

A Technological Gem: Materials, Medical, and Environmental Mineralogy of Apatite

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1811-5209/15/0011-0195\$2.50 DOI: 10.2113/gselements.11.3.195

Apatite has numerous applications that benefit society. The atomic arrangement of the apatite crystal structure and its rich and variable chemistry impart unique properties, which permit a wide range of technological and scientific applications in an array of disciplines outside of the traditional Earth sciences, including ecology, agronomy, biology, medicine, archeology, environmental remediation, and materials science. In our daily lives, apatite is essential for sustaining and enhancing human life through agricultural amendments, through bone replacements, through fluorescent lights, and through environmental remediation of contaminated soils. Apatite is truly a technological gem.

KEYWORDS: apatite, fertilizer, bone, fluorescent lights, bioceramics, radionuclide disposal

INTRODUCTION

It is difficult to think of a mineral with a historically longer-lasting and presently more diverse set of applications than apatite. The general term “apatite” in this paper refers to the calcium phosphate apatites, defined as fluorapatite, hydroxylapatite, chlorapatite, and the solid solutions among those end-members. As our dominant source of phosphorus, apatite is a critical mineral for sustaining human population through agricultural amendments. Extracted phosphorus is also essential to many industrial materials that rely on apatite ore. However, the significance of apatite to society is by no means limited to its role as a source of phosphorus (TABLE 1). Understanding the structure and chemistry of apatite and having an awareness of its current applications will help scientists to better refine its utility and to develop yet unforeseen uses of this technological gem.

AN APPETITE FOR APATITE: HUMAN NUTRITION

Feeding the World

Phosphorus is frequently the most limited of the essential element nutrients in the biosphere. Insufficient phosphorus can compromise, or even shut down, biological activity. Apatite is the most abundant naturally occurring phosphate mineral and, therefore, forms the foundation of the global phosphorus cycle (Filippelli 2008). It is the most important ore of phosphorus, which is used in many applications

(TABLE 1). The global biogeochemical cycling of phosphorus begins when phosphorus is released from apatite, naturally or anthropogenically, at the Earth's surface as phosphate (PO_4)³⁻. Free phosphate (i.e. not bound in crystal structures) is then able to cycle through the hydrosphere and biosphere where it is an essential constituent of life. Consequently, one of the most important uses of phosphorus, as extracted from apatite, is in the production of fertilizer to help grow our crops.

FIGURE 1 (Hughes 2015) illustrates the dramatic rise in world production of phosphorus since 1900, mined principally from apatite-rich sedimentary phosphorites. Superimposing the growth curve for human population on that of fertilizer use during the same period reveals that the two curves are essentially parallel. This highlights the profound human impact on the global phosphorus cycle in the past 150 years. Apatite-based fertilizer is necessary to help feed the world's population. The 2007 world average consumption was 3.7 kg of P per person per year, though this value varies widely by country, largely correlated with bovine meat consumption (of grain-fed herds) and, more recently, with the production of bioenergy. Ten percent of phosphate fertilizer in the US is used to produce ethanol (Elser et al. 2012). As the need for phosphate grows, concerned debate surrounds the time at which the maximum global phosphorus production rate is reached (“peak phosphorus”; Cordell et al. 2009). Dramatic price instability for “phosphate rock” began in 2007 and continues to this day (InvestMine 2014³), raising concerns by some about the eventual affordability of phosphate for fertilizer in the near future. Others, however, are estimating hundreds of years of phosphate ore availability.

Don't Waste It

Agricultural use of apatite can also have broad-ranging negative environmental implications. The widespread, and often intensive, application of synthetic fertilizer on fields produces phosphate-rich runoff. When such phosphate-contaminated runoff enters body of water, it can cause eutrophication because phosphorus encourages the rampant growth of algae (blooms). Such blooms cause the plants and animals in that ecosystem to die. Similarly, excess phosphate can be released into the environment

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3 InvestMine (2014) Historical Phosphate Rock Prices and Price Chart. www.infomine.com/investment/metal-prices/phosphate-rock/all/

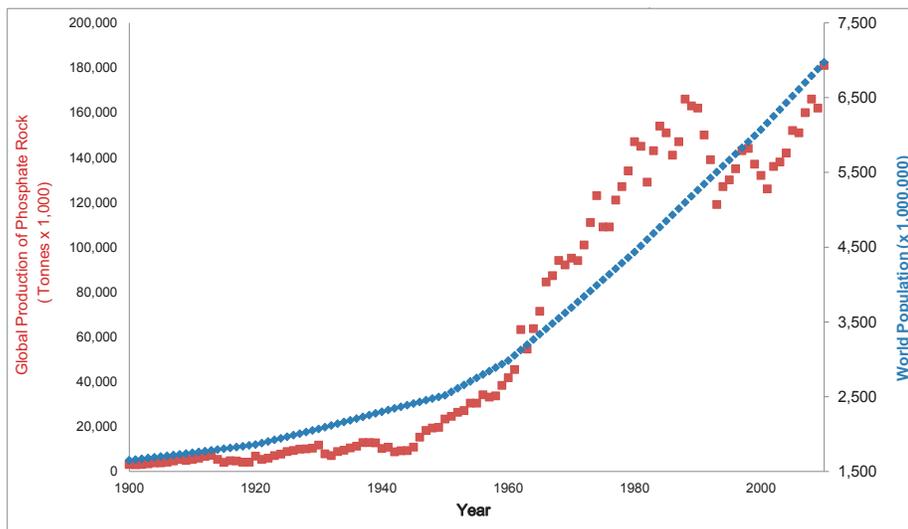


FIGURE 1 Diagram showing how the global annual production of phosphate rock (red) tracks the estimated world population (blue). FROM HUGHES (2015).

through either raw or treated sewage, which is enriched in phosphate because animals (including humans) consume plant and animal material.

The dual challenges of managing waste phosphate versus the increasing agricultural need for phosphate have created emerging technologies. For instance, as documented by the European Sustainable Phosphorus Platform (ESPP; www.phosphorusplatform.eu), there is now large-scale technical capability and increasing government encouragement to recycle the phosphate removed from wastewater and from agricultural waste.

BIOAPATITE AND BIOMATERIALS: SUPPORTING HUMAN HEALTH

Apatite is Us: Tooth and Bone

Teeth (dentin and enamel) and bones are composed of apatite (Fig. 2). Biologically precipitated apatite (nanocrystalline bioapatite) is structurally very similar to hydroxyl apatite but differs compositionally in the extensive substitution of carbonate for PO_4^{3-} (mostly) and the incorporation of ~3 wt% molecular water in the structure. Bioapatite in bone and in tooth dentin contains about 6 wt% CO_3^{2-} , whereas that in tooth enamel has only about 3.5 wt% CO_3^{2-} (LeGeros 2008). There is an intimate connection between apatite's composition and its properties. The additional carbonate in bone apatite makes its crystallites much smaller and more soluble than those in tooth enamel: this fulfills the need for bone apatite to be readily resorbable. Solubility is important for the bone remodeling/replacement process that is ongoing in our bodies and that is systematically regulated by our cells. Tooth enamel, in contrast, is a harder and more dissolution-resistant apatite that must protect the tooth and provide a durable chewing surface. Enamel consists almost totally of mineral; bone is only about 50% mineral by volume, the rest of the bone comprising water and a fibrous protein called collagen, which provides a physical framework and a spatial template for the incorporation of nanocrystals of bioapatite.

Bone is, in fact, a natural biological nanocomposite of carbonated apatite and collagen that is hierarchically ordered on several spatial scales from nanometers to centimeters (Weiner and Wagner 1998; Pasteris et al. 2008; Skinner and Ehrlich 2014). The nature of the two

component materials in bone, their mode of interfacing, and their hierarchical structure are what provide bone with its remarkable combination of strength and flexibility. The need for such mechanical properties, in addition to specialized biological and chemical properties, offers scientists a stiff challenge when attempting to create substitutes for diseased or damaged natural bones and teeth.

The term “biomaterial” has come to refer to a large, diverse group of synthetic organic and inorganic materials that are engineered to interact therapeutically with a biological system, either alone or as part of a complex system or nanoscale composite. Hydroxylapatite is the basis for the carbonated apatite that forms the mineral component of tooth and bone; thus, it is one of the

phases used alone or as part of a mineral-organic composite to repair or replace teeth or bones (Gross and Berndt 2002; Dorozhkin 2009, 2013).

The remarkably accommodating structure of apatite has allowed medical researchers and biomedical engineers to produce a wide array of medically useful apatites (as well as other calcium phosphate phases) that differ in crystallite size, degree of crystallinity/atomic order, and composition (e.g. with carbonate or silica substituting for phosphate); these are referred to as bioceramics (Fig. 3A,B,E). By its very nature, apatite is biocompatible with body tissue (see TABLE 1 BIOLOGY/MEDICINE SECTION). The variations in formulation can control how osteoinductive (encouraging of bone growth) and osteoconductive (providing a scaffold on which bone can grow) apatite can be (LeGeros 2008) (Fig. 3C,D). Researchers can synthesize biomimetic apatite

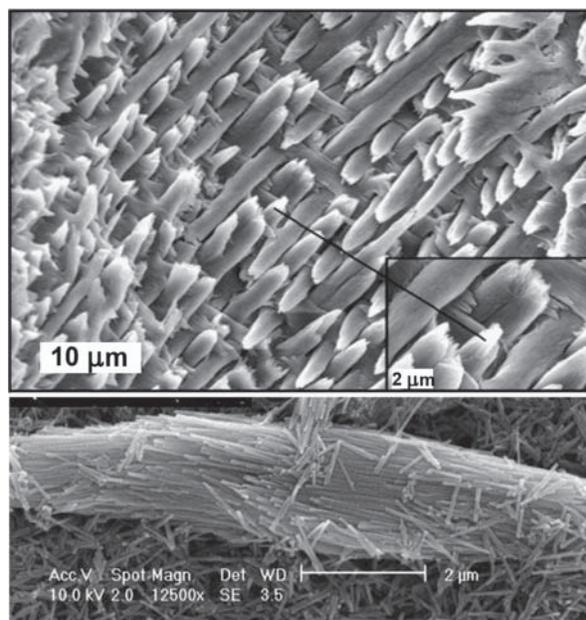


FIGURE 2 (TOP) SEM of tooth enamel from the acid-etched, ground-down surface of a mouse incisor. Shows the alignment of enamel prisms consisting of bundles of oriented carbonated apatite crystals. Scale bars = 10 μm and 2 μm . REPRINTED FROM FINCHAM ET AL. (1999) WITH PERMISSION OF ELSEVIER. (BOTTOM) SEM of tooth enamel, showing that one enamel prism consists of many apatite crystals. Scale bar = 2 μm . REPRINTED FROM CHEN ET AL. (2005) WITH PERMISSION OF ELSEVIER.

TABLE 1 THE PRINCIPAL TECHNOLOGICAL AND SCIENTIFIC USES OF APATITE.

	Application	Properties Utilized
Geology	Petrogenetic indicator	Major- and trace-element composition
	Geochronology (dating)	Radionuclide composition, fission tracks
	Ore of phosphorus and REE	Composition (P and REE)
Environmental	Heavy-metal and phosphate sequestration	Elemental affinity, chemical stability, insolubility
	Solid nuclear waste form	Thermal and chemical stability, annealing temperature, elemental affinity
	Water treatment	Elemental affinity, deflocculant
	Fertilizer	Constituent phosphate
Biology/Medicine	Orthopedics	Natural constituent of bone
	Dentistry	Natural constituent of teeth
	Nanoparticle drug delivery agent	Size, morphology, structure, solubility, biocompatibility
	Prosthetic coating, bone and tooth replacement media	Compositional and structural similarity to mineral in bones and teeth
Materials	Phosphors	Optical emission
	Lasers	Optical emission and lasing behavior
	Gems	Color, diaphaneity, chatoyancy

or can collect (from vertebrates) actual biological apatite, which would have the crystal size, the surface chemistry and texture, and the solubility of natural bone (FIG. 3E).

Many apatite biomaterials begin their fabrication as precipitates from aqueous solutions below 100 °C. However, they typically are then sintered at temperatures between 900 °C and 1200 °C. Such heating transforms the apatitic material structurally (reordering atoms, eliminating defects) and chemically (releasing CO₂ and H₂O) into well-crystalline stoichiometric hydroxylapatite, which causes the precipitate to be much less soluble, decreases its porosity, and greatly alters its surface chemistry.

The physical properties of apatite biomaterials are tunable. Another high-temperature form of biomaterial apatite is plasma-sprayed hydroxylapatite that is used, for example, as a coating on metallic devices to

improve their biocompatibility as surgically implanted prosthetics. The total porosity, pore sizes, and grain sizes of apatite are medically important. Fine-grained apatite, from nanocrystalline to millimeter-scale granules, can be created for packing into disease-induced gaps in bone. Hydroxylapatite-based injectable cements can, in turn, be introduced into voids in bone. These cements also can be molded or carved into appropriate shapes (Gross and Berndt 2002; Dorozhkin 2013). The success of such diverse bioactive calcium phosphate biomaterials seems to lie in their ultimate utilization by the body as if they were bone in need of remodeling. Such compounds can be resorbed (at a rate established by the details of their chemistry and crystallinity) and the released ions then reprecipitated as normal bioapatite by specialized bone cells (Pasteris et al. 2008; Skinner 2013).

“New and Improved Versions”

Materials scientists are unimpressed with the mechanical properties of hydroxylapatite ceramics, which are brittle and have a tensile strength less than that of bone (Dorozhkin 2009). This recognition accounts for the common use of metal rods and other metallic parts to fully or partially replace bone. Biomaterials designers do realize that the chemical and biological properties of bioapatite are important, but they feel free to augment naturally occurring phases with others that increase functionality. One such augmented bioapatite is biphasic calcium phosphate, which was developed as mixtures of highly crystalline hydroxylapatite plus beta tricalcium phosphate [Ca₃(PO₄)₂] in various proportions (LeGeros 2008; Daculsi et al. 2009). Upon introduction into the body, the more soluble beta tricalcium phosphate dissolves first, stimulating bone growth, whereas the less soluble hydroxylapatite acts both as an immediate stable construct and as a long-term, slow-release component to provide ongoing ion delivery for sustained bone formation. Biphasic calcium phosphate can be used to make a moldable, injectable, resorbable bone cement. Moreover, antibiotics or other drugs can be incorporated in bone cement to provide a site-specific slow release (Daculsi et al. 2009; Dorozhkin 2013).

There are many examples of how the properties of apatite are weighed against those of other compounds in the selection of the most appropriate biomaterial to address a specific medical condition. A particular challenge is to develop spherical implants for cosmetic (non-functional)

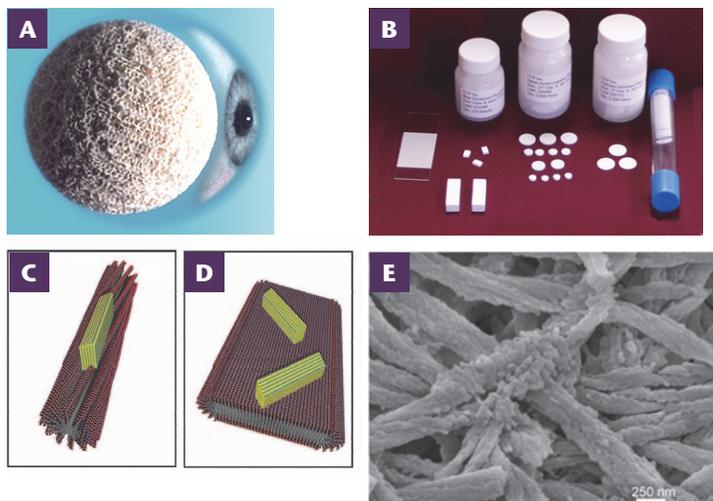


FIGURE 3 Apatite-based biomaterials. **(A)** Bio-Eye® “Hydroxyapatite orbital implant.” FROM WWW.IOI.COM **(B)** Commercial hydroxylapatite in disks, blocks, and powder. FROM WWW.CCPCORP.COM/PHOTOS/CCPCORP1_BIG.JPG **(C)** and **(D)** Schematic view of how the geometry of an organic template (red and gray) may control the orientation and alignment of hydroxylapatite crystals (yellow). REPRINTED FROM NEWCOMB ET AL. (2012) WITH PERMISSION OF JOHN WILEY AND SONS. **(E)** Biomimetically apatite-mineralized collagen fibers, after heating to 600 °C. The *c* axes of hydroxylapatite crystals align with collagen fibers. Scale bar = 250 nm. REPRINTED FROM LI AND APARICIO (2013)

eye replacements. Such replacements typically consist of two parts: the semi-spherical orbital implant, and the ocular prosthesis, which is a convex shell—having the appearance of the sclera, cornea, iris, and pupil—that fits on top of the orbital implant. Hydroxylapatite is often chosen to make orbital implants, though other implant materials are also used. What is unique to hydroxylapatite implants, however, is the self-healing they induce in small perforations that often occur in tissue surrounding an implant. This important property reflects hydroxylapatite's strong biocompatibility, which is related to its similarity to the mineral in bone (Baino et al. 2014).

Some special properties of hydroxylapatite were recognized long before we could produce it synthetically. Dating back to 1899 in Germany, trabecular (spongy) cow bone was used for orbital implants. Spheres of bone material were first heated to several hundred degrees Celsius to remove all organic tissue (mostly collagen), thereby leaving behind a highly crystalline framework of micrometer-scale hydroxylapatite crystals that mimicked the interconnecting pores of the original bone (Baino et al. 2014).

The manufacture of porous hydroxylapatite for implants requires the means to produce both the desired chemistry and porosity. Bone-derived material is no longer accepted due to concerns about bovine spongiform encephalopathy (“mad cow disease”) and other possible diseases that might be transmitted even by heated bone. The two materials now typically used are coral-derived hydroxylapatite and synthetic hydroxylapatite. The exoskeleton of a coral consists of finely crystalline aragonite (a polymorph of calcite) in a highly porous framework. Depending on the coral species, the pores are ~150–1000 micrometers in diameter. Decades ago it was determined that coral (CaCO_3) could be hydrothermally processed with $(\text{NH}_4)_2\text{HPO}_4$ to produce a slightly carbonated hydroxylapatite, the carbonate component making this apatite more bone-like than end-member hydroxylapatite. From a physical standpoint, what is produced is an apatite pseudomorph that retains the coral's macrostructure and porosity (Gross and Berndt 2002).

Creating Novel Composites with Apatite

Another way in which hydroxylapatite is used in biomaterials is in a variety of composites, typically with a synthetic or natural (collagen) polymer. The addition of a polymer to hydroxylapatite crystallites increases flexural strength and strain (% deformation), while decreasing Young's modulus (stiffness) compared to hydroxylapatite alone. The polymer is selected for its material properties and its biocompatibility and dissolution properties. Some hydroxylapatite composites have mechanical properties better than those of bone (Gross and Berndt 2002). Multiple laboratories have now created biomimetic collagen–hydroxylapatite composites by placing collagen fibers in solutions of simulated body fluid and allowing slightly carbonated (due to CO_2 in the air) hydroxylapatite crystallites to precipitate on and within bundles of collagen fibers.

PHOSPHORS, LASERS, AND VIBRANT COLORS

Lighting the World

Due to their physical and chemical properties, apatite and the apatite group minerals are used in many industrial materials applications, notably fluorescent lighting (FIG 4A). The presence of manganese, rare earth elements, lead, and other activators in apatite give it fluorescent properties (FIG. 4A) that make apatite useful in the phosphor and laser industries (Waychunas 2002; Rakovan and Waychunas 2013). Have you ever wondered why all fluorescent light

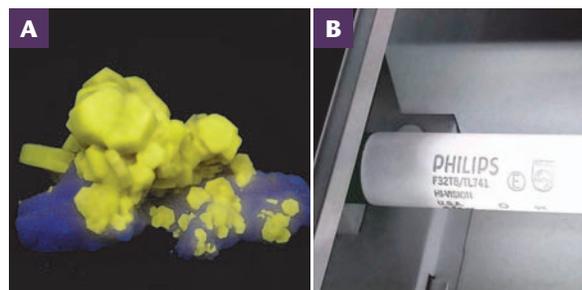


FIGURE 4 (A) Naturally fluorescent apatite under shortwave ultraviolet light, from Darrah Pech, Kunar Province, Afghanistan. Specimen is 10 cm across. (B) Fluorescent light bulb with Mn–Sb-doped apatite halophosphore. PHOTOS: JOHN RAKOVAN

bulbs are translucent rather than transparent? It is because of apatite. The inside of a fluorescent light bulb is coated with synthetic apatite that has been doped with manganese, antimony, or rare earth elements: the visible light emitted from the bulbs is created by the fluorescence of the doped apatite coating (FIG. 4B). Some of the rare earth elements used to dope this synthetic apatite may have been obtained from natural apatites that were mined as an ore of these elements (TABLE 1).

Fluorescent bulbs commonly consist of a tube containing mercury and a gas such as argon. At each end of the bulb is an electrode. When the bulb is energized, electrons flowing between the electrodes ionize the mercury vapor. The mercury then emits ultraviolet light that the apatite—the halophosphor—absorbs and converts into visible light. By slightly varying the apatite phosphor composition, the emission color balance can be tailored, allowing for bulbs with “warm white,” “white,” and “daylight” emissions.

Halophosphate fluorescent light bulbs have been in use for many decades. More recently, since the early 1990s, a new design of fluorescent light has come into use. Commercially known as “triphosphors,” these bulbs are based on fluorescence from three different phosphors that individually emit in the red, green, and blue. The blue-emitting phosphor is commonly europium-doped apatite.

Why so Many Colors?

The causes of luminescence and color in apatite are closely related. Substituents such as the first row transition elements and the lanthanides can lead to luminescence (they are activators) and impart color (are chromophores). Crystal imperfections such as site vacancies, vacancies with trapped electrons, and point defect clusters, can likewise



FIGURE 5 (A) A 10-carat (1.5 cm tall) faceted fluorapatite gemstone. PHOTO: TERRY HUIZING. (B) A 35-carat (1.5 cm wide) chatoyant fluorapatite cabochon, PHOTO: MARK MAUTHNER. Both are from a granite pegmatite located near Manambato, Ambilobe District, Madagascar.

influence color and luminescence. Because of its affinity for chromophoric substituents and its propensity for other defects, apatite is found in just about all colors of the rainbow (Rakovan and Waychunas 2013). Because of its beautiful and often intense color, natural apatite, not surprisingly, has been used as a gemstone (FIG. 5A). The use of apatite as a gem material (TABLE 1) dates back as far as the Neolithic. Beads of blue-green apatite have been found by archeologists at the sixth millennium BC Çatal Hüyük site in Turkey. Interestingly, early users of apatite did not recognize this mineral for what it is. Not until the late 18th century was apatite recognized as a distinct species (Werner 1788). Prior to this, apatites were mistaken for other similar-looking minerals, such as beryl. It is that confusion that led to the name “apatite,” which stems from a Greek word meaning “to deceive.”

Set to Stun!

The luminescence activated by various rare earth elements, such as Nd and Yb, has also been employed in the development of numerous types of apatite lasers. The structural and compositional complexity offered by apatite allows for tailoring of fundamental laser parameters, including the emission lifetime and cross section, as well as the pump line-width and saturation parameters, which in turn allow adjustment of the pumping, storage, and energy extraction characteristics (Payne et al. 1994).

ENVIRONMENTAL REMEDIATION: APATITE TO THE RESCUE

One of the most rapidly expanding areas of apatite science and technology is in the field of environmental mineralogy (TABLE 1): the study of the dynamic interaction between minerals and the environment and the effect of minerals on environmental chemistry, water quality, human health, contaminant remediation, and microbial processes (Brown and Calas 2011). The development of this science will encourage additional “mineral engineering” for environmental remediation and protection. One such application of apatite is the sequestration and stabilization of heavy metals, such as lead and arsenic, in contaminated sediments and water.

The heavy metal remediation strategy is based on reducing the bioavailability of these elements. If the metals are present in a form that cannot get into plants and animals or are nonreactive (cannot be metabolized), then they are *nonbioavailable*. Instead of removing the metals from the environment, which can be extremely laborious and expensive, the idea is to change their speciation to a stable (highly insoluble), nonbioavailable form, such as bound in the crystal structure of one of the apatite-group minerals. Once formed, such metal phosphates typically have very low solubility over a range of pH values, thereby retaining the contaminant metals, assuring their nonbioavailability, and substantially reducing their health risk.

Because apatite can incorporate such a large number of substituent elements (Hughes and Rakovan 2015 this issue), the potential use of apatite as a sequestration agent is broad. Apatite-based remediation can include the engineered in situ precipitation of a contaminant-incorporating apatite or the direct addition of apatite to a sediment by mixing or by restricted placement, such as in a permeable reactive barrier (FIG. 6A). The engineered formation of an apatite phase in contaminated soils and sediments is a new and promising method for sequestering harmful metals—including radionuclides—and for other types of environmental remediation (Magalhães and Williams 2007). In the case of in situ precipitation, individual concentrated solutions of calcium and phosphate are injected into contaminated sediments where they can mix, resulting in apatite formation (FIG. 6B).

The direct addition of apatite to a sediment, sometimes called phosphate-induced metal stabilization (PIMSTM), has been employed in many ways, one of which involves the use of cleaned fish bones, patented as Apatite IITM (Wright et al. 2005).

There are two fundamental mechanisms by which the direct addition of apatite to a contaminated soil may work to sequester metals. The first is adsorption of the contaminant to the apatite surface. The degree of dispersion retardation and, hence, the effectiveness of the remediation will vary depending on such factors as the nature of the adsorption mechanism, the metal speciation, and the state of overgrowth onto or aggregation of the particles to which the metal is adsorbed. Although this can be a useful methodology in metal remediation, adsorption typically provides less stable sequestration than incorporation, but both desorption and dissolution will release sequestered contaminants. The second mechanism is dissolution–precipitation, in which apatite that is added to the contaminated soil or water dissolves and releases phosphate that is free to combine with the contaminant metal to form another solid phase. The primary metal that has been remediated to date by this mechanism is lead, which is known to be a major health hazard and can cause nervous-system disorders in children. After apatite dissolves in the contaminated water or soil moisture, the phosphate combines with lead to form pyromorphite, $Pb_5(PO_4)_3Cl$ (Maneck et al. 2000), one of the apatite-group minerals with a particularly low solubility and, hence, high contaminant-retention capacity.

A related environmental problem is the disposal of contained liquid industrial waste. This problem is particularly germane to radioactive waste products from weapons manufacture or spent nuclear fuel. Another environmental application of apatite, which is not yet in use but is being actively investigated, is as a solid to incorporate nuclear

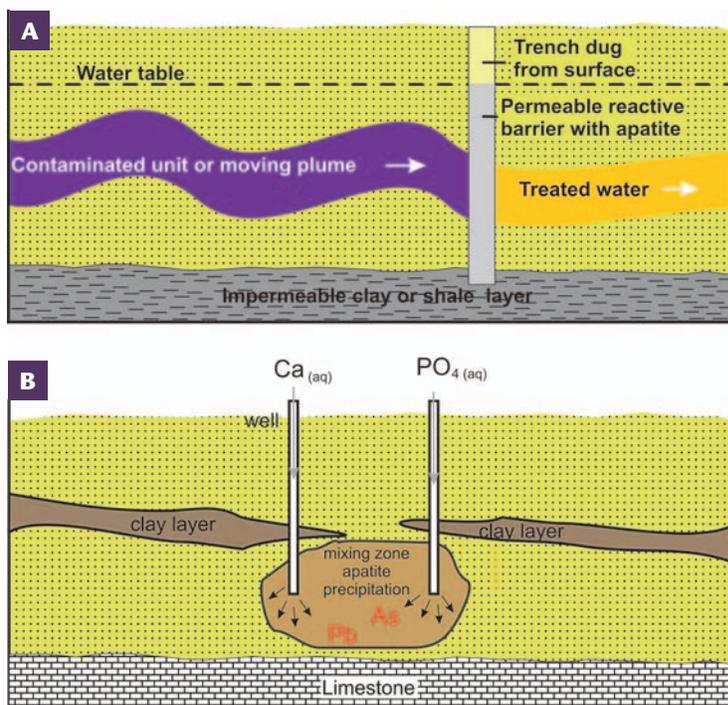


FIGURE 6 Schematics illustrating two fundamental methods of applying apatite to contaminant sequestration. (A) Isolated emplacement, in this case as a permeable reactive barrier, where sequestration occurs by sorption or dissolution–precipitation. (B) In situ precipitation and contaminant incorporation by injection of aqueous Ca^{2+} and PO_4^{3-} into contaminated soils.

waste (Ewing and Wang 2002). The idea is to put radionuclides into the stable apatite structure and then dispose of the apatite in deep geological repositories. Radionuclide disposal in the form of relatively insoluble apatite will greatly decrease the potential of the radioactive elements to disperse into the environment (e.g. through groundwater) after they are buried. Solid nuclear waste forms, in which apatite is one component of a composite material, are also being explored (Ewing and Wang 2002).

Apatite has three characteristics that make it useful for dealing with radioactive elements. First, a high capacity to incorporate many radionuclides of concern, as well as some of the fission products resulting from their decay. Second, a good chemical stability (e.g. low solubility in natural waters) depending on the geochemical environment for disposal. Third, a propensity to rapidly anneal radiation damage. These are the same characteristics that make apatite an important mineral for geological dating (Chew and Spikings 2015 this issue).

Thus, when it comes to environmental remediation, apatite could be our heavy metal hero.

APATITE: HOUSEHOLD TO HIGH-TECH

Apatite and its constituent phosphorus have not passed from the limelight into graceful semiretirement, as some geological materials have (due to lack of interest or banning of their usage). Phosphorus is essential for

feeding the world's population via its use in agriculture, and phosphorus has many vital industrial applications. Most modern rechargeable lithium batteries are based on lithium-iron-phosphate cathodes (synthetic triphylite, LiFePO_4). Every lithium-iron-phosphate battery in an electric car contains 60 kg of phosphorus (Elser et al. 2012). In addition, nearly 40 million metric tons of phosphoric acid are produced annually, which are used to make food and drink additives, to manufacture detergents, as gasoline (petrol) additives, to make insecticides, and to manufacture rust removers.

Phosphorus from apatite is also being used in an increasing number of industrial and scientific applications: from light bulbs to lasers, from prosthetic arms to cosmetic eyes, from heavy metal remediation agents to potential nuclear waste forms, and not forgetting the many geological applications of this ubiquitous mineral (see articles throughout this issue).

Apatite is a true technological gem.

ACKNOWLEDGMENTS

The authors wish to thank Gabriel Filippelli, Glenn Waychunas, and Catherine Skinner for their helpful reviews of an earlier version of this paper. We are grateful to John Hughes and Patricia Dove who also reviewed and contributed to this article. This work was partially supported by NSF grant EAR-0952298 to JR. ■

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