Phosphorus Chemistry of the Early Archean Ocean

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Why Phosphorus ?

- Phosphorus in life
  - Almost always as pentavalent P, though rarely as P^{3+}
  - In biology serves as a leaving group
  - Stores energy in anhydride bonds
  - Most rare of the major biogenic elements (universally)

31 (100%) ½

P

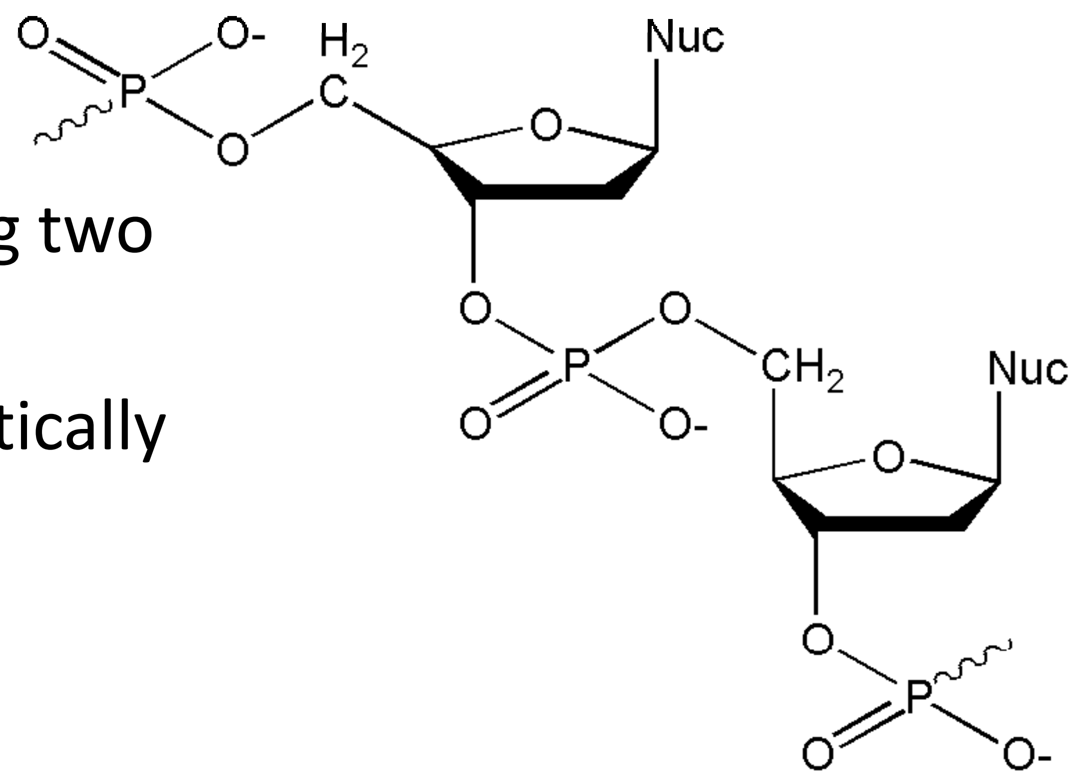
Phosphorus

15

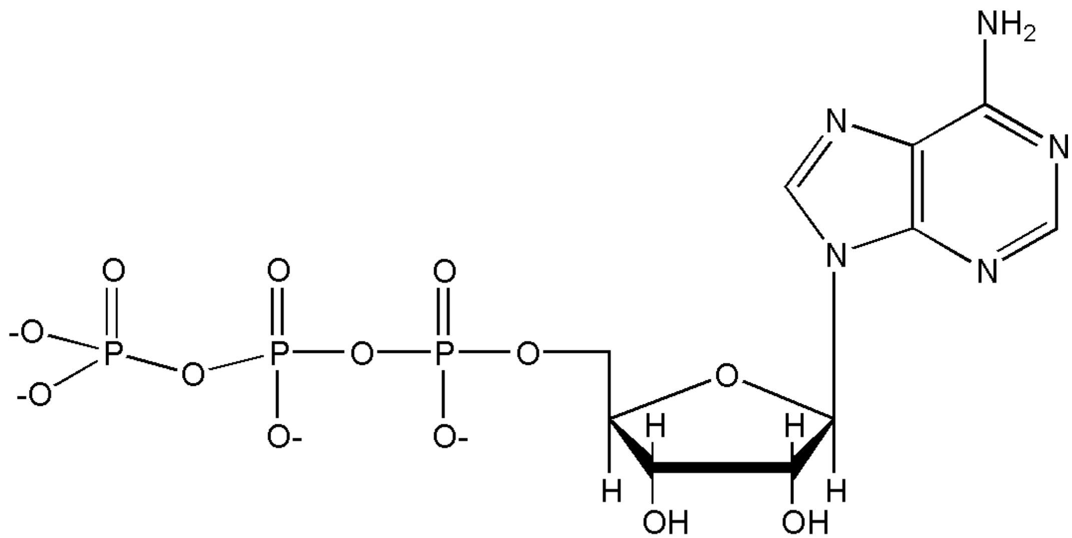
DNA + RNA

Why P?

- Charged
- Capable of forming two bridges
- Energetic but kinetically stable
- Soluble
- Achiral

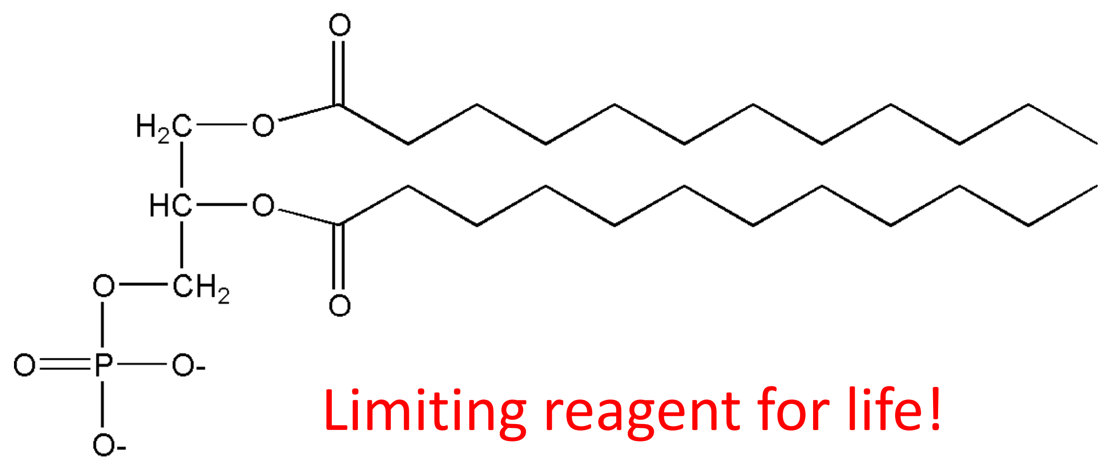


Phosphorus & Biochemistry



Metabolic molecules (ATP)

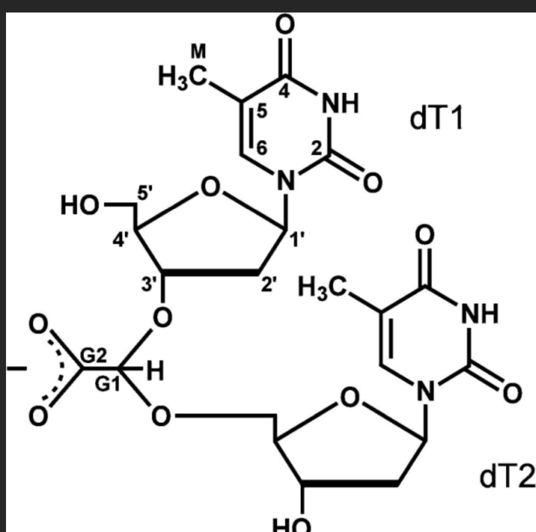
Structure (phospholipids)

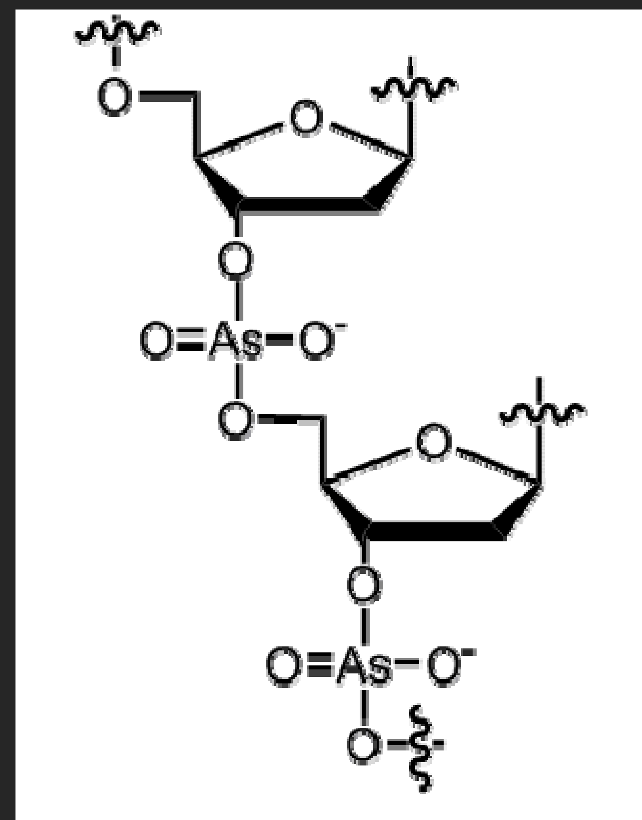


Limiting reagent for life!

Substitutes for Phosphorus

- Arsenate (Wolfe-Simon et al. 2011)
- Vanadate
- Glyoxylate (Bean et al. 2006)
- Citrate (Westheimer 1987)





http://2.bp.blogspot.com/_PZ-J57NWAyg/TQ91nFapkwI/AAAAAAAACic/xAkk0nQVh9I/s1600/notlikely.gif

Phosphorus is Critical to Life

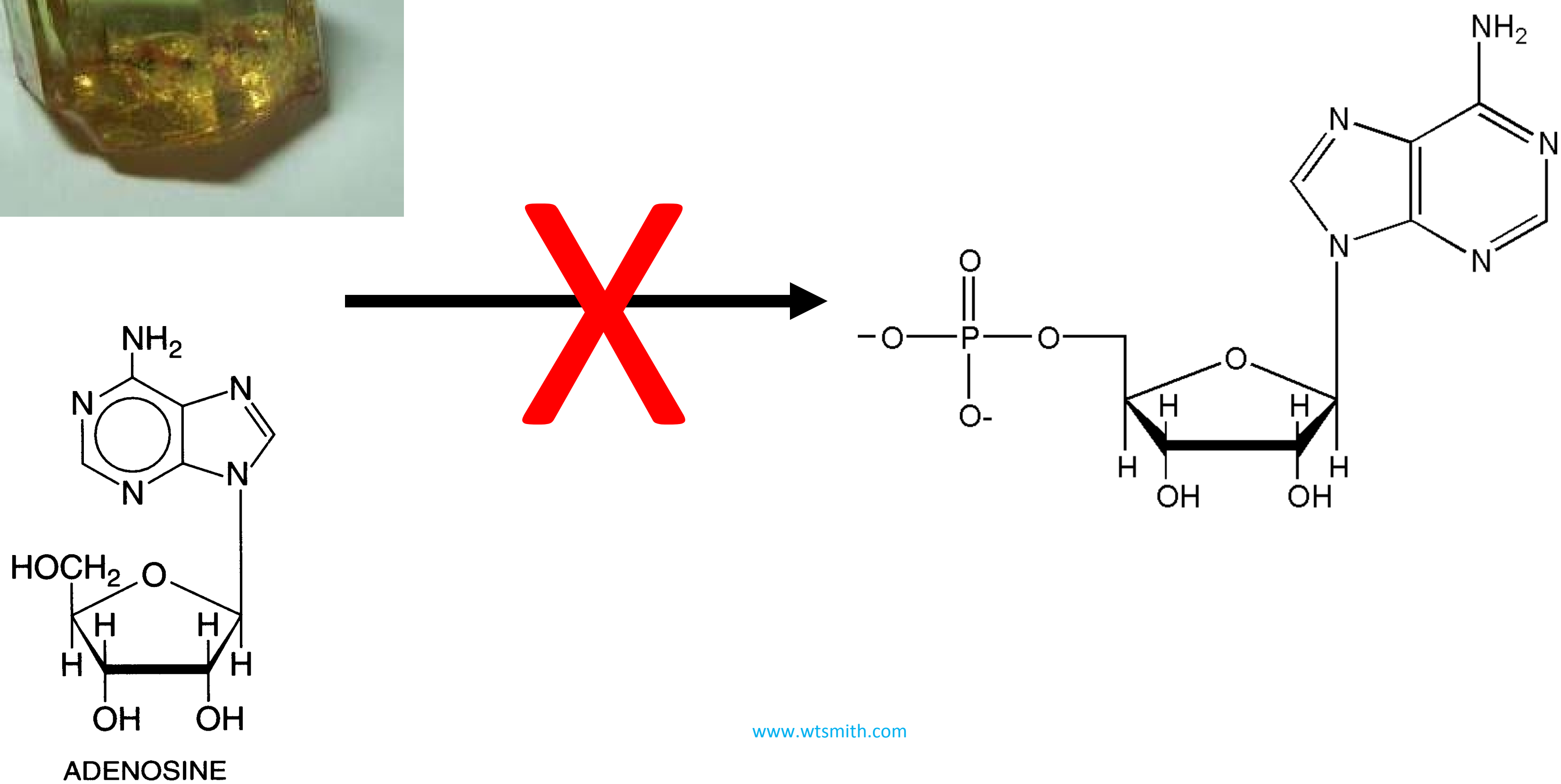
- P molecules are central to biochemistry
  - Metabolism, Replication, Structure
- P is the limiting nutrient in many ecosystems
  - Too little P, very little life
- Presumably P was important early in life's development
  - Changing Horses?
  - Earliest processes?

Sources of phosphate

- Phosphate had to come from a mineral
- Apatite- $Ca_5(PO_4)_3X$
- Monazite- $Ce(Ce,La,Nd,Th)PO_4$
- Whitlockite - $Ca_9Mg(PO_4)_6(PO_3OH)$
- Insoluble, inert
- These dominated Earth's surface and mantle 4 billion years ago

Phosphorus and the origin of life

www.wrightsrockshop.com



www.wtsmith.com

Where do we get our Phosphorus?

Phosphorus nucleosynthesis

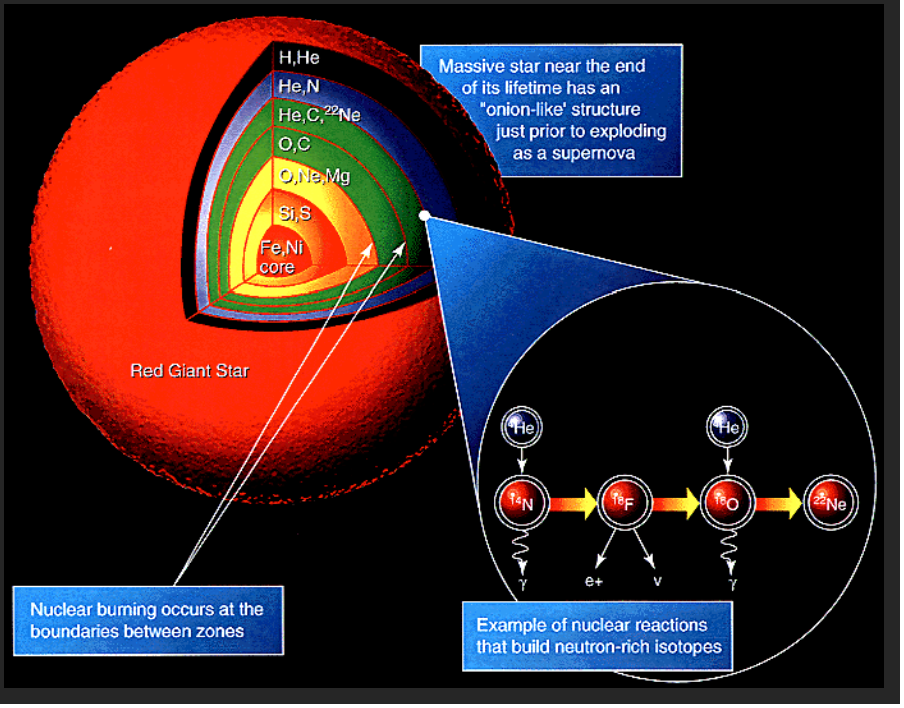
- Carbon Burning

$^{12}C + ^{12}C \rightarrow ^{24}Mg^* \rightarrow ^{23}Na + p \rightarrow$

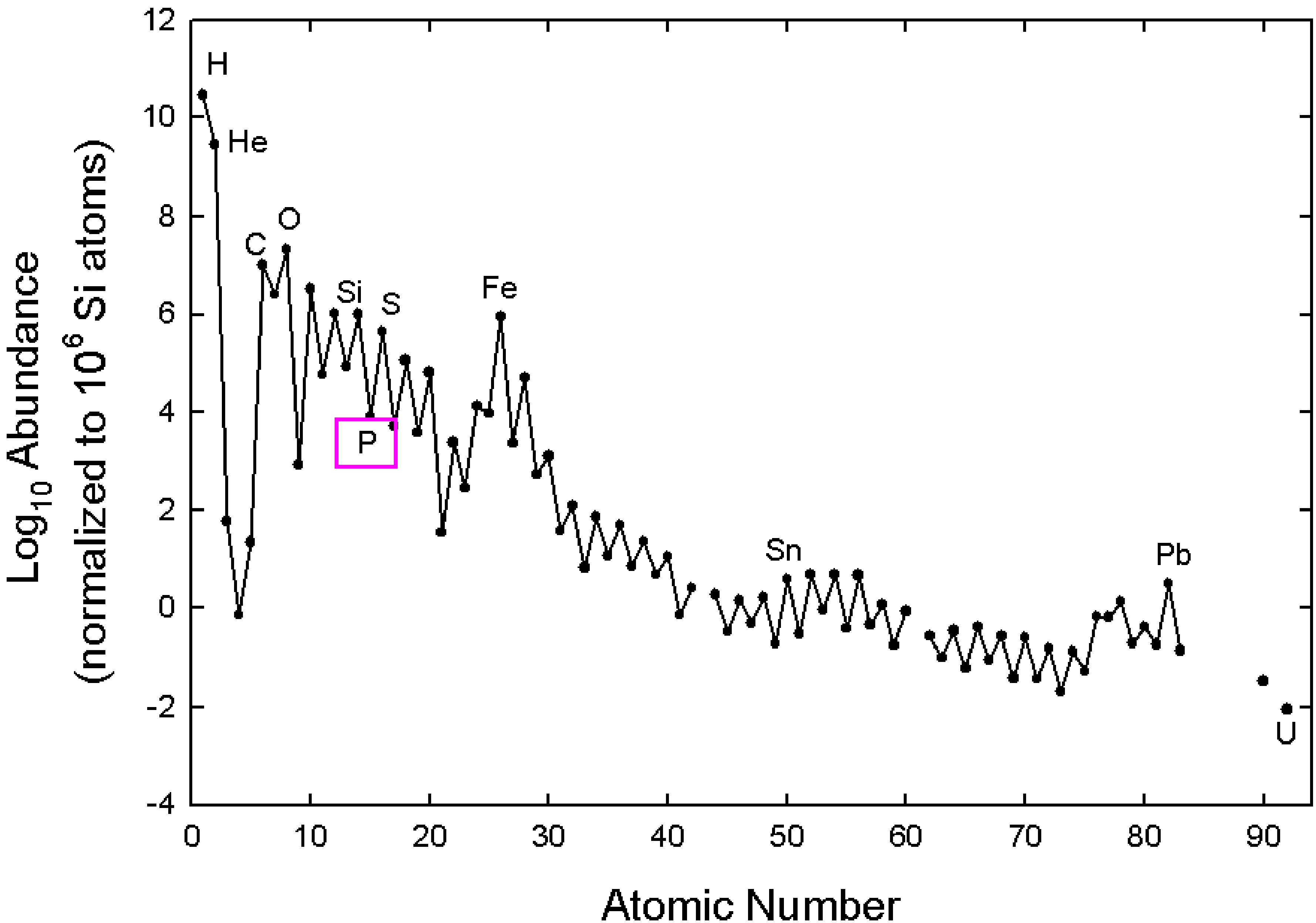
$^{23}Na\ (\alpha,p)\ ^{26}Mg\ (\alpha,\gamma)\ ^{30}Si\ (p,\gamma)\ ^{31}P$

- Oxygen Burning

$^{16}O + ^{16}O \rightarrow ^{31}P + p$



Anders and Grevasse 1989



Phosphorus Astrochemistry

- P is rare (680:1 C:P)
- 6 gaseous P compounds have been detected
  - Gases may form organic-P compounds
- P is sticky ($T_{condensation}$ ~1275 K)
  - Gas phase
  - Metal
  - Oxide (phosphate)

Phosphorus in Astrochemistry

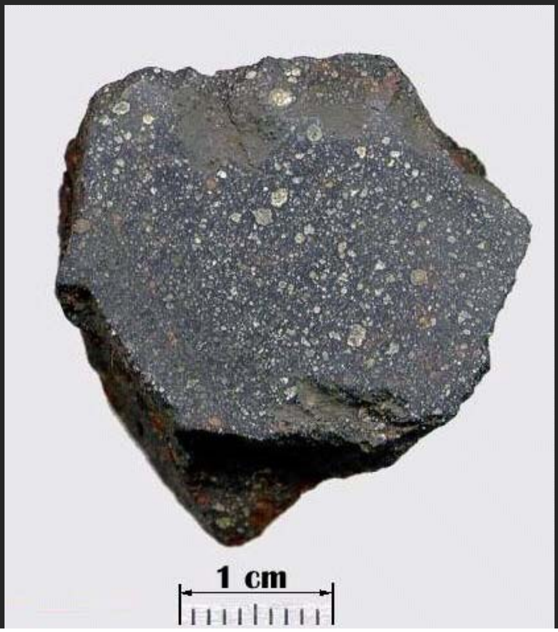
• PN	Ziurys 1987
• CP	Guelin et al. 1990
• HCP	Guelin et al. 1990
• PO	Tenenbaum et al. 2007
• PH_3	Agundez et al. 2008
• CCP	Halfen et al. 2008

Processing of ISM phosphorus

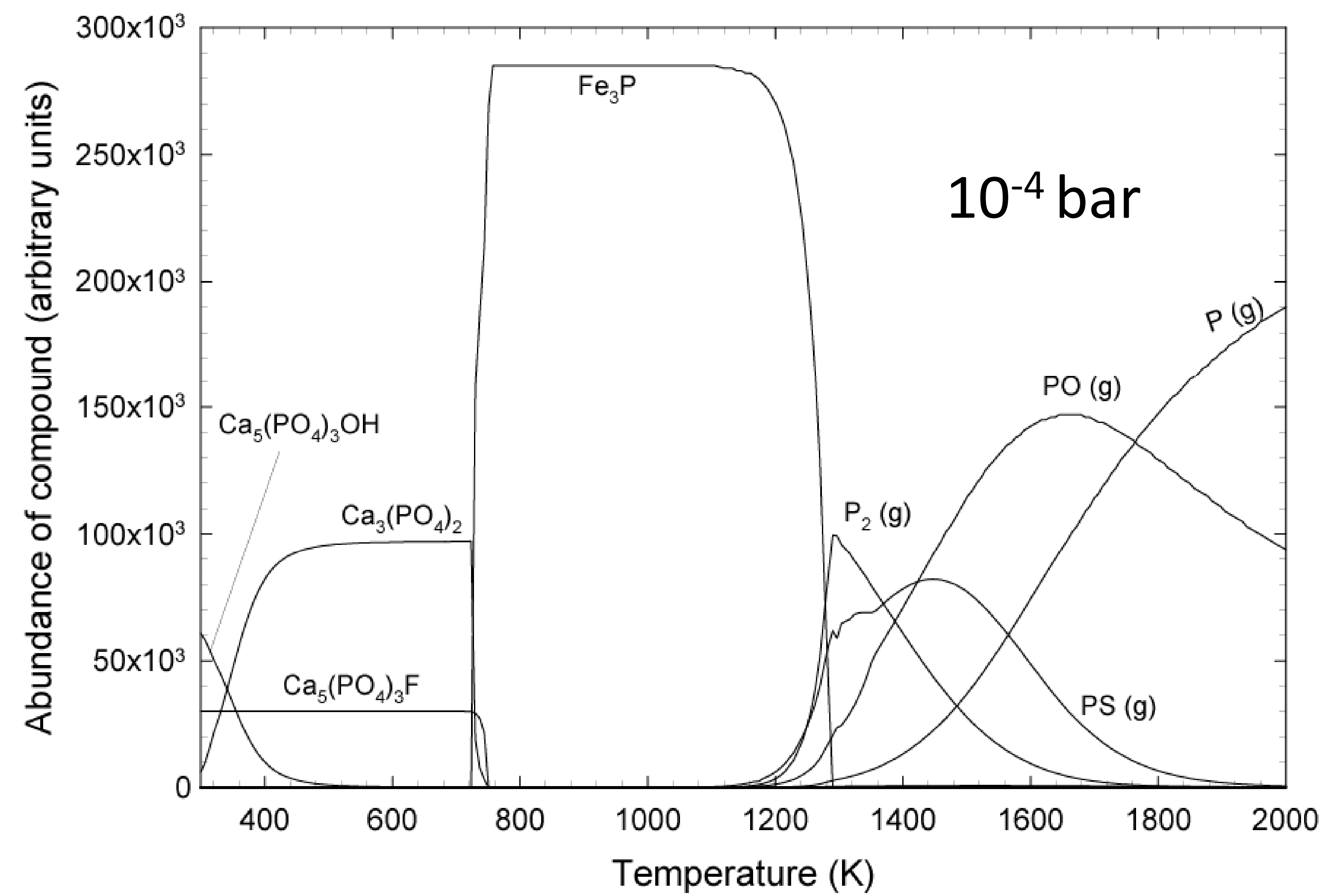
- Gaseous P species can react on dust/ice grains to form new P species
- $HCP + 3H_2O \rightarrow CH_3PO_3H_2 + H_2$
- Gorrell et al. *Chem Comm.* (2006)

- Murchison phosphonates (Cooper et al. 1992)

Low Temperature

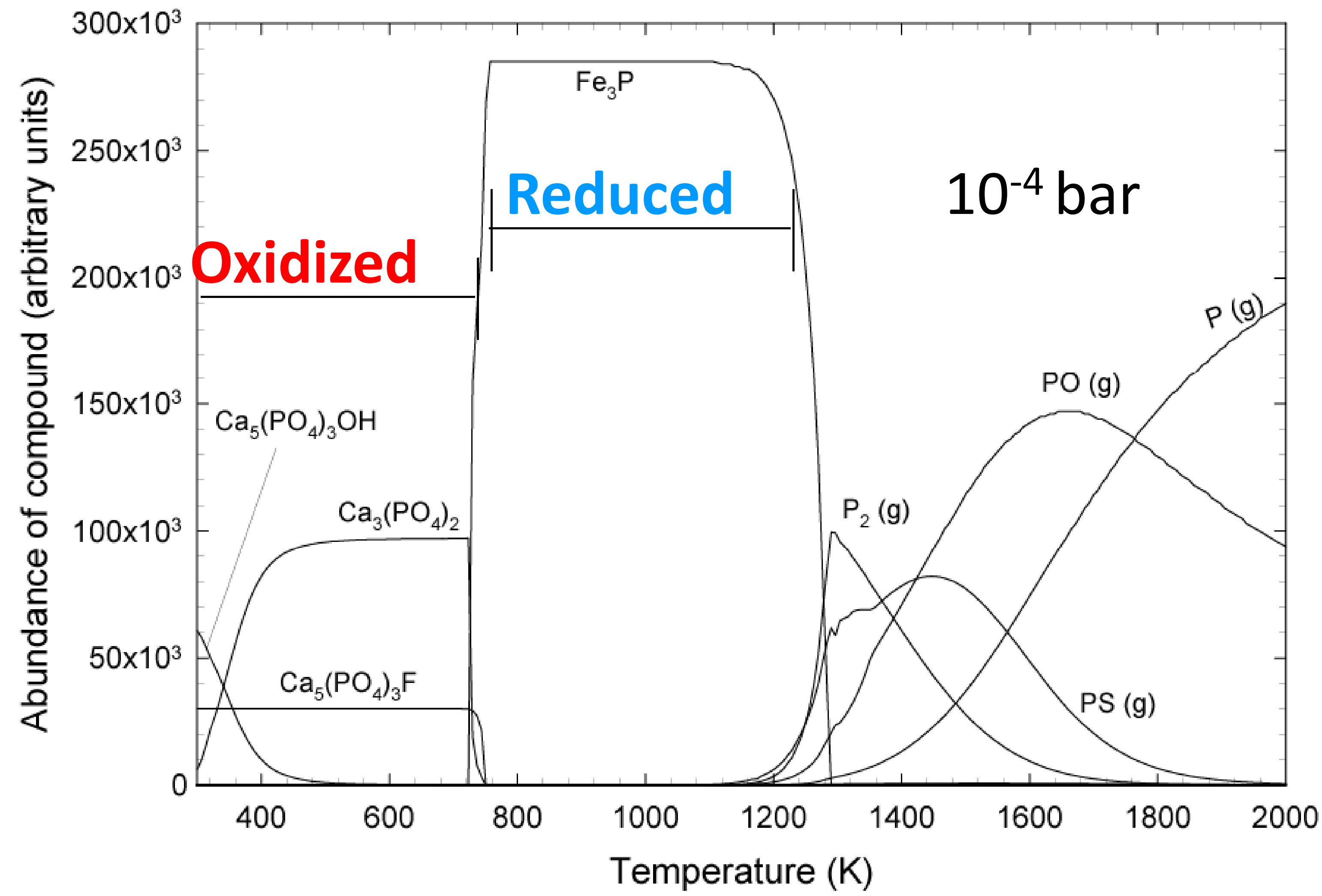


P Cosmochemistry- High T



Condensation sequence illustrating main forms of P in meteorites

Pasek *2008*



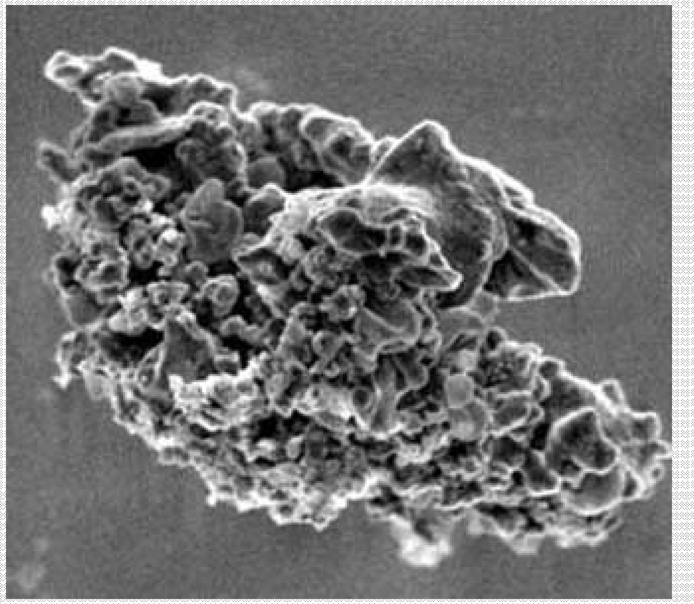
300x10³
250x10³
200x10³
150x10³
100x10³
50x10³
0
Abundance of compound (arbitrary units)
400
600
800
1000
1200
1400
1600
1800
2000
Temperature (K)
Oxidized
Reduced
10-4 bar
Fe3P
Ca5(PO4)3OH
Ca3(PO4)2
Ca5(PO4)3F
P2 (g)
PO (g)
P (g)
PS (g)

Meteoritic Phosphorus

- A mixture of non-equilibrium & equilibrium phosphorus
- Phosphates: Oxidized material
- Phosphides: Reduced material
- Phosphonates: Only in carbonaceous material, about 0.1%

IDPs and Stardust

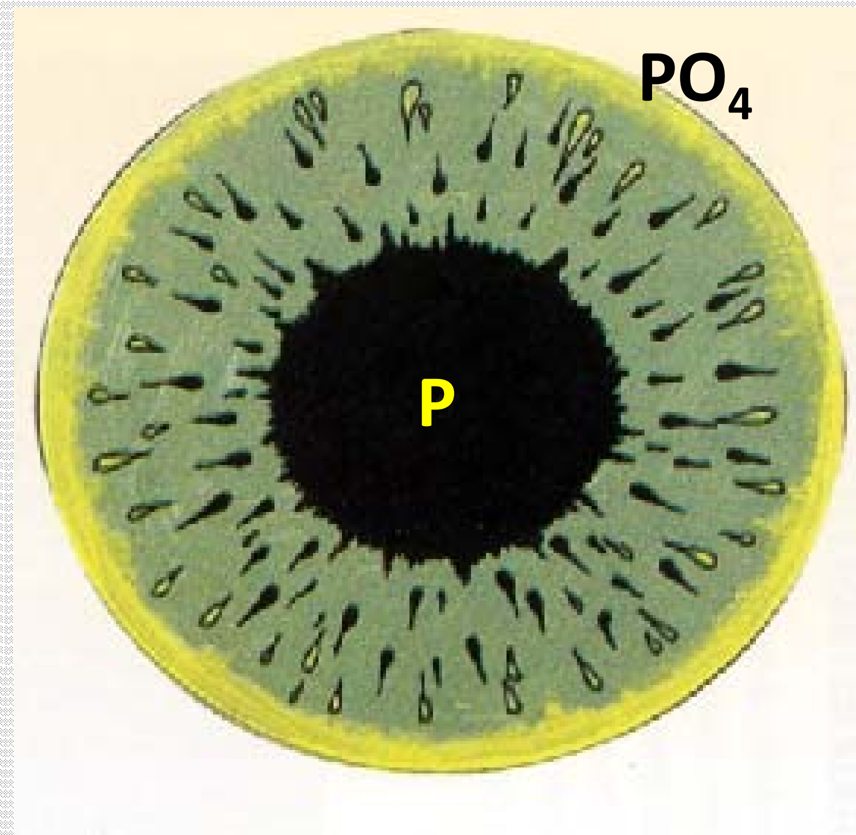
- IDPs: One grain of phosphate reported, one grain of phosphide



- Stardust: Schreibersite

Images from JPL

P during differentiation



- P is both siderophile and lithophile
  - Majority sinks to core
  - P incompatible in silicates, forms phosphates
  - 98% of P in core

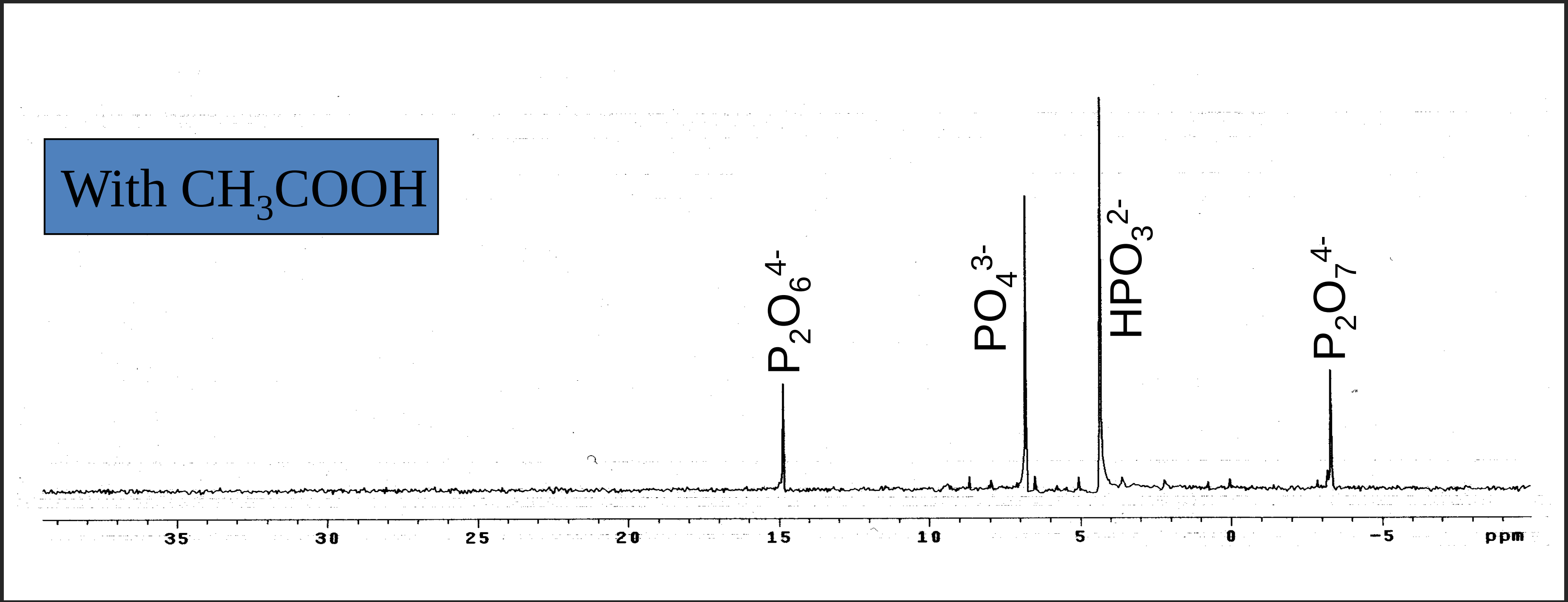
The Early Earth

http://images.encarta.msn.com/xrefmedia/aencmed/targets/illus/ill/T886125A.gif

Primary P sources on early Earth

- Phosphides
  - Ubiquitous constituent of meteorites
    - Schreibersite, $(Fe,Ni)_3P$
  - Abundant in meteorites falling to Earth
  - No O, hence reacting with O is favorable
  - Phosphorylation less thermodynamic battle?

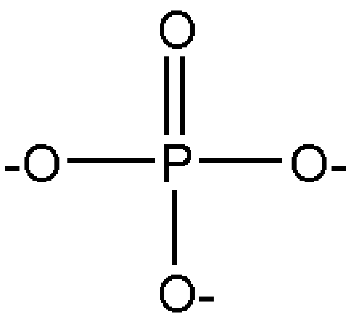
Aqueous Corrosion of Phosphide Powder (under Ar)



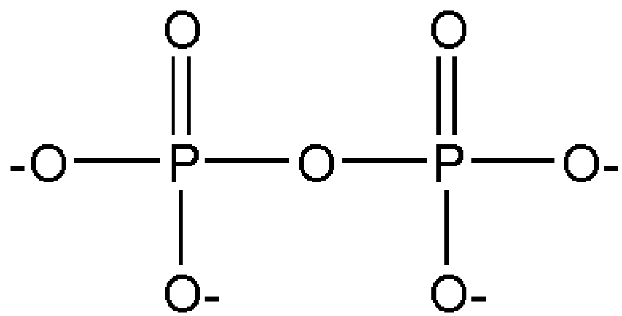
Pasek and Lauretta 2005

P Redox states and inorganic species

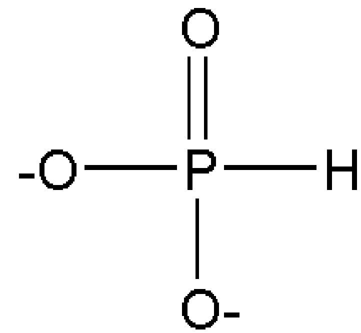
I. Orthophosphate



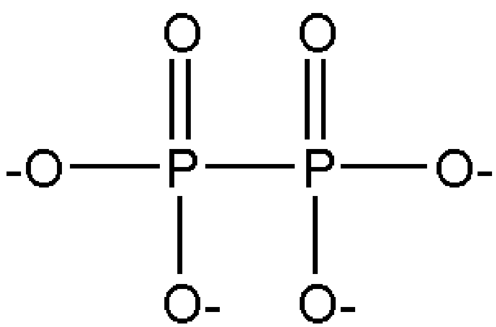
II. Pyrophosphate



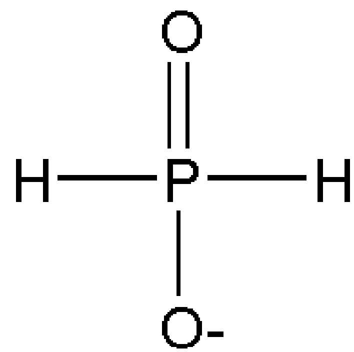
III. Phosphite



IV. Hypophosphate



V. Hypophosphite



VI. Phosphine

PH_3

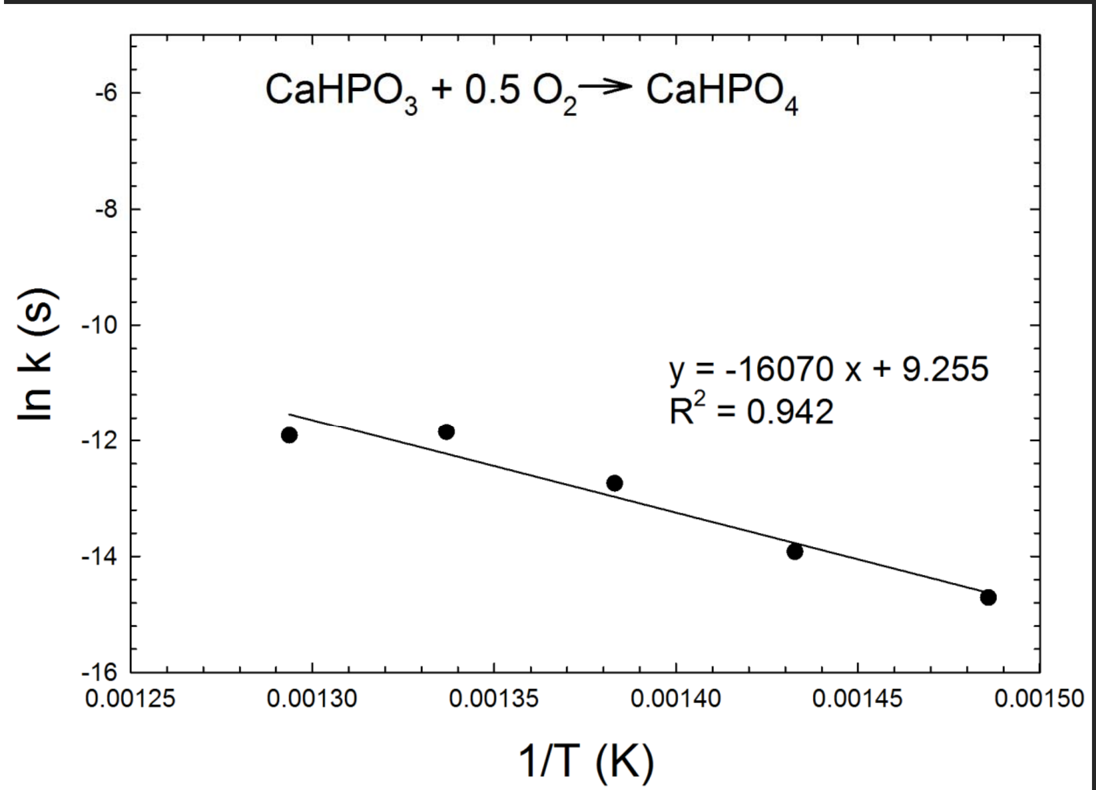
Pasek and Lauretta, Astrobiology 2005

Bryant and Kee 2006
Pech et al. 2011

Can we find these in old rocks?

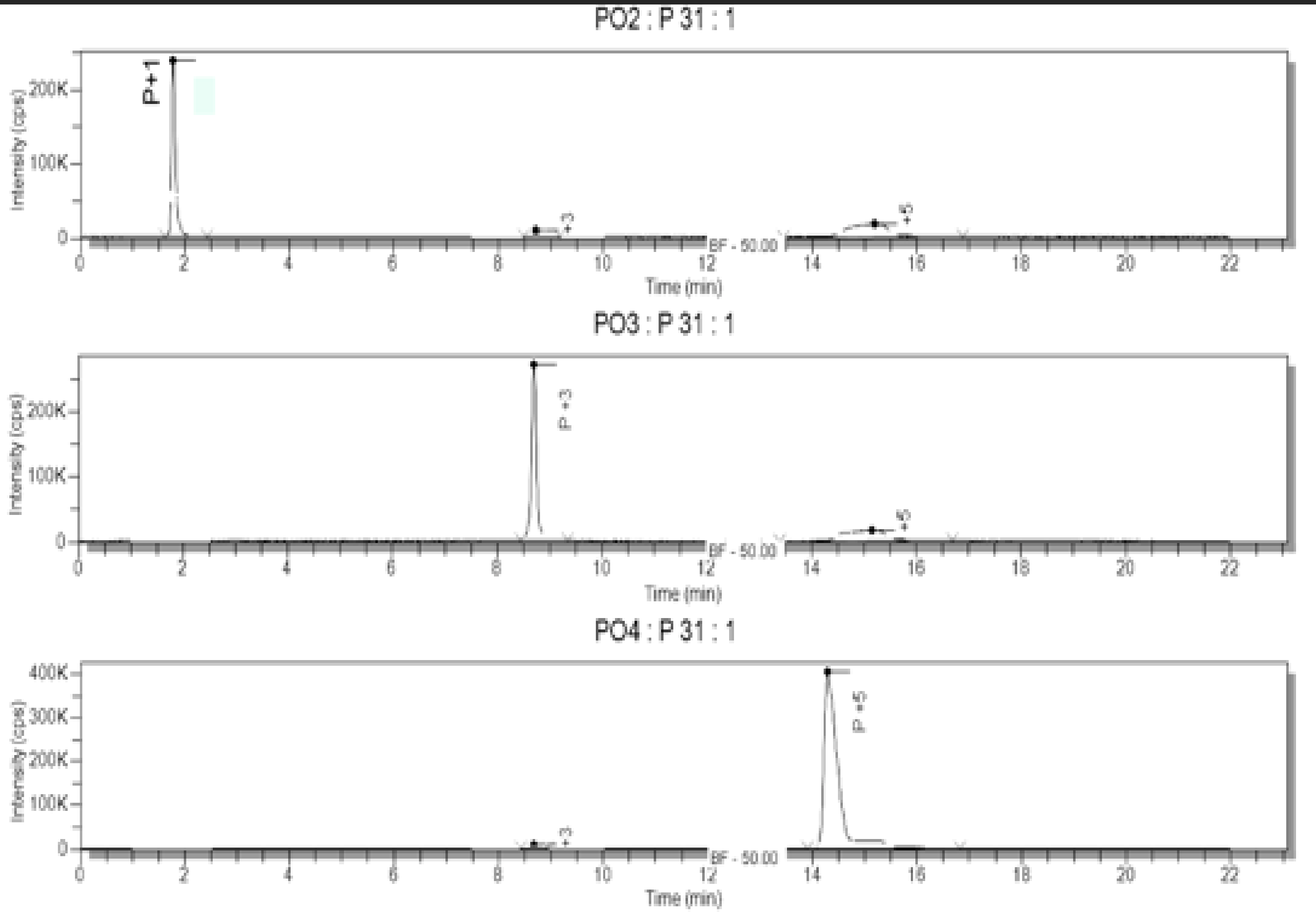
- If meteoritic phosphides played a role in early phosphorus geochemistry, can we see a signature of this?
- Does it last long enough?
- Can we detect it?

How long might reduced P last?



- $CaHPO_3$ a possible precipitate
- Phosphite oxidation directly proportional to f_{O2}
- Timescale of oxidation ~10^{12} years at Mag-Hem f_{O2}

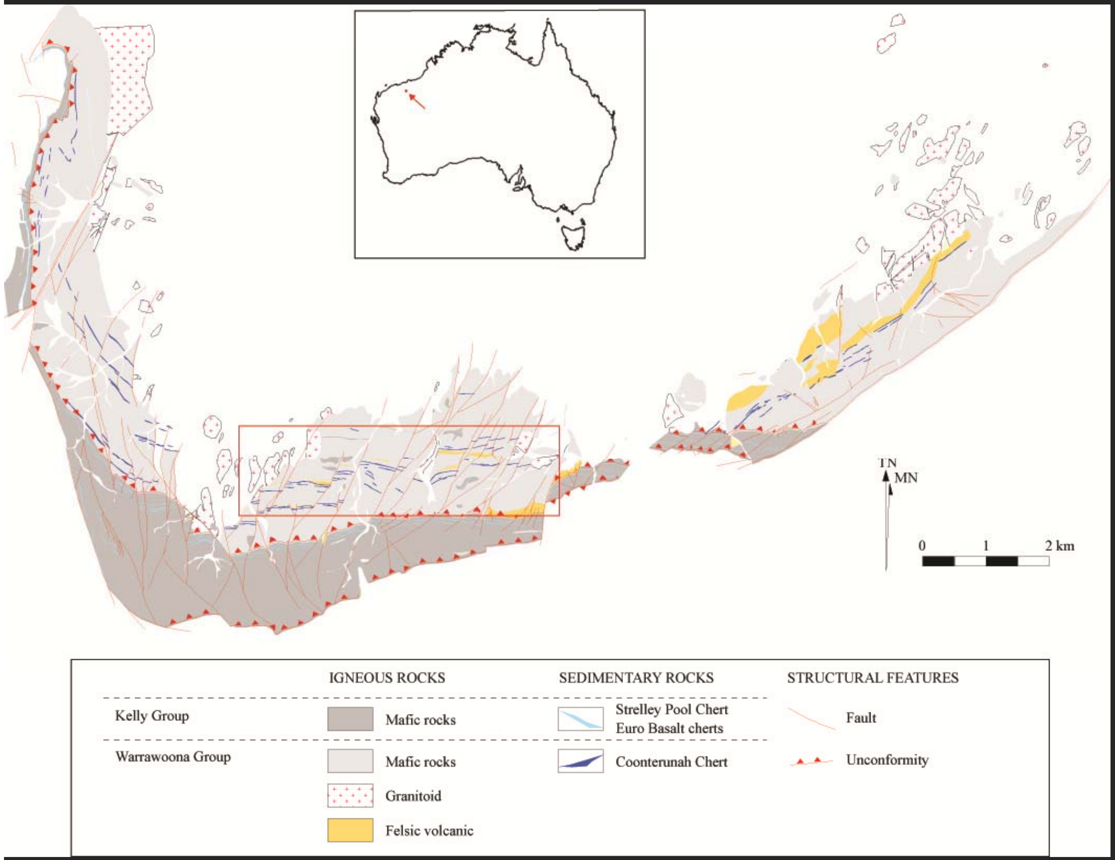
Detecting reduced P



Search for reduced P

Rock Locality	**Rock Type**	**Age (Ma)**
Coucal Fm., Coonterunah, Australia	Limestone (2 sample sites)	3,520
“	Hydrothermal chert	“
Goldman Meadows Fm., South Pass, Wyoming	Banded Iron Formation	2,870
Cheshire Fm., Belingwe, Zimbabwe	Carbonate	2,700
Brockman Iron Fm., Hamersley Basin, Australia	Banded Iron Formation	2,500
Millboro Fm., Charles Town West Virginia, USA	Shale	400-380
Green River Fm., Kemmerer, Wyoming, USA	Shale	50
Avon Park Fm., Citrus County, Florida, USA	Limestone	35

Geology of Coonterunah carbonates

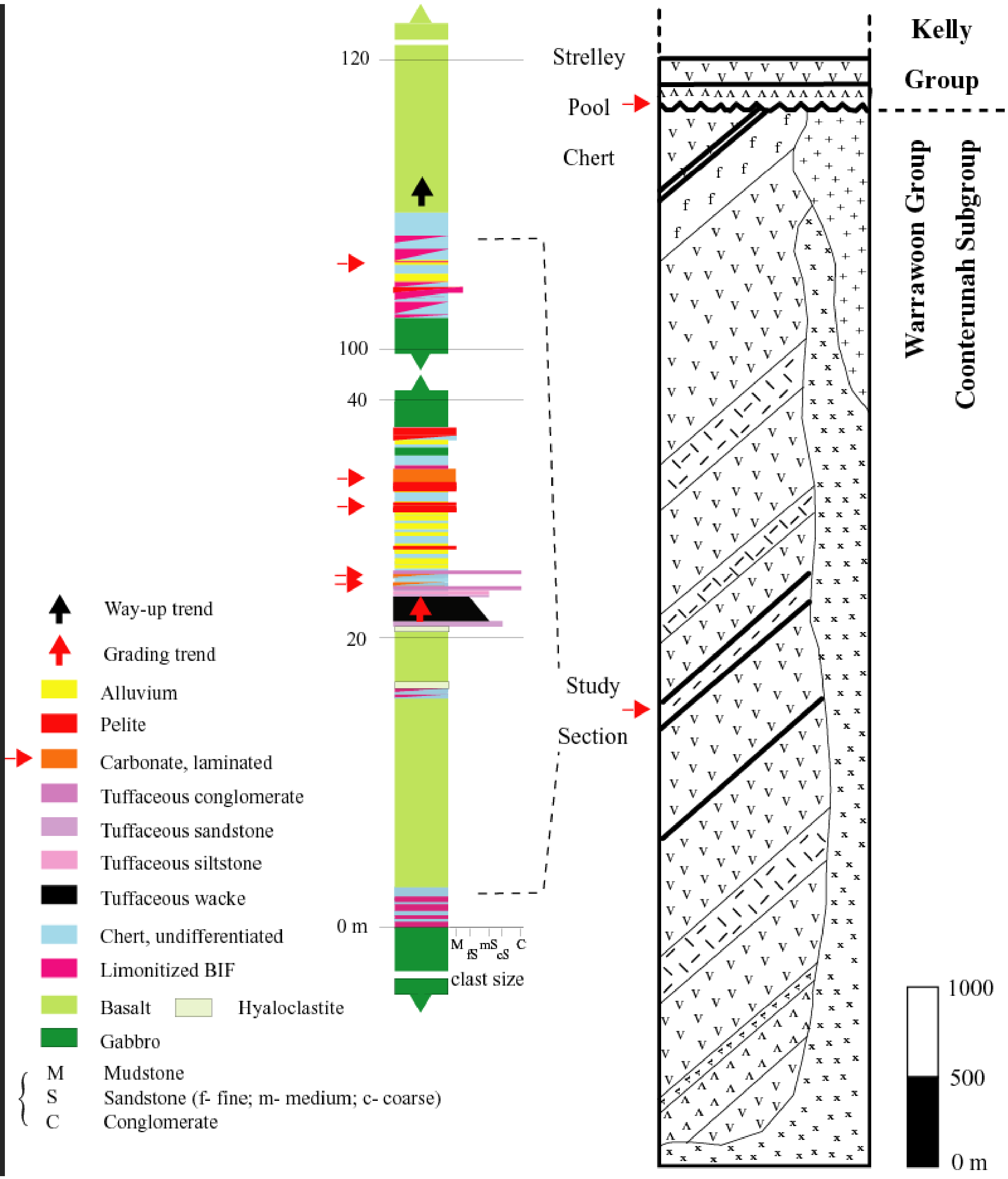


- Pilbara Craton
- East Strelley Belt
- Coucal formation

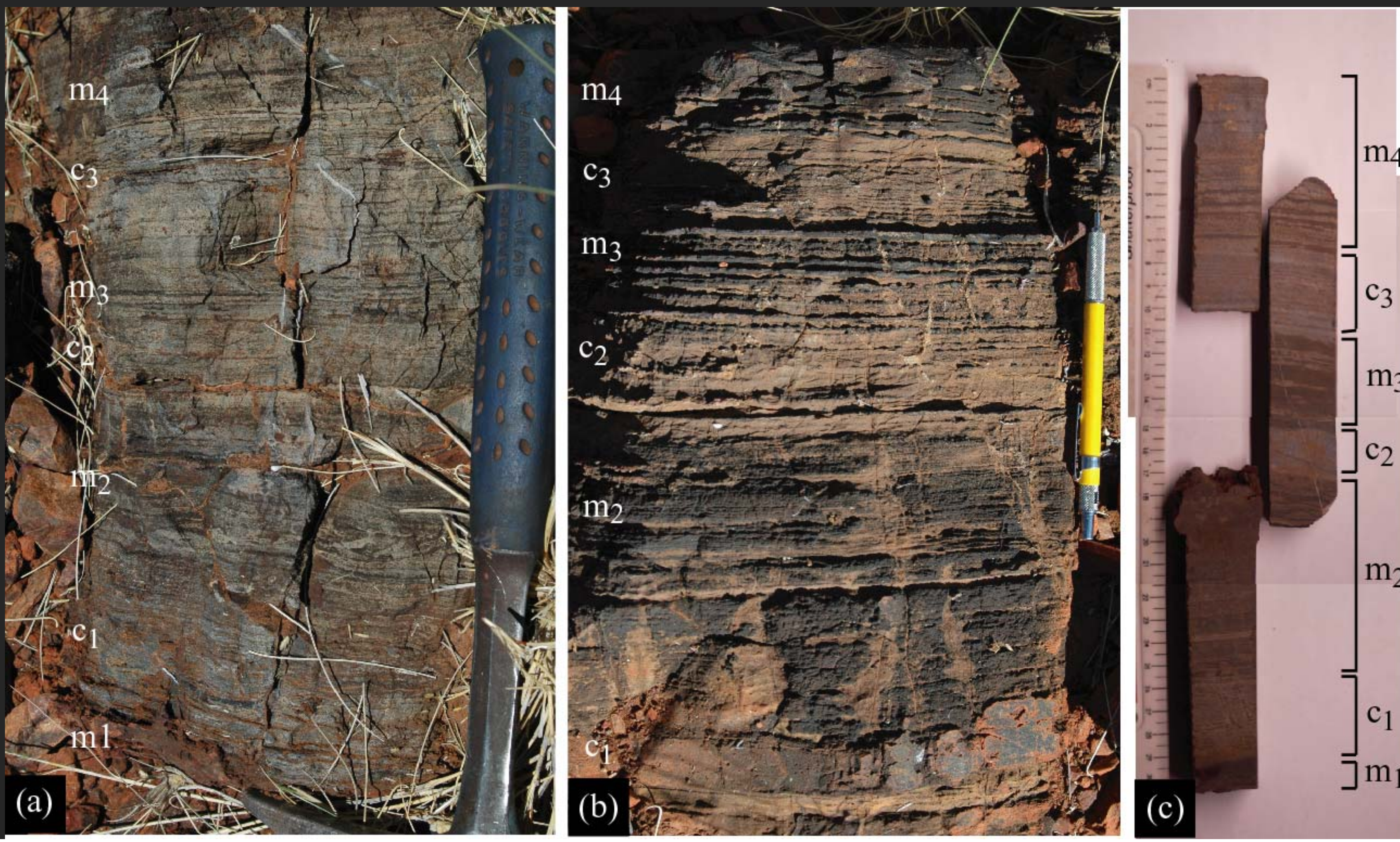
- Buick et al (Nature 1995)

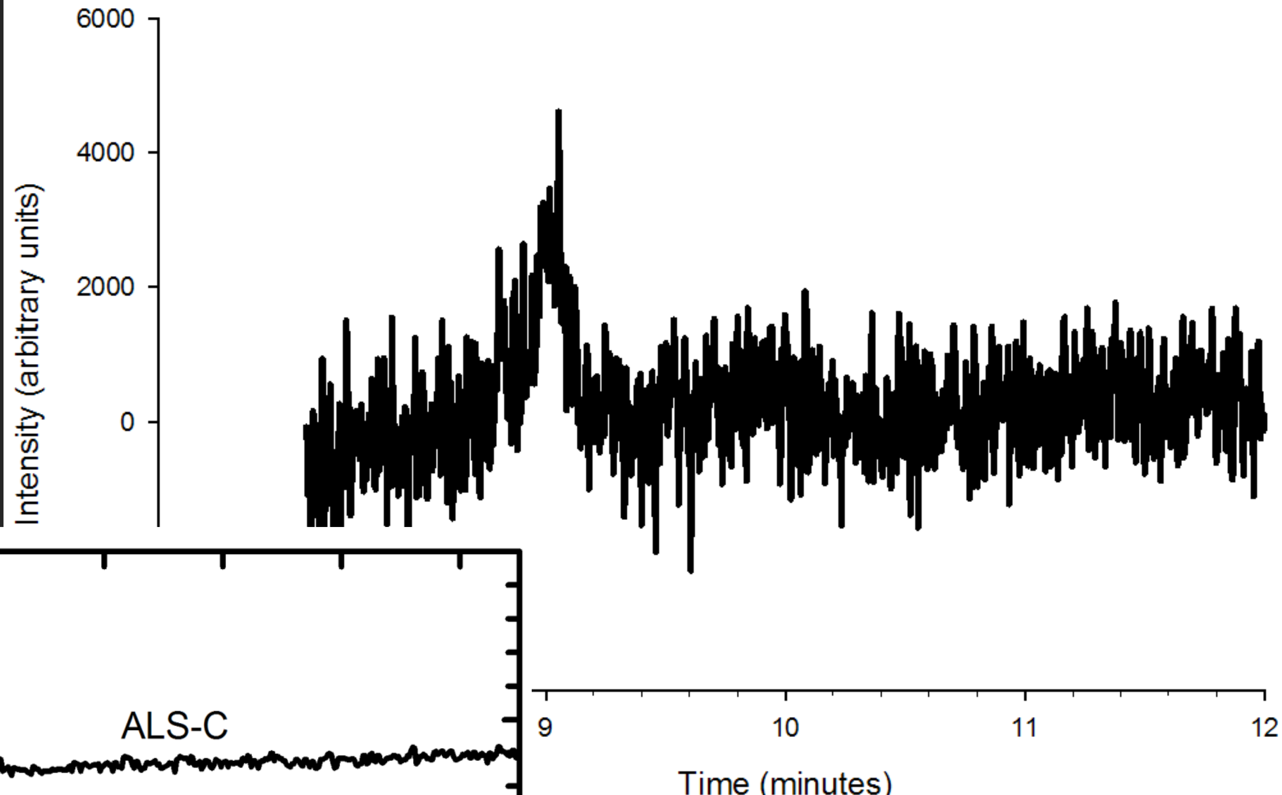
Cross-Section

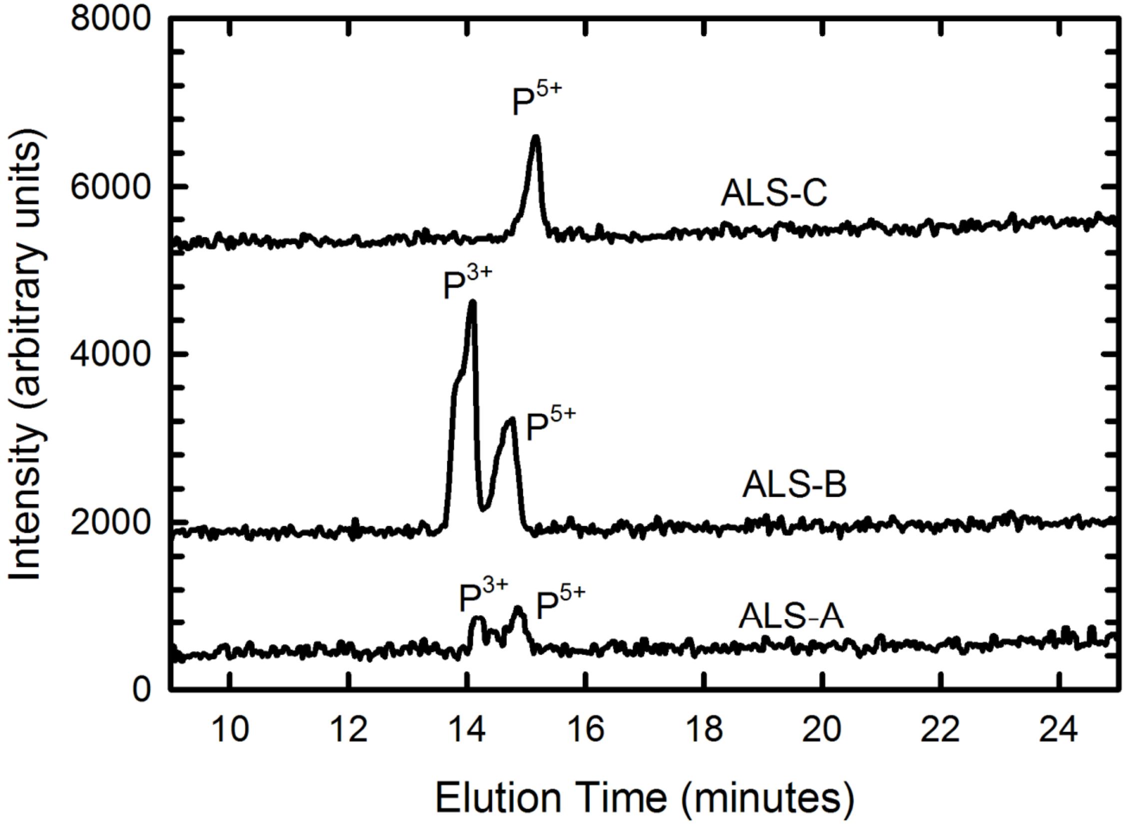
- Carbonates 32 cm or less in thickness
- ~5 km in lateral extent



- Magnetite + carbonate ± dolomite
- Both outcrop and core samples analyzed

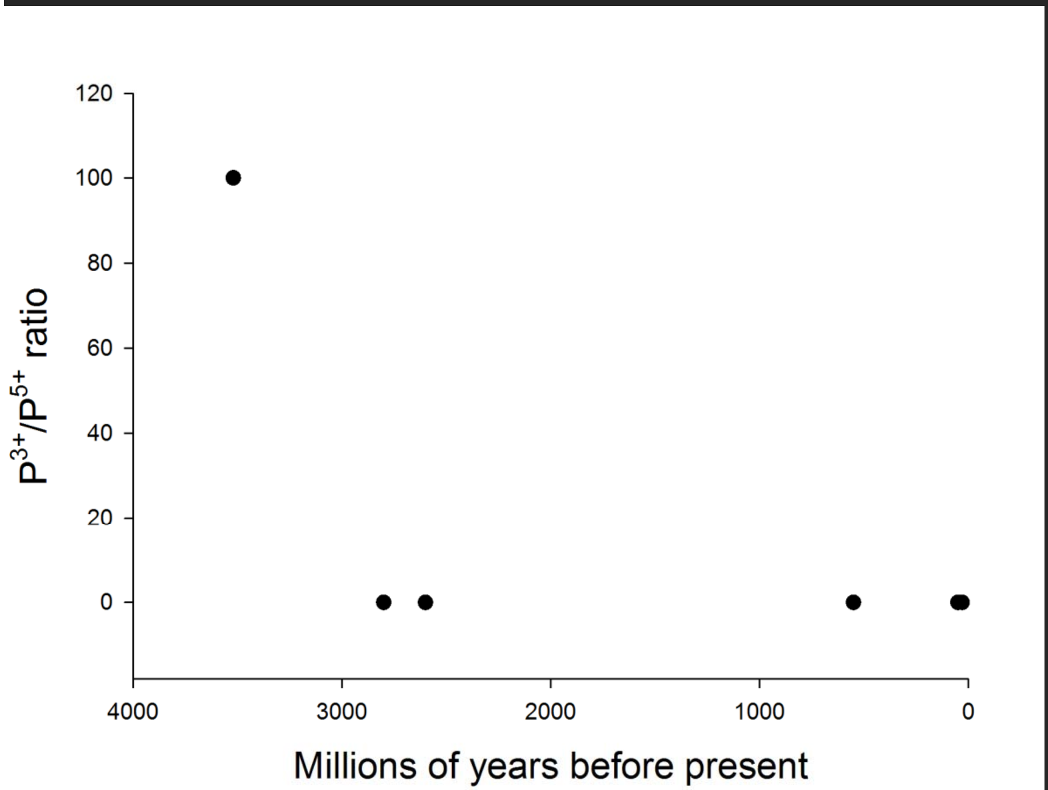






No phosphite in rocks 2.8 Ga and younger

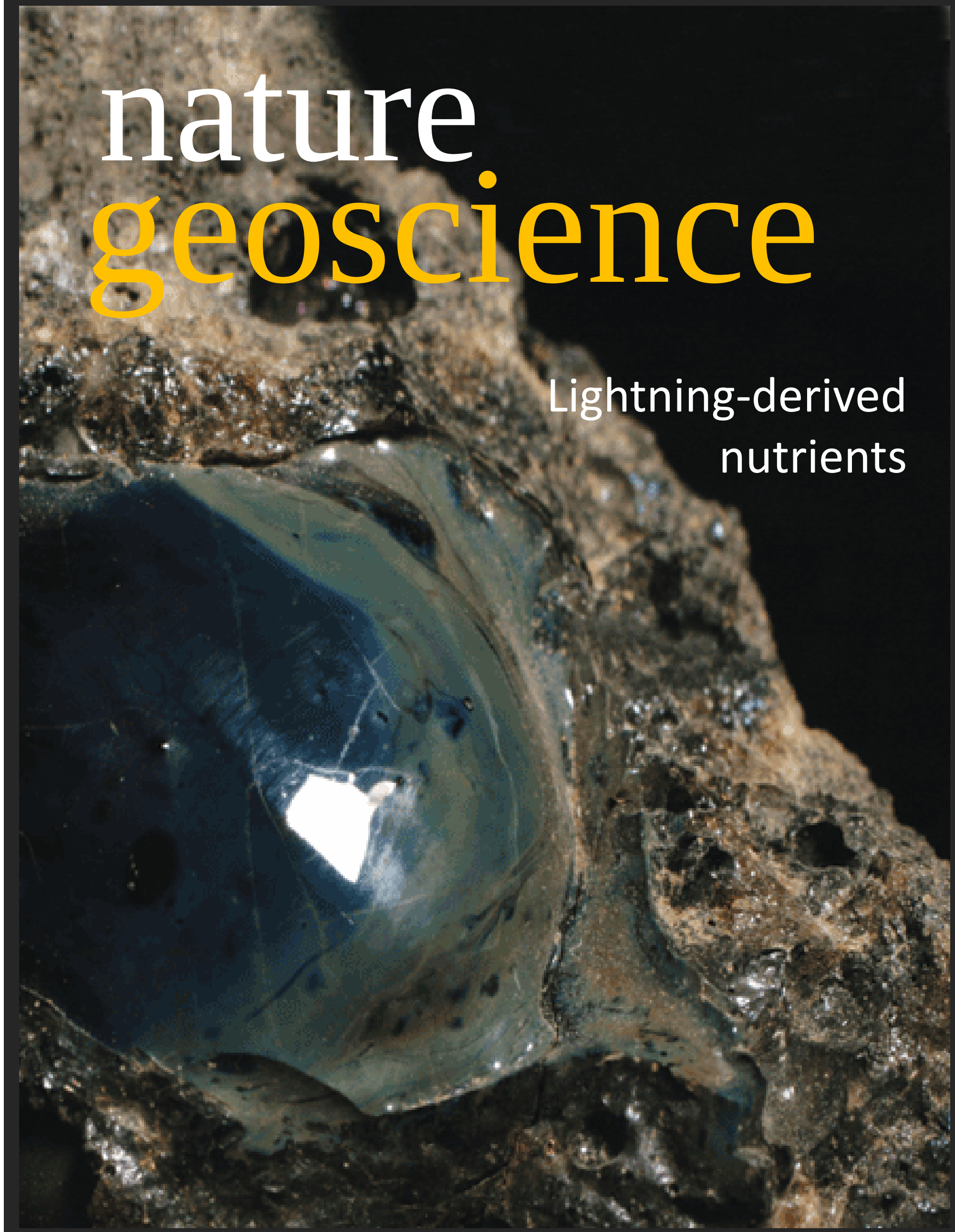
Early Archean P



- To precipitate phosphite in ocean water (0.01 M Ca^{2+}) requires a concentration of 10^{-4} M of phosphite
- More rocks being investigated

What is the source?

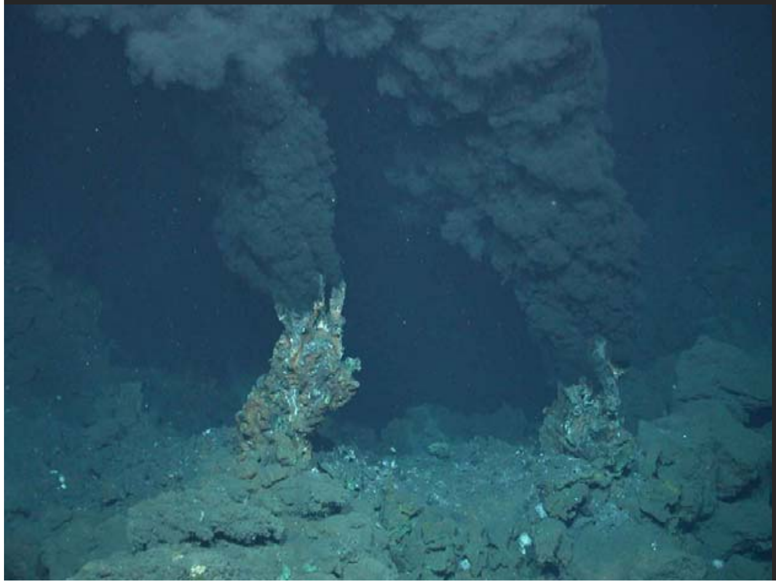
- High energy or low f_{O2} are necessary
- Phosphite is known from: Rice paddies (Tsubota 1959), phosphide corrosion (Morton et al. 2002, Pasek and Lauretta 2005), lightning (Pasek and Block 2009), Geothermal fluids (Pech et al. 2009, 2011), eutrophic lakes (Han et al. 2012)



Lightning and P redox

- Lightning is energetic enough to reduce P
  - Phosphites
  - Phosphides
- About $10^{3.5\pm1.5}$ kg/yr
- Pasek and Block (2009)

Hydrothermal sources?



- Pech et al. (2009) reported phosphite as a minor constituent (~4 × 10^{-8} M) of geothermal water (Hot Creek Gorge, Ca)
- Origin may be microbial
- Hydrothermal vents?

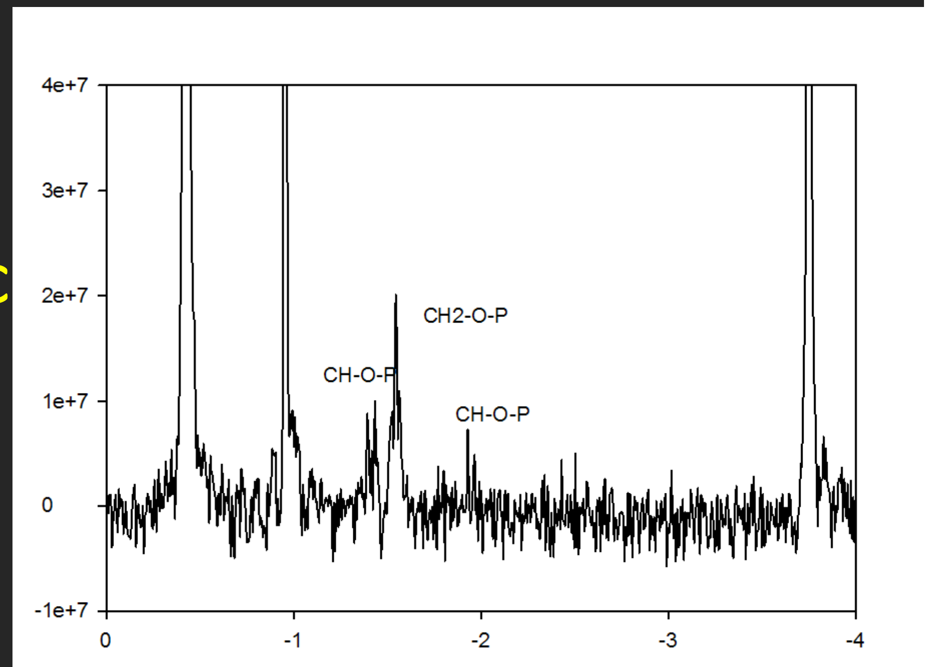
Implications for prebiotic chemistry

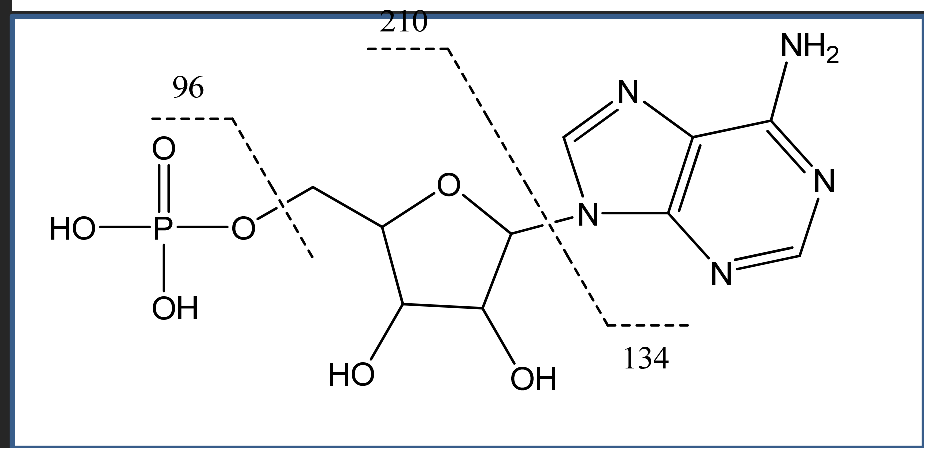
- Schreibersite is a good source of phosphorus
  - Creates soluble P as phosphite
  - Releases energy
  - Cations (iron) don't complex with phosphate at this pH

- Does it phosphorylate organic compounds?

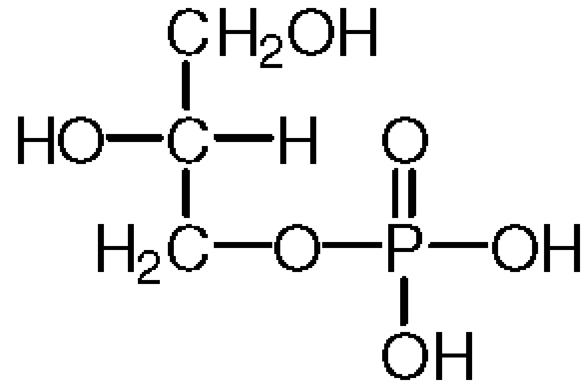
Prebiotic relevance

- If phosphite was formed from phosphides
- This allows new prebiotic chemistry
- Schreibersite reacts with organics to make organophosphates
- Earliest source of P for life?

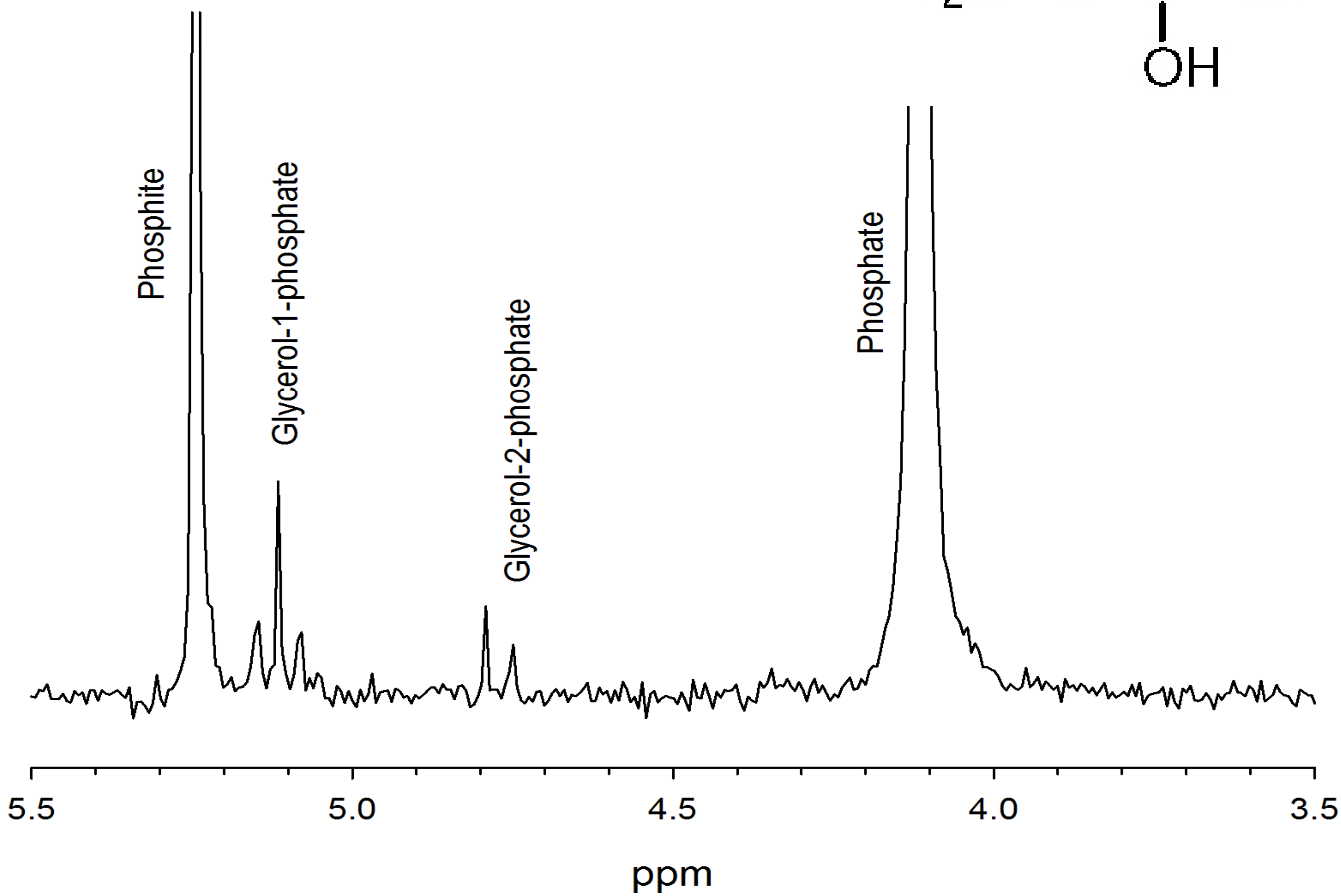




Glycerol

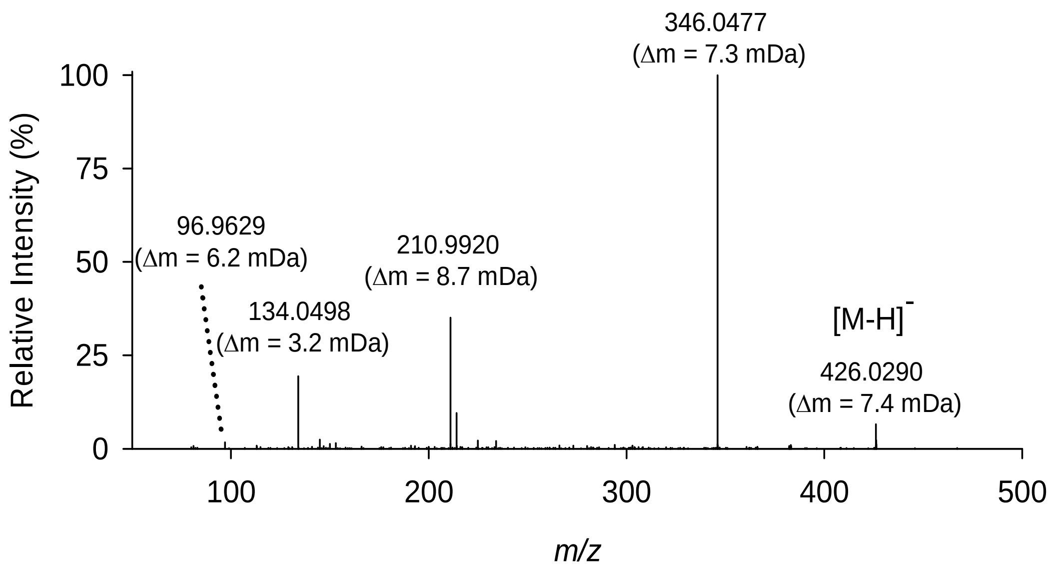


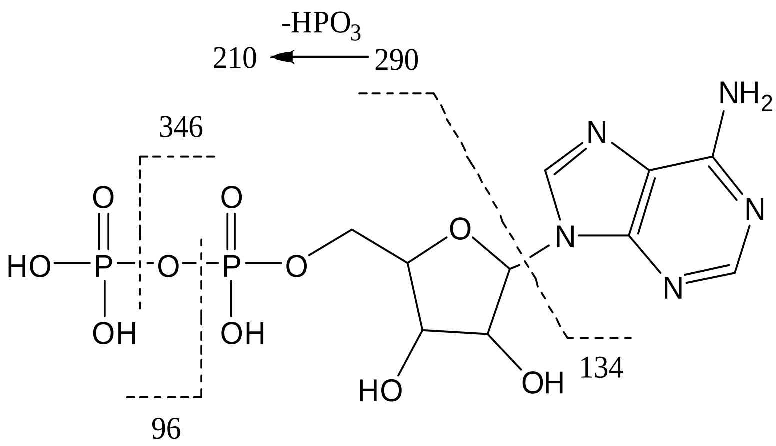
CH2OH
HO—C—H
O
H2C—O—P—OH
OH



Phosphite
Glycerol-1-phosphate
Glycerol-2-phosphate
Phosphate
5.5
5.0
4.5
4.0
3.5
ppm

ADP making



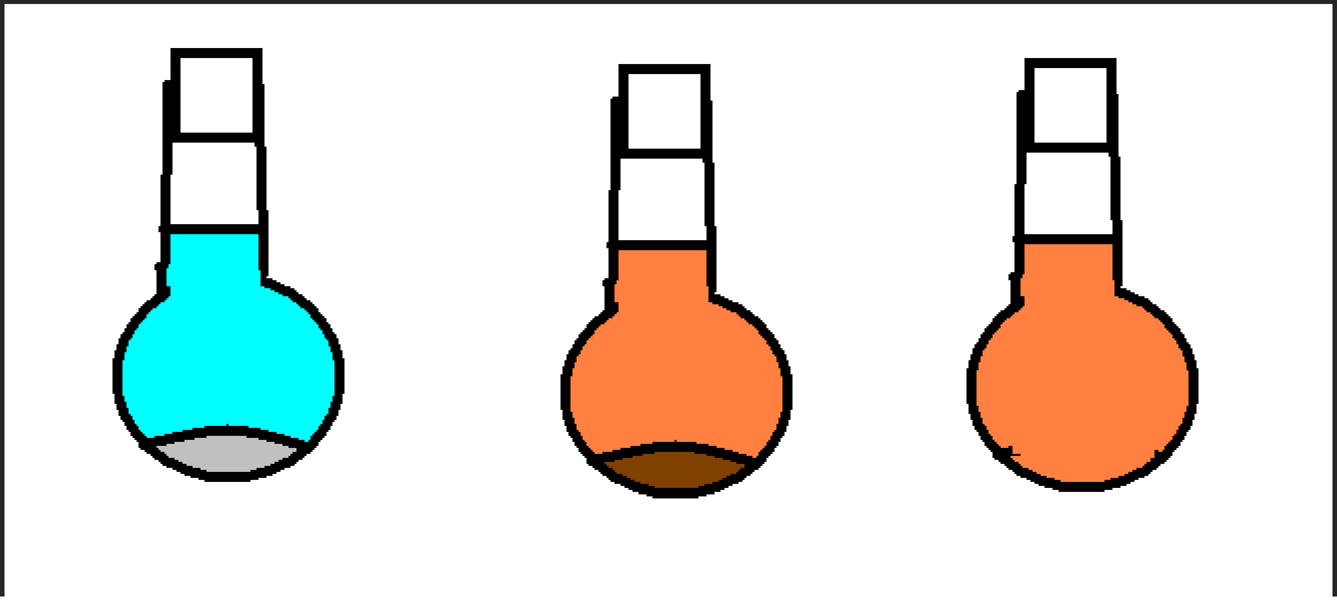


Chemical Formula: $C_{10}H_{15}N_5O_{10}P_2$

$[M-H]^-_{theoretical}$: 426.0216

Reaction pathway

- Unreacted Fe_3P necessary for nucleoside phosphorylation
- Reacted water okay for glycerol, alcohol phosphorylation- condensation



Phosphorylation of organics

- Phosphorylation yields are ~4% - ~25%
- Probably occurs via condensation (loss of water)
- Many prebiotic compounds can be phosphorlyated
- Paper to be submitted soon to *PNAS*

Practical Astrobiology

- We have recent results that suggest CO_2 fixation by phosphides
- $Fe_3P + CO_2 (g) + H_2O \rightarrow H_4CO_3P^- + Fe^{2+}$
- UV promoted
- Carbon-fixation, CO_2 sequestering, new synthetic pathways

Conclusions

- Early Archean phosphorus ocean chemistry included reduced oxidation state P
- Meteoritic phosphorus may have had significant impact on early earth
- Can provided needed P for biochemical reactions

Acknowledgements

- NASA Exobiology and Evolutionary Biology
- NSF Center for Chemical Innovation, Center for Chemical Evolution