Marine Phosphorites

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“There are no substitutes for phosphorus in agriculture.”

- United States Geological Survey\textsuperscript{167}, 2009

- Phosphorus is an element necessary for all life. Phosphorus is one of the three major nutrients required for plant growth: nitrogen (N), phosphorus (P), and potassium (K).

- Global phosphorus production most likely peaked in 1989. If global phosphorus production has not yet peaked, it will likely do so by 2033.

- The quality of remaining phosphate rock is decreasing and the production costs are increasing.

- Global reserves will start to run out within 50 – 100 years.

- Once phosphorus supplies are exhausted, phosphorus will need to be recovered and reused in order to avoid a massive global food security crisis. There are no substitutes for phosphorus in agriculture.

- In 2007 – 2008, the price of phosphate rock increased dramatically worldwide due to increased agricultural demand and limited supplies of phosphate rock.

- Most of the world's farms do not have or do not receive adequate amounts of phosphorus. Feeding the world's increasing population will accelerate the rate of depletion of phosphate reserves. Future generations ultimately will face problems in obtaining enough to exist.
Figure 30: Historical sources of phosphorus for use as fertilizers, including manure, human excreta, guano and phosphate rock (1800 – 2000). Reliability of data sources vary, therefore data points for human excreta, guano and manure should be interpreted as indicative rather than precise.
Why is Phosphorous So Important?

Original Source: Igneous Apatite

\[ \text{Ca}_5(\text{PO}_4)_3(\text{OH, F}) \]

The ATP Cycle

- Synthesis of cellular macromolecules (DNA, RNA, proteins, polysaccharides)
- Synthesis of other cellular constituents (such as membrane phospholipids and certain required metabolites)
- Cellular movements, including muscle contraction, crawling movements of entire cells, and movement of chromosomes during mitosis
- Transport of molecules against a concentration gradient
- Generation of an electric potential across a membrane (important for nerve function)

ATP

Adenosine triphosphate
Use of P in Chemical Fertilizers

Low-grade Ca-phosphate + Cheap sulphuric acid => Superphosphate (concentrate)

P added to Ammonium sulfate and Potassium sulfate => Chemical Fertilizer

N:P:K refers to mix or grade of biologically-available nitrogen, phosphorous, potassium (+ trace metals, Fe, Mn, Mg, Cu, Zn, etc.)

EROEI (plant yield) for chemical versus organic fertilizers = 10:1
Global reserve estimates of phosphate rock (thousands of metric tons)

Data source: USGS
From: EcoSanRes (2005)
Global phosphate consumption from 1920 - 1995

From: Phosphorus & Potassium, Issue No: 217 (September-October, 1998)
Distribution of Phosphate Sediments in North America

Global Marine Phosphorite Distribution

Cronan (1980)

US MMS (1983)
Peak Phosphorous: Island of Nauru

Insular Phosphorite = Guano from Ancient Seabirds
Phosphate is Lucrative

Nauru Towers, Honolulu

Air Nauru Route Map - 2009
Appearance of Marine Phosphorites

Phosphatized limestone, basalt-clast conglomerate, Hawaiian EEZ seamounts

Phosphatic nodules, East Pacific

(Burnett et al., 1987)
Do Recent Phosphorites Form on the Seafloor?
--Peru-Chile Shelf Study--

Microscopic and SEM-EDX Evidence for Phosphatization of Sedimentary Carbonates

P map (above)

W. C. Burnett (1974)
SEM-EDX Evidence for Phosphatization of Sedimentary Carbonates--Inorganic?

W. C. Burnett (1974)
U-series Dating Evidence for Recent Phosphorite Formation on Peru-Chile Shelf

Modern Seawater = 1.14 +/- 0.01

Open circles are corrected for common, initial $^{230}$Th

Burnett et al. (1987)
Depth Profile of PO$_4$ Saturation in North Pacific

W. C. Burnett (1974)
Spatial Distribution of Dissolved Phosphate, Oxygen and Sediment Bottom Type, Peru-Chile Shelf-Slope

Burnett et al. (1987)
Oxygen Minimum Zone Impingement upon Peru-Chile Margin

W. C. Burnett (1974)
Generalized Reactions to Describe Phosphatization

below:

\[(1) \quad SO_4^{2-} + \text{organic matter} \rightleftharpoons H_2S + HCO_3^- + HPO_4^{2-} + NH_4^+ + CH_4\]

and

\[(2) \quad 2 Fe^{3+} \text{Clay} + 3 Mg^{2+} + 4 S \rightleftharpoons 3 Mg^{2+} \text{Clay} + 2 FeS_2 \quad \text{(pyrite)}\]

and/or

\[(3) \quad 2 CaCO_3 + Mg^{2+} \rightleftharpoons CaMg(CO_3)_2 + Ca^{2+} \quad \text{(calcite)} (\text{dolomite})\]

and/or

\[(4) \quad Al_2Si_2O_5(OH)_4 + 5 Mg^{2+} + 10 HCO_3^- + H_4SiO_4 \rightleftharpoons \quad (\text{kaolinite}) \]

\[\quad Mg_5Al_2Si_3O_{10} (OH)_8 + 10 CO_2 + 5 H_2O\]

and

\[(5) \quad 5 Ca^{2+} + 3 HPO_4^{2-} + F^- \rightleftharpoons Ca_5(PO_4)_3 F + 3 H^+ \quad \text{(apatite)}\]

W. C. Burnett (1974)
The Global Distribution of Phosphorite is Not Uniform Over Time!
Sea Level Changes from Seismic Stratigraphy

Vail et al. (1977)
Phosphorite U-series Ages (arrows) vs. Paleo-Temperature & Sea Level

W. C. Burnett (1974)
Model for Origin of Seafloor Phosphatic Sediments & Nodules on the Continental Shelves

Richard Sheldon’s Model of Phosphogenesis at High Sea Levels followed by Glacial Events

Trade Wind & Equatorial Upwelling Models to Explain Origins of Ancient & Modern Shelf Phosphorites

Sheldon (1980)
Equatorial Upwelling Model to Explain Origins of Ancient Seamount Phosphorites

Sheldon (1980)
Cretaceous Seamount Paleotracks & Paleodepths Lead to Shallow-water Equatorial Settings of Summits

McMurtry et al., *EPSL* 125 (1994)
Peak Phosphorous: Island of Nauru

Use of Hubbert Linearization (HL) to Estimate Ultimate Recoverable Reserves (URR)

\[ P = \text{Annual Production (mass units)} \]
\[ Q = \text{Total Production to Date} \]

http://www.theoildrum.com/node/2882
(Patrick Déry and Bart Anderson)
Peak Phosphorous: USA

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http://www.theoildrum.com/node/2882
(Patrick Déry and Bart Anderson)
Phosphate Rock--Years of Extraction Left Based Upon Present Reserves and 2% Annual Increase

Data source: USGS
From: EcoSanRes (2005)
Peak Phosphorous: World*

* Excluding offshore deposits.

http://www.theoildrum.com/node/2882
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“It is concluded that global phosphate resources extend, for all intents and purposes, well into the future, but that depletion of current economically exploitable reserves can be estimated at somewhere from 60 to 130 years.”

From: Phosphorus & Potassium, Issue No: 217 (September-October, 1998)
Figure 28: Annual and cumulative phosphorus production predicted by Cordell et al.\textsuperscript{119}, based on URR = 24.3 billion tonnes (URR from the USGS\textsuperscript{167}). According to this graph global peak phosphorus occurs in 2033. Graph produced by Ward\textsuperscript{118}. 
Figure 29: Annual and cumulative phosphorus production predicted by Ward\textsuperscript{118}. Global peak phosphorus occurs in 1989.
Hey, It’s a Finite Planet!