Evidence goes against end-Permian impact (January 2005)

Last year I commented (see Bedout end-Permian “impact” hammered October 2004) on what appears to be a serious challenge to claims of geochemical evidence that would support a major impact associated with the largest of all Phanerozoic mass extinctions at the close of the Permian Period and the Palaeozoic Era, around 251 Ma ago. Newly published analyses from two other well-constrained P-Tr boundary sites found no signs of the elements that would be expected from a major collision with a metal or silicate-rich asteroid (Koeberl, C. et al. 2004. Geochemistry of the end-Permian extinction event in Austria and Italy: No evidence for an extraterrestrial component. Geology, v. 32, p. 1053-1056: DOI: 10.1130/G20907.1). Koeberl of the University of Vienna and colleagues from the US and UK focussed on platinum-group elements (PGEs), and osmium and helium isotopes. Both sites are stratigraphically similar and dominated by carbonate sediments, with evidence from one site for deepening water that laid down organic-rich marls. Sure enough, there is a “spike” in iridium at the level of these marls, which had been documented at the Austrian site in 1989, and there is another 50 m higher in the sequence. The new work confirmed both, and also found the marl-related “spike” in Italy. But the reason why iridium has been used to suggest extraterrestrial impacts is because, of all the PGEs, it is the easiest to analyse at very low concentrations.

That can give rise to “false positives”, for there are purely terrestrial processes that can concentrate PGEs. An unambiguous arbiter between these processes and impacts lies in the isotopic composition of the metal osmium. Rocks of the Earth’s crust have high rhenium (Re) and low osmium (Os) contents, whereas in meteorites the Re/Os ratio is very much smaller. The unstable isotope $^{187}$Re decays to produce a daughter $^{187}$Os that adds to the common $^{188}$Os isotope. Consequently, terrestrial rocks acquire high $^{187}$Os/$^{188}$Os rapidly after they crystallise from magmas and that “signature” is imparted to the entire surface environment through weathering and solution. On the other hand, meteorites have low $^{187}$Os/$^{188}$Os ratios, so the two influences on the geochemical record can be distinguished – if you have good enough analytical facilities. The two iridium spikes fail that test, as regards an impact origin. It seems likely that they originated through precipitation of PGEs from sea water under reducing conditions on the deep sea floor. The helium isotope data carry the same negative message; they are typically terrestrial.

Impact-induced extinctions, particularly ones that wipe out a sizeable proportion of all organisms, are likely to be unrelentingly sudden – direct effects being felt within hours over the whole planet, and secondary effects such as “nuclear winter” and acid rainfall over a matter of a few years or decades. Radiometric dating is incapable of resolving such short periods, and at the age of the P-Tr boundary probably not even several hundred millennia. Faunal sequences can give a better indication of abruptness. To most intents the marine record at the time does look as if extinction was very sharp, but it does not indicate anything by way of clear evidence for an impact, such as glass spherules, shocked quartz grains and other tell-tale signs. The continental record is pretty sparse, so has not figured much in the debate. However, the Karoo basin of South Africa contains thick continental sediments that span the boundary, and is famous for its primitive reptile fauna, some of
which became extinct around the time of the P-Tr event. Incidentally, this die-off created the genetic conditions for the adaptive radiation in the Mesozoic that led not only to the dinosaurs but also the mammals and birds.

Charting the timing of the Karoo extinctions has proved difficult, although it appears not to have been sudden in a stratigraphic sense. New age data has emerged from studies of palaeomagnetic field reversals in the sediments, together with variations in carbon isotopes, that allow timing to be better assessed through comparison with magnetic and carbon records from other sections (Ward, P.D. et al. 2005. Abrupt and gradual extinction among Late Permian land vertebrates in the Karoo Basin, South Africa. Science, v. 307, p. 709-714; DOI: 10.1126/science.1107068). The signs are that the proto-reptiles died off over tens to hundreds of thousand years due to some protracted crisis, probably connected with the giant continental flood basalt eruptions that formed the Siberian Traps. Those lavas overlap the timing of the P-Tr boundary, and would certainly have added sufficient CO₂ to give substantial global warming and also massive emissions of SO₂ that would have created chemically hazardous conditions on a global scale.

**New predators on the Mesozoic block (January 2005)**

Most people have been led to believe that, although the earliest mammals appeared in the Triassic fossil record, throughout the Mesozoic they were tiny and meekly scurried and skulked while the dinosaurs reigned supreme over land, sea and air. They had to wait for the K-T extinction to develop their full ecological potential. That is now a myth, for Chinese strata (yet again) have revealed much larger mammals than ever thought possible, and some of them ate dinosaurs (Hu, Y. et al. 2005. Large Mesozoic mammals fed on young dinosaurs. Nature, v. 433, p. 149-152; DOI: 10.1038/nature03102). One indisputable mammal skeleton (Repenomamus) contained the bones of dinosaur hatchlings in its body cavity. In fact so many that one wonders if it met its end through greed.

**Age range of early fossil treasure trove in China (February 2005)**

The Doushantuo Formation of southern China dates from just before the Cambrian Explosion, and has become a source of astonishing information about animals that preceded the appearance of those with hard parts. It contains fossil embryos, algae, acritarchs, and small bilaterians that are purportedly the Earth’s earliest animals. Moreover the formation rests on the cap carbonates of a diamictite reckoned to represent a late Neoproterozoic
glacial epoch, and provides a variable trend of carbon-isotope variation that extends up to the base of the Cambrian in southern China. Because the sequence contains a number of volcanic ash beds it is potentially dateable. Using a single-zircon U-Pb method, Daniel Condon of MIT and colleagues from the Chinese Academy of Science have established the ages of both top and base of the Doushantuo Formation with considerable precision (Condon, D. et al. 2005. U-Pb Ages from the Neoproterozoic Doushantuo Formation, China, Science, v. 308, p. 95-98; DOI: 10.1126/science.1107765).

Sedimentation is bracketed between 635 and 550 Ma, the oldest age coinciding with that for the Ghaub tillite in Namibia. There is one snag; within the sequence is a formation boundary that signifies non-deposition, which the authors correlate with a glacial epoch recognised in Newfoundland (the Gaskiers diamicite), citing sea-level withdrawal as the cause of non-deposition in China. Time-calibration using the carbon-isotope record at Doushantuo allows it to be matched with others in Namibia, Oman and Newoundland. A well-constrained correlation suggests a major, global increase in the burial of $^{12}$C that produced a marked negative excursion in $\delta^{13}$C that spans around 90% of the Ediacaran Period that saw the rise of large soft-bodied animals shortly before the emergence of shelly faunas. The interpretation placed by the authors on this signature of burial of dead organic matter, which relates to no sign of glaciation, is that it would have elevated oxygen levels in the Late Neoproterozoic oceans. That might have increased productivity by primitive eukaryotes, and possibly opportunities for predation. The uppermost part of the Doushantuo Formation broadly coincides with the first appearance of complex trace fossils and mollusk-like bilaterians, and elsewhere there are signs of the first reef formation by weakly calcified metazoans at around that time. Clearly, it is well-dated sections such as these that may hold the key to what exactly prompted the general secretion of skeletal material; the hallmark of the 10 Ma later explosion in fossil animals.

**No graphite in Akilia apatites and no sign of life? (February 2005)**

In December 2004 I reported evidence that weighed against a sedimentary origin for the ~3.8 Ga ironstones of West Greenland from which isotopically light carbon had been claimed to indicate the earliest signs of life (see *Iron isotopes enter the Archaean life debate* December 2004). The original work that claimed a biological signature in carbon from the oldest known metasedimentary rocks focussed on carbon-isotope analyses of apatites in them, in the belief that they would have withstood intense metamorphic alteration because of the resistance of that mineral to chemical reactions. Following close on the heels of that revelation comes one a great deal more worrying for aficionados of biogeochemistry. Geoscientists from Estonia, France, the US and Sweden have systematically made petrographic observations on apatite grains from the rocks of the Akilia Association, including those originally reported as carrying geochemical signs of life existing at that time (Lepland, A. et al. 2005. Questioning the evidence for Earth’s earliest life – Akilia revisited. Geology, v. 33, p. 77-79; DOI: 10.1130/G20890.1). Of the 190 individual apatite grains extracted from 17 rocks, not one showed the slightest trace of carbonaceous material. It seems that apatite is unlikely to have been the host for the low $\delta^{13}$C that caused such a stir in palaeobiological circles when it was first announced. Isua may well not be a good place to look for biomarkers. It also throws into question what did produce the signal. If it was the bulk rock, then the depletion in $^{13}$C could have resulted from temperature induced isotopic
fractionation. Another possibility is that the samples were contaminated with modern biological materials, despite the precautions taken to avoid that.

**Evolutionary rhythms (March 2005)**

The late Jack Sepkoski did a lasting service for those who study life’s record by combing the literature to compile the first and last appearance of each marine fossil genus. It is from this archive that we have been able to visualise numerically mass extinctions and those lesser in magnitude. As well as the “Big Five” there are other die-offs, particularly through the Mesozoic and Cenozoic Eras. To some extent the extinction patterns also appear among terrestrial taxa that have been less well documented, partly because few have had Sepkoski’s determination and partly because land organisms leave fewer traces. It quickly became apparent to him and other palaeontologists that extinction occurred sharply, which is why the biologically-determined division of Phanerozoic time since 542 Ma is so well defined world-wide. What also emerged from inspection of the time series of genus and family numbers was a pulse in the timing of significant extinctions, which appears to have been between 25 and 30 Ma. That struck a chord with specialists in volcanic activity, and there is a good correlation between the occurrence of flood-basalt outpourings and extinctions. But at least one of the five largest extinctions, at the K-T boundary, coincides with abundant evidence for a major impact by an extraterrestrial body. Planetary scientists then began looking for a pulsed variation in the intensity of bombardment of the Inner Solar System. There is no tangible evidence of that, although there are theoretical arguments that suggest that the Sun in its ~250 Ma orbit around the galactic centre wobbles through dust arranged in bands close to the galactic plane every 30 Ma.

![Sepkoski’s plot of changes in marine faunal diversity during the Phanerozoic. Colours indicate groups of families that reached the acme in the Cambrian (Cm), Palaeozoic (Pz) and Mesozoic to modern (Md). Numbers indicate the major mass extinctions.](image)
Extinctions are not, of course, the only features of the fossil record. Primarily it charts variations in diversity, of which suddenly lowered numbers are one aspect in broader fluctuations. Each extinction precedes an increase in biodiversity as adaptive radiation from surviving taxa fills ecological niches left vacant or under-populated. That part of the record has its fascinations, as complexity seems to have emerged in three great pulses, through the Palaeozoic, Mesozoic and Cenozoic Eras, each producing more diverse forms than its predecessor. There are also slackenings in the pace and periods of apparent stasis. Getting to numerical grips with the full record requires analysis that uses similar mathematical techniques to that which unlocked proof of Milankovich’s theory of astronomical pacing of climate from finely calibrated oceanic-sediment records. It is possible to analyse time series in terms of discrete frequencies from which the curves can be reconstructed. Physicists Robert Rohde and Richard Muller of the University of California have used this Fourier analysis on the 36 thousand strong catalogue published after Sepkoski’s death, with some recalibration of the time scale and some pruning of data – they removed genera with only a single record or whose age is poorly known (Rohde, R.A. & Muller, R.A. 2005. Cycles in fossil diversity. Nature, v. 434, p. 208-210: DOI: 10.1038/nature03339).

There are definitely distinct frequencies that dominate the record, and they cannot be present by chance, although that is a purely statistical view. But to their surprise, and everyone else’s, they are completely unexpected ones at 62 and 140 Ma. It is proving exceedingly difficult to come up with plausible Earthly or extra-terrestrial explanations. There are two interesting features: the 62 Ma periodicity dominates the record of relatively short-lived genera; and the “Big Five” seem to fit neatly into the patterns of diversity, albeit at unequally spaced intervals, when the effects of background fluctuations have been removed. That filtering may allow for increasing preservation towards recent times. One major control over diversity is, logically, a mixture of the number of potential niches and their geographic isolation, and both are probably related to plate tectonic activity. Unfortunately, fluctuations in 2 and even 3 geographic dimensions have only the broadest calibration to time. Added to that is the complex way in which global sea level has changed with time. So we can expect a great deal of head scratching, and it may come as a relief that the crowing of some volcanologists and impact theorists may have been silenced at a single stroke!


New twist for end-Permian extinctions (April 2005)

The old adage, “There are more ways of killing a cat than drowning it in butter” seems apt for mass extinctions, particularly the most severe on that ended the Palaeozoic. A new hypothesis points the finger towards breathing problems, but nothing to do with massive, ground-hugging emissions of sulphur dioxide from the Siberian flood basalts that coincide with the P-Tr extinction. Raymond Huey and Peter Ward of the University of Washington reckon a major contributing factor for terrestrial extinctions was a fall in atmospheric oxygen (Huey, R.B. & Ward, P.D. 2005. Hypoxia, global warming and terrestrial Late Permian extinctions. Science, v. 308, p. 398-401; DOI: 10.1126/science.1108019).

For most of the Carboniferous and Early Permian, Earth flipped in and out of glacial conditions that dominated the southern supercontinent of Gondwana. Tropical latitudes
were cloaked in dense vegetation for the first time. Rapid sedimentation buried vast amounts of carbon in the form now taken by the world’s largest and most extensive coal deposits. Net carbon burial for 90 to 100 Ma resulted in extraordinary oxygen concentrations in the atmosphere. One line of evidence for that is the huge size of Carboniferous and Early Permian insect fossils, such as those of dragonflies. Insects do not breathe, but take in oxygen by a diffusive process through spiracles on the underside of their bodies. The more oxygen the larger they can grow. Carbon burial also links in with the global cooling that made the Carboniferous and Early Permian susceptible to astronomic forcing of glacial-interglacial cyclicity because CO₂ and the greenhouse waned.

The present-day oxygen concentration in the air is about 22%, whereas estimates for the Carboniferous Permian peak concentration are around 30%. Most land animals today, including ourselves, have an altitude limit to permanent life of around 4 to 5 km, though the vast majority live much lower. In the Early to Middle Permian, the availability of oxygen for respiration would have raised that to around 6 km altitude, and the top of a mountain the height of Everest would not constitute the “Death Zone”. The limit to the altitude range of animals would have been temperature rather than oxygen availability. So, given sufficient warmth, the area available for animal life would have been very high. Estimates of the oxygen level at the end of the Permian are as low as about 16%. Even living at sea level would have demanded an ability to survive at about 2.7 km today and at 6 km during the oxygen-rich Early and Middle Permian. Evolution of land animals during the 100 Ma long “global winter” would have adjusted to elevated oxygen availability, which Huey and Ward believe would have led to at least a limited altitude stratification of available ecosystems, governed by temperature. Their hypothesis is that declining oxygen forced extinctions by reducing the habitable range severely, and increased competition among those taxa able to live in the reduced, low-altitude land area: probably patches of “refugia”.

The decline in oxygen was accompanied by global warming. Permian and Triassic sedimentary records show a dramatic increase in red terrestrial sediments, coloured by iron oxide. Iron had been released and oxidised to insoluble iron(III), possibly by increased continental weathering, which would have sequestered oxygen by the formation of iron oxide coatings to sedimentary grains. Increased oxidation would also have encouraged biodegradation by aerobic bacteria, which may have run-away to help boost atmospheric CO₂ levels. One testable outcome of such events is the rate of extinction during the Late Permian, which should have risen slowly, rather than plummeting at the P-Tr event. Another is that survivors might show signs of adaptation to low oxygen levels, and indeed some Triassic reptiles do. All in all, those times were stressful on land. Yet the extinctions were just as severe in marine ecosystems, where the fossil record is more complete. Less oxygen and warmer seas would have resulted in similar hypoxia for aquatic animals.
Lichen-like fossils from the Doushantuo Formation (Credit: Yuan et al. 2005; Fig. 1)

Lichens are not individual species, although they are given Linnaean names, but symbiotic associations of two or more species. In the lichens the mutual relationship is between entirely different organisms: fungi with either algae or blue-green bacteria. Although lichen form one of the plagues set to try field geologists, their fossil record is extremely sparse. Once again, Chinese lagerstätten in the Doushantuo Formation establish a first, in this case preserved in phosphorites (Yuan, X. et al. 2005. Lichen-like symbiosis 600 million years ago. Science, v. 308, p. 1017-1020; DOI: 10.1126/science.1111347). The fossils show exquisite detail, sufficient to reveal both fungus-like hyphae and cells that resemble those of cyanobacteria. They are from the late Neoproterozoic, Ediacaran period, when all manner of evolutionary developments were taking place. One question that is unanswered is whether or not these fossils were marine or subaerial (could they be the earliest life on land?). Modern lichens are intolerant of salt water.

Methuselah (May 2005)

Since the 1960s claims have been made for the oldest living organism being found in brine inclusions from salt deposits, and most have been dismissed as modern contaminants. In 2000 that easy avoidance was ruled out by super-sterile culturing of the contents of a fluid inclusion in a Permian halite crystal from New Mexico (see The undead: ancient bacteria in salt October 2000). The research produced a culture of the salt-tolerant bacterium Virgilbacillus. However, the odd nature of the crystal could have formed much later than the deposition of the salt beds. Confirming a Permian age for a fluid inclusion is not easy. One approach is by comparing the composition and formation temperature of the bacterium-hosting fluid with that from other, more usual inclusions in the same deposit and from fluids that form when salt deposits are exposed to air (“weeps”), as might be included when salt deposits recrystallise long after their formation (Satterfield, C.L. et al. 2005. New evidence for 250 Ma age of halotolerant bacterium from a Permian salt crystal. Geology, v. 33, p. 265-268; DOI: 10.1130/G21106.1). The study found that the inclusion fluids along with others from halite at the same level in the salt deposit have significantly different compositions from “weeps”. The latter reflect the composition of the salts in the deposit which formed by precipitation of the less soluble components of seawater. The inclusions have compositions more like sea water that has been concentrated by evaporation, albeit different from that of modern halite inclusions. So it does indeed seem as if the revived
Virgilbacillus is a Permian creature. Yet to emerge are DNA analyses that can be compared with modern Virgilbacillus species.

**Zircon and the quest for life’s origin (May 2005)**

At a rough estimate the material that has pushed back the oldest direct dating of supposedly continental material is about the size of a pinch of salt. It consists of detrital zircon grains contained in Archaean sedimentary quartzites from Western Australia, the oldest of which give U-Pb ages of 4.4 Ga, 400 Ma older than the earliest rocks of the continents. Arguably, the zircons are products of repeatedly recycled debris from the earliest silica-rich magmas formed in the Hadean: zircon is hard and not affected by sedimentary processes. Any subduction processes in the early Earth might well have produced silicic magmas by a variety of petrogenetic processes: modern ocean crust contains tiny amounts of plagiogranites. Minute inclusions of quartz, mica and feldspar in the zircons suggest that such igneous rocks may have formed by partial melting of the clay-rich sedimentary veneer on Hadean oceanic crust when it descended. So, the only surprise in a chronological sense is that a few grains have been found among those formed in the 1.4 Ga until the deposition of the 3 Ga old Jack Hills quartzite in which they found a resting place. The zircons are controversial for another reason. They contain high concentrations of $^{18}$O that indicate a role for water in their formation.

Bruce Watson and Mark Harrison of the Rensselaer Polytechnic Institute, New York and the Australian National University have devised a way of establishing the temperatures at which the zircon formed, from their content of titanium (Watson, E.B & Harrison, T.M. 2005. Zircon thermometer reveals minimum melting conditions on earliest Earth. *Science*, v. 308, p. 841-844; DOI: 10.1126/science.1110873). Their results from 54 zircons aged from 4.0 to 4.35 Ga cluster around 700°C, which is what would be expected had their parent magmas formed at the minimum temperature for partial melting of sediments to form granite-like magmas in the presence of a water-rich fluid (the “wet-granite minimum”): they look very similar to modern zircons. This confirms the results from earlier oxygen-isotope studies. Because the oldest of the Jack Hills zircons are only 75 Ma younger than the mighty thermal effect of the Earth’s collision with a smaller planetary body that excavated matter that formed the Moon, the influence of water in the zircons’ formation has been interpreted as having monumental significance for the effectively vanished 400 Ma-long Hadean Eon. It has been taken as support for oceans at the Earth’s surface, as well as “normal” plate tectonic processes that can generate continental crust, but also that conditions amenable to pre-biotic chemistry and even the origin of life existed.

The Earth could not have escaped the massive Hadean bombardment of the lunar surface by planetesimals that climaxed between 4.0 and 3.8 Ga. Rocks from the lunar highlands preserve ages back to 4.45 Ga, close to the time of its origin, and at that time the Moon must have had a solid crust below about 400°C for radiogenic isotopes to accumulate in minerals. The Earth equally must have had at least a surface veneer of relative cool rock at that time. So, since the Apollo samples yielded these dates in the 1970’s, the popular image of a long-lived magma ocean has been insupportable, even though it probably existed shortly after the cataclysm of the formation of the Earth-Moon system. In that sense, evidence in ancient zircons for plate-like processes is not a surprise, although an interesting confirmation of long-held beliefs. Nor does their showing the influence of water come as a
shock. The Earth is tectonically active partly through it not having been thoroughly dried by Moon formation; lunar rocks are a great deal drier and the Moon is as dead as a doorknob. At 700°C water cannot exist as a liquid, so its influence in partial melting is not evidence for surface water. However, the most efficient means of heat loss from any heated body is by radiation to space, and simple calculations show that it would be highly unlikely for Earth not to have had liquid surface water about 100 Ma after Moon formation. That in itself indicates that there would have been a water-rich atmosphere too.

No matter how much “shock and awe” might colour our view of repeated bombardment during the Hadean, no sane impact theorist has suggested that sufficient energy was delivered to recreate a global magma ocean. Water may have been boiled off to the atmosphere by the biggest, but only to fall again as rain between major impacts. Given favourable chemical conditions and liquid water, the route to surface liquid water might well have opened up in the Hadean itself: some have suggested that it happened again and again until the Inner Solar System became a safer place after 3.8 Ga. The real mystery of the aged zircons concerns the rocks in which they crystallised: where on Earth are they? Four decades of radiometric dating of actual rocks has failed to break the 4.0 Ga barrier, so if relics do remain they are either buried or have been reduced to sediments, as the Jack Hills quartzite so nicely demonstrates.

See also: Reich, E.S. 2005. What the hell…? New Scientist 14 May 2005, p. 41-43.

Hydrogen sulfide and mass extinction (June 2005)

Naughty school kids once used to hurl glass vials that launched a pervading smell of rotten eggs when they smashed. Stink bombs produce hydrogen sulfide. Interestingly, if you can smell it you are more or less safe – though not from flying glass shards. When H₂S is more concentrated, it becomes an odourless and stealthy killer; ‘sour gas’ emitted from oil drilling rigs. A group of anaerobic bacteria generate the gas when there are abundant sulfate ions in oxygen-starved conditions. They use these ions as electron acceptors in their metabolism, thereby reducing sulfate to sulfide ions; a common phenomenon in stagnant swamps, and especially prevalent at depth in the Black Sea. Several times during the Phanerozoic global ocean depths became anoxic, when thermohaline circulation shut down. The consequences show up in black mudrocks, rich in partially broken down hydrocarbons and iron sulfide. Some of these are major source rocks for petroleum. Unstirred by deep current flow, bottom waters pervaded by H₂S are covered by oxygenated water, so it might seem that there is little threat to surface dwellers and air breathers, although any animal unwarily entering toxic bottom water would instantly die. That is why black mudrocks are repositories of exquisite fossils. Should H₂S build up in deep water, however, there might be chemical instability that would result in large-scale emissions to the upper ocean and to the atmosphere. Geochemists from the universities of Pennsylvania and Colorado have made some simple chemical calculations to see if such a potentially catastrophic leakage is within the bounds of possibility (Kump, L.R. et al. 2005. Massive release of hydrogen sulfide to the surface ocean and atmosphere during intervals of oceanic anoxia. Geology, v. 33, p. 397-400; DOI: 10.1130/G21295.1). Theoretically it is, once a threshold concentration of around 1 mmol kg⁻¹ of H₂S dissolved in deep water is exceeded. There would be sulfidic upwellings involving emissions of the order of teratonnes
of sulfide per year to the atmosphere; more than 2000 times that today from volcanoes, with the added risk that it would also permeate upper-ocean water.

As well as witnessing mass extinctions, the Late Devonian, end-Permian and Middle Cretaceous were characterized by widespread anoxia. Leakage of H2S would not only have killed directly, but would have destroyed the ozone layer that protects from UV radiation. Inevitably, methane produced by other anaerobic bacteria would also have been released in the same way to force global warming. Rather than being the result of dramatic impacts or monstrous flood basalt effusions, mass extinctions at these times would have been quiet, but efficient nonetheless

**Potted history of atmospheric oxygen (June 2005)**

The most likely hallmark of an inhabited planet is an atmosphere that contains oxygen; a simple rule of thumb made popular by James Lovelock. By assembling complex molecules based on carbon, life increases the degree of chemical reduction in its environment. Effectively it draws in electrons, and the counterpart of that must be that some other component loses them through oxidation. On Earth the source of electrons needed to make organic molecules through the action of photosynthesis is predominantly the oxygen atoms locked in molecules of water and carbon dioxide. By losing 4 electrons, 2 oxygens bonded in those two simple compounds are oxidised to become the gas O2, which itself has become the commonest and most active acceptor of electrons from reduced ions and compounds. Oxygen gives its name to oxidation, which is the inevitable fate of most organisms, thereby reversing the process of photosynthesis. A planet whose surface topography is continually changing, because more radioactive energy is produced in its mantle than can be lost to space by radiation, generates physical conditions that continually bury and store some unoxidised carbon compounds. Carbon burial together with continued living processes keeps the photosynthetic chemical equation weighted in favour of free oxygen.

Since the domain of living things to which we and all advanced organisms belong, the Eukarya, is almost wholly one to which oxygen is vital in metabolism, there can be few more important geoscientific topics than how and when oxygen emerged as a free element. There have been major recent developments in addressing these questions, so it is useful and fascinating to find an up-to-date and easily read review (Kerr, R.A. 2005. *The story of O2*. *Science*, v. 308, p. 1730-1732; DOI: 10.1126/science.308.5729.1730). Among its highlights is evidence that although cyanobacteria (the most primitive oxygenic photosynthesisers) were definitely around at 2.7 Ga, they may not have produced oxygen until about 300 Ma later, when the first signs of free environmental oxygen appear. Photosynthetic release of oxygen during life’s early period was not the only reduction-oxidation regime adopted by organisms. Another of huge importance was generation of methane, which can rise to the limits of the atmosphere unlike the other major hydrogen-bearing gas, water, which is condensed out at quite low altitudes. Photochemical breakdown of methane at the limits of outer space would release hydrogen to leak away from the Earth, removing a reductant gas that would otherwise consume highly reactive oxygen: without this process, modelling suggests that Earth’s atmosphere would never have accumulated free oxygen, even had primitive life emerged.

Once free oxygen appeared, about 2.4 Ga ago, it took almost 2 billion years for enough to accumulate so that complex, multicelled Eukarya could use its potential (see *The
Malnourished Earth hypothesis - evolutionary stasis in the mid-Proterozoic (August 2002).

What kept the levels down? Quite probably it was oxidation of sulfide minerals on exposed land. That supplied sulfate ions to a still reducing ocean, so that sulfide ions formed again to become metal sulfide precipitates, which drew from ocean water several essential nutrients for Eukarya. Oxygen-producing Eukarya (algae) would not be able to bloom because of this ‘starvation’. Nonetheless, about 600 Ma ago, surface oxidation potential soared to almost modern levels, sufficient for large organisms to appear and evolve, to lead to life as we know it. Another series of questions surrounds this tremendous event, but they remain to be answered convincingly.

Oxygen and mammalian evolution (October 2005)

So much in the geological history of surface processes depends on either the dearth or the superabundance of oxygen. That is no surprise for a host of reasons, one being that it is the most reactive common element when free of bonds, and another is that the most powerful means of releasing oxygen is the capture of energetic solar photons by the pigments residing at the heart of photosynthesis. To grossly paraphrase James Lovelock, the principal reason for not sending people to Mars to search for life is that the planet’s atmosphere tells us that even if was there, it wouldn’t be very exciting. Oxygen gas is at vanishing low levels on the Red Planet, even if there is lots locked up in its iron-oxide rich surface.

The greatest event in the history of terrestrial life, apart from its emergence, was exploitation of the means of breaking hydrogen-oxygen bonding in water, which is what common photosynthesis is all about. It opened the entire planet to life from the restricted, though diverse habitats of most Bacteria and Archaea in the earlier anoxic world. First, oxygen-excreting cyanobacteria were able to colonise the entire ocean surface, depending on available nutrients. In doing so and generating free oxygen they threatened every other organism that used metabolisms based on other kinds of chemistry: oxygen is highly toxic because of it propensity to grab free electrons. Balanced by its oxidation of iron in early oceans, severe oxygen stress did not emerge until halfway through Earth’s history. Once it did become able to accumulate in air and water, all ecosystems faced havoc. Dominant prokaryotes slunk to rare places of refuge, while others seem to have combined in resisting oxidation. Their creation of the Eucarya that depend completely on available oxygen led, through the emergence of algae and then plants, to an accelerated stoking up of oxygen generation.

Once vegetation began to cloak the land, an extra 30% of the planet’s surface opened new vistas for animals and increased oxygen production and complementary burial of carbon. Indeed, explosive growth of atmospheric oxygen during the Carboniferous resulted in animal expansion to the air, through ominously huge insects. The first clearly traced ancestors of mammals seem to have appeared in the Permian, though their descendants only got the chance to dominate once reptiles, especially dinosaurians, lost their grip as a result of the K-T extinction. At the time of a far greater loss of living diversity, at the end of the Permian, it is now clear that in a relatively short time oxygen levels had fallen from their highest to one of the lowest in the Phanerozoic record (see New twist for end-Permian extinctions above).

Anoxic oceans were a regular feature of the Mesozoic and early Cenozoic. It is their preservation of abundant buried carbon that holds a key to, in an anthropocentric sense,
the greatest of evolutionary leaps; the rise of large mammals and ourselves. A large team of US scientists has used the now abundant records of carbon isotopes in both buried organic matter and marine carbonates to reconstruct changes in atmospheric oxygen content (Falkowski, P.G. and 8 others 2005. The rise of oxygen over the past 205 million years and the evolution of large placental mammals. *Science*, v. 309, p. 2202-2204; DOI: 10.1126/science.1116047). Their modelling suggests that at the start of the Jurassic, atmospheric oxygen stood at around only 10%. Through that period it rose dramatically to 16%, fell equally abruptly and then rose again to about 18%, thereby creating the conditions for some of the largest sources of petroleum. Cretaceous times saw a slow rise, until around the time of the global warming at the Palaeocene-Eocene boundary (55 Ma). The middle of the Cenozoic was a further period of dramatic increase in oxygen levels, to their highest (~23% in the Oligocene) since the peak during the Carboniferous. Latterly atmospheric oxygen has waned to around 21% today.

Falkowski *et al.* compare their new atmospheric oxygen curve with evolutionary spurts among mammals, of which the simplest to understand is the parallel rise of mammalian average size. The metabolism of all mammals, like birds, has 3 to 6 times the oxygen demand of reptiles. Not only were Mesozoic mammals challenged in stature by the air they breathed, reptiles were easily able to grow to monstrous proportions because of their less demanding physiological processes. The first signs of the placental nurturing of mammalian foetuses, which requires a high oxygen level, coincides roughly with the Mesozoic maximum (100-65 Ma). The end-Cretaceous extinction of the dominant dinosaurian reptiles removed the main competition against the subtle advantages of placental mammals, and was followed by further increase in oxygen. The Cenozoic permitted terrestrial mammals to reach sizes almost comparable with dinosaurs, and to go beyond them among whales. Moreover, it saw explosive diversification, one branch of which, the primates, leads to ourselves.

**Fig leaves over Palaeocene-Eocene boundary (November 2005)**

Methane-induced warming around 55 Ma ago was one of the greatest environmental upheavals of recent geological time. Pretty quickly, all the methane belched out by destabilisation of sea floor gas hydrates would have forced up atmospheric CO₂ concentrations. The estimated climatic effect was astonishing: a global temperature rise of the order of 5-10°C in 10-20 thousand years. The early Eocene world would have become a steamy place, and the changes certainly tally with shifts in a range of faunas, from foraminifera to large mammals. Not many people have reported any coincident changes in plant fossils, even though a moist atmosphere charged with CO₂ would have encouraged growth enormously. A reflection of the changed conditions does come from rapidly changing leaf shapes and sizes, however. One of the key sections that does reveal floral change is in terrestrial sediments preserved in the Bighorn Basin of Wyoming, USA (Wing, S.L. *et al.* 2005. Transient floral change and rapid global warming at the Palaeocene-Eocene boundary. *Science*, v. 310, p. 993-996; DOI: 10.1126/science.1116913). Tied down from a dramatic change in carbon isotopes, the boundary section not only shows the rapid dominance of leaves with extended ‘drip tips’ that allow rainwater to be shed quickly, but an influx of genera unknown from the Palaeocene below. The invasive groups are known from sediments of that age from much further south in the US, and even from Europe at the other side of the opening Atlantic Ocean. So it seems that there was a rapid northward plant
colonisation over 4 to 20 degrees of latitude. The section perhaps gives a flavour of floral changes that might occur should modern anthropogenic warming go unchecked.

**Dinosaur dung, the Deccan Trap and grass (November 2005)**

Yes, it has to come to a pretty pass when geologists will tramp to the very base of the Deccan continental flood basalts, dig up and then finger through dinosaur crap. The temptation of a bed consisting of little other than coprolites deposited by sauropods, especially beneath the very lavas implicated by some in their demise, is huge. It isn’t the first time that coprophilia has struck the vertebrate palaeontological community, for a very good reason: if dinosaurs grew so darned big what did they eat? That it included grass is a surprise for palaeobotanists, but would have been a great treat for the thunder lizard, for there is nothing more toothsome to a herbivore than a hay snack; much better than a monkey puzzle leaf. Indian and Swedish geologists hit the headlines with their discovery (Prasad, V. *et al*. 2005. *Dinosaur coprolites and the early evolution of grasses and grazers*. *Science*, v. **310**, p. 1177-1180; DOI: 10.1126/science.1118806). The lithified dung contains unmistakable traces of silica-rich phytoliths that occur only in grasses. Some possible grass pollen has been found before in Late Cretaceous sediments, but the crown-group *Poaceae*, that still thrive today, had been thought to have appeared later than the Early Eocene. It now seems likely that grasses appeared first in Gondwana, being transferred to Eurasia by the collision of its wandering fragment India around 50 Ma ago – India had already begun to move independently at the time of Deccan eruptions. Genetic studies of grasses points to their origin about 80 Ma ago, so it is likely that those in the dung are among the earliest. The Indian titanosaurids that ate them were not grazers, however, because the dung is also full of remains of conifers, palms and other vegetation that would have been abundant in those times. Interestingly, mammals from palaeosols within the Deccan lava sequence have cheek teeth reminiscent of the dominant grazers of later time.

**Clay minerals and the origin of life (November 2005)**

J.D. Bernal, a former student of J.B.S. Haldane, had as wide a range of interests as his mentor. Though a member of the Communist Party of Great Britain at the height of its loyalty to Stalin, during World War II he was a scientific advisor to Churchill. Among his many contributions was an idea inspired by Haldane’s conviction that life emerged from the inorganic world through simple chemical processes. Bernal thought in terms of a template sufficiently complex to shape early organic molecules, and clay minerals fitted that particular bill because they contain loosely bonded, yet complex passageways between the sheets of linked SiO₄ tetrahedra that form the bulk of their structure. A group of geochemists from Arizona State University have experimented on the organic catalytic potential of clays by simulating conditions around sea-floor vents that may have been the haven in which terrestrial life first formed (Williams, L.B. *et al*. 2005. *Organic molecules formed in a ‘primordial womb’*. *Geology*, v. **33**, p. 913-916; DOI: [10.1130/G21751.1](https://doi.org/10.1130/G21751.1)). Their ‘feedstock’ was dilute methanol and the clays that they chose were montmorillonite, illite and saponite, the last a member of the smectite group with high magnesium that forms by hydrothermal alteration of olivine and pyroxene in basalts. More complex hydrocarbons, with up to 20 carbon atoms per molecule, did indeed form in their experiments. The results suggest that smectite clays protect such unstable hydrocarbons from thermal decay, but no
distinct life-forming molecules, such as amino acids, showed up. The products were polycyclic aromatic hydrocarbons, but it is possible that they would have formed a diverse feedstock for other processes once the hydrothermal clays were deposited in cooler conditions.

Yet more on the end-Permian extinction (December 2005)

Sequences that reveal the Permian-Triassic boundary continue to receive a great deal of attention, spurred by the seemingly cryptic nature of the conditions that caused up to 90% of all living things to die 251 Ma ago. Globally, the boundary is marked by a sudden and large fall in the proportion of $^{13}$C in carbonates and sedimentary organic matter. Since the $\delta^{13}$C anomaly follows the biotic decline, it is less likely to reflect any cause of the extinction, such as a massive methane release from destabilised gas hydrates and global warming, than an effect of whatever went on. Joint research by UK, Dutch and US organic geochemists focused on the P/Tr boundary in northern Italy, where it is dominated by shallow-marine carbonates (Sephton, M.A. et al., 2005. *Catastrophic soil erosion during the end-Permian biotic crisis*. Geology, v. 33, p. 941-944; DOI: 10.1130/G21784.1). They analysed the organic compounds preserved in the section, and found that the extinction zone coincides with a major increase in total organic carbon, which is dominated by large amounts of compounds (polysaccharides) that typify soils and leaf litter. They explain the anomaly as the result of a short period of rapid soil erosion from the terrestrial hinterland of the shallow Late Permian sea. Since virtually all continental crust had stabilised in the Pangaea supercontinent, tens of millions of years beforehand, such erosion was unlikely have been a result of some sudden tectonic uplift. But it might have been triggered by sudden loss of the vegetation that retards soil erosion on the continental surface. The P/Tr extinction affected both marine and terrestrial organisms, and Sephton et al recognise that their discovery of evidence for soil stripping on a grand scale reflects that unified fate. Acid rain from the massive Siberian continental flood volcanism could well have been the trigger for ill thrift of land vegetation, or maybe removal of stratospheric ozone by release of halogen (chlorine and bromine) compounds let in destructive UV radiation.