Phosphate Mineral Reactivity and Global Sustainability

Eric H. Oelkers¹ and Eugenia Valsami-Jones²

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Phosphorus is a unique element. It is the limiting nutrient controlling
biological productivity in many terrestrial and marine environments.
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biological **biological productivity in many terrestrial and marine environments. When in excess, however, dissolved phosphate leads to uncontrollable biological growth and water-quality problems through a process called eutrophication. The use of phosphate minerals and their products as fertilizers has increased tremendously global food production; it would not be possible to feed the current world population without phosphate fertilizers. Yet phosphate is a limited global resource; current estimates suggest economic phosphorus supply may be severely depleted over the next 100 years. Nevertheless, mineralogists and geochemists have invested little time investigating phosphate mineral stability, reactivity, and transformations. This issue attempts to bring phosphates to the forefront of our scientific endeavours.**

> **KEYWORDS: phosphate minerals, eutrophication, apatite, fertilizer production, global sustainability**

INTRODUCTION

This thematic issue provides an overview of biotic and abiotic reactions involving phosphate minerals and discusses the consequences of these reactions for global sustainability. It is motivated by the importance of the role phosphate minerals play in natural and industrial processes. Phosphorus (P) is the 11th most abundant element in the lithosphere. It occurs as an oxyanion (phosphate, $PO₄³$) under the conditions prevailing on Earth, commonly as a constituent of either an inorganic mineral phase or an organic molecule. Phosphorus is a major constituent of deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine diphosphate (ADP), and adenosine triphosphate (ATP). Phosphorus is required for life to occur. Reactions at phosphate mineral surfaces play a major role in making fertilizers work (Becker 1989). As part of our bones, phosphate minerals keep us upright (Mann et al. 1989; Driessens and Verbeeck 1990) and, as the main component of our teeth, they enable us to chew our food (LeGeros 1991). Phosphate minerals provide an effective way to remediate metal-contaminated waters (Xu et al. 1994; Chen et al. 1997) and contribute to materials/medical technologies, such as bioceramics (Hench and Wilson 1993), and to medicine (Aoki 1991). Moreover, phosphate minerals are currently being considered both as possible additives to backfill for confinement of nuclear

waste (Perrone et al. 2002) and as potential actinide and iodine storage hosts (e.g. Boyer et al. 1998; Guy et al. 2002; Chaïrat et al. 2006).

Human activities have seriously impacted the natural cycling of phosphorus on Earth, not unlike that of carbon although one that is far less understood and discussed. Gabriel Filippelli presents in this issue the scale and significance of these effects (Filippelli 2008). Phosphorus is also recycled constantly at a far smaller scale within soils; as discussed in this issue by David Manning, this cycle has also been disrupted by humans, mostly as a result of agriculture (Manning 2008). Simon Parsons and Jennifer

Smith outline how phosphate minerals may hold the key to solving a major modern challenge: treatment strategies for removing nutrients from wastewaters before their release into the environment (Parsons and Smith 2008). Jill Pasteris and co-authors explore how evolution has optimised phosphate minerals to form the hard parts of mammalian anatomy (Pasteris et al. 2008). Finally, Eric Oelkers and Jean-Marc Montel provide a mechanistic approach to the contribution that phosphate mineral reactivity can make to nuclear waste disposal (Oelkers and Montel 2008). All these topics require some basic understanding of the behaviour of natural phosphate, which is summarized below.

THE MAJOR PHOSPHATE MINERALS

Huminicki and Hawthorne (2002) tabulated the names, chemical formulae and lattice parameters of nearly 400 phosphate compounds, but relatively few such compounds control phosphate concentrations in natural systems. The names, compositions and photos of selected minerals are presented in TABLE 1 and FIGURE 1. The most abundant phosphates on Earth are the apatite group minerals, $Ca₅(PO₄)₃(F,OH,Cl)$. Of these, fluorapatite, usually called simply apatite, is the most abundant. It is present in almost all igneous rocks, typically comprising 0.1 to 1 volume percent (vol%), though in some cases it may be significantly higher. Apatite occurs in both thermally and regionally metamorphosed rocks and reflects the phosphorus composition of the original rock. In sedimentary rocks, apatite occurs as a detrital mineral and as a primary chemical precipitate. Some extensive sedimentary deposits contain up to 80% apatite and are locally interbedded with limestone. Such deposits, called phosphorites, are commonly exploited as phosphate ore. Much of the phosphate in these deposits is formed directly from P-rich aqueous solutions via diagenetic and

¹ Biogéochimie et Géochimie Expérimentale LMTG-Université Paul Sabatier-CNRS-IRD-OMP 14 av. Edouard Belin 31400 Toulouse, France E-mail: oelkers@lmtg.obs-mip.fr

Department of Mineralogy The Natural History Museum London, United Kingdom E-mail: e.valsami-jones@nhm.ac.uk

biochemical processes in the sediments, although significant phosphorus deposits can originate from skeletons and guano. Apatite minerals also form the hard parts of many living organisms. Hydroxylapatite makes up 65 to 70% of mammal bones, the remainder being mostly organic compounds (Turek and Buckwatler 1994). The apatite crystal structure is very accommodating, allowing the incorporation of nearly half of the elements in the periodic table. Thus apatite serves as a repository for minor and trace elements in rocks (Hughes and Rakovan 2002).

The heavy-metal phosphate minerals monazite, xenotime and rhabdophane are widely distributed as microcrystals in crystalline and sedimentary rocks. Monazite occurs as an accessory mineral in granitic rocks and as large crystals in

REE stands for rare earth elements

pegmatites. Because monazite and xenotime are resistant to weathering (e.g. Oelkers and Poitrasson 2002), they can be concentrated in stream and beach sands. Together with apatite, they are a major source of rare earth elements (REE), uranium and thorium. As such they play a significant role in U–Th–Pb dating of rocks and minerals (Parrish 1990). These minerals have served as thorium and uranium ores and their solubility controls to a large degree the REE signature of natural waters (cf. Johannesson et al. 1995; Köhler et al. 2005). The low solubility and slow dissolution rates of the anhydrous heavy-metal phosphates have led many to propose their use in radioactive waste storage (Sales et al. 1983).

Many phosphate minerals are popular with collectors and are used in jewellery. Perhaps the phosphate mineral best known to the general public is turquoise, an opaque, bluegreen mineral, prized as a gem for thousands of years because of its unique color. Autunite is one of the more attractive radioactive minerals. Its green and yellow colour, fluorescence and crystal aggregates that resemble inflated mica books make this distinctive mineral very popular with collectors. Wavellite, with its classical radiating, globular crystal habit, is another sought-after phosphate mineral.

AVAILABILITY IN NATURAL WATERS

Phosphorus is an essential nutrient for all life forms and a key element in many physiological and biochemical processes. It is taken up by most living organisms from natural waters, but its dissolved concentration is limited by the low solubility of phosphate minerals. An estimate of the solubility of metal phosphate minerals is presented in FIGURE 2. In natural waters with $pH > 6$, apatite is the least soluble species, whereas in more acidic waters, variscite and strengite may limit phosphate availability. The concentration of aqueous phosphate in equilibrium with these minerals also varies dramatically with pH. At extremely low pH, aqueous phosphate in equilibrium with strengite can reach 100 ppm, but

Images of selected phosphate minerals: (**A**) apatite, Wolley Farm, Devon, UK; (**B**) autunite, Spokane Co., Washington, USA; (**C**) pyromorphite, Wheal Alfred Phillack, Cornwall, UK; (**D**) turquoise, **FIGURE 1**

West Phoenix Mine, Linkinhorne, Cornwall; (**E**) vivianite, Blackbird mine, Lemhi Co., Idaho, USA; (**F**) wavellite, Trenice, near Horovice, Bohemia, Czech Republic. COPYRIGHT NHM PICTURE LIBRARY

at near-neutral conditions, the concentration of phosphate in equilibrium with variscite and apatite ranges from 1 to 40 ppb. At high pH, phosphate in equilibrium with apatite becomes even less soluble. As a result of its low solubility, phosphorus is the critical limiting element for animal and plant productivity in most environments on Earth's surface. Historically this limitation was overcome by recycling manure, but more recently, phosphate-rich fertilizers have been used to dramatically increase global agricultural productivity, greatly increasing dependence on phosphate production.

In response to the low concentration of phosphate in natural waters, some microorganisms have developed methods to enhance phosphate liberation from minerals (e.g. Newman 2001). Such processes have been shown to modify reaction rates at mineral surfaces (e.g. Hutchens et al. 2006). The ability of microorganisms to exploit minerals for essential elements may define which environments can sustain life, both on Earth and on other planets, and they have likely played a role in the origin of life itself.

PHOSPHATE CONCENTRATIONS: ESSENTIAL AND TOXIC

Although phosphorus is critical for life, excess phosphorus causes environmental destruction in both fresh and marine ecosystems. Overabundance in natural waters results from phosphate fertilizers, human sewage, and detergents. Because phosphorus is often the limiting nutrient for plant growth, an oversupply can trigger rapid growth of aquatic plants and algae (Smith et al. 1999). The organic mat that forms blocks sunlight. When the nutrients are depleted and the plants or algal blooms die, they are decomposed aerobically by bacteria. This releases phosphorus but depletes the dissolved oxygen in the water. In the dark, $O₂$ -depleted water, plankton and fish die, destroying the food chain. The overall process is called eutrophication. An example of a eutrophic river is shown in FIGURE 3.

Although a concentration of 0.08 to 0.10 mg/L orthophosphate (PO₄⁻³) may trigger periodic blooms, long-term eutrophication is usually prevented if total phosphorus and orthophosphate levels are below 0.5 mg/L and 0.05 mg/L, respectively (Dunne and Leopold 1978). To minimize eutrophication risk and limit algal growth, the U.S. Environmental Protection Agency water quality criteria require that phosphate not exceed 0.05 mg/L if streams discharge into lakes or reservoirs, 0.025 mg/L within a lake or reservoir, and 0.1 mg/L in streams or flowing waters not discharging into lakes or reservoirs (U.S. Environmental Protection Agency 1986).

GLOBAL PHOSPHATE MINERAL RESOURCES

Phosphate rock is the only economic source of phosphorus for production of fertilizers and chemicals. About 80% of world phosphate production is derived from deposits of sedimentary marine origin. About 17% comes from igneous rocks and their weathering derivatives and the remainder comes from residual sedimentary and guano deposits. In sedimentary deposits, the main phosphate mineral is microcrystalline carbonate-fluorapatite (formerly known as francolite), which occurs in association with a variety of accessory minerals and impurities (McClellan and Van Kauwenbergh 1990).

Economically produced ore typically contains 20–30% P₂O₅. Like natural phosphate minerals, phosphate rock is sparingly soluble, and fertilizer production requires creating a more soluble form. In the typical treatment, sulfuric acid

Solubility of mineral species that control aqueous phosphate concentration at 25ºC as a function of pH (after Stumm and Morgan 1996). The calculations assume equilibrium with $AI(OH)3$ and α -FeOOH and concentrations of aqueous Ca and F fixed at 0.01 and 0.0001 molal, respectively. **FIGURE 2**

The eutrophic Verdouble River near Les Gorges de Gouleyrous in southern France. PHOTO BY TERESA RONCAL-HERRERO **FIGURE 3**

is used to produce phosphoric acid, the basic material for fertilizer production. More than 90% of the phosphate rock mined in the United States is used for making fertilizer.

A summary of global phosphate production is provided in TABLE 2. The United States, China and Morocco collectively produce more than 60% of global supplies. The United States is the leading exporter of fertilizers, accounting for approximately 45% of global exports (Prud'homme 2005), but US dominance of the export market is currently declining as a result of competition from other countries. It is interesting that there are no major phosphate deposits in Europe. Global production of phosphate rock (FIG. 4) increased dramatically during the last century to meet the demands of agriculture. Production peaked during the mid-1980s, in part as a response to global concerns about eutrophication. The price of phosphate ore remained close to \$20–30 (inflation adjusted) per metric ton over much of the past century (FIG. 5).

PHOSPHATE ROCK PRODUCTION AND RESOURCES FOR 2005 (Jasinski 2006) **TABLE 2**

FIGURE 4 Global phosphate production (U.S. Geological Survey 2007)

Cost of phosphate rock from 1900 to 2005 in constant 1998 US dollars (U.S. Geological Survey 2007) **FIGURE 5**

Estimates of the future of global resources

Because most phosphate is used for fertilizer, estimates of the duration of global phosphate reserves are linked to estimates of future agricultural needs and efficiency. Increased life expectancy, decreased child mortality and improved farming methods, which have increased food production, have led to exponential world population growth over the last 150 years, raising our numbers from 1 billion to 6 billion by the beginning of this century. Currently, world population is growing by 1.5% per year. Although difficult to estimate accurately, UN population projections suggest a decrease in this rate, such that the population will remain roughly constant at 10 billion after 2050 (United Nations 1998). Agricultural production and phosphate consumption may, however, increase faster than global population. As the world becomes richer, increased demand for meat, dairy products and other 'higher quality' foodstuffs will modify existing consumption patterns. Thus, global phosphate demand may increase by as much as 2–2.5% annually over the next several decades. Such estimates suggest that half the global phosphate resources will be consumed during the next 60 to 70 years. This depletion will set off a progressive increase in prices, as extraction and processing costs rise and as countries holding deposits become conscious of their value. Decreased agricultural production, because of dwindling fertilizer availability, could have grave consequences for society in the future.

CHALLENGES FOR EARTH SCIENTISTS

One of the obvious roles for Earth scientists is to improve our ability to limit the mobilization of phosphorus from agricultural and other human sources to natural waters where it causes eutrophication. This may be achieved by developing 'designer' fertilizers with formulations that allow better control of the rate of phosphorus release. Alternatively, if methods are developed to recycle phosphorus from waste forms (e.g. sewage sludge and effluents), it may be possible to use current resources more effectively and conserve the limited global phosphate reserves (Valsami-Jones 2004). Another area of active research is finding ways to take advantage of the low solubility of many metal phosphate minerals, such as pyromorphite and actinide phosphates, to design better methods to immobilize toxic and radioactive waste (cf. Valsami-Jones et al. 1998).

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Adenosine Triphosphate (ATP): The Currency of Life

Adenosine triphosphate (ATP) is probably the most important phosphate compound of all. It is the universal energy "currency" for all known life forms. ATP and its reaction products provide or store energy for all organism activity. The reaction takes place within the cell and is responsible for a range of functions, including metabolism, DNA synthesis, and cellular motility.

ATP consists of a central sugar molecule, ribose (which also happens to be the foundation for DNA) (green in the figure) bounded to a base, adenine (purple), on one side (adenine plus ribose = adenosine) and to three phosphate groups on the other (red). The three phosphate atoms are the key to ATP's worth. The bonds between P and O are very strong, so when the end phosphate is released by the activity of an enzyme, the cell gains a lot of energy. The adenosine diphosphate (ADP) that is produced can further react, loosing a second phosphate, releasing more energy, and leaving adenosine monophosphate, AMP.

When the cell needs to store energy gained from food or sunlight, reverse reactions reattach two phosphate groups. This molecular "rechargeable battery" is essential for life, explaining

why phosphate supply is critical. In order to ensure a ready reservoir, vertebrates have developed a storage system that doubles as the skeleton's building material. In bones, we carry around our emergency stockpile of phosphorus.

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