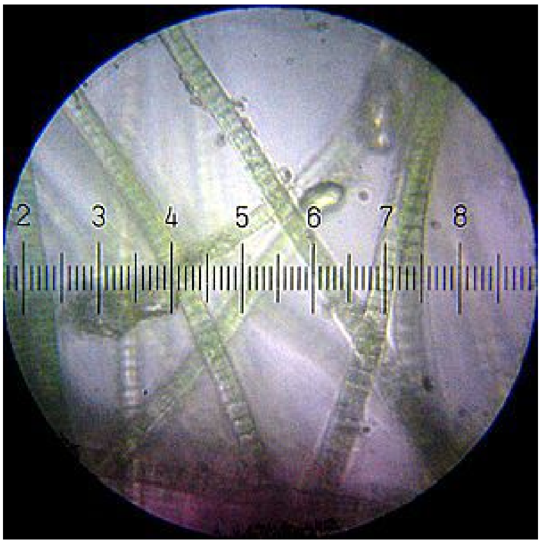
Climate change and palaeoclimatology

Massive event in the Precambrian carbon cycle (*January 2012*)

The entire eukaryote domain of life, from alga to trees and fungi to animals, would not exist had it not been for the emergence of free oxygen in the oceans and atmosphere about 2.4 billion years ago; thanks in large part to the very much simpler photosynthetic blue-green bacteria. The chemistry behind this boils down to organisms being able to transfer electrons from elements and compounds in the inorganic world to build organic molecules incorporated in living things. Having lost electrons the inorganic donors become oxidised, for instance ferrous iron (Fe^{2+} or Fe-2) becomes ferric iron (Fe^{3+} or Fe-3) and sulfide ions (S^{2-}) become sulfate (SO_4^{2-}) and the organic products that receive electrons principally involve reduction of carbon, on the OilRig principal – **O**xidation **i**nvolves **l**oss of electrons, **r**eduction **i**nvolves **g**ain. Since the Great Oxygenation Event (GOE), ferric iron and sulfate ions now account for 75% of oxidation of the lithosphere and hydrosphere while free oxygen (O_2) is a mere 2-3 % (Hayes, J.M. 2011. Earth's redox history. *Science*. V. **334**, p. 1654-1655; DOI: 10.1126/science.1216481); an excellent introduction to the geochemistry involved in the GOE and the carbon cycle. Free oxygen is around today only because more of it is produced than is consumed by its reacting with ferrous iron and sulfide ions supplied mainly by volcanism, and with carbon-rich material exposed to surface processes by erosion and sediment transport.



Cyanobacteria: earliest producers of oxygen in the Precambrian.

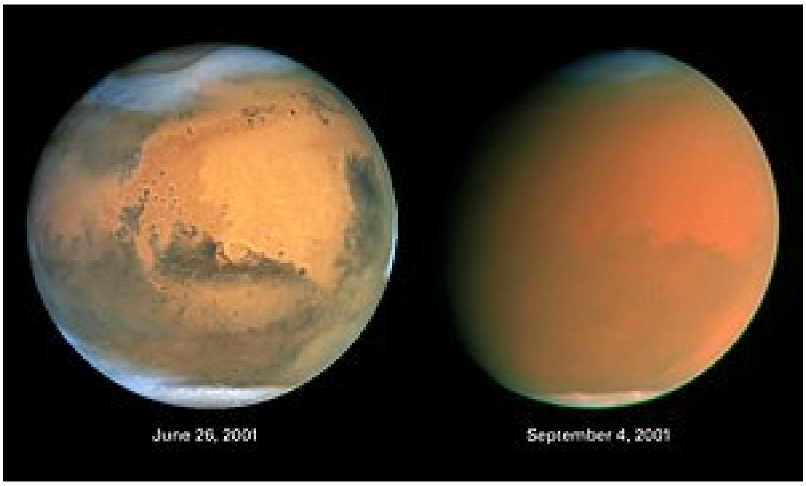
Eukaryote life has never been snuffed out for the last two billion years or so, but it has certainly had its ups and downs. To geochemists who take the long view, oxygen might well seem to have steadily risen. But that is hardly likely in the hugely varied chemical factory that constitutes Earth's surface environments, involving major geochemical cycles for carbon, iron, sulfur, nitrogen, phosphorus and so on, that all inveigle oxygen into reactions. Tabs can be kept on one of these cycles – that involving carbon – through the way in which the proportions of its stable isotopes vary in natural systems. If all geochemistry was in balance all the time, all materials that contain carbon would show the same proportions of ^{13}C and ^{12}C as the whole Earth, but that is never the case. Living processes that fix carbon in organic compounds favour the lighter isotope, so they show a deficit of ^{13}C relative to ^{12}C signified by negative values of $\delta^{13}C$. The source of the carbon, for instance CO_2 dissolved in sea water, thereby becomes enriched in ^{13}C to achieve a *positive* value of $\delta^{13}C$, which may then be preserved in the form of carbonates in, for instance, fossil shells that ended up in limestones formed at the same time as organic processes were favouring the lighter isotope of carbon. Any organic carbon compounds that ocean-floor mud buried before they decayed (became oxidised) conversely would add their *negative* $\delta^{13}C$ to the sediment. Searching for $\delta^{13}C$ anomalies in limestones and carbonaceous mudrocks has become a major means of charting life's ups and downs, and also what has happened to buried organic carbon through geological time.

A most interesting time to examine C-isotopes and the carbon cycle is undoubtedly the period immediately following the GOE, in the Palaeoproterozoic Era (2500 to 1600 Ma). From around 2200 to 2060 Ma the general picture is roughly constant, high positive values of $\delta^{13}C$ (~+10‰): more organic carbon was being buried than was being oxidised to CO_2. However, in drill cores through the Palaeoproterozoic of NW Russia carbonate carbon undergoes a sharp *decline* in its heavy isotope to give a negative $\delta^{13}C$ (~-14‰) while carbon in organic-rich sediments falls too (to~-40‰): definitely against the general trend (Kump, L.R. *et al*. 2011. Isotopic evidence for massive oxidation of organic matter following the Great Oxidation Event. *Science*. v. **334**, p. 1694-1696; DOI: 10.1126/science.1213999). Oxygen isotopes in the carbonates affected by the depletion in 'heavy' carbon show barely a flicker of change: a clear sign that the ^{13}C $\delta^{13}C$ deficit is not due to later alteration by hydrothermal fluids, as can sometimes cause deviant $\delta^{13}C$ in limestones. It is more likely that a vast amount of organic carbon, buried in sediments or dissolved in seawater was oxidised to CO_2 faster than biological activity was supplying dead material to be buried or dissolved. In turn, the overproduction of carbon dioxide dissolved in seawater to affect C-isotopes in limestones. Such an event would have entailed a sharp increase in oxygen production to levels capable of causing the oxidation (~ 1% of present levels). Yet this was not the time of the GOE (2400 Ma) but 300-400 Ma later. A possible explanation is a burst in oxygen production by more photosynthetic activity, perhaps by the evolution of chloroplast-bearing eukaryotes much larger than cyanobacteria.

Related articles: Rise of atmospheric oxygen more complicated than previously thought (eurekalert.org); The Great Oxygenation Event (olivermeredithcox.wordpress.com)

Dust: heating or cooling? (*January 2012*)

Roughly every 13 years dust blots out most of the surface of Mars turning it into an orange ball. The last such planet-encircling dust storm occurred in 2001, but lesser storms spring up on a seasonal basis. Yet Martian seasons have very different weather from terrestrial ones because of the greater eccentricity of Mars's orbit, as well as the fact that its 'weather' doesn't involve water. When Mars is closest to the Sun, solar heating is 20% greater than the average, for both hemispheres. The approach to that perihelion marks the start of the dust season which last for half the Martian year. Unsurprisingly, the sedimentary process that dominates Mars nowadays is the whipping up and deposition of sand and dust, though in the distant past catastrophic floods – probably when subsurface ice melted – sculpted a mainly volcanic landscape pockmarked with impact craters. Waterlain sediments on early Mars filled, at least in part, many of the earlier craters and probably blanketed the bulk of its northern hemisphere, which is the lowest part of the planet and now devoid of large craters. Erosion and sedimentation since that eventful first billion years has largely been aeolian. Some areas having spectacular dunes of many shapes and sizes, whereas more rugged surfaces show streamlined linear ridges, or yardangs (see *Winds of change* May 2011), formed by sand blasting. Most of the dust on Mars is raised by high winds in the thin atmosphere that sweep the great plains and basins and, by virtue of Stokes's law, the grains are very much smaller than on Earth.



Mars: with and without dust storms in 2001

The dustiest times on Earth in the last million years, which might have blotted out sizeable areas from alien astronomers, have been glacial maxima, roughly every 100 ka with the latest 20 ka ago. Layering in the Antarctic ice core records such dust-dominated frigid periods very precisely. Less intricate records formed away from the maximum extent of ice sheets as layers of fine sediment known as loess, whose thickness variations match other proxy records of palaeoclimate nicely. Loess, either in place or redeposited in alluvium by rivers, forms the most fertile soil known – when the climate is warm and moist. The vast cereal production of lowland China and the prairies of North America coincides with loess: it may seem strange but a large proportion of 7 billion living humans survive partly because of dust storms during glacial periods of the past.

Being derived from rock-forming minerals dust carries with it a diverse range of chemical elements, including a critical nutrient common on land but in short supply in ocean water far offshore: iron in the form of oxide and hydroxide coatings on dust particles – the dust coating your car after rain often has a yellow or pinkish hue because of its iron content. Even when the well-known 'fertilizer' elements potassium, nitrogen and phosphorus are abundant in surface ocean water, they can not encourage algal phytoplankton to multiply without iron. Today the most remote parts of the oceans have little living in their surface layers because of this iron deficiency. Yet oceanographers and climatologists are pretty sure that this wasn't always the case. They are confident simply because reducing the amount of atmospheric carbon dioxide and its greenhouse effect to levels that would encourage climate cooling and glacial epochs needed more carbon to be buried on the ocean floors than happens nowadays, and lifeless ocean centres would not help in that.

Saharan dust carried over the Atlantic Ocean by a tropical cyclone affecting NW Africa.

At present, the greatest source of atmospheric dust is the Sahara Desert (Bartholoet, J. 2012. Swept from Africa to the Sahara. *Scientific American*, v. **306** (February 2012), p. 34-39). Largely derived from palaeolakes present during a Holocene pluvial episode, Saharan dust accounts for more than half the two billion metric tonnes of particulate atmospheric aerosols dispersed over the Earth each year. Located in the SE trade-wind belt, the Sahara vents dust clouds across the Atlantic Ocean, most to fall there and contribute dissolved material to the mid-ocean planktonic biome. Yet an estimated 40 million t reaches the Amazon basin, contributing to fertilising the otherwise highly leached tropical rain-forest soils. While over the ocean, the high albedo of dust adds a cooling effect to the otherwise absorbent sea surface. Over land the fine particles help nucleate water droplets in clouds and hence encourage rainfall. The climatic functions of clouds and dusts are probably the least known factors in the climatic system, a mere 5% uncertainty in their climatic forcing may mean the difference between unremitting global warming ahead or sufficient cooling by reflection of solar radiation to compensate for the cumulative effects of industrial CO_2 emissions.

Recording amounts of dust from seafloor sediments is difficult, and impossible from terrestrial sediments, but superb records tied accurately to time at annual precision exist in ice caps. Low dust levels in Greenland and Antarctic ice tally well with the so-called 'Medieval Climate Anomaly' (a warm period) whereas through the 13th to 19th centuries (the 'Little Ice Age') more dust than average circulated in the atmosphere. Crucially, for climate change in the industrial era, there has been a massive spike in dust reaching near-polar latitudes since the close of the 18th century during the period associated with signs of global warming: a counterintuitive relationship, but one that is difficult to interpret. The additional dust may well be a result of massive changes in land use across the planet following industrialised agricultural practices and growing population. There are several questions: does the additional dust also reflect global warming with which it is correlated, i.e. evaporation of the huge former lakes in the Sahara (e.g. Lake Chad); is the dust preventing additional greenhouse warming that would have taken place had the atmosphere been clearer; is it even the 'wrong kind of dust', which may well reflect short-wave solar radiation away but also absorbs the longer wavelength thermal radiation emitted by the Earth's surface, i.e. an aerosol form of greenhouse warming. Needless to say, neither clouds nor dust can be factored into climate prediction models with much confidence.

Related articles: Evan, A.T. *et al* 2011: Influence of African dust on ocean–atmosphere variability in the tropical Atlantic. Nature Geoscience, v. **4**, p. 762-765; DOI: 10.1038/ngeo1276.