The Sad Fate of the Ancient, Well-Shelled Mariners

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Five hundred million years ago, soft-bodied sea animals used phosphate to build elaborate, protective armor. Then their resource dried up, and evolution moved on.

An array of fossils, including a large Leptaena brachiopod at left, that lived during the Ordovician to the Devonian Period, 485 million to 444 million years ago.Credit...Biophoto Associates/Science Source

By Natalie Angier

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In the Cambrian Period, 500 million years ago, the armored set ruled the seas. Soft-bodied animals secreted a mineral paste that hardened into protective shells of immense strength and deco beauty, some shaped like rams' heads or eagles' wings, others like champagne flutes studded with dagger-sharp spines.

But by the Devonian Period some 70 million years later, most of these brachiopods, briopods and related well-shelled mariners had gone extinct, victims of theft and their own extravagant ways.

As researchers recently proposed in the journal Trends in Ecology and Evolution, the collapse of the brachiopod empire exemplifies a struggle that has defined life from the start: the quest for phosphorus. Scientists have long known that the element phosphorus is essential on many fronts, here holding the DNA molecule together, there powering the cell's every move. The new report emphasizes yet another way that phosphate — the biochemically useful form of phosphorus — has shaped the course of evolution as an arbiter of nature's hard parts, its shells and teeth and bones.

"Phosphorus was stolen by the vertebrates, the bony fishes," said Petr Kraft, a paleontologist at Charles University in the Czech Republic and an author of the new report. "And once this happened, they diversified quickly and took over." Dr. Kraft collaborated with Michal Mergl of the University of West Bohemia.

The research is part of a renaissance of phosphate studies, an enterprise that spans disciplines and time frames. Chemists are exploring how phosphates managed to season the prebiotic broth that gave rise to life in the first place, while materials scientists are manipulating the element into startling new colors and forms.

"If you heat phosphorus under different conditions, different temperatures, different pressures, strange things start to happen," Andrea Sella, a professor of inorganic chemistry at University College London, said. "You get red fibrous forms, metallic black forms, purple forms." You can also stack up layers of phosphorus atoms and then pull them apart into ultrathin and flexible sheets called phosphorenes, all with the goal of controlling the flow of electrons and light particles on which technology depends. “We’ve only scratched the surface of what this element can do,” Dr. Sella said.

Phosphorus was discovered in the late 17th century by a Hamburg alchemist, Hennig Brand, who inadvertently isolated it while seeking the storied “philosophers’ stone” that would transform ordinary metals into gold. Experimenting doughtily with large quantities of the golden liquid he knew best — human urine — Brand emerged with an eerie substance that lacked any Midas touch but did glow in the dark, prompting Brand to christen it phosphorus, Greek for “bringer of light.”

Editors’ Picks

A phosphorous bomb detonated during exercises in Gondrecourt, France, during World War I. Credit...U.S. Army Signal Corps, via Library of Congress

This pure form of the element, called white phosphorus, turned out to be toxic and flammable and so has been used in warfare, to make tracer bullets, smoke screens and the Allied fire bombs that destroyed Brand’s hometown during World War II.

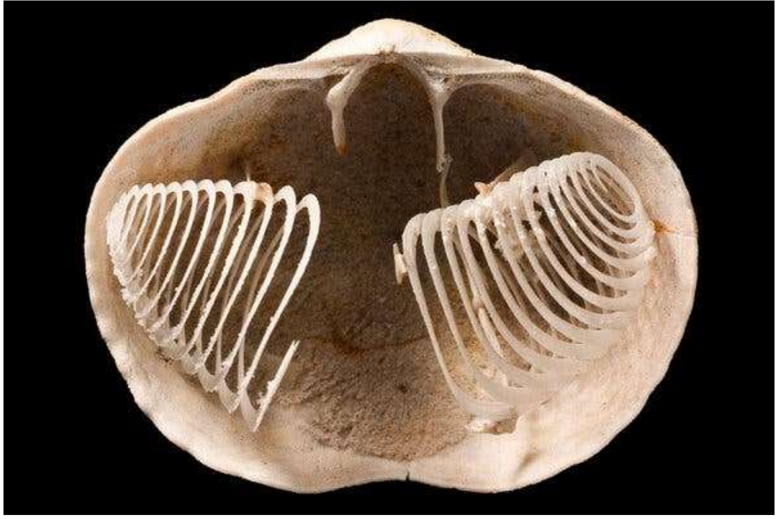
White phosphorus also won grim Dickensian fame in the 19th century, when it was added to the tips of matchsticks to produce “strike anywhere” matches. The girls and women who toiled in poorly ventilated factories churning out the enormously popular product were sometimes exposed to so much phosphorus vapor that they contracted “phossy jaw,” a horrifying condition in which their gums receded, their teeth fell out and their jawbones dissolved. According to the historian Louise Raw, matchstick makers’ struggle for safer working conditions helped galvanize the modern trade union movement.

Pure phosphorus does not exist in nature, but instead is bound up with oxygen, as phosphate, and this molecular trade union, the phosphorus-oxygen bond, “is central to why biology works,” Matthew Powner, an organic chemist at University College London, said. The body stores and burns energy by perpetually making and breaking the phosphate bonds found in the cell’s little cash machines, its adenosine triphosphate molecules, better known as ATP. The phosphate recycling operation is so relentless, Dr. Powner said, “you basically turn over your body weight in ATP every day.”

Phosphate conjoins with sugar to form the backbone of DNA, holding in meaningful order the letters of genetic information that would otherwise collapse into alphabet soup. Phosphate colludes with lipid molecules to encase every cell in an ever vigilant membrane that dictates what gets in and what must be kept out. Proteins send messages to one another by exchanging phosphate parcels.

Behind phosphate’s spectacular, jack-of-all-trades utility is a negative charge that prevents unwanted leakage. “You can put energy in and only take it out when you want to,” Dr. Powner said. “It won’t leach into the environment.” By contrast, he said, the equivalent carbon-based molecule, called carbonate, dissolves readily in water: “If you were to stitch DNA together with carbonate rather than phosphate it would all fall apart.” Dr. Powner has joked that we should consider life phosphate-based rather than carbon-based.

Image



A fossil of the brachiopod Spiriferida, showing its brachidium, a support structure that connected to the lophophore, an organ that helped in feeding.Credit...The Natural History Museum, London/Science Source

Yet unlike the other major ingredients of life — carbon, nitrogen, oxygen, hydrogen — phosphate molecules do not have a gas phase. “They’re too big to fly,” Dr. Sella said. Phosphates jump into the game of life through the erosion of rocks, the breakdown of living organisms, or waste products like urine or guano. Understanding the impact of phosphate fluxes over time is a major research endeavor.

One lingering mystery is how early life got hold of phosphate initially. Given how essential phosphate is to every aspect of biology, the primordial watery setting in which the first cells arose must have been rich in phosphate. “Yet most natural waters on Earth today are pretty lean in terms of phosphate,” Nicholas Tosca, a geochemist at Cambridge University, said. “We had expected the same to be true of the early Earth.” Iron, he explained, was thought to sequester the phosphates away.

Dr. Tosca and his colleagues at Cambridge addressed the origin-of-life conundrum in a study published recently in Nature Communications. The researchers decided to revisit the assumption, asking: What about early on, when there was much less oxygen around? Oxygen, they knew, turns iron into a form that tenaciously hoards phosphate. What would happen if oxygen were removed from the equation? The researchers created artificial seawater in a large oxygen-free glove box and discovered that, sure enough, under those conditions the dissolved iron left most of the phosphate alone, presumably available to any proto-cells in the neighborhood.

In the Trends in Ecology and Evolution paper, Dr. Kraft similarly proposed that the Cambrian seas were comparatively glutted with phosphates. Animals could soak up so much, in fact, that they could fashion thick and durable shells, as hard as the hardest tissue in the human body — the phosphatic enamel of our teeth.

“It’s a big advantage to have these shells,” Dr. Kraft said. By comparison, the shell of a modern mollusk, made of calcium carbonate, cracks easily beneath a beachcomber’s feet. But as the seas grew crowded and bony fishes appeared, phosphate supplies dwindled, and brachiopods could no longer freely scavenge what they needed to construct their expensive housing. Bony fishes were judicious in their use of phosphate as a building material: their teeth, a few parts of the skeleton, and that was it. And being mobile, fish could trap whatever phosphate and other nutrients filtered down from land to sea, before they reached the lumbering hard shells below.

The vertebrates had seized control of phosphate, and nothing could stop them now.