OILS" (1.5-2%S)
HEAVY OILS (~4%S)
IMMATURE ASPHAILS (8-12%S)
IMMATURE KEROGENS (8-12%S)
Massada
Zohar
Lot
Kidod 3
BD* Sdom SH5
BD IPRG 1
Amiaz
Nahal Heimar
Wadi Hemar
Float
Amiaz 3 samples 3452-3600m
Zefa Efe
Nabi Musa
-10
0
+10
$\delta^{34}S$

# Conclusions - diagenetic stages

- **The largest pool of sulfur in the geosphere is sulfate $SO_4^{2-}$ marine sulfates are $\delta^{34}S_{CDT}$ +20 ± 5‰ depending on geological era. The supply of sulfate open or closed systems determines the interstitial $\delta^{34}S$ recorded.**

- **The main source of reduced sulfur in sediments is the SRB dissimilatory process. The bacterial process has a marked isotopes selectivity -20 to -60‰, this is kinetically recorded by the formation of pyrite depending on iron availability.**

## Conclusions- diagenetic stages

- **$S^{2-}$ and $S^0$ form (pH ~8-9) polysulfides of the $S_x^{2-}$ structure (x=3,4,5) that are the most chemically active, these in turn react with the SOM to form sulfur rich-SOM. The isotopic signature of the organic bound sulfur has a wide range relating to some parameters discussed in the papers $\delta^{34}S$ recorded for the organically bound sulfur is on average +10‰ heavier then the pyrite.**

- **Type II-S kerogens are formed by the secondary sulfur enrichment dominated by polysulfides, these reactions produce the poly-cross-linked-macromolecules (PCLM). The isotopic mixing and discrimination at each geological setting still needs further studies**

# Conclusions- catagenetic stages

- The evolved $H_2S$ from the kerogen is always $^{32}S$ -enriched. Very small, if any, pyritic light sulfur is contributed.
- On average the $H_2S$ released is 5‰ lighter than the original $\delta^{34}S$ of the organic matter.
- All liquids are by +5 to +8‰ heavier $^{34}S$ than the original kerogen. The residual kerogen (isolated) is somewhat Isotopically heavier.
- In comparison to the carbon isotope changes with maturation from kerogen to petroleum the proposed scheme is reversed.

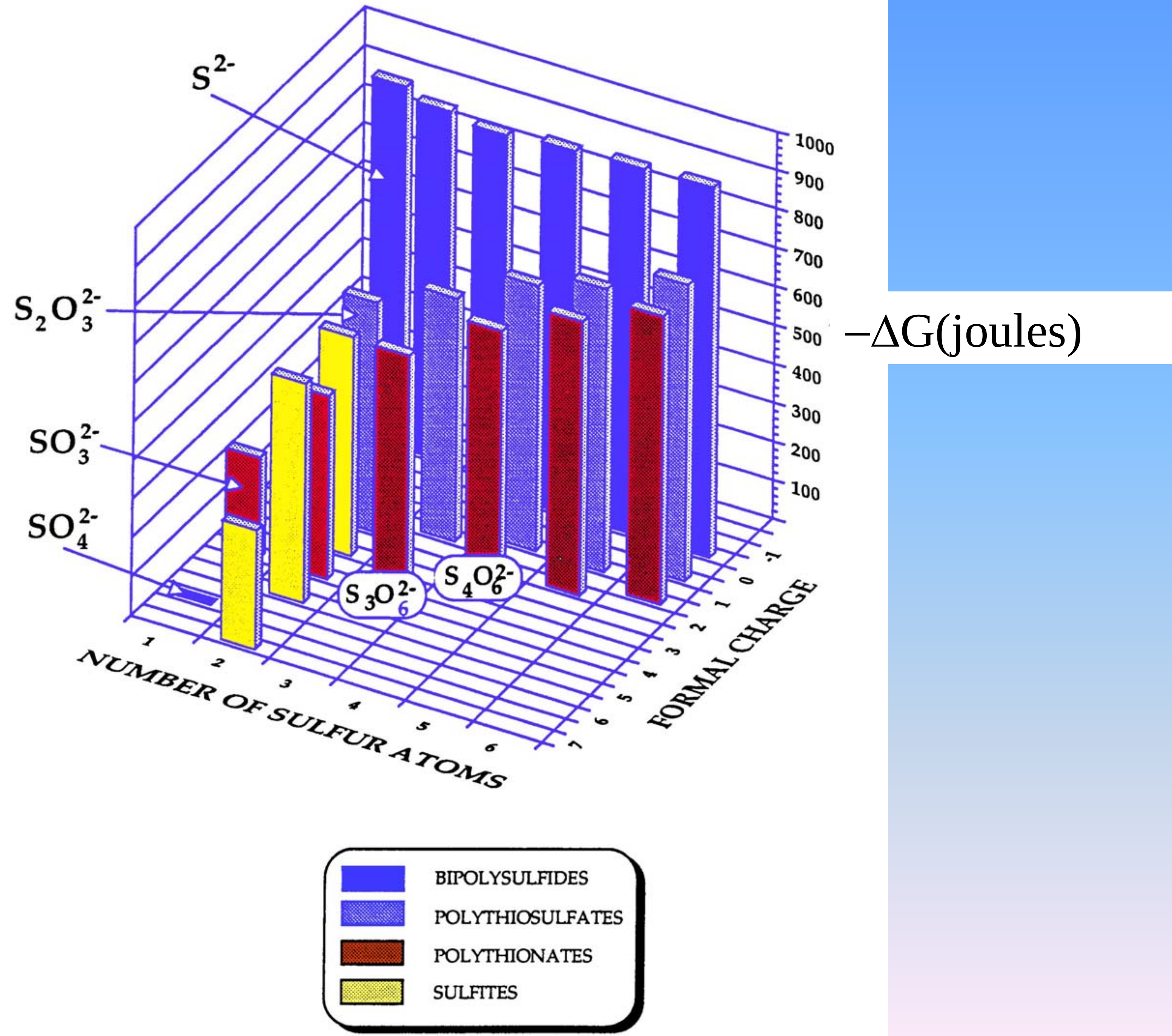
# Catagenesis and TSR

- **The closed or open systems at the catagenesis stages (thermally controlled) transformations have a marked difference.**

- **TSR depends on mineral matrix, high temperatures and pH changes.**

- **Mixing of the various reduced species of sulfur is recorded by sulfur isotope ratio changes.**

- **The source of organically bonded sulfur under TSR conditions can derive from inorganic sulfur such is the case for Type I kerogens under *insitu* shale oil production.**


$S^{2-}$
$S_2O_3^{2-}$
$SO_3^{2-}$
$SO_4^{2-}$
$S_3O_6^{2-}$
$S_4O_6^{2-}$
1000
900
800
700
600
500
400
300
200
100
$-\Delta G$(joules)
NUMBER OF SULFUR ATOMS
1
2
3
4
5
6
FORMAL CHARGE
BIPOLYSULFIDES
POLYTHIOSULFATES
POLYTHIONATES
SULFITES

## NUMBER OF SULFUR ATOMS

| AVERAGE FORMAL CHARGE ON SULFUR | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| -2 | $S^{2-}$ | | | | | | |
| -1 | | $S_2^{2-}$ | $S_3^{2-}$ | $S_4^{2-}$ | | | |
| 0 | | | | | $S_5^{2-}$ | $S_6^{2-}$ | $S_7^{2-}$ |
| +1 | | | $S_3O_3^{2-}$ | $S_4O_3^{2-}$ | $S_5O_3^{2-}$ | $S_6O_3^{2-}$ | $S_7O_3^{2-}$ |
| +2 | | $S_2O_3^{2-}$ | | | $S_5O_6^{2-}$ | $S_6O_6^{2-}$ | $S_7O_6^{2-}$ |
| +3 | | $S_2O_4^{2-}$ | $S_3O_6^{2-}$ | $S_4O_6^{2-}$ | | | |
| +4 | $SO_3^{2-}$ | $S_2O_5^{2-}$ | | | | | |
| +5 | | $S_2O_6^{2-}$ | | | | | |
| +6 | $SO_4^{2-}$ | $S_2O_7^{2-}$ | | | | | |
| +7 | | $S_2O_8^{2-}$ | | | | | |