Climate change and palaeoclimatology

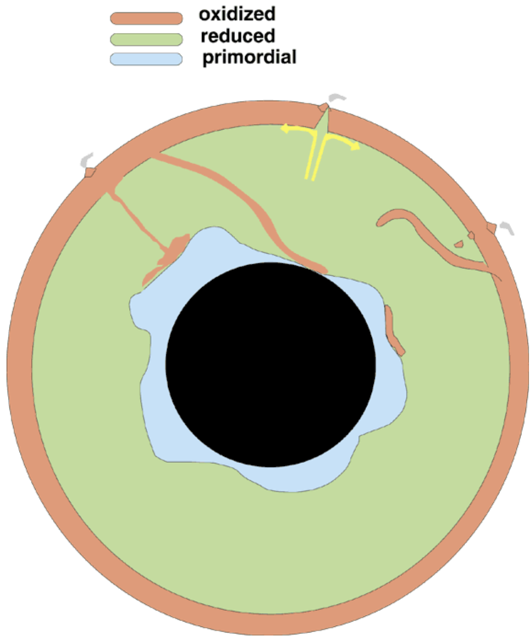
Mantle overturn and oxygenation of the atmosphere *(March 2001)*

The presence of abundant oxygen in Earth's atmosphere defies Le Chatelier's Principle - it should react rapidly with the rest of the environment through oxidation. That it does not is sufficient evidence for an alien observer to conclude that our planet is dominated by photosynthetic life at its surface and the burial of carbohydrate by geological processes. So, Le Chatelier is not defied on the long term, because the CO_2 + H_2O = carbohydrate + oxygen equilibrium does not reach a balance because of continual removal of organic material from the right-hand side! That Mars has no atmospheric oxygen bears witness to its lifelessness, as regards photosynthesis, in that respect, as concluded decades back by James Lovelock.

Before 2.5 Ga ago, in the Archaean, atmospheric oxygen was a trace gas. Preservation of detrital grains of sulphides and uranium oxides in Archaean clastic sequences, which would have broken down in an oxidizing environment, is the main evidence for that. The other side of the coin is that oxygen-producing photosynthesizers - the cyanobacteria - were abundant throughout the Archaean, leaving their trace as common stromatolitic carbonates and signs of the crucial enzyme rubisco in kerogens and the carbon-isotope record.

If cyanobacteria generated oxygen, then why did it not build up in the atmosphere throughout the Archaean, instead of from about 2.2 Ga ago? The most likely explanation is that Archaean magmatism released vast amounts of soluble Fe-II or ferrous iron to sea water, which then reacted with available oxygen to form the insoluble ferric oxide of banded iron formations (BIFs), with the biproduct of hydrogen gas that further drove Archaean environmental chemistry into a reducing condition. Seawater circulating through Archaean ocean crust would also have enriched basalts in ferric iron by the same oxidizing reaction. Such a chemical model still leaves unexplained the shift to an oxygenated atmosphere after the Archaean.

Lee Kump of Pennsylvania State University and his co-workers suggest that, rather than relating to a change in palaeoecology, the shift arose from subduction of dense ferric oxide-rich lithosphere to settle at the core-mantle boundary (Kump L.R., *et al*. 2001. Rise of atmospheric oxygen and the "upside-down" Archean. *Geochemistry, Geophysics, Geosystems*, v. **2**, online; DOI: 10.1029/2000GC000114). By the end of the Archaean oxidized material filled the lower mantle. Heating reduced its density so that it became buoyant. If that deep oxidized layer rose to displace more primitive, reducing mantle, later magmatism would have released less Fe-II, thereby allowing biologically generated oxygen to build up. The converse effect would have been to bring down levels of reducing atmospheric gases, such as hydrogen, methane and carbon monoxide, to trace levels.



Model of Late Archean mantle structure and dynamics, depicting heterogeneity of mantle redox states. Basalts erupted at Earth's surface become oxidized. The oxidized slabs of oceanic lithosphere are subducted, penetrating into the lower mantle and accumulate at the core-mantle boundary. Plumes carry oxidized mantle back to the surface. Source regions for mid-ocean ridge basalts remain reduced through the Archean. Interior structure (but not redox characteristics) after *Albarede and van der Hilst* [1999].

Except to its primitive producer - cyanobacteria - oxygen would have been anathema to the dominant anaerobic Bacteria and Archaea that constituted Archaean life. An end-Archaean mantle overturn, implicated by the tectonic pandemonium from 2.7 Ga, could well have triggered accelerated extinction and evolution that encouraged the rise of the eukaryote cell that requires oxygen for its basic metabolism. Nonetheless, such an upheaval would have been directly connected with earlier living processes. That is something which will delight followers of the Gaia hypothesis.

Related article: Sleep, N.H. 2001. Oxygenating the atmosphere. *Nature*, v. 410, p. 317-319).

Atmospheric oxygen: yet more *(April 2001)*

Following last month's *Mantle overturn and oxygenation of the atmosphere* (above) Nature has run a news feature on competing theories for when oxygen began to accumulate in Earth's atmosphere (Copley, J. 2001. The story of O. *Nature*, v. **410**, p. 862-864; doi: 10.1038/35073794). The paradox between evidence for oxygen production by photosynthetic cyanobacteria since 3.5 Ga and that supporting the first major influence of oxygen in redbeds at 2.2 Ga may be resolved by the ideas of Hiroshi Ohmoto of Pennsylvania State University (Ohmoto, H. 1996. Evidence in pre–2.2 Ga paleosols for the early evolution of atmospheric oxygen and terrestrial biota. *Geology*, v. **24**, p. 1135-1138; doi: 10.1130/0091-7613(1996)024<1135:EIPGPF>2.3.CO;2)

Redbeds - terrestrial sediments containing abundant ferric hydroxides - form when iron enters its Fe-3 state and are insoluble. That results in weathering processes being unable to leach soils of their iron content, unless the waters involved have been rendered reducing by bacterial activity. The most dramatic expression of this is laterite that blankets ancient erosion surfaces of most of the Gondwanan continents, much of which formed in Palaeocene times. Palaeosols older than 2.2 Ga do not show the characteristic laterite ferricrete cap, implying that iron existed consistently in its soluble Fe-2 form and could be leached away. Most geochemists regard that as evidence for a reducing atmosphere, lacking oxygen except as a trace. Ohmoto suggests that organic acids formed by terrestrial cyanobacteria might also create the reducing conditions necessary for iron leaching.. He sees such “blue-greens” as having had a dual role, fixing iron in soils through oxidation and then releasing it to solution by formation of organic acids. Ohmoto and Antonio Lasaga are developing a geochemical model for the iron, oxygen, carbon and sulphur cycles during the Archaean. Early runs suggest that only 30 Ma after the appearance of cyanobacteria at 3.5 Ga their release of oxygen would have built up high levels in the early atmosphere.

That bucks the evidence for low oxygen provided by detrital sulphides and uranium oxide grains in Archaean high-energy sediments, such as the conglomerates of the Witwatersrand basin in South Africa: in the presence of oxygen, both should break down quickly in water. Archaean banded iron formations, thought to form by reaction between Fe-2 ions in ocean water and oxygen produced locally by shallow-water cyanobacteria, have a dual significance: abundant oceanic Fe-2 suggests global lack of oxygen, and BIF deposition of ferric oxide would have formed a sink for any oxygen in the environment. Ohmoto cites the re-appearance of BIFs at several times in the Proterozoic Eon as a sign that BIF formation was possible when atmospheric oxygen was abundant.

The debate seems destined to run, for two reasons. Studies of sulphur isotopes - Ohmoto’s speciality - give evidence for fractionation through the influence of ultraviolet radiation. Once oxygen rose in the air, its formation of ozone gas would have blocked UV and ended this kind of selective take-up of sulphur isotopes. James Farquhar of the University of California in San Diego has found its effects common in Archaean rocks, but no sign in later rocks. That favours an oxygen-poor early atmosphere. Ohmoto counters with abundant evidence in the Archaean for the activity of bacteria that reduce sulphate ions to sulphide - in an oxygen-poor world, sulphate formation would have been suppressed.

Oxygen build-up demands complementary burial of organic matter formed by photosynthesis before it oxidized. The influence of organic carbon burial is to take with it ^{12}C that biological processes favour over heavier ^{13}C, so that carbon-rich rocks show higher ^{12}C than carbonates precipitated from the seawater that was left. Such enrichment in ^{12}C shows up most clearly after 2.7 Ga ago, when carbon burial must have been stoked up somehow. That points to a late build-up of oxygen in the air. But why? James Kasting, also of Pennsylvania State University, suggests a change in the Earth's mantle from reducing to oxidizing conditions. Before that time volcanic gases would have been dominated by reduced gases that could mop up any free oxygen. Afterwards, oxidized volcanic gases could have co-existed with free oxygen.

The start of North Atlantic Deep Water formation *(April 2001)*

The most favoured means whereby the weak fluctuation in solar radiation due to the Milankovich-Croll effect become amplified to affect climate's ups and downs is the switching on and off of thermohaline circulation in the North Atlantic Ocean. The key to such ocean circulation is formation today of dense, cold brine through cooling and sea-ice formation around Iceland. To set circulation in motion, however, depends on these brines being able to move southwards, which they do now through a sea-floor channel between Shetland and the Faeroe Islands. When the North Atlantic began to open, this route was blocked by a ridge between Greenland and Shetland, buoyed up by residual warmth in the lithosphere from volcanic activity at the Iceland plume.

It is important to assess when the Shetland-Faeroe "gateway" formed, so that the effects of thermohaline circulation on pre-glacial climate can be assessed. Petroleum exploration using high-resolution seismic reflection profiles and drilling has resolved this particular issue. Geologists and geophysicists from Exxon and Cardiff University have found signs that sediment drift dragged by such a deep flow began in the early Oligocene (about 35 Ma ago) (Davies, R. *et al*. 2001. Early Oligocene initiation of North Atlantic Deep Water formation. *Nature*, v. **410**, p. 917-920; doi: 10.1038/35073551). The evidence takes the form of multiple, moat-like erosion surfaces down to the base of sediment fill between the Faeroes and Shetland, shown superbly by the seismic data. Drilling shows that these signs of deep-water flow stop abruptly in Early Oligocene sediments.

Astrology and ice *(April 2001)*

The early Oligocene marked the onset of serious ice cover on Antarctica, and it shows as a dramatic increase in $\delta^{18}O$ values in the ocean-floor record of benthic forms - lighter ^{16}O had been trapped in land ice. That may or may not be a coincidence with the finding about the start of North Atlantic thermohaline flow in the previous item. A lesser, but still dramatic increase marks the Oligocene-Miocene boundary, suggesting further growth of the Antarctic ice sheet, which is not so readily matched empirically. Detailed study of the isotopic "blip" at this time by a team from the Universities of California, Cambridge and South Florida (Zachos, J.C. *et al*. 2001. Climate response to orbital forcing across the Oligocene-Miocene boundary. *Science*, V. **292**, p. 274-278; DOI: 10.1126/science.1058288) suggests that it related to a remarkable coincidence in the astronomical record of solar heating.

Round 23 Ma ago, the orbital eccentricity dropped almost to zero - Earth's orbit would have been circular - at the same time as its axial tilt became very stable, the one reinforcing the climatic effect of the other. The isotopic "blip" coincides exactly with the coincidence. The detailed record also shows very clearly that minor fluctuations in climate at that time were in step with the 400 and 100 ka periods in the eccentricity variations, and with those of 41 ka that relate to changes in axial tilt. If nothing else, these results confirm that it is unnecessary to turn to extraterrestrial influences over climate other than those which are predictable from Milankovich's theory (*see Impacts and human evolution*, above).

Additional source: Kerr, R.A. 2001. An orbital confluence leaves its mark. *Science*, v. **292**, p. 191; DOI: 10.1126/science.292.5515.191.

Start of Pleistocene environmental change in tropical Africa ***(April 2001)***

Pollen records from an ODP core drilled off the Congo estuary provide a record of the fluctuation in the monsoon of western tropical Africa (Dupont, L.M. *et al*. 2001. Mid-Pleistocene environmental change in tropical Africa began as early as 1.05 Ma. *Geology*, v. **29**, p. 195-198; doi: 10.1130/0091-7613(2001)029<0195:MPECIT>2.0.CO;2). Before 1.05 Ma there is little sign of a glacial-interglacial pulse in the fluctuation of vegetation in the Congo Basin. Thereafter, ups and downs in pollen from various vegetation groups correlate well with the benthic foram oxygen-isotope time series. However there are a few surprises.

Conventional wisdom is that Africa experienced drying during glacial epochs, rain forest expanding during interglacials. In the Congo basin, grasses and savannah trees increased during interglacials while mountain trees fell in their influence, up to 600 ka. This suggests the *opposite* trend of warm, dry interglacials and cool, humid conditions during glacial periods, similar to the record for tropical South America. In the later Pleistocene, the fluctuation switched to that indicated by fluctuating lake levels throughout the continent. The pollen variations are backed up by variations in dinoflagellate cysts, which show that discharge from the Congo dropped during interglacials. The other surprise is that the onset of astronomically paced environmental change in West Africa predated the change to a 100 ka domination of global climate, and the increase in amplitude of changes in land-ice volume at 900 ka by a hundred thousand years. Dupont *et al*. suggest that the changes in albedo in tropical West Africa in response to vegetation changes could have had an influence on global climate when the fluctuations began.

As well as being interesting in terms of climate change, the new data throw doubt on the hypothesized link between climate in Africa and pulses of migration of early human species, such as *H. ergaster* and *H. erectus*. There were fluctuations in humidity in the earlier Pleistocene, but they show no link to global climate change. So, it seems unwise simply to look to the Milankovich forcing as a pacemaker in early human affairs.

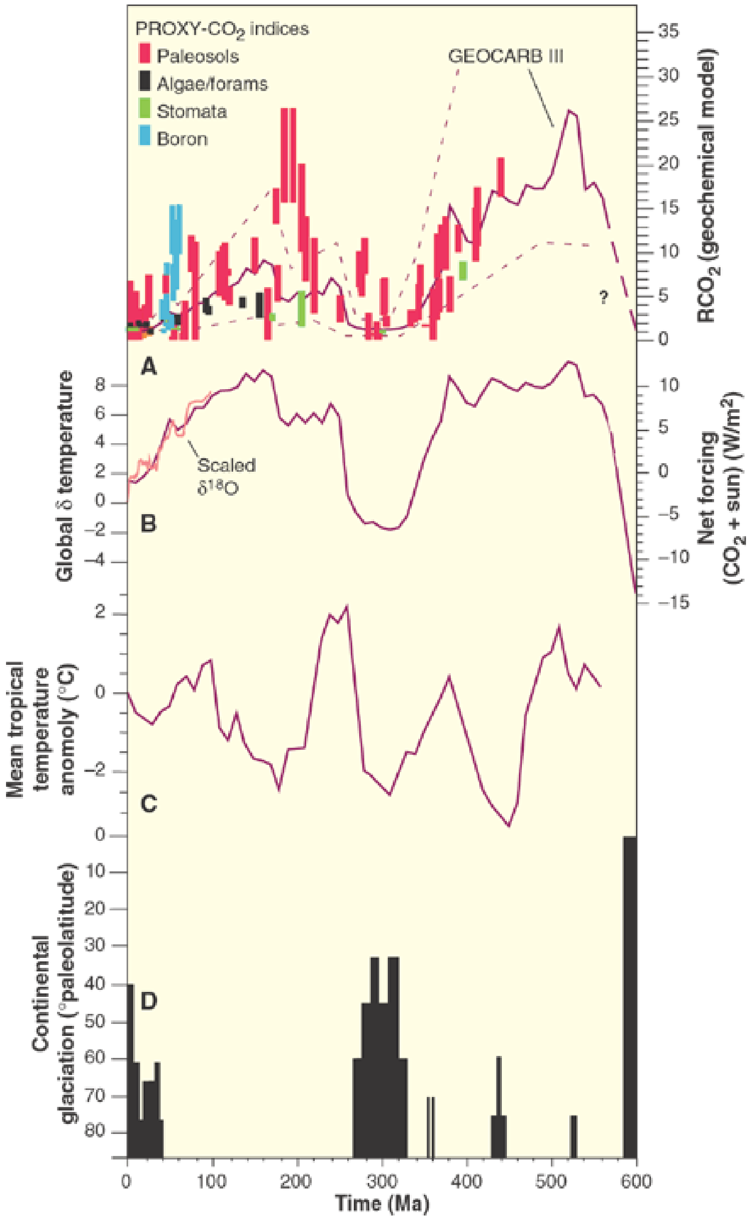
A Late-Jurassic methane "gun" ***(April 2001)***

Massive releases of methane from gas hydrate layers beneath the ocean floor, and its subsequent oxidation to carbon dioxide have been implicated in major climatic and oceanographic changes in the mid-Jurassic, Cretaceous and Palaeocene. They can be detected by drops in the ^{13}C content of marine carbonates, caused by the "light" carbon trapped in biogenic methane. All those known also correlate with evidence for climatic warming.

The Swiss Jura mountains are a repository of great thicknesses of Jurassic carbonates, whose ammonite faunas allow fine stratigraphic division. Between 157 and 156 Ma (late Middle Oxfordian) there is a major negative excursion in $\delta^{13}C$ whose duration was as short as 180 ka (Padden, M. *et al*. 2001. Evidence for Late Jurassic release of methane from gas hydrate. *Geology*, v. **29**, p. 223-226; doi: 10.1130/0091-7613(2001)029<0223:EFLJRO>2.0.CO;2). The Swiss-French geochemists who discovered the anomaly believe that the release may have linked to opening of the ocean gateway that connected currents between Tethys and the easter Pacific oceans through what is now the Atlantic.

Phanerozoic CO_2 levels *(May 2001)*

Because climate depends partly on the retention of solar heat by carbon dioxide in the atmosphere, a record of past CO_2 fluctuations is important in linking evidence for shifting climate and environments to models. Conversely, models that seek to mimic climates of the past depend heavily on the assumption that the "greenhouse" effect and the carbon cycle underpin global temperature and precipitation. Current theorists consider that shifts in CO_2 content of the atmosphere reflect a balance between its release through volcanism (itself a reflection of the rate of plate tectonics) and its removal by weathering of silicate minerals and burial of dead biomass.



(A) CO_2 concentrations calculated using GEOCARB III through the Phanerozoic compared with values based on various proxies; (B) Estimated mean global temperature; (C) Deviations from mean temperature; (D) Episodes of glaciation (Credit: Crowley & Berner 2001, Fig 1)

The GEOCARB III model predicts rising atmospheric CO_2 following the ice-house condition of the late-Precambrian, when rapid sea-floor spreading broke up and began to reassemble supercontinents during the Lower Palaeozoic. In the early Cambrian CO_2 levels come out at 25 times the modern amount. Colonization of the land by plants through the Upper Palaeozoic, and the burial of a proportion of the increased amount of carbon fixed by them, allows the model to predict a massive fall in CO_2. That tallies very well with the long period of glaciation in southern Pangaea during the Carboniferous and Permian. GEOCARB III suggests a recovery in levels through the Mesozoic, punctuated by extraordinary releases from plume activity, such as that implicated in the formation of ocean plateaux beneath the Pacific about 120 Ma ago.

From GEOCARB modelling stem predictions of the overall forcing of global temperatures. However, only the last 100 Ma can be assessed as regards temperatures, by using accurate proxies provided by oxygen isotopes and the Ca:Mg ratio of marine carbonates. Two of the leading climatic theorists, Thomas Crowley and Robert Berner of Texas A&M and Yale universities usefully summarise the range of other proxies that help validate their kind of modelling (Crowley, T.J. and Berner, R.A. 2001. CO_2 and climate change. *Science*, v. **292**, p. 870-872; DOI: 10.1126/science.1061664). These include estimates from fossil soils, carbon isotopes in sediments, the pores in plant leaves (see *Plant respiration and climate* below) and how much boron is taken up in the shells of fossil animals. There are considerable discrepancies with modelling, albeit encompassed by the high uncertainties in the calculations. Crowley and Berner acknowledge the complexity of other factors that affect the global redistribution of heat, such as continental configurations in terms of area, geographic position, their effects on ocean circulation and even on the pace of the carbon cycle. They see the need to expand climate models, taking other factors on board, in an attempt to quantify the discrepancies.

Methane and escape from Snowball Earth *(May 2001)*

Palaeomagnetic pole positions determined from areas characterized by thick glacigenic deposits around 750 Ma old leave little doubt that large volumes of ice covered the Earth to tropical latitudes. Such evidence suggests an ice-bound world from which escape would have been very difficult because much of the Sun's energy would have been reflected back to space. Extreme and prolonged frigidity, from which Earth's climate did escape is seen by a growing number of palaeobiologists as the most profound influence over later evolution and diversification of life. The first fossil metazoans appear in the record shortly after a "Snowball Earth" event at 650 Ma, and the Cambrian explosion of animals with hard parts followed close on the heels of the last. Carbon isotope studies from marine carbonates suggest that each global glaciation witnessed massive extinctions of single-celled organisms, and surviving life was presented with a virtual *tabula rasa* of niches to fill. Such survivors, possessing characters that had ensured their survival - at which we can only guess - exploited them to the full. It is reasonable to speculate that without such climatic upheavals life would not be as it is now, and that our eventual appearance depended on them.

That Earth's climate broke out of runaway ice-house conditions is obvious, the question being how was that possible. Volcanic emissions of carbon dioxide, which neither the Neoproterozoic biosphere nor silicate weathering were able to draw down into ocean water and sediments, would have accumulated in the atmosphere, to create "greenhouse" conditions. That simple scenario, envisaging a spectacular shift from frigid to hot conditions, has its problems. In order for climate to stabilize, without rushing into runaway heating along the path followed by Venus, demands implausibly high rates of silicate weathering to draw down CO_2 in the period following the end of each "Snowball" event, and strontium isotopes that record the rate of continental weathering show no sign of anything so dramatic. It also poses the question of how global ice cover could remain while CO_2 slowly built up. The key seems to lie in carbonates that everywhere cap the glacigenic deposits of this age. The cap carbonates record rapid falls in the ^{13}C proportion of the carbon in carbonate. ^{13}C shows a rise in the glacial epochs that signifies massive burial of dead organic matter (enriched in lighter ^{12}C), probably through mass extinction. In a review of the geochemical basis for changes in oceanic carbon isotopes, and high-resolution data from cap carbonates, scientists from the University of California and the Lamont-Doherty Earth Observatory, suggest that the isotopic excursions could reflect massive release of methane from gas-hydrate layers in sediments that were frigid during the Snowball event (Kennedy, M.J. *et al*. 2001. Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals? *Geology*, v. **29**, p. 443-446; doi:10.1130/0091-7613(2001)029<0443:APCCAI>2.0.CO;2). Backing up this hypothesis are examples of structures in cap carbonates that are identical to those formed in modern sediments affected by break down of gas hydrates and release of methane from the sea floor.

Plant respiration and climate *(May 2001)*

Leaf surfaces are pockmarked by pores (stomata), through which cell metabolism draws in the carbon dioxide involved in photosynthesis and transpires its products, including oxygen. When CO_2 levels are low, more pores are needed, and vice versa. Surprisingly, museum specimens of leaves collected since the start of the Industrial Revolution do show a decrease in the density of such pores that matches the documented rise in atmospheric CO_2 levels. Were it possible to find fossils of the same plant species, pore density would be an excellent proxy for the "greenhouse" effect. That is not possible, because of evolution. However, plants related to the *Ginkgo* have a pedigree that goes back about 300 Ma. Morphologically, the four genera of *Ginkgo*-like leaves are very similar, so using them potentially gives an independent record of the "greenhouse" effect.

Eye-shaped leaf stomata (Credit: http://www.ilovegrowingmarijuana.com/structure-function-stomata/)

Gregory Retallack of the University of Oregon has measured the stomatal index of sufficient *Ginkgo* and related leaves to assess CO_2 levels in a broad-brush sense for the period since the early Permian (Retallack, G.J. 2001. A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles. *Nature*, v. **411**, p, 287-290; doi: 10.1038/35077041). His results tally broadly with oxygen-isotope and other proxies for palaeotemperature variations, and to some extent with CO_2 modelling (see *Phanerozoic CO_2 levels* above). However, the stomatal record shows changes up to 10 Ma in advance of shifts in temperature. That might be due to coarse resolution in Retallack's data, but could signify other forces at work other than the "greenhouse" effect. The most significant advance provided by leaf studies is that they help account for mismatches between evidence for cooling and predictions of highCO_2 by modelling, for the Jurassic and Cretaceous, that have been a thorn in the side of the modellers. Given fossil leaves more closely spaced in time, and using other plant groups, Retallack's method potentially could revolutionize climate analyses and extend them back as far as 400 Ma ago.

See also: Kürschner, W.M. 2001. Leaf sensor for CO_2 in deep time. *Nature*, v. **411**, p. 247-248; doi: 10.1038/35077181.

Climate and heavy breathing *(June 2001)*

The kingdom of the eukaryotes rests on a very simple environmental economy. Plants are producers of carbohydrate through photosynthesis, thereby generating excess oxygen from the photo- and molecular chemistry involved. Animal consumers use up oxygen in their metabolism and return carbon dioxide, the ultimate source of carbohydrate, to the air. A simple view is that animals contribute to global warming, whereas plants help cool the world. Perhaps because of that "common sense" view, most environmental scientists take a very different line, linking it with volcanic exhalation of CO_2, "capture of carbon through rock weathering and the burial of dead organic matter in the global carbon cycle. Greg Retallack of the University of Oregon has reappraised the animal versus plant part of the C-cycle (Retallack, G.J. 2001b. Cenozoic expansion of grasslands and global cooling. Journal of Geology 109(4), 407-426; DOI: 10.1086/320791) that is based on observed imbalances between the two opposed kinds of respiration. Specialists in the C-cycle hold that there is an overall balance, taking all components into account, whose inevitable result is the build up of oxygen in the atmosphere of an inhabited world. Yet oxygen is extremely reactive and should quickly combine in mineral oxides and hydroxides - after all, the iron in an untended car reverts to its oxide ore in the space of a few decades at most.

Partly following James Lovelock's Gaia hypothesis, Retallack focuses on the major fluctuations in atmospheric chemistry evidenced in the geochemical record, the most immediate being the see-saw fluctuation of modern levels of CO_2 in the atmosphere - a 2% annual variation controlled by the waxing and waning of vegetation in the northern hemisphere (where plant cover is greatest) according to season. One of the largest shifts in atmospheric CO_2 concentration followed the evolution of land plants from about 450 Ma ago. To thrive, they had to develop hard cellular material (lignin) that formed stems and trunks, which animals of the Palaeozoic were unable to oxidise efficiently. Both living biomass and burial of undigested lignin drew down CO_2 and boosted oxygen levels. Animal evolution eventually exploited this "free lunch" through the humble termite and reptilian and then mammalian megafaunas. Retallack believes that heavy breathing that resulted from lignin digestion reversed the declining CO_2 trend for the 200 Ma following the Carboniferous to Permian glacial epoch in Gondwana. Though displaying some ups and downs, the Mesozoic saw a "greenhouse" world. Removal of the mighty and extremely abundant herbivorous dinosaurs by the K-T mass extinction provided and opportunity for plant diversification. Many Mesozoic plants evolved armour against browsing dinosaurs, exemplified by the surviving Andean "monkey puzzle" tree *Araucaria*. Their demise removed the need, and the plant Kingdom's evolutionary response was the appearance of grasses. Reatallack points out that grass itself is not as good as lignin-rich plants in holding CO_2, but grasslands encourage the development of thick carbon-rich soils that hold more than the soils of the forest floor. It is this development that Retallack believes lay at the base of the decline in average global temperature through the Cainozoic, to culminate in the present Ice Age. Unsurprisingly, proponents of the complexity and diversity of the C-cycle, particularly in the oceans, are disinclined to have truck with the hypothesis.

Source: Pearce, F. The Kingdoms of Gaia. *New Scientist*, 16 June 2001, p. 30-33.

Carbonates and biofilms *(June 2001)*

Above the low level that is essential for their role in molecular "information" transfer, calcium ions pose a fatal threat to cell processes. That is simply because excess calcium combines with carbonate ions to form minute calcium carbonate crystals within the cell when the solubility product of calcite is exceeded. The solubility product is the concentration of calcium ions multiplied by that of carbonate ions, so that increase in one or the other can lead to supersaturation of calcium carbonate and imminent precipitation. Because CO_2 is an essential need for photosynthesis and a product of animal metabolism, this risk is always present. In the most common photosynthesising bacteria, the cyanobacteria that have been around for at least 3.6 billion years, the drawing in of CO_2 in the form of carbonate (CO_3^{2-}) or bicarbonate (HCO_3^-) ions in water can result in supersaturation immediately around the cell. When it occurs, the "blue-green" bacterial biofilms induce precipitation of calcium carbonate. That is why such micro-organisms can act as reef builders, as they did to great effect during the early Precambrian (stromatolites), and also from Cambrian to Cretaceous times.

Calcite mineralization by biofilms is, however, a complicated process. It is connected with highly reactive substances that cyanobacteria exude outside their cell walls. Depending on their degree of ordering and the supply of calcium ions, these substances control the manner in which calcium carbonate precipitates. The detailed biochemistry and the form of calcite biofilms obtained by study of modern cyanobacteria in different watery environments has allowed Gernot Arp and co-workers at the University of Göttingen to evaluate varying calcium and CO_2 concentrations in ocean water since 540 Ma, and suggest differences in Precambrian oceans (Arp, G. *et al*. 2001. Photosynthesis-induced biofilm calcification and calcium concentrations in Phanerozoic oceans. *Science*, v. **292**, p. 1701-1704; DOI: 10.1126/science.1057204).

Their studies suggest that up to the Cretaceous, the Phanerozoic oceans must have had higher calcium contents than they do today. Microbial reefs formed in that period preserve details of the "blue-green's" cell structure, suggesting that calcite was nucleated directly by the extracellular substances. Vast burial of the calcite shells of planktonic metazoan organisms to form the Chalk deposits of Cretaceous age reduced very high levels to give the calcium-depleted oceans that prevailed during the Cenozoic. Microbial carbonates of these younger ages show no structure. The stromatolites that are so characteristic of

Precambrian limestones are stuctureless too, although they show evidence of progressive build-up from myriads of thin layers. Irrespective of the Precambrian oceans' calcium content, this lack of structure can be explained by more dissolved CO_2 that resulted from its higher concentration in the atmosphere. About 700-750 Ma ago, stromatolites that contain calcified cyanobacterial cells appear, and that may signify the massive drawdown of CO_2 from the atmosphere that is implicated in creating icehouse conditions on a global scale during the late Proterozoic.

Strontium load of Himalayan rivers *(November 2001)*

One process connected to long-term climate change is the way that weakly acid rainwater (containing dissolved CO_2) weathers silicates in continental rocks, one product being carbonate in soils. The process should draw CO_2 from the atmosphere, thereby reducing its "greenhouse" effect. The idea is by no means new, but received a boost in the mid 1990's from Maureen Raymo and William Ruddiman's suggestion that fluctuations in the strontium-isotope composition of the oceans through geological time should be a proxy for changes in the rate of continental weathering. The $^{87}Sr/^{86}Sr$ of marine carbonates does show clear correlation with long-term climate shifts during the Phanerozoic..

Continental weathering should increase as topographic relief becomes greater through mountain building episodes. The Himalaya's rise through the late-Tertiary has been suggested as a major influence over climatic deterioration, partly by its effect on the Asian monsoon and partly as a huge site for the sequestration of atmospheric CO_2 by chemical weathering. Himalayan rivers have enormous flows and equally large sediment and dissolved element loads. In particular they carry far more strontium than other rivers, and it has a highly radiogenic content of ^{87}Sr. There are three means of attaining these levels: from average continental crust which has a higher $^{87}Sr/^{86}Sr$ ratio than oceanic crust (the other main source of seawater strontium); from strontium rich limestones that acquired their isotopic signatures from the ocean when they were deposited; or from sources with unusually high $^{87}Sr/^{86}Sr$ ratios. The Himalaya are well known for carbonate sediments, and for granites formed by melting of deeper, older continental material that gives them very high proportions of radiogenic strontium. Recent work now shows that a significant contribution of highly radiogenic strontium to Himalayan rivers is hydrothermal activity (Evans, M.J. *et al*. 2001. Hydrothermal source of radiogenic strontium to Himalayan rivers. *Geology*, v. **29**, p. 803-806; doi: 10.1130/0091-7613(2001)029<0803:HSORST>2.0.CO;2). Hot springs feeding a major tributary of the Ganges contribute up to 30% of its strontium load, and incidentally a great deal of CO_2. Both result from hydrothermal alteration of deeper rocks, and are unrelated to weathering if the water involved emanates from the deep crust. It seems that these waters are recycled rainwater, so this is a case of a high-temperature chemical weathering. Whatever, it further complicates the original notion of linkage between mountain building and climate.

Methane and Snowball Earth *(November 2001)*

The well-publicized "Snowball Earth "model for Neoproterozoic glaciogenic rocks that occur at tropical palaeolatitudes has to involve an escape mechanism from global frigidity.

Without some means of warming, the high albedo of widespread ice would have locked the Earth into perpetual glaciation, which of course did not happen.

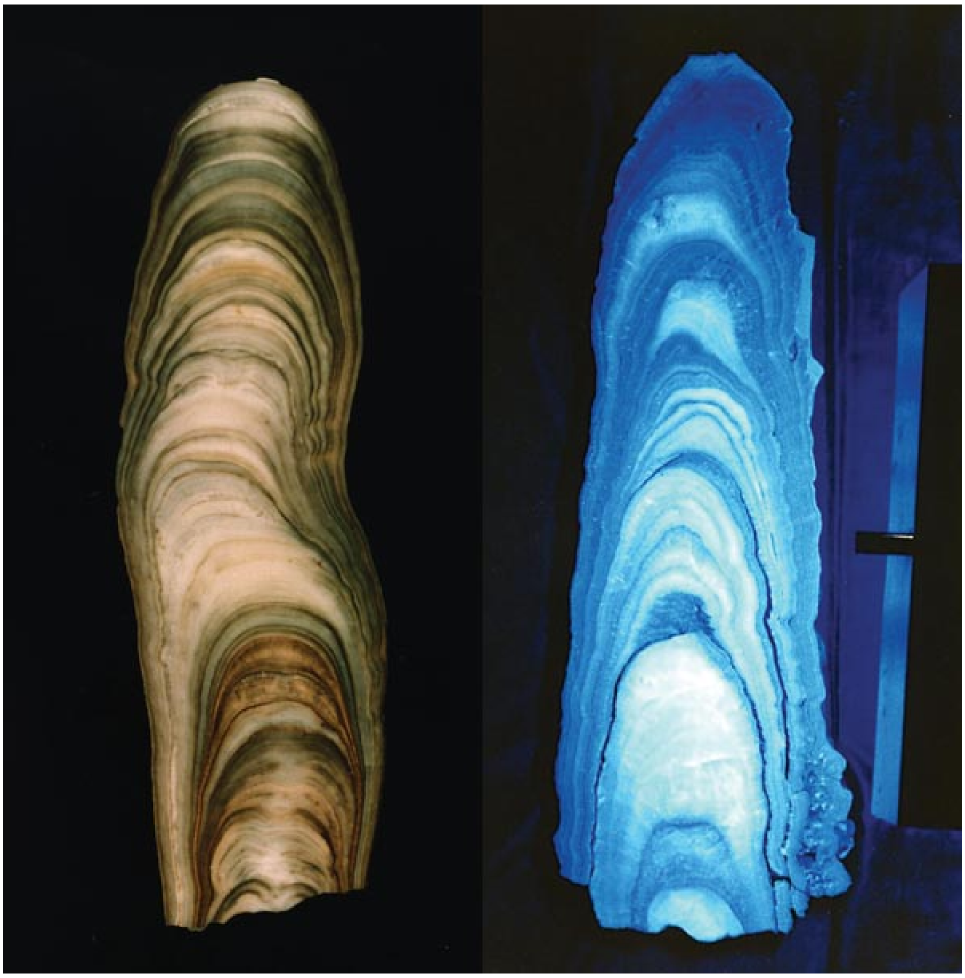
The main proponents of the model, Paul Hoffman and Dan Schragg of Harvard University suggested a gradual build up of volcanogenic CO_2 during "Snowball" conditions, when a dry atmosphere would have retained the "greenhouse" gas instead of its being sequestered to the oceans and carbonate rocks by acid rain and continental weathering. Gradually, atmospheric temperatures would have risen due to trapping of outgoing, long-wave radiation by CO_2. This simple aspect of the model leads to scenarios where warming overruns once ice sheets disappeared, to give extremely high-temperature conditions. Using carbon-isotope data from marine carbonates is a means of supporting or refuting this escape mechanism, and also of detecting the influences of other components of the carbon cycle. Carbonates take up carbon dissolved in seawater without fractionating its different isotopes, and provide measures of the degree to which organic processes did contributed to fractionation. Cell processes preferentially take up ^{12}C, and if large masses of undecayed organic matter ends up in seafloor sediments, the proportion of "heavier" ^{13}C (indicated by the standardized ratio of the two main isotopes $\delta^{13}C$) increases in seawater and the atmosphere. Carbon of mantle origin, that emerges as volcanic CO_2, has a constant $\delta^{13}C$ of about -5‰. So these two processes contribute to an isotopic balance, which for most of the Mesozoic and Cenozoic Eras established a $\delta^{13}C$ of between 0 and +4 ‰ in sea water and limestones. This is interpreted as a sign that the recent carbon cycle achieved a balance between volcanic additions and organic carbon burial weighted towards trapping of undecayed carbohydrate in sea-floor sediments. Explanations for broad climate changes since 250 Ma therefore rely more on other mechanisms than on the carbon cycle

The most comprehensive study of Neoproterozoic carbon (Walter, M.R. *et al*. 2000. Dating the 840-544 Ma Neoproterozoic interval by isotopes of strontium, carbon and sulfur in seawater, and some interpretative models. *Precambrian Research*, v. **100**, p. 371-433; doi: 10.1016/S0301-9268(99)00082-0) does indeed show dramatic see-sawing of $\delta^{13}C$ through supposed "Snowball" events, from highly positive values (<+10‰) before glaciogenic sedimentation to highly negative (>-10‰) in the immediate aftermath. However, few data were available from within glaciogenic sediments, and resolution is insufficient to detect tell-tale trends. The key approach needs detailed carbon isotopes through a single event, and such data appeared recently for the famous Neoproterozoic glaciogenic-cap carbonate sequence of Namibia (Kennedy, M.J. *et al*. 2001. Are Proterozoic cap carbonates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals. *Geology*, v. **29**, p. 443-446; doi: 10.1130/0091-7613(2001)029<0443:APCCAI>2.0.CO;2)

Kennedy *et al*. measure $\delta^{13}C$ in carbonate cements in the glaciogenic diamictites, in overlying cap carbonates and in cement to later clastic rocks. Interestingly, there is little sign of a gradual decrease in ^{13}C through the glaciogenic rocks. Constant oceanic carbon composition would be expected if no volcanic CO_2 entered seawater during frigid, dry conditions, and living processes were minimal. In the cap carbonates $\delta^{13}C$ plummets from +3‰ to -4‰. One simple explanation would be massive "rain-out" of volcanic CO_2 ($\delta^{13}C$ of -5‰) that had built up in the air during the "Snowball" episode.

Irish stalagmite reveals high-frequency climate changes *(December 2001)*

Much of the information about glacial and interglacial climate change has come from cores drilled either from ocean-floor sediments or ice caps. However, both suffer from limits to time resolution of the order of more than 100 years, although ice younger than about 5 thousand years clearly shows annual layers. While groundwater is able to flow, speleothem (flowstone) grows continuously in caves, under conditions of extremely stable temperature and humidity. Depending on how they are analysed and how thick the deposits are, stalagmites and stalactites should give fine time resolution. A half-metre long stalagmite from an Irish cave has grown since the start of the Holocene. Using high-precision uranium-series dating, its length has been calibrated in calendar years before present. A laser probe that releases oxygen from the speleothem calcite has provided oxygen isotope data whose resolution (between 7 and 18 years) is an order of magnitude better than sea-floor sediments and between 5 to 20 times better than from pre-5 ka ice cores (McDermott, F., Mattey, D.P. and Hawkesworth, C. 2001. Centennial-scale Holocene climate variabilty revealed by a high-resolution speleothem $\delta^{18}O$ record from SW Ireland. *Science*, v. **294**, p. 1328-1331; doi: 10.1126/science.1063678).



Growth lines in a vertical slice through a stalagmite: normal light (left); ultraviolet light (right). (Credit: King *et al*. 2004)

Until recently, the best documented climate variations that are more rapid than can be explained by the Milankovich effect are the Dansgaard-Oeschger cycles in the Greenland ice cap. They are of the order of 1 ka, but somewhat variable in their periodicity. The Irish stalagmite shows that there were climate shifts throughout the once supposedly stable Holocene, with frequencies equivalent to periods of 625, 169 and 78 years, the latest of which coincide with warm and cool periods since Roman times. One caution is that the oxygen isotope variations cannot be ascribed directly to variations in air temperature, because they would have been affected by differences in the surface seawater from which water vapour evaporated to fall as rain in SW Ireland. Before about 4.5 ka 8 clear peaks and troughs occur at the same times in both the Irish stalagmite and the Greenland ice core; clear signs of regional changes. These probably reflect releases of glacial meltwater to freshen surface waters of the North Atlantic. Over Greenland they resulted in atmospheric cooling, in response to weakening of the effects of the Gulf Stream by reduced thermohaline circulation. The correlation breaks down for the last 4 ka, and the fluctuations in the Irish data do not show features that coincide with ice-rafting events known from sea-floor sediment cores. That suggests that ice-rafting was no longer able to cap the North Atlantic with fresher water. Nonetheless, something was going on to impart isotopic changes to rain falling on Ireland, and that did coincide with the widespread climate changes of the recent past. What the driving processes were is not known, but it seems inescapable that underlying the drive to global warming through industrial CO_2 emissions is a more fundamental process. Should anthropogenic warming reinforce it, as seems to be happening, their combined effects could flush fresh water into the North Atlantic's surface layers, thereby slowing thermohaline circulation and the warming effect of the Gulf Stream.