BIOGEOCHEMISTRY

Phosphorus burial

The formation and burial of calcium phosphate minerals removes large quantities of phosphorus from the ocean. Radiotracer experiments reveal that bacteria in marine sediments mediate the production of these mineral phases at remarkably fast rates.

Ellery D. Ingall

Phosphorus is a central component of biological systems. It is key to the formation of membranes, the transfer of genetic information and the cycling and storage of energy. Phosphorus availability can therefore limit the growth and abundance of organisms in all environments. In the ocean, variations in phosphorus levels correlate with variations in primary productivity over decadal[1] and geologic timescales[2]. The formation of calcium phosphate minerals in marine sediments is thought to constitute the largest phosphorus-removal pathway in marine waters over geologic time[2,3]. However, although marine sediments typically contain high levels of dissolved calcium and phosphate, sediment chemistry is not kinetically conducive to the formation of these minerals[4]. Indirect evidence suggests that calcium phosphate formation is biologically mediated[5,6], but direct evidence for bacterial participation is lacking. As they report in *Nature Geoscience*, Goldhammer and colleagues[7] use a radioactive phosphorus tracer to show that bacteria catalyse the conversion of phosphorus to calcium phosphate in marine sediments.

Studies of phosphorus speciation in marine sediments have typically relied on sequential chemical extraction[8] or nuclear magnetic resonance techniques[9]. These methodologies have revealed that phosphorus exists in a wide variety of organic, inorganic and mineral phases in marine sediments. These phases can undergo many transformations in response to environmental change.

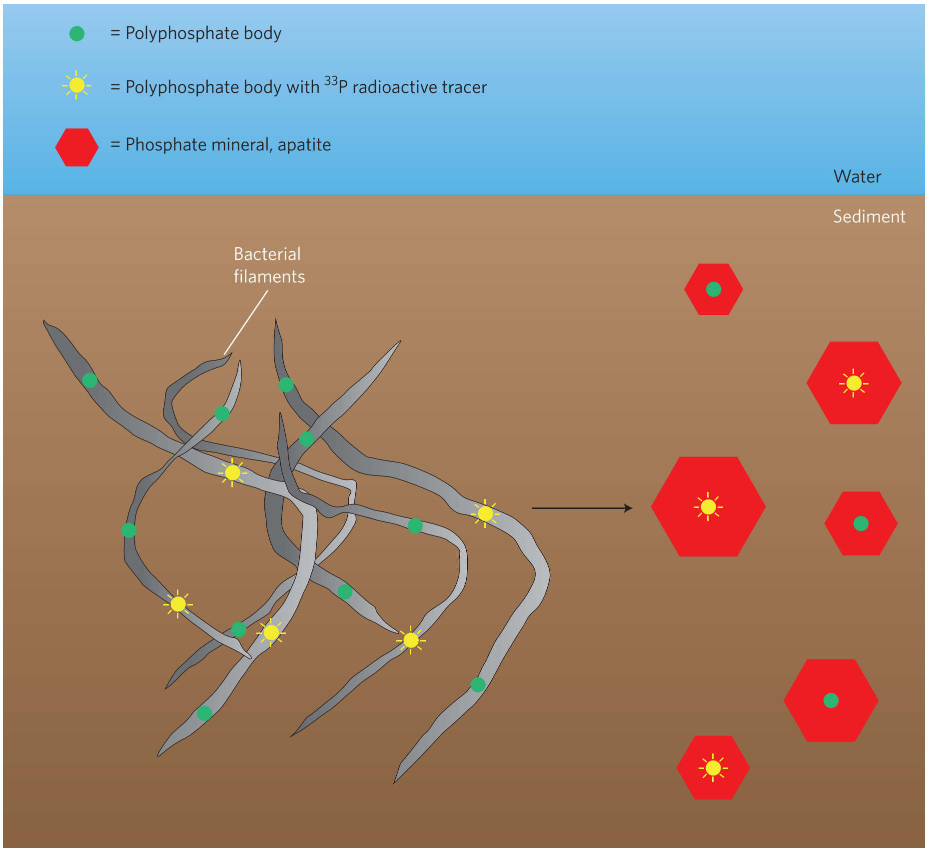

Figure 1 | Radioactive phosphorus taken up by filamentous bacteria is incorporated into polyphosphate bodies, and ultimately the calcium phosphate mineral apatite. Goldhammer and colleagues[7] use radiotracer incubation experiments to show that bacteria in marine sediments catalyse the conversion of phosphorus to apatite on very short timescales (hours to days), thereby removing phosphorus from the biologically active pool.

One particular form of phosphorus — the calcium phosphate mineral group called apatite — is increasingly recognized as the most significant sink for phosphorus in marine sediments[3]. Apatite forms in two environmental regimes, each producing a distinct type of deposit. Dispersed, micrometre-sized grains form in marine sediments worldwide. Macroscopic, apatite-rich grains and sediment layers are found in coastal upwelling regions characterized by high levels of nutrients and sediment organic matter. Recent studies in both environments suggest that apatite tends to form in the presence of a biogenic compound called inorganic polyphosphate[5,6]. Polyphosphate congregates in the cells of most organisms[10]. A key feature of these polyphosphate aggregations is their high levels of calcium — also an important component in apatite. Polyphosphate bodies therefore provide a great template for apatite growth, because much of the calcium needed to form apatite is already present.

Goldhammer and colleagues[7] present direct evidence for apatite formation by polyphosphate-producing bacteria in an upwelling region characterized by high nutrient levels and large quantities of sediment organic matter. Using a radioactive form of phosphorus, they traced the pathway of apatite formation in sediment samples collected from the Benguela upwelling system off the coast of Namibia. In the presence of sulphide-oxidizing bacteria, up to 11% of the phosphorus radiotracer spike was converted into apatite. In the absence of these bacteria, most of the radioactive phosphorus remained in the abiogenic phosphorus pool, and none was found in apatite. The findings therefore provide direct evidence for the involvement of bacteria in apatite formation (Fig. 1). Most importantly, they were able to show that the radioactive tracer added to their incubations was incorporated into newly formed apatite on the relatively short, 48-hour timescale of their experiments.

Surprisingly, apatite formation was greatest under anoxic, rather than oxic, conditions[7]. This finding contradicts studies in both modern and ancient sediments, which suggest that phosphorus-burial efficiencies decrease in sediments overlain by anoxic waters, leading to an enhanced flux of phosphorus from sediments to the water column under anoxic conditions[11]. Enhanced phosphorus burial under anoxic conditions could have significant oceanographic and atmospheric implications, given the importance of phosphorus levels for oceanic productivity and the stability of atmospheric oxygen levels over geologic timescales[2,12].

The unexpected findings of Goldhammer and colleagues may be specific to nutrient-rich upwelling systems such as Benguela. Nevertheless, long-term models of ocean circulation — most of which project an expansion of present-day oxygen-minimum zones — should consider the possibility that phosphorus burial increases under anoxic conditions, similar to those in the Benguela upwelling system.

Goldhammer and colleagues[7] present unique evidence for a bacterially mediated mechanism of apatite formation in a nutrient-rich upwelling system. The next step is to determine whether bacterially mediated processes govern the production of dispersed micrometre-sized apatite grains that occur in more typical marine sediments worldwide. ❐

Ellery D. Ingall is in the School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340, USA.
e-mail: ingall@eas.gatech.edu

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EARLY EARTH

Microbes and the rise of oxygen

Reconstructions of atmospheric chemistry and microbial life early in the Earth's history have been contentious. Observations increasingly point to the evolution of complex and variable environments earlier in time.

Andrew D. Czaja

Unravelling the history of life on Earth in the eons before the Cambrian explosion about 542 million years ago is as fascinating as it is challenging. Direct evidence for life in the Precambrian was first convincingly identified from the 1.9-billion-year-old Gunflint Iron Formation in the 1960s[1]. The biologic origin of these microfossils is undisputed, and it is now commonly — though not universally — accepted that life existed as early as 3.5 billion years ago, based on not only morphological evidence, but also detailed geochemical and palaeoecological studies. Further evidence of ancient life is provided by geochemical and biological constraints on metabolic diversity. The study of ancient life and how it made its living requires pulling together data from numerous lines of enquiry to understand these ancient organisms and the palaeoenvironments in which they existed (Fig. 1). A series of presentations at the Goldschmidt 2010 conference[2] held in June in Knoxville, Tennessee, and in particular those of a session titled 'Life before the rise of oxygen', attempted to do just that.

Essentially the full gamut of metabolic pathways in operation today is thought to have arisen early in the Precambrian. Perhaps most important to life as we know it today, it has been suggested that organisms that produced or consumed free oxygen had evolved by 2.67 billion years ago[3]. However, it is unclear whether oxygen production resulted in a significant flux to the atmosphere and oceans or remained a local phenomenon at this time. According to the present majority view, oxygen levels in the atmosphere of the early Earth remained below 10^{-5} times the present atmospheric level until sometime between 2.4 and 2.2 billion years ago, and then rose to between 10^{-1} and 10^{-2} times present-day levels in the Great Oxidation Event[4,5]. However, evidence is emerging that the transition from anoxic to oxic was far from simple.

Despite the title of the session at Goldschmidt[2], many of the early signs of life seem to have been accompanied by 'whiffs of oxygen'[6–10], long before the Great Oxidation Event. The earliest putative microfossils of possible cyanobacteria occur in the 3.5-billion-year-old Apex Chert of Western Australia[11], at essentially the same time as the first — controversial — evidence for oxygen in the Archaean oceans[12]. The purported oxygenated oceans are recorded in the 3.46-billion-year-old Marble Bar Chert, also of Western Australia. Isotopic, mineralogical and elemental evidence from these rocks are all consistent with the presence of microbes that are capable of producing oxygen (Y. Watanabe, Pennsylvania State