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

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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.

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

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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[a]	0.09		
Marine sediments[b]		8.4×10^{11}	
Continental margins	0.11		
Phosphorites	10–20		
Deep Sea	0.18		
Hydrothermal	0.6–1.5		
Soils[c]	0.015	40–50	
Ocean[b]	~0	93 000	
Phosphate Rock Ore[d]	13	2300	20
Morocco and Western Sahara		820	3.4
China		531	7.9
USA		158	3.9
Manure (cow)[e]		0.4	>15
Sewage[e]		2–3	3
Human demand of phosphate rock ore			
Human demand 2000[e]			20
Human demand 2050[e]			30
Time to reserve exhaustion 2010 demand	115 years		
Time to reserve exhaustion 2050 demand	77 years		

[a] Blatt and Tracy (1996).
[b] Ruttenberg (2003).
[c] Schlesinger (1997).
[d] USGS (2009).
[e] 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