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)
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)
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 - $\text{Ca}_5(\text{PO}_4)_3X$
- Monazite - $\text{Ce}({\text{Ce,La,Nd,Th}})\text{PO}_4$
- Whitlockite - $\text{Ca}_9\text{Mg}(\text{PO}_4)_6(\text{PO}_3\text{OH})$
- Insoluble, inert
- These dominated Earth’s surface and mantle 4 billion years ago
Phosphorus and the origin of life
Where do we get our Phosphorus?
Phosphorus nucleosynthesis

- **Carbon Burning**
  \[ ^{12}\text{C} + ^{12}\text{C} \rightarrow ^{24}\text{Mg}^* \rightarrow ^{23}\text{Na} + p \rightarrow ^{23}\text{Na} (\alpha, p) ^{26}\text{Mg} (\alpha, \gamma) ^{30}\text{Si} (p, \gamma) ^{31}\text{P} \]

- **Oxygen Burning**
  \[ ^{16}\text{O} + ^{16}\text{O} \rightarrow ^{31}\text{P} + p \]
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 ($T_{\text{condensation}} \sim 1275$ 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 + 3H₂O → CH₃PO₃H₂ +H₂

- Murchison phosphononates
  (Cooper et al. 1992)

*Low Temperature*
Condensation sequence illustrating main forms of $P$ in meteorites

Pasek 2008
Reduced

Oxidized

$10^{-4}$ bar

Temperature (K)

Abundance of compound (arbitrary units)

Ca$_5$(PO$_4$)$_3$OH

Ca$_3$(PO$_4$)$_2$

Ca$_5$(PO$_4$)$_3$F

Fe$_3$P

PO (g)

P (g)

P$_2$ (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
Primary P sources on early Earth

• Phosphides
  – Ubiquitous constituent of meteorites
    • Schreibersite, (Fe,Ni)$_3$P
  – 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)

With CH₃COOH

Pasek and Lauretta
2005
P Redox states and inorganic species

I. Orthophosphate

II. Pyrophosphate

III. Phosphite

IV. Hypophosphate

V. Hypophosphite

VI. Phosphine

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 $f_{O_2}$
- Timescale of oxidation $\sim 10^{12}$ years at Mag-Hem $f_{O_2}$
Detecting reduced P
<table>
<thead>
<tr>
<th>Rock Locality</th>
<th>Rock Type</th>
<th>Age (Ma)</th>
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<tbody>
<tr>
<td>Coucal Fm., Coonterunah, Australia</td>
<td>Limestone (2 sample sites)</td>
<td>3,520</td>
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<td>&quot;</td>
<td>Hydrothermal chert</td>
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<td>Goldman Meadows Fm., South Pass, Wyoming</td>
<td>Banded Iron Formation</td>
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<td>Cheshire Fm., Belingwe, Zimbabwe</td>
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<td>Brockman Iron Fm., Hamersley Basin, Australia</td>
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<td>Millboro Fm., Charles Town West Virginia, USA</td>
<td>Shale</td>
<td>400-380</td>
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<tr>
<td>Green River Fm., Kemmerer, Wyoming, USA</td>
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<tr>
<td>Avon Park Fm., Citrus County, Florida, USA</td>
<td>Limestone</td>
<td>35</td>
</tr>
</tbody>
</table>
Geology of Counterunah 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 $f_{O_2}$ 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 (~$4 \times 10^{-8}$ 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?
ADP making

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

$[\text{M-H}]^{-}$

$\Delta m$ values:
- 346.0477 (7.3 mDa)
- 210.9920 (6.2 mDa)
- 96.9629 (6.2 mDa)
- 134.0498 (3.2 mDa)
- 426.0290 (7.4 mDa)

$[\text{M-H}]^{-}$ theoretical: 426.0216
Reaction pathway

- Unreacted Fe$_3$P 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
We have recent results that suggest CO\textsubscript{2} fixation by phosphides

Fe\textsubscript{3}P + CO\textsubscript{2} (g) + H\textsubscript{2}O \rightarrow H\textsubscript{4}CO\textsubscript{3}P\textsuperscript{-} + Fe\textsuperscript{2+}

UV promoted

Carbon-fixation, CO\textsubscript{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

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