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Biogeochemistry

Oxygenating the atmosphere

Norman H. Sleep

Photosynthesis is the main source of oxygen in Earth's atmosphere. But it may have been geological activity that first allowed an oxygen-rich atmosphere to develop.

We usually give little thought to the air we breathe. Yet the Earth's atmosphere was not always as rich in oxygen as it is today. Oxygen now constitutes about 20% of the gas in the atmosphere, but before about 2,500 million years ago it was only a trace constituent. Writing in the new journal *Geochemistry, Geophysics, Geosystems*, Kump, Kasting and Barley[1] propose that changes in the deep interior of the Earth affected the composition of volcanic gases, and that this led to the rise in atmospheric oxygen levels at the Archaean–Proterozoic transition, 2,470 million to 2,450 million years ago. In turn, the increase in oxygen allowed complex life to evolve.

The Earth is unique among the planets in the Solar System in having an oxygenated atmosphere. The atmospheres of the other planets are anoxic because oxygen levels are kept comparatively low by an equilibrium system involving chemical processes — in, for instance, volcanic gases, and the planets' crusts and mantles. On the Earth, oxygen levels built up over geological time as a result of photosynthesis, which can be expressed as the reaction $CO_2 \rightarrow C + O_2$. Over the years, a vast amount of organic carbon has become locked up in sedimentary rocks, a small part of it as coal and oil, so preventing the reverse reaction to equilibrium that would create CO_2 and lower atmospheric levels of oxygen. Today, carbon burial is an inefficient process — only 0.1% of the carbon produced by photosynthesis ends up in sedimentary rocks, the rest being oxidized — which helps to keep today's oxygen levels stable.

But the advent of oxygen-producing photosynthesis cannot be the whole story. Photosynthesis existed long before the Archaean–Proterozoic transition and the well-documented rise in oxygen levels, as is evidenced by the existence of photosynthetic bacteria 3,500 million years ago. But it is possible that these bacteria were part of a global microbial ecology that used sulphate as the main oxygen carrier, and so would consume only trace amounts of oxygen.

Instead of looking at what processes might produce oxygen, Kump *et al.*[1] consider the materials and reactions that consume it and might have kept its levels low. They outline a scheme in which the reduced, oxygen-consuming gases carbon monoxide (CO), hydrogen (H_2) and methane (CH_4) were vented from arc volcanoes on land and midocean ridges beneath the sea (Fig. 1, overleaf). These reducing gases emanating from the mantle were a major sink for the oxygen resulting from photosynthesis in the Archaean, each reacting with oxygen to produce CO_2, water or both.

In addition, rocks containing a reduced form of iron — iron(II) or ferrous iron — were another sink for the oxygen produced by photosynthesis. These rocks were basalts that erupted on the ocean floor or land surface, and they sequestered the oxygen from water using the oxidation reaction that turned ferrous iron into its ferric — iron(III) — counterpart.

$$2FeO + H_2O \rightarrow Fe_2O_3 + H_2$$

This reaction is key to Kump *et al.*'s hypothesis because it traps oxygen through oxidation of mantle rock, and regenerates a reducing gas.

Kump *et al.* believe that subsequent events in the Earth's mantle explain the transition to an oxygen-rich atmosphere. This transition began abruptly at the Archaean–Proterozoic boundary, which is thought to coincide with a change in tectonic conditions in the Earth. In the authors' model, the sudden change is a consequence of the poor mixing — stratification — in the mantle.

The idea is that cold, dense, oxidized slabs, containing high amounts of iron(III) oxide, sank rapidly from close to the surface of the Earth and settled near the boundary between the Earth's core and mantle. Eventually, most of the lower mantle was filled with this oxidized material. As today, the mantle was heated from below by the core and from within by radioactivity. Heating from the core meant that the base of the mantle became buoyant about 2,700 million

100 YEARS AGO

Sir Courtenay Boyle objects, in the March number of *Macmillan's Magazine*, to many words in common use in science. His objections are partly etymological and partly to the vagueness of connotation of the words. Pliocene, miocene and phonolite are incorrectly formed; and the first two, together with palaeozoic, mesozoic, kainozoic, jurassic and triassic are condemned because they are purely relative terms. Electron is objected to because there is sometimes a doubt whether it signifies a minute corpuscle having an electric charge or an electric charge without the corpuscle. Kion and autokion are suggested as preferable to the unsatisfactory words motor and the hybrid automotor.

From *Nature* 14 March 1901.

50 YEARS AGO

Mr. Ritchie Calder, the science editor of the *News Chronicle*, was sent by Unesco to North Africa and the Middle East to report on what is being done to reclaim the deserts. The strange aura of romance and the mystery that surrounds the desert attracted much attention to the assignment, which was reported (according to the publisher's note) in thirty-two countries… In Israel… and to a lesser extent in Iraq and Persia, desert reclamation is a matter of urgent practical politics. Those beings whom Mr. Calder calls "the scientists" and who correspond to the gods who wrought wonders in former ages are being called upon to shower their blessings on mankind. Iraq and Persia have in their oil great wealth, some of which can be diverted to restoring the productivity of the land by modern adaptation of ancient methods. Israel has no mineral wealth, and her greatest resource in conquering the desert is the ingenuity of her people, and particularly of "the scientists" who are not only planning great irrigation and hydroelectric schemes but also are working on the large-scale desalinization of salt water by ionic exchange and by distillation through nylon. Promising experiments are being made to use the opacity of flake nylon to light and heat to reduce evaporation from reservoirs. There seem to be possibilities that nylon may become a key material in the conservation of water in Israel, and schemes are being considered for the large-scale cultivation of the castor-oil plant as a source of raw material for nylon manufacture.

From *Nature* 17 March 1951.

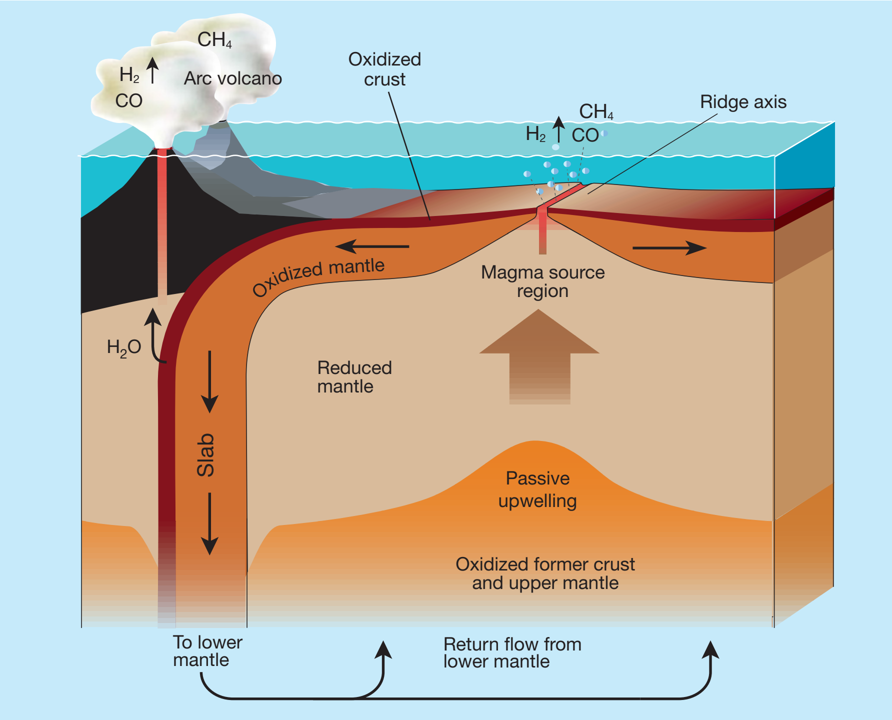

Figure 1 **Events near the end of the Archaean, around 2,500 million years ago, which led from an oxygen-depleted to an oxygen-rich atmosphere. Volcanic gases emanating at arc volcanoes and midocean ridges from a reduced mantle were themselves reduced and hence were an oxygen sink. In the crust and mantle, the oxidation of iron(II) oxide to iron(III) oxide also helped to keep oxygen levels low. According to the course of events outlined by Kump *et al.*[1], slabs of cold, dense, oxidized upper mantle and crust sank by subduction deep into the lower mantle. Heating from the core led to the rise of this oxidized material. Eventually, by overturn of the lower mantle into the upper mantle, or by filling the mantle completely, this oxidized material became the source of gases released at arc volcanoes and midocean ridges. As a result, the gases were insufficiently reduced to be a significant sink for oxygen — hence the rise in oxygen concentrations in the atmosphere.**

years ago, causing plumes of oxidized rocks to ascend towards the surface. Kump *et al.* suggest that the Archaean ended when the whole oxidized lower mantle became buoyantly unstable and overturned into the upper mantle, so that oxidized material replaced the reduced iron(II).

An alternative explanation, which gives the same outcome as far as oxygenation of the atmosphere and chemical mass balances are concerned, is that oxidized slabs filled the entire mantle by the end of the Archaean, replacing the reduced upper mantle that had never existed in slab form[2].

These events made the mantle source regions for magmas less reducing, which in turn had the same effect on the volcanic gases emanating from them. Eventually, the mantle became oxidized to the extent that volcanoes and midocean ridges vented gases that were an ineffective oxygen sink. Oxygen levels could then build up in the air, and the levels of H_2, CH_4 and CO were brought down to their present status as trace constituents of the atmosphere.

The basic geometry of the scheme proposed by Kump *et al.* works out; a plausible amount of oxidized slab material could have filled the mantle in the given time. It is also the case that the Earth's mantle is more oxidized than the material from which it formed. The success of Kump and colleagues'[1] hypothesis hinges on the time that the Earth's mantle became oxidized. At present, data from Archaean rocks come only from volcanic rocks generated by mantle plumes, which — as expected from the authors' reasoning — are oxidized. What are needed are data from Archaean volcanic rocks from an upper mantle source (such as the basalts erupted at mid-oceanic ridges), which according to Kump *et al.* should be reduced. In other words, their hypothesis is testable with data that are mostly independent of the surface carbon–oxygen cycle.

As well as looking at the rise of photosynthesis, traditional approaches to the increase of oxygen in the atmosphere have concentrated on surface biogeochemical processes. Carbon burial has been the subject of especial attention because, if free to react, the amount of carbon now sequestered in sediments would be a huge oxygen sink[3]. But although carbon burial is a necessary condition for maintaining a high-oxygen atmosphere, it may not have been a sufficient one for generating it in the first place. Controls on the process — which in part depends on availability of the nutrient phosphorus from rock weathering[4] — are not well understood.

Finally, it is also plausibly the case that weathering of volcanic rocks at the surface was a controlling factor in lowering the effectiveness of the oxygen sink at the Archaean–Proterozoic transition. Quite simply, the surface sink provided by the reaction of iron (II) to iron (III) might have diminished, as basalt (an Fe(II)-rich rock) became a subordinate part of the material subjected to weathering. The process is independent of

Animal behaviour

Greensleaves

Bats are usually thought of as roosting in caves or buildings. But there are several do-it-yourself tropical species that create tents out of large leaves. They do this by biting the leaf in such a way that the sides collapse downwards and create a sheltered area — as shown here (from within, complete with bat occupants).

These tents can stay healthy for long periods, even though much of the leaf's water supply has been cut off. How? Carol A. Peterson, Brock Fenton and colleagues have tackled the question by looking at the leaves of three plant species used by bats in Costa Rica (*Biol. J. Linn. Soc.* **72,** 179–191; 2001).

The group examined the water-conduction system in the leaves, and the damage caused to it by bats, and also performed tests with a tracer dye to follow water flow in damaged and undamaged tissue. The vein system in the leaves is complex, consisting of an apparent hierarchy of some five conducting elements. But it seems that water conduction by the smallest elements is enough to sustain the leaf, even when more major veins are severed. The authors point out that the advantage for the leaf is that it can survive damage from, say, wind or heavy rain; for the bats, it means that they are not forever making new tents.

Tim Lincoln

MICHAEL & PATRICIA FOGDEN/CORBIS

the precise oxidation state of the mantle as all basalts are Fe(II)-rich. It does, however, depend on the volcanic and tectonic processes in the mantle that control the amount of basalt that ascends to the surface where it can be weathered and hence oxidized.

It was over two centuries ago that Antoine Lavoisier figured out that we breathe oxygen. But we still don't know how an oxygen-rich atmosphere arose. Clearly, processes at both the Earth's surface and in its bowels were involved. Exactly how and by how much each contributed remain open questions, but Kump and colleagues' stimulating ideas should prompt further investigation. ■

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Cognitive neuroscience

Repression revisited

Martin A. Conway

The idea that unwanted memories can be repressed has been controversial. An adaptation of an old technique provides an unambiguous model for exploring memory repression in the laboratory.

The concept of repressing unwanted memories is central to psychoanalytic theory, and Freud, in a definition memorable for its clarity, wrote "the essence of repression lies simply in turning something away, and keeping it at a distance from the conscious"[1]. Freud provided many examples of memory repression from clinical cases, and documented its effects in day-to-day behaviour[2]. Yet evidence from case studies and vignettes from everyday life are often open to alternative interpretations, and may not be accepted as credible scientific data because they arise from 'uncontrolled' conditions. What was needed was a way to investigate memory repression in the laboratory, and Anderson and Green provide just that on page 366 of this issue[3]. Their methods offer a way of exploring the underlying inhibitory mechanisms, and may ultimately shed light on how repression comes about.

Attempts to study repression in the 1960s and early 1970s produced mixed results, sometimes supporting the idea that unwanted memories can be repressed, and sometimes not. By contrast, more general experimental studies have consistently shown that powerful inhibitory processes are at work in other aspects of human memory[4]. For example, there are inhibitory mechanisms that support the selection of competing items stored in memory.

Anderson and Green's procedure[3] is an elegant way of experimentally inducing memory repression. They adapted the well-known 'go/no-go' procedure used to study so-called executive control — which regulates the encoding, manipulation and recall of information in working memory — of movements in primates. In the authors' adaptation, human participants first learned a list of pairs of unrelated words (paired associates), such as 'ordeal' and 'roach'. They then undertook a 'think/no-think' task. They were presented with one of the words from a previously learned pair, and asked either to say aloud the associated word ('think') or to avoid thinking about it ('no-think'). So, the no-think condition had two components that had to be inhibited: thinking about the unpresented word, and saying it aloud. Before the words were presented, the participants were told which words would cue avoidance and which would not, so that they knew whether, on being shown the word 'ordeal', for example, they were to say aloud 'roach' or to avoid thinking about it. Different paired associates were tested a varying number of times (1, 8 or 16 times, or not at all for 'baseline' words).

Some time after the think/no-think phase, participants were presented again with all the cues seen in the previous phase, as well as with cues from baseline pairs. They were then asked to recall the words with which the cues had originally been paired, regardless of whether they had been told to avoid or recall those words in the think/no-think phase. Not surprisingly, participants fared best at recalling words from the 'think' category; paired associates that had been practised most often (that is, in 16 trials) were recalled best of all. The next best recall was of the baseline paired associates. Words in the 'no-think' category were recalled badly, with the words avoided most often being recalled worst of all. In other words, the more rehearsal, the better the recall (this has been found previously), and the more active the avoidance of rehearsal, the greater the inhibition of recall.

Next, Anderson and Green presented the participants with cues related to the paired associates, and asked them to recall the relevant word. For example, instead of 'ordeal–r_____' to cue recall of 'roach', the participants were presented with 'insect–r_____'. Again, words in the no-think category of the original test were poorly recalled, and again, inhibition of recall was strongest for those items for which avoidance had been most practised. This crucial finding shows that it is the avoided word ('roach', in this example) that is inhibited, rather than the whole paired associate.

In short, Anderson and Green have shown in a laboratory setting that if a memory that is associated with something familiar (here a word) is actively avoided every time that familiar object is seen, then the memory becomes repressed and the avoided item is later difficult to remember. This is an important result, which lends support to Freud's original definition of repression: it unambiguously shows the existence of consciously initiated, executive inhibition of memory. Even more surprising is that this occurs for unrelated pairs of words — hardly comparable to psychodynamic (primitive) motives or to the amnesia that can result after the trauma of childhood abuse. The results therefore further demonstrate the ubiquity of inhibitory processes in human memory.

More generally, memory researchers[4] have concluded that inhibition is not only widespread but also habitual, and that, when an item is retrieved from memory, associated items are temporally inhibited. Indeed, the functional arrangement of the brain also suggests the widespread existence of inhibition. As many as 20–25% of cells in the cerebral cortex may be inhibitory and serve to prevent other neurons from becoming overexcited[5]. Such networks of inhibitory neurons could give rise to the type of repression proposed by Freud to underlie neuroses[6].

In this respect, it is interesting that Anderson was led to his present research by a cognitive analysis of a pattern of amnesia seen in abused children[7]. Children abused by a trusted caregiver are more likely eventually to forget the abuse than those maltreated by strangers. This led to the insight that a trusted caregiver might represent an unavoidable cue for memory retrieval. The only way to prevent persistent recall of damaging memories would be to adapt internally and to deliberately avoid thinking of such memories — in Freud's terms, to push them away from consciousness. Anderson and Green have now shown[3] that, even in the innocuous setting of the laboratory, and with stimuli as trivial as randomly paired words, powerful inhibition can be evoked. How much stronger must this inhibition be for objects central to our thoughts and emotions. ■

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