

PALAEOLOGY

Late to the mix

Marine sediments underlying oxygenated waters are usually a soupy mix. They are often poked, prodded or digested by creatures in the substrate and the waters above. Tiny foraminifera and ostracods crawling through the sediments, larger animals burrowing, and even puffer fish creating sand art, all rework the sea floor to depths of eight or more centimetres. In stark contrast, sediments underlying anoxic waters tend to be neatly layered, undisturbed since deposition.

Before the evolution of digging creatures, sediments were unmixed, too. Generally, early records of fossilized burrows and feeding trails, evident from the earliest Cambrian period about 550 million years ago, are considered the onset of sediment mixing. This Cambrian substrate revolution is thought to have ushered in the era of the oxygenated sediment column, with substantial implications for biogeochemical cycles, particularly for the amount of phosphorus retained in the sediments. Lidya Tarhan and Mary Droser, however, suggest there may have been a considerable delay between the onset of burrowing and the full bioturbation of marine sediments (*Palaeogeogr. Palaeoclim. Palaeoecol.* <http://doi.org/rt7>; 2013).



Tarhan and Droser assessed the sedimentary fabric of large sections of early and middle Cambrian-aged rocks. The sections, from the Great Basin (USA), southern Spain and Newfoundland, were deposited in shallow, oxygenated marine settings. Even in individual beds with high concentrations of burrows, the fabric of the surrounding sediment was minimally disrupted. So it seems that little mixing

occurred outside the burrows. The earliest evidence for a prominent sedimentary mixed layer occurred no earlier than the middle Cambrian. This is at least 30 million years after the inferred evolution of trilobites, whose search for food in the sediments was thought to have churned the sea floor.

Without significant mixing that could have brought oxygen-rich water down, the sediment column should have been largely anoxic, even though the overlying waters were oxygenated. Largely anoxic sediments, in turn, could explain the sulphur isotope signature of seafloor minerals at this time, and would also have promoted the preservation of soft-bodied organisms, whose fossils are relatively abundant in early Cambrian-aged rocks.

The coexistence of anoxic sediments and an oxygenated water column throughout much of the shallow oceans represents a highly unusual state. This anomaly is one of the factors that mark the early Cambrian oceans as the unique and irreversible transition from an anoxic microbial domain to the oxygenated multicellular world.

ALICIA NEWTON

EARLY EARTH

Cyanobacteria at work

Oxygen-producing photosynthesis must have evolved before the pervasive oxidation of the atmosphere around 2.4 billion years ago, but how long before is unclear. Geochemical analyses of ancient sedimentary rocks now suggest that cyanobacteria generated oxygen at least 3 billion years ago.

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With every breath, we and other animals are indebted to the cyanobacteria. These microbes developed the capacity to harness light energy to harvest electrons and hydrogen from water and use them to fix carbon into organic matter in the process of oxygenic photosynthesis. As an unintended consequence of this biochemical innovation, surplus oxygen was released, and slowly built up in the ocean and atmosphere. The antiquity of this microbial process, as well as the path to the ultimate rise of oxygen to modern

levels, has long been a source of debate. Complicating the issue, the key biochemical fingerprint for cyanobacteria, found in 2.7-billion-year-old organic-rich sedimentary rocks from Western Australia, is likely to be a contaminant^{1,2}. Searching for an alternative barometer of ancient oxygen levels, Planavsky and colleagues³ present in *Nature Geoscience* a study of molybdenum isotopes in middle Archaean and late Palaeoproterozoic banded iron formations (Fig. 1), and suggest that oxygenic photosynthesis evolved at least 3 billion years ago.

The molybdenum isotope signature of ancient marine sediments may be used to assess past oxygen concentrations in the overlying water column. The concentration of the trace element molybdenum in sea water is expected to scale with the oceanic oxygen level. This scaling occurs because the molybdate anion (MoO_4^{2-}) is more soluble in oxidized sea water than the reduced form of the element, which is found in water lacking oxygen. The adsorption of molybdate anions to the surface of manganese-rich oxides and oxyhydroxides, such as the nodules that