



# Phosphate rock formation and marine phosphorus geochemistry: The deep time perspective

Gabriel M. Filippelli\*

Department of Earth Sciences, Indiana University – Purdue University Indianapolis (IUPUI), 723 W. Michigan St., Indianapolis, IN 46202, USA

## ARTICLE INFO

### Article history:

Received 12 October 2010  
 Received in revised form 7 February 2011  
 Accepted 8 February 2011  
 Available online 4 March 2011

### Keywords:

Phosphorus  
 Phosphate rock  
 Ore  
 Phosphogenesis  
 Phosphorite  
 Global sustainability

## ABSTRACT

The role that phosphorite formation, the ultimate source rock for fertilizer phosphate reserves, plays in the marine phosphorus (P) cycle has long been debated. A shift has occurred from early models that evoked strikingly different oceanic P cycling during times of widespread phosphorite deposition to current thinking that phosphorite deposits may be lucky survivors of a series of inter-related tectonic, geochemical, sedimentological, and oceanic conditions. This paradigm shift has been facilitated by an awareness of the widespread nature of phosphogenesis—the formation of authigenic P-bearing minerals in marine sediments that contributes to phosphorite formation. This process occurs not just in continental margin sediments, but in deep sea oozes as well, and helps to clarify the driving forces behind phosphorite formation and links to marine P geochemistry.

Two processes come into play to make phosphorite deposits: chemical dynamism and physical dynamism. Chemical dynamism involves the diagenetic release and subsequent concentration of P-bearing minerals particularly in horizons, controlled by a number of sedimentological and biogeochemical factors. Physical dynamism involves the reworking and sedimentary capping of P-rich sediments, which can either concentrate the relatively heavy and insoluble disseminated P-bearing minerals or provide an episodic change in sedimentology to concentrate chemically mobilized P. Both processes can result from along-margin current dynamics and/or sea level variations. Interestingly, net P accumulation rates are highest (i.e., the P removal pump is most efficient) when phosphorites are not forming. Both physical and chemical pathways involve processes not dominant in deep sea environments and in fact not often coincide in space and time even on continental margins, contributing to the rarity of high-quality phosphorite deposits and the limitation of phosphate rock reserves. This limitation is becoming critical, as the human demand for P far outstrips the geologic replacement for P and few prospects exist for new discoveries of phosphate rock.

© 2011 Elsevier Ltd. All rights reserved.

## 1. Introduction

Phosphate rocks, also referred to as phosphorites, are sedimentary deposits with high phosphorus (P) concentrations. These rocks are one of the primary ore sources for P (Fig. 1), which in turn is a critical and non-renewable element for fertilizer production, upon which global fertility depends. The startling limitation of phosphate rock reserves has led to a renewed intensity of research in mitigating P loss from landscapes, recycling P from waste streams, and exploring new P ore potentials. From a human perspective, this situation is one of taking an element from a high-concentration source and distributing it broadly—although the elemental P mass is conserved, it is now scattered across the globe and effectively diluted. The ecological impact of intense fertilization and loss from

landscapes has been documented extensively in eutrophication literature (e.g., Bennett et al., 2001; Schindler et al., 2008), but the impacts from a resource conservation standpoint are just becoming apparent (Smil, 2000; Cordell et al., 2009).

From a geologic standpoint, P also is a vital fertilizing agent for biological productivity on land and in the sea, and indeed is considered the ultimate limiting nutrient in the ocean on timescales exceeding 1000 years (Tyrell, 1999). As with all resources, geology had millions of years to act to form sedimentary deposits with high P concentrations, but humans have extracted these resources at rates so high that the current phosphate rock reserves might be largely depleted in this century (Table 1; Cordell et al., 2009). Typical sedimentary rocks have an average P concentration of about 0.1 wt.%, whereas phosphate rocks have P concentrations 100× that amount. Phosphate rocks are indeed unique from many perspectives, not least their high P content.

This paper describes the current understanding of the geochemical process, phosphogenesis, at the root of phosphate rock

\* Tel.: +1 317 274 3795; fax: +1 317 274 7966.

E-mail address: [gfilippe@iupui.edu](mailto:gfilippe@iupui.edu)



Fig. 1. Dragline mining of phosphate ore in Florida.

**Table 1**  
Components of the Phosphorus Cycle in comparison to modern demand.

Material	P content (%)	Reservoir MT	Production/formation MT/yr
Average continental rocks <sup>a</sup>	0.09		
Marine sediments <sup>b</sup>		8.4 × 10 <sup>11</sup>	
Continental margins	0.11		
Phosphorites	10–20		
Deep Sea	0.18		
Hydrothermal	0.6–1.5		
Soils <sup>c</sup>	0.015	40–50	
Ocean <sup>b</sup>	~0	93 000	
Phosphate Rock Ore <sup>d</sup>	13	2300	20
Morocco and Western Sahara		820	3.4
China		531	7.9
USA		158	3.9
Manure (cow) <sup>e</sup>		0.4	>15
Sewage <sup>e</sup>		2–3	3
Human demand of phosphate rock ore			
Human demand 2000 <sup>e</sup>			20
Human demand 2050 <sup>e</sup>			30
Time to reserve exhaustion 2010 demand	115 years		
Time to reserve exhaustion 2050 demand	77 years		

<sup>a</sup> Blatt and Tracy (1996).

<sup>b</sup> Ruttenberg (2003).

<sup>c</sup> Schlesinger (1997).

<sup>d</sup> USGS (2009).

<sup>e</sup> Cordell et al. (2009).

formation, along with the multiple geochemical and sedimentological steps that marine sediments must undergo before the rare few ultimately become phosphate rocks. A significant paradigm shift in our understanding of phosphogenesis and phosphate rock formation has occurred over the past several decades, in line with increased understanding of the marine P cycle (Ruttenberg, 1993; Delaney, 1998; Benitez-Nelson, 2000; Colman and Holland, 2000; Compton et al., 2000; Ruttenberg, 2003). Both revolutions have provided a more consistent picture of phosphate rock formation, and indeed might guide the way to determine the position and extent of phosphate rock reserves that are not currently economically viable. Various aspects of phosphorus geochemistry and phosphate rock formation have been considered before (e.g., Sheldon, 1981; Föllmi, 1996), but not from the viewpoint of critical resource limitation.

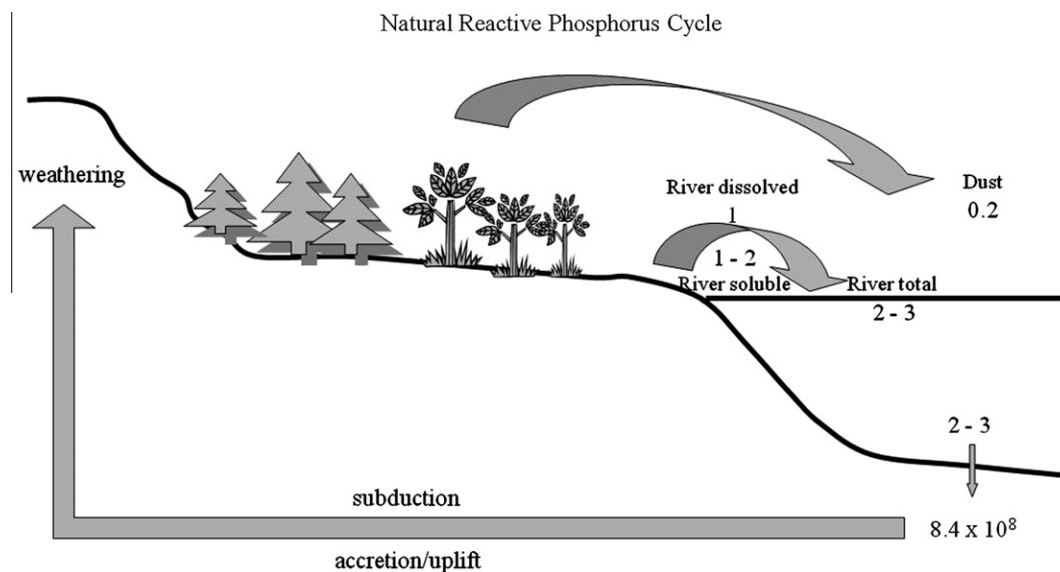
## 2. The phosphorite paradigm shift: out with the old, in with the new

The processes responsible for phosphate rock formation have been the focus of research for the past century, owing to the importance of this fertilizer resource. Several key early observations were made about phosphorite deposits, especially the massive phosphorite formations that constitute the bulk of our phosphate rock reserves, called “Phosphorite Giants.” First, “Giants” contain P at extremely high concentrations (Sheldon, 1981). This alone seemed important, because in the modern ocean P is a limiting nutrient that is in such high demand by marine ecosystems that the element is recycled heavily and not typically found in high concentrations in modern marine sediments. The amount of P in the Permian Phosphoria Formation, for example, was commented to be equivalent to 5× that present in the modern ocean (Sheldon, 1981). Second, the deposition of phosphorites is apparently episodic through geologic time, with certain intervals (i.e., the Permian, the Eocene, the Miocene) being marked by active phosphorite formation (Cook and McElhinny, 1979; Riggs, 1984; Riggs and Sheldon, 1990; Sheldon, 1989). These observations led geologists to assume that intervals of phosphorite formation reflected unique intervals of Earth history where the rate of weathering and input of P from the continents to the oceans must have been extremely high to allow for ‘excess’ P burial in phosphorites. An extension of this paradigm was that marine biological productivity and carbon burial must have been high in these intervals of extensive P fertilization, and thus they constituted unique climatic events as well (Vincent and Berger, 1985).

It was with the development of better stratigraphic models, a deeper understanding of P geochemistry, and the examination of P burial in several modern high productivity regions that the old paradigm of atypical conditions driving deposition of “Phosphorite Giants” began failing. As will be discussed in the remaining portion of the paper, the initiation of P mineralization in marine sediments follows a predictable pathway seen in most (and perhaps all) marine sediments. The geochemical concentration of these disseminated P minerals into discrete laminae and nodules occurs in relatively unique environments of high biological production and organic matter burial flux with little detrital input. And finally, the concentration of these P-rich laminae and nodules into “minable” phosphorites is the result of periodic disruption and winnowing of marine sediments caused by dynamic sedimentary conditions which are also relatively unique. Thus, the finding of discrete intervals marked by massive phosphorite deposition likely reflects the uniqueness of these processes acting in unison, and not necessarily the uniqueness of global conditions with respect to P weathering and cycling. The Permian Phosphoria Formation P estimate was robust, but the analogy to 5× the modern marine P inventory does not actually merit surprise given that the Phosphoria Formation was deposited over a period of 6 million years and thus had a net P burial rate that puts it along the lines of modern upwelling environments on the Peru margin, for example (Garrison and Kastner, 1990; Föllmi and Garrison, 1991). In so much as the modern ocean is not considered atypical, then weathering and oceanographic conditions that resulted in the deposition of the Phosphoria Formation were not atypical either. This new paradigm does not discount that global changes in P weathering and cycling occurred in the past, but simply documents that this is not a prerequisite for phosphorite formation.

## 3. The marine phosphorus cycle and phosphorus sedimentation

The cycling of P in the ocean is marked by: (1) the relative paucity of input dissolved and sediment-bound sources, (2) the role of



**Fig. 2.** Natural cycle of reactive phosphorus, with phosphorus input to the oceans from riverine and dust sources, output via sedimentation, and recycling via tectonics (after Ruttenberg, 2003; fluxes in Tg P/year, sedimentary reservoir in Tg P).

P in limiting biological productivity, and (3) the recycling and ultimate burial processes affecting P. Global assessments of P cycling reveal that P weathering and release from terrestrial landscapes to the ocean is the dominant mechanism for the input of new P to the marine environment (Fig. 2; Ruttenberg, 2003). Only a portion of that P is potentially bioavailable, however, and indeed much of the P is removed in estuarine biogeochemical processes (Froelich, 1988). The only other input of P to the oceans is via dust, and this source likely comprises less than 10% of the total P input. Anthropogenic activities have increased the P erosion rates from land to ocean by about 300% (Bennett et al., 2001), dwarfing the 50% variation due to the extreme changes in landscapes and erosion during glacial cycles (Tsandev et al., 2008) and revealing the domination of global P transfers by humans.

Phosphate concentrations are near zero in most surface waters, as this element is taken up by phytoplankton as a vital component of their photosystems (phosphate forms the base for ATP and ADP, required for photosynthetic energy transfer) and their cells (cell walls are comprised of phospholipids). Dissolved P has a nutrient profile in the ocean, with a surface depletion and a deep enrichment. Furthermore, deep phosphate concentrations increase with the age of deep water, and thus values in young deep waters of the Atlantic are typically  $\sim 1.5 \mu\text{M}$  whereas those in the older Pacific are  $\sim 2.5 \mu\text{M}$  (Broecker and Peng, 1982). Once incorporated into plant material, P roughly follows the organic matter loop, undergoing active recycling in the water column and at the sediment/water interface.

Riverine P is present in particular and dissolved forms. Most of the P contained in the particulate load of rivers is held within mineral lattices and never participates in the active biogenic cycle of P. This will also be its fate once it is delivered to the oceans, because dissolution rates in the high pH and heavily buffered waters of the sea are exceedingly low. Roughly 50% of the total P entering the ocean suffers exactly this fate (Compton et al., 2000). Of the remaining P input, some is removed via the export of organic matter (with included P) to the seafloor, and a smaller portion is removed via scavenging by marine oxyhydroxides, especially near ocean vent environments (Feely et al., 1990; Wheat et al., 1996). Some of the particulate P is adsorbed onto soil surfaces, held within soil oxide, and incorporated into particulate organic matter. This P likely interacted with the biotic P cycle on land, and its fate upon

transfer to the ocean is poorly understood. For example, P adsorbed onto soil surfaces may be effectively displaced by the high ionic strength of ocean water, providing an additional source of P into the ocean. Furthermore, a small amount of the P incorporated into terrestrial organic matter may be released in certain environments during bacterial oxidation after sediment burial. Finally, some sedimentary environments along continental margins are suboxic or even anoxic, conditions favorable for oxide dissolution and release of the incorporated P. Several important studies have examined the transfer of P between terrestrial and marine environments (e.g., Froelich, 1988; Ruttenberg and Goñi, 1997), but more work clearly needs to be done to quantify the interactions between dissolved and particulate P forms and the aquatic/marine interface. The net pre-human flux of dissolved P to the oceans is  $\sim 1 \text{ Tg P/year}$ , with an additional 1–2 Tg P/year of potentially soluble P, bringing the total to about 2–3 Tg P/year (Fig. 2).

Variations in the marine phosphorus cycle through time have certainly occurred, but these variations are difficult to determine due to a lack of effective marine proxies for the P cycle. No useful P isotopes exist to constrain the P cycle in deep time, nor are fossil-based proxies adequate to determine past changes in the P cycle. This is due to elemental mass balance differences between P and other nutrient-type proxies—these proxies are, however, excellent for determining the horizontal and vertical distribution of dissolved P in ancient ocean waters. Our only direct measure of P input changes to the ocean, for example, is P accumulation in marine sediments. Because accumulation rates vary tremendously in different settings, and because it is difficult to isolate P that is detrital in origin from that which has been involved in past biological processes, many important questions remain unanswered about P cycle variations. Nevertheless, several key events in Earth's evolution have likely impacted the rate of P input to the ocean and the cycling of P within the ocean. For example, the Snowball Earth glaciations approximately 700 million years ago may have resulted in a substantial and sustained increase in P input to the ocean, ultimately driving high rates of organic matter burial and the observed increase in atmospheric oxygen critical to the evolution of animal life (Planavsky et al., 2010). Additionally, the development of 'rootedness' in land plants during the Devonian Era must have affected the rate and style of erosion of P from landscapes and input to the ocean, which in turn affected marine biogeochemistry (Algeo et al.,

1995). Finally, a several million year long global marine biogenic bloom centering around 6 million years ago (Farrell et al., 1995), was likely the result of a P erosional pulse driven by the onset of the Asian Monsoon and intensification of chemical weathering of vast floodplain and front range deposits (France-Lanord and Derry, 1994) eroded from the uplifting Himalayan–Tibetan Plateau. Föllmi (1995) document many of these changes in the P cycle over the past 160 million years, and others have examined P cycle changes on glacial timescales (Tsandev et al., 2008; Tamburini and Föllmi, 2009).

#### 4. Phosphate rock formation: from phosphogenesis to phosphorite formation

The pathway from a dissolved phosphate molecule in the ocean to a P-rich phosphorite is long, and indeed is rarely travelled. But following this pathway is critical if we want to understand what controls the presence and distribution of phosphate rock reserves and consider what additional P-bearing resources might be available and where they might be found to fuel our P-hungry planet.

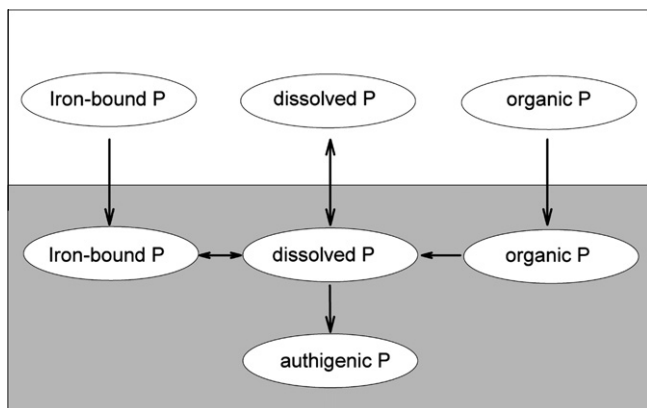
##### 4.1. Phosphogenesis

Phosphogenesis is defined as the authigenic formation of phosphate minerals—in marine environments, this is largely of the form carbonate fluorapatite, or CFA. This geochemical process was long considered unique (the “old” paradigm), because our understanding of phosphogenesis was limited to the product (phosphate minerals) instead of the process. Owing largely to the development by Ruttenberg (1992) of a geochemical technique to isolate the various fractions of P-bearing materials in marine sediments, researchers have now documented systematic patterns in P geochemistry and P geochemical transformations that reveal the basic process of phosphogenesis (Ruttenberg and Berner, 1993; Delaney, 1998; Schenau et al., 2000). Basically, phosphogenesis involves diagenesis of P-bearing phases in marine sediments, the release of P to interstitial waters, the local supersaturation of P and the authigenic formation of CFA (Fig. 3). This process can involve intermediaries, like iron oxyhydroxides, and is not 100% efficient, as P loss is seen from the sediments to the overlying water column (McManus

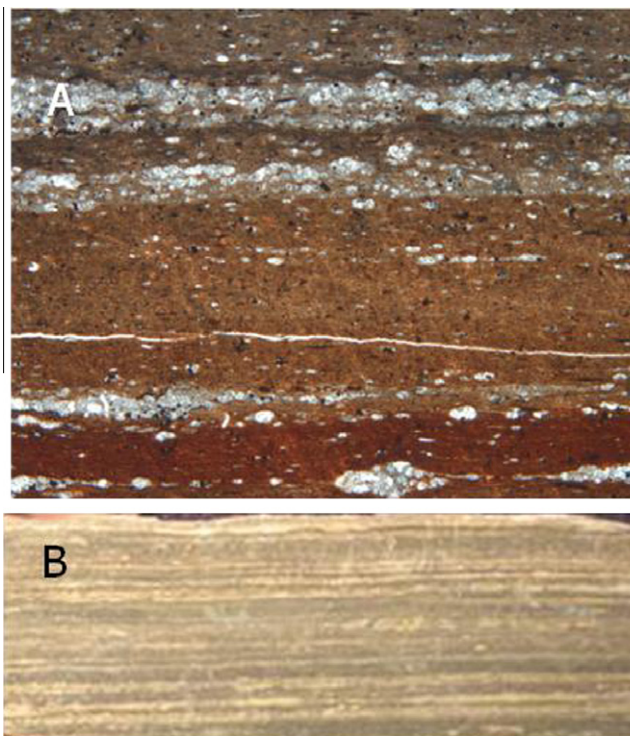
et al., 1997). But ample evidence exists to support an interpretation of authigenic CFA formation in marine sediments, spanning many oceanographic settings.

Phosphatic shales might be considered the “type section” for phosphogenesis, because the CFA end-product of the process is visibly apparent in these rocks (Fig. 4). In this case, phosphatic laminae and micronodules form authigenically from the release of P from organic matter during remineralization and the migration of this dissolved P to sites of CFA mineralization. Based on the morphological characteristics of this visible CFA mineralization, this process seems to be controlled by a number of factors, including the rate of mineralization, bio-irrigation of the sediments, microbiological density, permeability and porosity of the sediments, the presence or absence of viable mineral templates for CFA mineralization (e.g., calcite can be easily converted to CFA via phosphate substitution), and other competitive geochemical reactions (e.g., Föllmi, 1996).

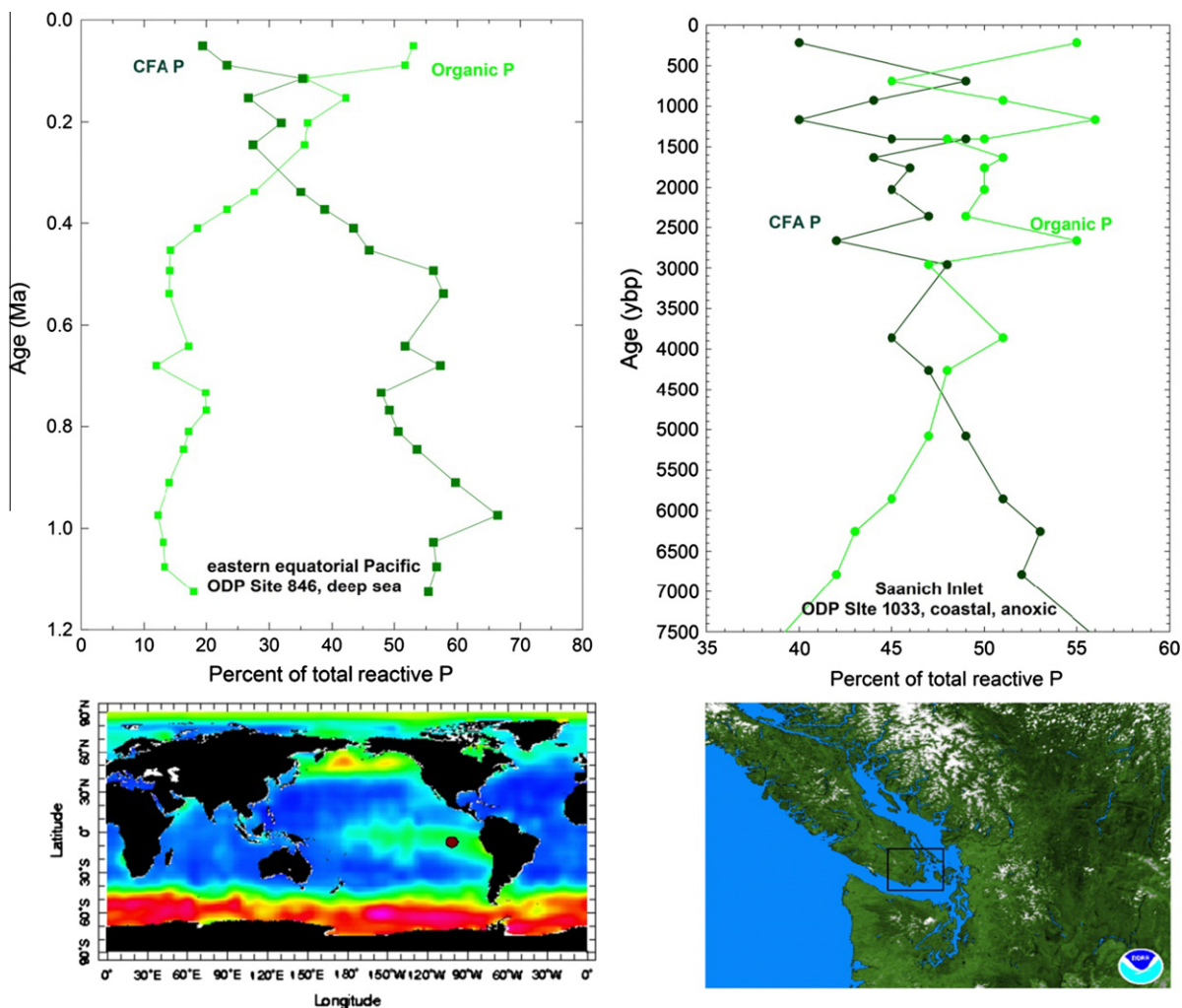
With the application of P geochemical techniques, however, it is clear that although phosphatic shales may be the type section for field geologists, they are in fact just one of many environments where CFA formation can be inferred. These environments range from deep marine sediments, where the formation of CFA at the expense of other P-bearing phases (so-called “sink switching”) occurs on timescales of millions of years (Fig. 5), to anoxic marginal basins where the process occurs on timescales of thousands of years (Fig. 5). Indeed, over the past two decades researchers have revealed that the process of phosphogenesis is common and occurs in many sedimentary environments, although it should be noted that scant effort has been made to observe the morphology and mineralogy of the disseminated CFA that is the presumed product of this process.



**Fig. 3.** A conceptual diagram of P geochemistry in oceanic sediments (after Delaney, 1998). Phosphorus associated with organic matter is the primary source of P to the sediments, although the depositional flux of iron-bound P is commonly similar to that of organic P in continental margin settings. Organic matter degradation leads to the release of P to interstitial waters. Dissolved P in interstitial waters appears to be involved in several processes, including adsorption to grain surfaces, diffusion back to bottom waters, binding to iron oxyhydroxide minerals (which also scavenge some P from deep waters during particle formation in the water column), and incorporation in authigenic P, most likely as the mineral carbonate fluorapatite (CFA).



**Fig. 4.** Phosphatic shales of the Miocene Monterey Formation (Shell Beach, California, USA). Sample A displays white nearly pure cellophane in the form of phosphate nodules and weak lamination in an organic shale host. Sample B displays tan phosphate-rich laminations in a shale host which contains about 15% organic carbon by mass.



**Fig. 5.** The progressive diagenesis of sedimentary phosphorus as a function of time in two ocean sediment cores, revealing the progressive decreases in organic-associated P and the increase in CFA-associated P with increased time (and depth). Left—Ocean Drilling Program Site 846, eastern equatorial Pacific Ocean; Right—Ocean Drilling Program Site 1033 in the Saanich Inlet, British Columbia. Note that significant diagenetic transformations of P occur in less than 8000 years in the Saanich Inlet setting, driven by high organic matter input, whereas they occur on timescales of a million years in the relatively organic poor deep sea sediments of the eastern equatorial Pacific.

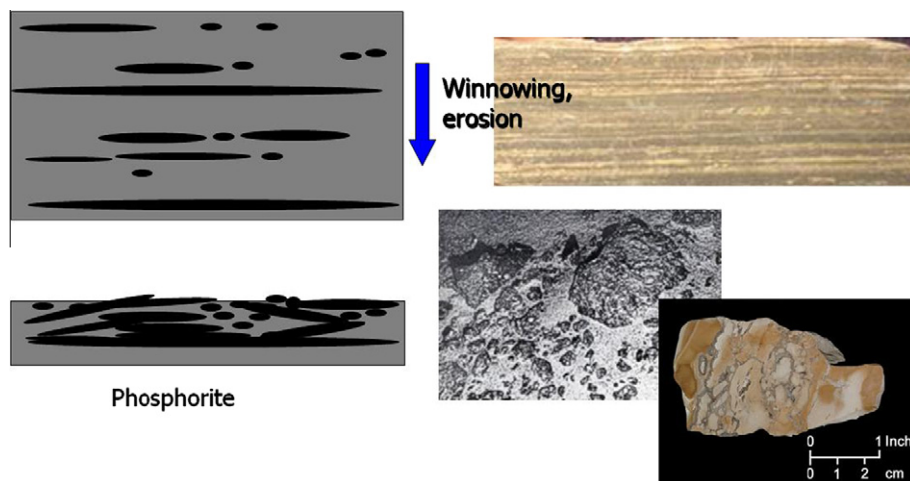
#### 4.2. Phosphorite formation

Marine sediments with disseminated CFA, or even those with more concentrated occurrence of CFA as in the phosphate shale example, do not constitute phosphate rock reserves, at least given modern mining and purification economics. Indeed, the phosphate rock reserves are exclusively phosphorites, defined as a rock with P concentrations exceeding 9% (Blatt and Tracy, 1996). Most marine sediments have relatively constant concentrations of reactive (i.e., non-detrital) P, whereas the P concentration in phosphorites is about  $100\times$  higher (Table 1). Thus, the sedimentological process that “mines” and concentrates widely disseminated CFA or even more concentrated accumulations, as in the phosphatic shale example above, is a critical component of phosphorite formation.

The typical marine setting for phosphorite formation is a continental shelf-slope environment with extremely high surface productivity, limited dilution by terrigenous sedimentation, and periodic winnowing and reworking. The modern analogy for this ideal environment is the Peru Margin. This setting has high coastal upwelling which produces tremendous phytoplankton blooms and high burial rates of organic matter with incorporated P. Terrigenous input is limited by terrestrial dynamics—the Andes Mountains create a rain shadow effect for easterly storm jets, and thus

the western Andes are extremely arid resulting in little river input into the Pacific. Additionally, a number of off-shore basins exist along the Peru margin, with proximal basins effectively trapping what little terrigenous input occurs in the setting (Garrison et al., 1990). Finally, variations in sea level driven by glacial cycles drive periodic migration of longshore and along-margin eddies. This allows for the accumulation of organic-rich material and related phosphogenesis within these sediments, followed by high current activity and winnowing of the lighter clay and organic material away from (in this case, off-shore of) the sediments and the concentration of phosphatic materials into hardgrounds and lag deposits characteristic of phosphorites.

This dynamic, multi-stage process of sedimentation, phosphogenesis, and winnowing, repeated many times, yields the characteristic sedimentology of phosphorites and results in their extremely high P concentrations (Fig. 6). This is the truly unique aspect of phosphorites, and the reason why phosphorites cannot be formed in deep sea environments, which have slow CFA formation rates and typically lack the energy for concentration, or in proximal environments like the Saanich Inlet in British Columbia which experience too much dilution from terrigenous runoff. Some past environments were well-suited for phosphorite formation, often for different reasons, as can be seen in contrasting the major



**Fig. 6.** The sediment reworking process of converting sediments that have undergone high rates of phosphogenesis, as in the phosphatic shale model and example in the upper portion, into phosphorite deposits, as in the phosphorite model and the photos of off-shore phosphatic crusts (black and white photo, Blake Plateau) and the high-grade phosphorite hand sample (Bone Valley Member, Hawthorne Formation, Florida).

phosphatic deposits of the USA. The Miocene Hawthorne Formation was deposited along the open continental shelf of the southeastern US and experienced early diagenetic phosphogenesis, but was the product of significant mid-Miocene sea level variation and related extensive reworking (Compton et al., 1993). The Permian Phosphoria Formation of Utah, Wyoming and Idaho was deposited along the margins of an intracontinental seaway, where productivity may have been influenced by wind-blown sediment input and the flux of evaporative brines that pulled nutrient-rich water further into a shallow embayment setting (Hiatt and Budd, 2001). The depositional setting of the Phosphoria Formation resulted in a number of discrete beds, related to deeper water settings with high concentrations of vanadium, cadmium, selenium, and uranium—age equivalent phosphorites deposited in near-shore settings are relatively free of these toxic metals (Hiatt and Budd, 2003). Finally, the phosphatic sediments of the Miocene Monterey Formation were deposited under highly anoxic conditions in transform sedimentary basins along the California margin that were caused by tectonic movement related to early San Andreas faulting. Although proximal basins trapped most of the terrigenous sediments, allowing for extremely pure organic matter sediments in the basins farther off-shore, the lack of reworking energy in these deep basins limited the formation of true phosphorites to a few horizons and hardgrounds—the rest of the CFA remains in laminae and nodules interbedded with organic-rich shale and dolomite.

An interesting aspect of phosphorite formation is that it occurs during an interval of non-deposition or even sediment removal, via working or winnowing. Thus, although net P accumulation might be high during sedimentation and during the actual process of phosphogenesis, it is low or even zero during times of phosphorite formation. Thus, intervals of phosphorite formation are not necessarily driven by high P input from weathering or even intervals of high biological production.

### 5. Phosphate rock reserves: a reflection on economic and environmental viability

Most of the reserves with the highest economic viability have been exploited. The clean high-quality guano phosphates from low-lying atolls in the central Pacific like Banaba Island and Nauru have been completely exploited for over a decade now, although

there is some discussion of re-mining the spoil piles given the high phosphate prices today. Many of the more P-rich horizons from standard phosphate rocks have also been depleted, resulting in average P content of mined phosphate ore to decline from 15% P in 1970 to less than 13% P by 1996 (Smil, 2002). The declining quality of current reserves and the inherently low economic viability of and environmental consequences of extraction for other potential phosphate rock resources signals a need for a careful examination of P usage.

In the state of Florida (USA), the well-known Bone Valley Member of the Hawthorne Formation has been mined since the late 1800s. Since that time, extraction operations have not changed significantly. The main deposit lies under about 10–20 m of soil, so after removal of this top layer, the phosphate rocks are extracted using large draglines, and processed to purify the P and remove various impurities (like uranium and cadmium) before final processing for the raw P fertilizer ingredient. The waste produced from processing is in the form of phosphogypsum, which contains enough radioactive material that it is unusable for any other purpose and is stored in large stacks and settling ponds on site. These settling ponds, and indeed even the piles, have inherent environmental risks, as evidenced by several dam bursts which have transported the phosphogypsum material and clays into waterways, causing large fish kills. But in terms of resource limitation, the bottom line is that the Bone Valley Member is simply running out. About 730 km<sup>2</sup> of the deposit within the Peace River watershed has already been mined and now is reclaimed. Mining companies are seeking permits to mine additional portions of the member to the south, but as this area of Florida becomes increasingly developed, the potential for expanded mining diminishes. This situation is the particular case for phosphate given that it is only economic as a surface-based extraction operation. Ironically, the people who depend on a P-limited food production system are further limiting that production by developing on top of the resource.

Along the west coast of North America the extensive Miocene Monterey Formation stretches from the Central Coast of California into Baja California. The Monterey Formation hosts organic- and P-rich sedimentary rocks, and is found both on-shore and off-shore (Föllmi and Garrison, 1991). Although the phosphatic shales of the Monterey Formation (Fig. 2) contain a reasonable amount of P (~6%), intervals of phosphatic hardgrounds exists within the formation which are classic examples of phosphorite formation due to

sedimentation variations and can contain up to 20% P (Föllmi and Garrison, 1991). By all measures, the P content of the Monterey Formation makes it at least a candidate for extraction should the price of phosphate be favorable. But it is difficult to conceive of such an economically favorable situation for several reasons. First, much of the on-land coastal Monterey Formation is developed. Second, off-shore-mining of phosphate rock has never been attempted, and thus the vast portions of the off-shore Monterey Formation are out of reach—as are the exposed phosphatic ledges of the Blake Plateau and the Peru margin, for example. Finally, the active tectonics of coastal California results in the sedimentary deposits being folded and faulted, and not flat-lying and easily accessible as is the case for the Bone Valley Formation of the Hawthorne Formation.

Clearly, economics engenders innovation, and we will see technologies and environmental controls in the next century that will open up some currently uneconomic phosphate rock resources to extraction. Off-shore mining of phosphorites will be a top target as land-based reserves are depleted and price increases. For example, off-shore Namibia and South Africa have large estimated P reserves with very high P contents related to reworked Neogene phosphorites on the middle and outer shelf and are being targeted by for potential mining by Namibian Marine Phosphate, a joint venture between several Australian and Namibian companies (Namibian Sun, November 22, 2010). But we should be equally clear in realizing that there is no technological “out” for the P problem. There simply are limited resources on the earth’s surface, there is no biological replacement for elemental P, and the global population’s demand for P continues to increase with global population (Table 1; Gilbert, 2009).

## 6. Conclusions

Determining the mechanisms for phosphate rock formation in the context of marine geochemistry is important to understanding the limited availability of P-rich rock deposits on Earth. The biogeochemical process of phosphogenesis has been found to be widespread in marine sediments, overturning previous concepts of its uniqueness. But the combination of phosphogenesis plus sedimentologically favorably conditions for sedimentary phosphate accumulation plus dynamic oceanographic conditions for winnowing and concentration of P into phosphorites leads to the geographically and temporally restricted occurrence of phosphate rock reserves on Earth. Those reserves are being rapidly depleted at current usage, and this likely will be accelerated with continued global population growth. Given the resource limitation, drastic steps should be taken to increase the efficiency of P use in agriculture, reduce the loss of P from agricultural soils, consider crops that more effectively mine the P that has been over-applied (e.g., perennial crops), and effectively recycle P from our waste streams (Smil, 2002; Cordell et al., 2009). It is surprising that so much global attention has been paid to “peak oil” that we have missed noticing the threat of “peak phosphorus”—it is time to turn that trend around, as we will have to wait tens of millions of years for geological processes to restore the concentrated P that we have disseminated in two centuries.

## Acknowledgements

I would like to thank a fantastic set of colleagues and organizers who participated in the Phosphorus Cycle workshop of the Aspen Global Change Institute for introducing me to the P scarcity literature and for being interested in the geologic aspects of phosphate reserve formation. Reviews by John Compton, Eric Hiatt, and David

Vaccari were extremely helpful. I acknowledge research support from the NSF (OCE9711957, BCS9911526, OCE0452428).

## References

- Algeo, T.J., Berner, R.A., Maynard, J.P., Scheckler, S.E., 1995. Late Devonian oceanic anoxic events and biotic crises: “Rooted” in the evolution of vascular land plants? *GSA Today* 5, 64–66.
- Benitez-Nelson, C.R., 2000. The biogeochemical cycling of phosphorus in marine systems. *Earth Sci. Rev.* 51, 109–135.
- Bennett, E.M., Carpenter, S.R., Caraco, N.F., 2001. Human impact on erodible phosphorus and eutrophication: a global perspective. *Bioscience* 51, 227–234.
- Blatt, H., Tracy, R.J., 1996. *Petrology*, second ed. Freeman, New York.
- Broecker, W.S., Peng, T.-H., 1982. *Tracers in the Sea*. Eldigio Press, Palisades, New York.
- Cook, P.J., McElhinny, M.W., 1979. A reevaluation of the spatial and temporal distribution of sedimentary phosphate deposits in the light of plate tectonics. *Econ. Geol.* 74, 315–330.
- Colman, A.S., Holland, H.D., 2000. The global diagenetic flux of phosphorus from marine sediments to the oceans: Redox sensitivity and the control of atmospheric oxygen levels. In: Glenn, C., Prévôt-Lucas, L., Lucas, J. (Eds.), *Marine Authigenesis: From Microbial to Global*, vol. 66. SEPM Special Publication, pp. 53–76.
- Compton, J., Mallinson, D., Glenn, C., Filippelli, G., Föllmi, K., Shields, G., Zanin, Y., 2000. Variations in the global phosphorus cycle. In: Glenn, C., Prévôt-Lucas, L., Lucas, J. (Eds.), *Marine Authigenesis: From Microbial to Global*, vol. 66. SEPM Special Publication, pp. 21–34.
- Compton, J.S., Hodell, D.A., Garrido, J.R., Mallinson, D.J., 1993. Origin and age of phosphorite from the south-central Florida Platform: Relation of phosphogenesis to sea-level fluctuations and  $\delta^{13}\text{C}$  excursions. *Geochim. Cosmochim. Acta* 57, 131–146.
- Cordell, D., Drangert, J.-O., White, S., 2009. The story of phosphorus: Global food security and food for thought. *Global Environ. Change* 19, 292–305.
- Delaney, M.L., 1998. Phosphorus accumulation in marine sediments and the oceanic phosphorus cycle. *Global Biogeochem. Cycle* 12, 563–572.
- Farrell, J. et al., 1995. Late Neogene sedimentation patterns in the eastern equatorial Pacific Ocean (Leg 138). In: Blum, P., Gersonde, R., Hodell, D. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results*, vol. 138. College Station, Texas, pp. 717–756.
- Feely, R.A., Massoth, G.J., Baker, E.T., Cowen, J.P., Lamb, M.F., Krogsland, K.A., 1990. The effect of hydrothermal processes on midwater phosphorus distributions in the northeast Pacific. *Earth Planet Sci. Lett.* 96, 305–318.
- Föllmi, K.B., 1995. 160 m.y. Record of marine sedimentary phosphorus burial: Coupling of climate and continental weathering under greenhouse and icehouse conditions. *Geology* 23, 859–862.
- Föllmi, K.B., 1996. The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. *Earth Sci. Rev.* 40, 55–124.
- Föllmi, K.B., Garrison, R.E., 1991. Phosphatic sediments, ordinary or extraordinary deposits? The example of the Miocene Monterey formation (California). In: Muller, D.W. et al. (Eds.), *Controversies in Modern Geology*. Academic Press, London, pp. 56–84.
- France-Lanord, C., Derry, L.A., 1994.  $\Delta^{13}\text{C}$  of organic carbon in the Bengal fan: source evolution and transport of C3 and C4 plant carbon to marine sediments. *Geochim. Cosmochim. Acta* 58, 4809–4814.
- Froelich, P.N., 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: a primer on the phosphate buffer mechanism. *Limnol. Oceanogr.* 33, 649–668.
- Garrison, R.E., Kastner, M., 1990. Phosphate sediments and rocks recovered from the Peru margin during ODP Leg 112. In: Suess, E., von Huene, R. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results*, vol. 112. College Station, Texas, pp. 111–134.
- Garrison, R.E., Kastner, M., Reimers, C.E., 1990. Miocene phosphogenesis in California. In: Burnett, W.C., Riggs, S.R. (Eds.), *Phosphate Deposits of the World. Neogene to Modern Phosphorites*, vol. 3. Cambridge University Press, pp. 285–299.
- Gilbert, N., 2009. The disappearing nutrient. *Nature* 461, 716–718.
- Hiatt, E.E., Budd, D.A., 2001. Sedimentary phosphate formation in warm shallow waters: new insights into the paleoceanography of the Permian Phosphoria Sea. *Sediment. Geol.* 145, 119–133.
- Hiatt, E.E., Budd, D.A., 2003. Extreme paleoceanographic conditions in a Paleozoic oceanic upwelling system: organic productivity and widespread phosphogenesis in the Permian Phosphoria Sea. In: Chan, M.A., Archer, A.W. (Eds.), *Extreme Depositional Environments: Mega End Members in Geologic Time*, vol. 370. Geological Society Special Paper, pp. 245–264.
- McManus, J., Berelson, W.M., Coale, K.H., Johnson, K.S., Kilgore, T.E., 1997. Phosphorus regeneration in continental margin sediments. *Geochim. Cosmochim. Acta* 61, 2891–2907.
- Planavsky, N.J., Rouxel, O.J., Bekker, A., Lalonde, S.V., Konhauser, K.O., Reinhard, C.T., Lyons, T.W., 2010. The evolution of the marine phosphate reservoir. *Nature* 467, 1088–1090.
- Riggs, S.R., 1984. Paleocceanographic model of Neogene phosphorite deposition, US Atlantic continental margin. *Science* 223, 123–131.
- Riggs, S.R., Sheldon, R.P., 1990. Paleocceanographic and paleoclimatic controls of the temporal and geographic distribution of Upper Cenozoic continental margin

- sediments. In: Burnett, W.C., Riggs, S.R. (Eds.), *Phosphate Deposits of the World. Neogene to Modern Phosphorites*, vol. 3. Cambridge University Press, pp. 53–61.
- Ruttenberg, K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* 37, 1460–1482.
- Ruttenberg, K.C., 1993. Reassessment of the oceanic residence time of phosphorus. *Chem. Geol.* 107, 405–409.
- Ruttenberg, K.C., 2003. The global phosphorus cycle. In: Schlesinger, W.H. (Ed.), *Treatise on Geochemistry*, vol. 8. Elsevier, NY, pp. 585–643.
- Ruttenberg, K.C., Berner, R.A., 1993. Authigenic apatite formation and burial in sediments from non-upwelling continental margin environments. *Geochim. Cosmochim. Acta* 57, 991–1007.
- Ruttenberg, K.C., Goñi, M.A., 1997. Phosphorus distribution, C:N:P ratios, and  $\delta^{13}\text{C}_{\text{oc}}$  in arctic, temperate, and tropical coastal sediments: Tools for characterizing bulk sedimentary organic matter. *Mar. Geol.* 139, 123–146.
- Schenau, S.J., Slomp, C.P., De Lange, G.J., 2000. Phosphogenesis and active phosphorite formation in sediments from the Arabian Sea oxygen minimum zone. *Mar. Geol.* 169, 1–20.
- Schindler, D.W., Hecky, R.E., Findlay, D.L., Stainton, M.P., Parker, B.R., Paterson, M.J., Beaty, K.G., Lyng, M., Kasian, S.E.M., 2008. Eutrophication of lakes cannot be controlled by reducing nitrogen input: results of a 37-year whole-ecosystem experiment. *Proc. Natl. Acad. Sci. USA* 105, 11254–11258.
- Schlesinger, W.H., 1997. *Biogeochemistry: An Analysis of Global Change*. Acad. Press, San Diego.
- Sheldon, R.P., 1981. Ancient marine phosphorites. *Annu. Rev. Earth Planet Sci.* 9, 251–284.
- Sheldon, R.P., 1989. Phosphorite deposits of the Phosphoria Formation, western United States. In: Notholt, A.J.G. et al. (Eds.), *Phosphate Deposits of the World. Phosphate Rock Resources*, vol. 2. Cambridge University Press, pp. 53–61.
- Smil, V., 2000. Phosphorus in the environment: Natural flows and human interferences. *Annu. Rev. Energy Environ.* 25, 53–88.
- Smil, V., 2002. Phosphorus: global transfers. In: Douglas, P.I. (Ed.), *Encyclopedia of Global Environmental Change*. John Wiley & Sons, Chichester, pp. 536–542.
- Tamburini, F., Föllmi, K.B., 2009. Phosphorus burial in the ocean over glacial-interglacial time scales. *Biogeosciences* 6, 501–513.
- Tsandev, I., Slomp, C.P., Van Cappellen, P., 2008. Glacial-interglacial variations in marine phosphorus cycling: Implications for ocean productivity. *Global Biogeochem. Cycle* 22, GB4004.
- Tyrell, T., 1999. The relative influence of nitrogen and phosphorus on oceanic primary productivity. *Nature* 400, 525–531.
- USGS, 2009. *Mineral Commodity Summaries: Phosphate Rock*, United State Geological Survey, Reston, VA.
- Vincent, E., Berger, W.H., 1985. Carbon dioxide and polar cooling in the Miocene: the monterey hypothesis. In: Sundquist, E.T., Broecker, W.S. (Eds.), *The Carbon Cycle and Atmospheric CO<sub>2</sub>: Natural Variations Archean to Present*, vol. 32. American Geophysical Union Monograph, pp. 455–468.
- Wheat, C.G., Feely, R.A., Mottl, M.J., 1996. Phosphate removal by oceanic hydrothermal processes: An update of the phosphate budget of the oceans. *Geochim. Cosmochim. Acta* 60, 3593–3608.