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Phosphorus: From the Stars to Land & Sea

Christopher C. Cummins

Abstract: The chemistry of the element phosphorus offers a window into the diverse field of inorganic chemistry. Fundamental investigations into some simple molecules containing phosphorus reveal much about the ramifications of this element's position in the periodic table and that of its neighbors. Additionally, there are many phosphorus compounds of commercial importance, and the industry surrounding this element resides at a crucial nexus of natural resource stewardship, technology, and modern agriculture. Questions about our sources of phosphorus and the applications for which we deploy it raise the provocative issue of the human role in the ongoing depletion of phosphorus deposits, as well as the transfer of phosphorus from the land into the seas.

CHRISTOPHER C. CUMMINS, a Fellow of the American Academy since 2008, is Professor of Chemistry at the Massachusetts Institute of Technology. His research focuses on innovating new methods of inorganic synthesis, as well as the synthesis of new simple substances. His work has recently appeared in *Inorganic Chemistry, Science, Journal of the American Chemical Society*, and *Chemical Science*, among other journals.

Inorganic chemistry can be defined as “the chemistry of all the elements of the periodic table,”¹ but as such, the field is impossibly broad, encompassing everything from organic chemistry to materials science and enzymology. One way to gain insight into and appreciate the rapidly moving and diverse field of inorganic chemistry is to view the science from the perspective of the elements themselves, since they are the basic ingredients for assembling molecules or materials – and indeed, all matter, living or inanimate. Although phosphorus may be less celebrated than carbon or hydrogen, it joins those elements (along with nitrogen, oxygen, and sulfur) to constitute the six “biogenic elements” (those needed in large quantities to make living organisms; see Figure 1).² Let us take a look at some of the issues that arise in inorganic chemistry from the perspective of phosphorus, illustrating in the process the notion that each element has its own story to tell.

Many phosphorus-containing chemical compounds are commercially valuable and have interesting or important applications.³ Lithium hexafluorophosphate, for example, is the electrolyte in common

Phosphorus: Figure 1

From the Stars to Land & Sea
Periodic Table with Nonmetals, Including Biogenic Elements, Above the Stair-Step Line

Group→	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides			57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
Actinides			89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Biogenic elements are H, C, N, O, P, S in the “nonmetals” region of the periodic table, indicated by the heavy line.
Source: Adapted from a graphic found on <http://www.openclipart.org>.

lithium-ion batteries, which are used in consumer electronics (such as laptops) and automotive applications.⁴ So how is it made? The synthesis route begins with the white form of elemental phosphorus, a simple molecular form of the element consisting of tetrahedral P_4 molecules (Figure 2).⁵ White phosphorus is combined with elemental chlorine in order to bring the phosphorus to the correct oxidation state (+5), and then, in a second step, chloride is replaced by fluoride.

This process is also frequently used to synthesize many organo-phosphorus compounds that are important components of catalysts used in the chemical industry.⁶ In these applications, again, white phosphorus is first oxidized using chlorine, and then the chloride provides the basis for the formation of carbon-phosphorus bonds.⁷ But notably, elemental chlorine is hazardous to use and ship, and environmental groups have called for an outright ban on it.⁸ So why use chlorine to oxidize phos-

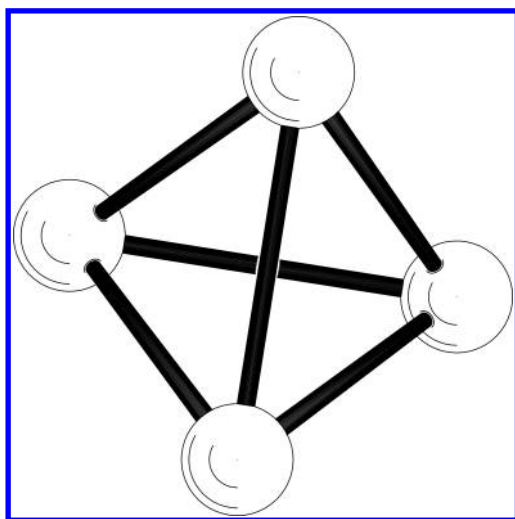
phorus if chlorine is not even present in the products, such as lithium hexafluorophosphate, that are the target of synthesis? These industry standard processes suggest there is room for improvement: if manufacturers eliminated the use of chlorine in the synthesis of important phosphorus compounds in which chlorine is absent, both hazards and waste would be significantly reduced.

Because our research has shown that it is indeed possible to derive organo-phosphorus compounds directly from white phosphorus, this is an opportunity for inorganic chemistry to improve the safety and efficiency of the manufacturing process. In one advance, we showed that phosphorus-carbon bonds can be generated by using white phosphorus together with a source of organic radicals.⁹ Each of the six phosphorus-phosphorus bonds present in a molecule of white phosphorus absorbs two organic radicals in the process of being broken; each P_4 tetrahedron is broken

Figure 2

Tetrahedral Arrangement of Atoms in a P_4 (White Phosphorus) Molecule

Christopher
C. Cummins



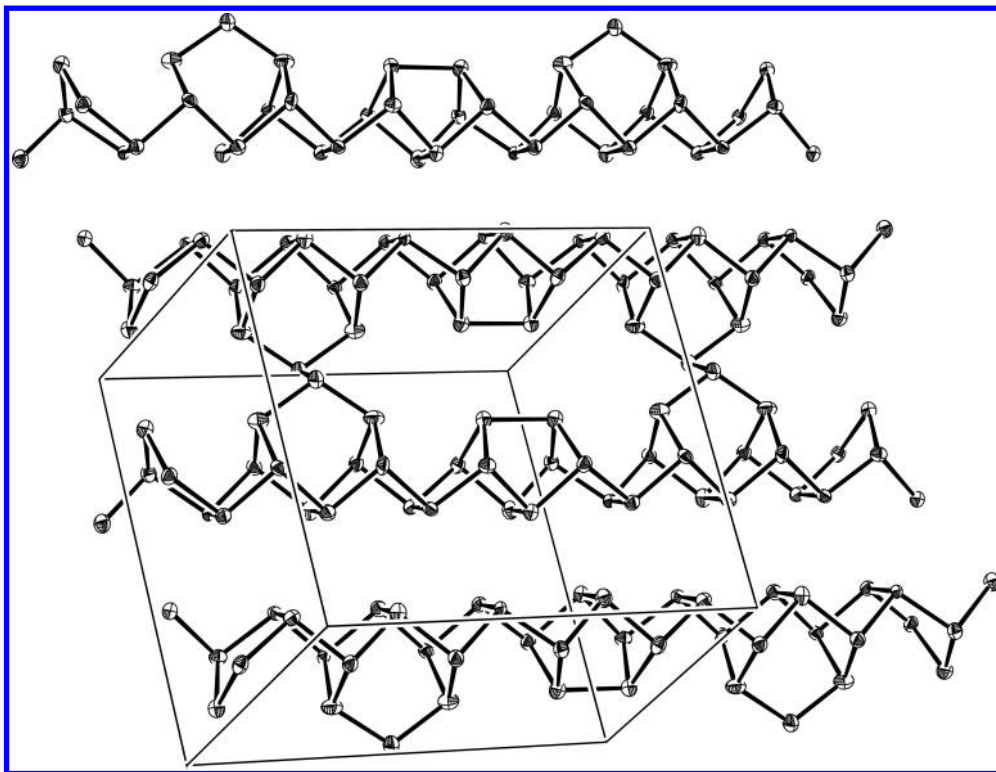
Source: Generated by the author using the PLATON program. See A. L. Spek, "Single-Crystal Structure Validation with the Program PLATON," *Journal of Applied Crystallography* 36 (2003): 7–13.

completely apart, and each phosphorus atom becomes incorporated into a freshly formed organo-phosphorus compound.

Our method for developing this new process was derived from basic inquiries into phosphorus's relationship to the elements neighboring it on the periodic table. Phosphorus is immediately beneath nitrogen on the periodic table, suggesting that these elements should have some similarities in their chemical properties. Then why, we wondered, was it the case that, while Earth's atmosphere consists mainly of triply-bonded N_2 molecules, a similar diatomic molecular form of phosphorus is neither prevalent nor even particularly stable?¹⁰ Part of the answer is that nitrogen is unusual because the stability of its multiple bond far exceeds that of the sum of an equivalent number (three) of its single bonds. So the only stable form of elemental nitrogen is the diatomic molecular form floating innocuously about in the atmosphere we breathe; in contrast, phosphorus (like its diagonal relative, carbon)¹¹ exists

in a wide variety of structural arrangements, all of which are networks exclusively based upon phosphorus-phosphorus single bonds, three for every phosphorus node. The variant known as red phosphorus, for example, has cages of phosphorus atoms connected into linear tubes (see Figure 3),¹² which in turn are cross-linked together to form a polymeric network.

Knowing this, we were inspired to ask: can we design and synthesize a molecule that would be prone to a fragmentation reaction wherein one of the fragments produced would be the diatomic molecule P_2 ? If we could, we would have the opportunity to study the properties and chemical characteristics of an all-phosphorus molecule structurally analogous to the main constituent of Earth's atmosphere. In our first attempt to produce it, the selected design incorporated a feature patterned after the reaction used to inflate an automobile airbag in the event of a collision, a process that rapidly generates nitrogen gas from a solid precursor. Our target molecule em-



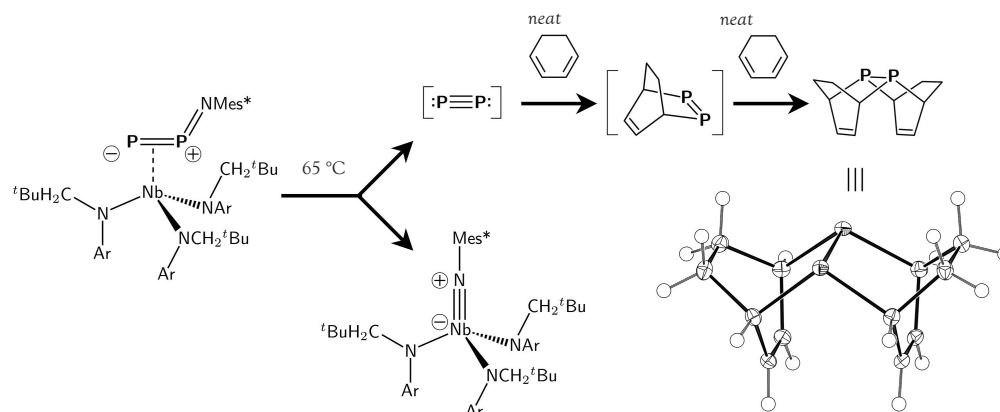
The box encloses one crystallographic unit cell. Source: Generated by the author using crystallographic coordinates from M. Ruck et al., "Fibrous Red Phosphorus," *Angewandte Chemie International Edition* 44 (2005), doi:10.1002/anie.200503017.

bedded a diphosphorus moiety into the stabilizing environment of a niobium complex (niobium is a transition metal; it forms complexes by arranging sets of molecules or ions – called ligands – around itself), from which it could be released by a stimulus of mild heating.¹³ Carrying out the fragmentation reaction in the presence of other molecules permitted the mapping of the reactivity patterns of diatomic phosphorus. One important result was the discovery that P_2 easily undergoes addition to unsaturated organic molecules, such as 1,3-cyclohexadiene (see Figure 4).

If diatomic molecular phosphorus is indeed capable of direct combination with organic molecules, then the means of its

generation should not matter. Could there be a way to access the P_2 molecule by starting from a stable form of the element, rather than from an exotic niobium complex? We found the suggestion in a lightly cited 1937 paper that the photochemical conversion of white phosphorus into the red form of the element may occur with P_2 as the key intermediary, which is initially generated and subsequently polymerizes.¹⁴ We found by experiment (see Figure 5) that the addition of methyl isoprene to a solution of white phosphorus during irradiation both inhibits the production of red phosphorus *and* yields molecules in the same class of organo-phosphorus compounds that we studied earlier in connec-

Figure 4

A Niobium Complex that Can Act as an “Eliminator” of P_2 under Thermal FragmentationChristopher
C. Cummins

In the depicted sequence, transient P_2 (not observed) combines with two molecules of 1,3-cyclohexadiene resulting in four new P-C single bonds in the stable final product (shown both as a line drawing and in a thermal ellipsoid representation from a single-crystal X-ray diffraction analysis). Abbreviations: tBu is tert-butyl, Ar is aryl (specifically 3,5-Me₂C₆H₃), and Mes* is supermesityl. Source: Adapted from material published in N. A. Piro, J. S. Figueroa, J. T. McKellar, and C. C. Cummins, “Triple-Bond Reactivity of Diphosphorus Molecules,” *Science* 313 (2006), doi: 10.1126/science.1129630.

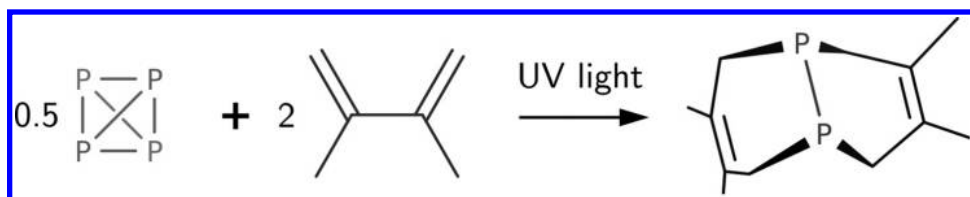
tion with niobium-mediated access to diphosphorus molecules.¹⁵ Hence, in effect and in principle, we have shown that in certain cases the hazardous and wasteful use of chlorine in the synthesis of organophosphorus compounds can be replaced with a process relying on ultraviolet radiation.

After viewing the beautiful tetrahedral molecular form of elemental phosphorus in Figure 2, one might wonder whether this arrangement of phosphorus is unique to this particular element. Arsenic (As) lies just below phosphorus on the periodic table, separated from it by the stair-step line dividing the metals from the nonmetals (see Figure 1). Once again, the periodicity of chemical properties suggests that molecular arsenic might adopt a similar tetrahedral structure to that of phosphorus. Indeed, it does, but only in the gas phase where the molecules are well isolated from one another, or in solution at low temperature and in the dark. To generate gas-

phase As₄ molecules, one heats grey arsenic (which has a layered sheet structure reminiscent of graphite or black phosphorus) to about 550 degrees C while flowing a carrier gas over it. The As₄ molecules, entrained in the carrier gas, can be led into a solvent and used for reaction chemistry before re-polymerization to grey arsenic can take place. If condensed to a solid on a cold surface, the As₄ condensate is “yellow arsenic,” but it cannot be kept. Warming to room temperature or exposure to light brings about a facile return to the grey form.¹⁶

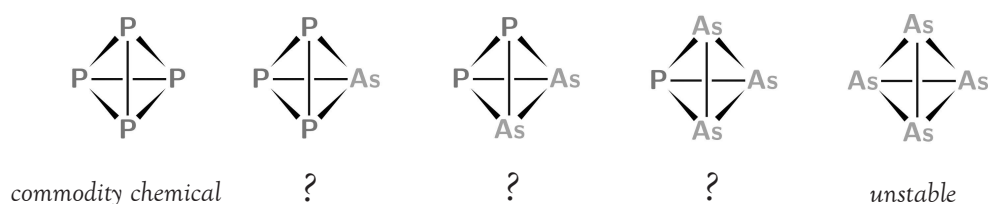
Phosphorus and arsenic lie on either side of the divide (marked on Figure 1) separating the metals from the non-metals. White phosphorus is stable enough that it can be stored as a pure liquid above its melting point of 44 degrees C and pumped into tank cars for shipping; while, conversely, samples of yellow arsenic are evanescent. We therefore wondered: would it be possible to synthesize a stable substance whose tetrahedral molecules would be composed of

Combination of Phosphorus with Methyl Isoprene under the Action of Ultraviolet Light



Methyl isoprene is the precursor to the original synthetic rubber. The reaction mechanism may involve P_2 as a reactive photo-generated intermediate.¹⁷ Source: Generated by the author using data from Daniel Tofan and Christopher C. Cummins, "Photochemical Incorporation of Diphosphorus Units into Organic Molecules," *Angewandte Chemie International Edition* 49 (2010), doi:10.1002/anie.201004385.

Figure 6

From the Commodity-Chemical P_4 Molecule to the Unstable As_4 Molecule

What are the properties of substances composed of tetrahedral molecules of mixed composition? Source: Adapted from Brandi M. Cossairt and Christopher Cummins, "Properties and Reactivity Patterns of AsP_3 : An Experimental and Computational Study of Group 15 Elemental Molecules," *Journal of the American Chemical Society* 131 (42) (2009), doi:10.1021/ja906294m.

a mixture of phosphorus and arsenic (see Figure 6)? To test this idea, we made a niobium complex carrying a P_3^{3-} unit, and combined this with a source of arsenic (3+), effectively knitting together the neutral AsP_3 molecule in a selective fashion.¹⁸ The new substance turned out to have a waxy appearance much like that of white phosphorus, and it could be purified by sublimation, wherein the pure material is condensed onto a cold probe. Because of the volatile nature of AsP_3 , we and our collaborators determined its properties by a variety of techniques, including electron diffraction, microwave spectroscopy, and photoelectron spectroscopy.¹⁹ Obtaining gas-phase property data on a simple molecule containing a heavy element (arsenic)

provides a benchmark for theorists working on the *a priori* prediction of properties; heavy elements pose the greatest challenge in this regard. The elements in the AsP_3 molecule are packaged together in a 1:3 ratio at the molecular level; and now this substance is readily available as a starting material. Substitution of a single nitrogen atom into the P_4 tetrahedron has scarcely been considered; one possibility involves stabilization inside a recently discovered spherical B_{80} molecule that is analogous to Buckminsterfullerene (C_{60}).²⁰

To ask why diatomic phosphorus is neither stable nor prevalent is really to ask a larger question: why is elemental phosphorus not found on Earth as a pure substance,

uncombined with other chemical elements? It is because elemental phosphorus is especially prone to oxidation, a process encouraged by Earth's atmosphere at this point in history. Elements that form very stable oxides (such as aluminum, phosphorus, and silicon) are not found in uncombined form on our planet unless they can be formed by biological or geological processes taking place under anaerobic conditions (as in the case of volcanic sulfur, or carbon in the form of coal and diamond). If we cannot obtain phosphorus in pure form directly by digging it out of the ground, where do we get it?

Phosphate rock (also known by its mineral name apatite) is essentially the bones and teeth of ancient marine organisms formed into concentrated deposits where long-evaporated seas once stood.²¹ It is extracted through strip mining and forms the basis for the phosphorus fine chemicals industry. One of the principal methods for white phosphorus²² production is the "thermal process," which involves use of an electric arc furnace, carbon in the form of coke as a reducing agent, and silica to absorb the oxide ions liberated in the heating process.²³ The elemental phosphorus is thus extracted from the rock in what is essentially an expensive purification process. Note that most phosphorus-containing commercial chemicals contain phosphorus in the +5 oxidation state: the same as is found in phosphate rock when it is dug out of the ground. The typical purification process reduces phosphorus's oxidation state from +5 to zero; however, when it is converted to other chemicals, chlorine is often used to return the phosphorus to its highest oxidation state (zero back to +5). (This method of making white phosphorus is, in fact, reminiscent of the one used by the alchemist Hennig Brand, who made phosphorus the thirteenth element to be obtained in pure form.²⁴ In search of the philosopher's stone, the alchemist collect-

ed great quantities of human urine, which he concentrated to a paste and subjected to reductive distillation.)

Phosphate rock is not only the basis for the fine chemicals industry of phosphorus; it is also the starting point for the (much larger) phosphorus side of the fertilizer industry. The "wet process" of purification uses sulfuric acid to generate phosphoric acid from phosphate rock, after which it can be made into critical fertilizers such as monoammonium phosphate, or MAP. Around 1940, the human population of our planet began to rise more rapidly than it had previously (since my birth in 1966 the population has doubled).²⁵ This critical rise in population growth coincided with two important developments in the fertilizer industry: the worldwide commercial deployment of the Haber-Bosch ammonia synthesis (whereby ammonia for agricultural applications is obtained by direct combination of the elements hydrogen and nitrogen); and the large-scale mining of phosphate rock deposits, mainly for fertilizer applications. Prior to the mid-twentieth century, humankind had been largely limited to locally available nutrients for crop production. Now, ammonia can be had in essentially limitless supply by combining the atmosphere's inexhaustible supply of nitrogen with hydrogen (which is currently derived from natural gas by steam reforming). Can phosphorus keep up?

Stars are the element factories.²⁶ They consist mainly of our universe's lightest and most abundant elements: hydrogen and helium. Red giants are more evolved stars with an onion-like layered structure; the most abundant metallic elements, iron and nickel, make up their core, and layers of progressively lighter elements surround them, moving outward to the surface. Elements heavier than iron and nickel are formed by neutron capture when a massive star explodes in a supernova, and these (in-

*Christopher
C. Cummins*

cluding the precious gold sought by the alchemist) are of minimal cosmic abundance. It is one of the peculiarities of nuclear physics that nuclei of odd atomic number (odd Z) are generally less stable and less abundant than those of even Z . The only stable isotope of phosphorus is ^{31}P ($Z=15$), and the ^{31}P nucleus is the product of an extremely improbable sequence of nuclear reactions (the final reaction in the sequence converts ^{31}Si into ^{31}P by proton capture), only taking place during an explosive neon burning phase in the core of massive, hot stars.²⁷ Accordingly, the cosmic abundance of phosphorus is lower – by orders of magnitude – than that of the other five biogenic elements. Indeed, to quote astrobiologist Douglas Whittet: “The only biogenic element present in the human body (and in biological tissue generally) at a concentration substantially above its solar abundance is P. If one were to attempt to place an upper limit on the total biomass present in the Universe at large, on the basis of cosmic abundances, then the critical element would be phosphorus.”²⁸ This is in keeping with the observation that, in many of the ecosystems on Earth, phosphorus is life-limiting. This means that the addition of phosphorus (usually in the form of phosphate) will bring about an abrupt bloom of life, since the absence of phosphorus was all that was holding it back.

Our land reserves of phosphorus are finite. And given the ongoing depletion of phosphate rock reserves, it is natural to ask what is left, where it is, and how long it will last. The U.S. Geological survey indicates that roughly three-quarters of the available reserves are concentrated in Morocco and Western Sahara.²⁹ Mining locations in Florida and Idaho contain the most significant amount of phosphate rock in the United States, but these constitute a small percentage of global reserves. And Central Florida’s mines have been largely

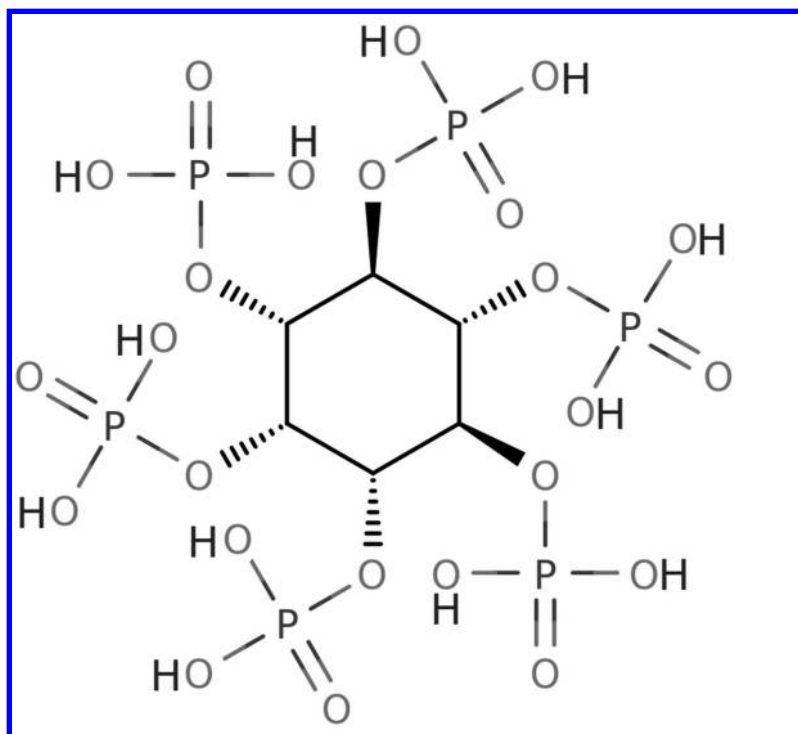
exhausted, leaving behind a legacy of radioactive phosphogypsum stacks and collapsing sinkholes.³⁰ The term “peak phosphorus” is now used with reference to the point in time when phosphate rock production (mining) will inevitably begin to taper off.³¹ Current estimates place peak phosphorus some time later in the twenty-first century.

Off the coast of Brittany, France, there are sometimes blooms of marine algae vast enough to be visible from space.³² Brittany is a livestock-producing region where large amounts of phosphate from feed is transferred to the ground water and ultimately to the ocean. This perfectly illustrates two consequences of the large-scale mining of phosphate rock and industrialized agricultural activity: first, we are depleting the concentrated reservoirs of this key nutrient; second, its dispersal into the world’s oceans can have negative effects on marine ecosystems, chiefly by causing eutrophication through overgrowth of certain species of phytoplankton.

What can we do to mitigate the movement of phosphorus from land to sea? Efforts are being directed at optimizing the separation and recovery of phosphorus from waste water, which is an important direction.³³ In some countries (such as India and Sweden), the use of toilets that separate liquid from solid waste is being adopted; phosphate can then be recovered from urine as the crystalline mineral struvite, while solid waste is composted.³⁴ Pigs cannot digest plant-derived phosphate because of the phytic acid form in which plants store it (see Figure 7), so researchers at the University of Guelph in Canada developed the Enviropig.³⁵ This genetically engineered pig secretes the enzyme phytase in its saliva, enabling the pig to digest the plant phosphate, whereupon its excreta are phosphate-poor, leading to an improvement in waste water quality. While the meat of the Enviropig is the same as that of

Figure 7
Molecular Structure of Phytic Acid

Christopher
C. Cummins



Source: Generated by the author using the program MarvinSketch. Marvin is used for drawing, displaying, and characterizing chemical structures, substructures, and reactions. See ChemAxon, Marvin 6.1.3 (2014), <http://www.chemaxon.com>.

an unmodified pig, concerns about this creative kind of genetic engineering have effectively blocked its adoption thus far.

The chemistry of an element is a fascinating thing, and we have explored several of the issues that flow naturally from asking questions about where an element comes from, what we use it for, and how we might gain an improved understanding of it. Motivated to study phosphorus by curiosity and a desire to expand on fundamental science, we have come to appreciate the vital role played by this relatively precious element that forms the inorganic backbone of DNA, the energy currency of ATP, and the main component of bones and teeth. We have demonstrated the ability to

identify ways of using this limited resource that minimize waste, but we acknowledge our limited ability to grapple with the consequences of enormous demand for phosphorus – a markedly limited resource – stemming from a rapidly rising human population. Phosphorus, therefore, is interesting not only for its chemistry but also in light of the rich texture of its larger story, only one of the many stories that emerge when we view inorganic chemistry from the perspective of a single element.

- Author's Note: I am grateful for stimulating conversations with Professor Brandi M. Cossairt, Professor Anna Frebel, Professor Jerrold Meinwald, and Dr. Willem Schipper. This material is based upon work supported by the National Science Foundation under CHE-1362118.
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²² White phosphorus is a commodity chemical that is also in demand for military applications, in which setting it is valued for its incendiary effects (including the production of smoke screens) and is known as "Willy Pete." Small quantities of white phosphorus for research purposes were previously available from many chemical suppliers. After 2001, white phosphorus ceased to be available from catalog suppliers in the United States, but since red phosphorus was still available and can be converted to the white form by simple thermal depolymerization, this was not a major impediment to researchers. Now, both red and white phosphorus are Drug Enforcement Agency (DEA) List 1 controlled chemicals, which has led to difficulty in purchasing either form of the element. Why is phosphorus on this list? While there is no phosphorus whatsoever in the chemical composition of the much-abused drug methamphetamine, a popular street method for synthesizing the drug involves a combination of phosphorus and hydrogen iodide as a reducing agent for ephedrine. For the same reason, elemental iodine is also a DEA List 1 chemical. My research group was fortunate to receive a gift of white phosphorus from Thermphos (see endnote 23); after arriving from the Netherlands, however, the shipment (which was around half a kilogram) was held up in customs in New Jersey until, with the assistance of MIT's general council and a customs broker properly licensed to receive shipments of List 1 chemicals, we were able to free the shipment.

For more on the conversion of red to white phosphorus, see J. Brodtkin, "Preparation of White Phosphorus from Red Phosphorus," *Journal of Chemical Education* 37 (2) (1960), doi:10.1021/ed037pA93.1. For more on the use of phosphorus in methamphetamine synthesis, see Harry F. Skinner, "Methamphetamine Synthesis via Hydriodic Acid/Red Phosphorus Reduction of Ephedrine," *Forensic Science International* 48 (1990): 123–134, <http://www.sciencedirect.com/science/article/pii/0379073890901047>.

²³ A company called Thermphos (recently gone out of business) in the Netherlands was situated adjacent to a nuclear power plant for the cheap electricity, and took its phosphate rock shipments from Florida, now mostly mined out. Thermphos was taking a leadership role toward the exciting goal of making phosphorus from waste and thereby realizing a vision of a sustainable phosphorus industry. White phosphorus is made in the United States as the first step in the synthesis of glyphosate. See A. D. E. Grossbard, *The Herbicide Glyphosate* (London; Boston: Butterworths, 1985).

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