# Climate change and palaeoclimatology

#### Freezing the Antarctic (January 2003)

Records of seawater oxygen isotopes and its Ca/Mg ratio shows that a substantial permanent ice sheet first formed in Antarctica in the Oligocene Epoch, about 34 Ma ago. The favoured explanation, until this month, was that the South polar continent became thermally isolated from the rest of the planet when circumpolar currents were able to flow around it, once South America and Australia had separated from Antarctica and opened the "gateways" of the Drake and Tasmanian Passages. But what if atmospheric CO₂ played a role? A drop in the "greenhouse" effect and global cooling could have driven polar temperatures low enough for ice formation without an oceanographic influence. Once established, the albedo effect of a large ice sheet would seal Antarctica into permanent freeze-up. Factoring all the likely components in a general circulation model leads to a surprise (DeConto, R.M. & Pollard, D. 2003. Rapid Cenozoic glaciation of Antarctica by declining atmospheric CO<sub>2</sub>. Nature, v. 421, p. 245-249; DOI: 10.1038/nature01290). The opening of the Drake and Tasmanian Passages was not accompanied by a sufficient depth of water to support massive current reorganisation until several million years after the ice cap left its clear imprint on the marine record. DeConto and Pollard's model shows that even with closed gateways an ice cap would have formed, if CO<sub>2</sub> levels had fallen below three times those that prevailed in the Holocene, before industrial emissions began. Global cooling had begun somewhat earlier than Antarctic freeze-up, following the high around the Palaeocene/Eocene boundary (~55 Ma), falling to a plateau about 40 Ma ago. Undoubtedly CO<sub>2</sub> concentrations had fallen globally for this to have happened. Of course, there is no Oligocene ice, from which glaciologists might extract trapped bubbles and samples of ancient air with which to refute or confirm the model. However, a decrease in carbon dioxide would also cause the acidity of rainfall to decrease as well as the amount of rainfall globally, and that might show up in changed weathering processes, especially in the tropics of the time.

## When did southern Tibet get so high? (February 2003)

For about a decade it has been suggested that the Tibetan Plateau, which rises to more than 5000 metres, has a profound effect on climate. This may be partly due to the way such a high and enormous area deflects regional wind patterns, but largely to its profound interconnection with the South Asian monsoon. When such a circulation barrier arose is critical to understanding how it relates to climate evolution in the latter part of the Cenozoic. There are various suggestions, based on aspects of its structural and magmatic evolution. Theory suggests that the southern part came into being in Eocene times, possibly because a segment of the lithosphere beneath broke off to subside into the mantle - there are volcanic rocks whose chemistry does suggest such a mechanism. About 8 Ma ago the southern Plateau began to spread laterally, producing a series of N-S extensional basins, which suggests that by then sufficient gravitational potential had accumulated to make the thickened crust unstable. About that time various signatures arose in foraminifera of the Indian Ocean and sediments derived by erosion, which suggest that the monsoon increased in intensity.



Satellite image mosaic of the Tibetan Plateau

When the Plateau attained sufficient elevation above sea level to start spreading sideways and affect atmospheric circulation largely rests on these theoretical judgements. For the ideas to firm up needs some means of estimating topographic elevation, which is not easy to do. One way is to use plant remains that can give clues, either because the species involved are sensitive to elevation today, or the morphology of their leaves shows signs of physiological adaptation to elevation. The first is ruled out in old sediments, simply because the species present are now extinct. Plants metabolism is dependent on diffusion of water and CO<sub>2</sub> into their leaves during photosynthesis, and features, such as stomata density, give clues to the conditions for such diffusion. Luckily, sediments from southern Tibet do contain well-preserved plants, and a multinational group led by Bob Spicer of the British Open University have attempted to assess palaeo-elevation for the time at which they were deposited (Spicer, R.A. and 7 others 2003. Constant elevation of southern Tibet over the last 15 million years. Nature, v. 421, p. 622-624; doi: 10.1038/nature01356). Their method relies on linking leaf morphology to a property of the atmosphere, known as moist static energy (MSE), through estimates of atmospheric enthalpy from the leaves. That is not the end of the estimation, because MSE needs to be related to elevation and the only way is to use climatic modelling for the past. Whatever, Spicer and colleagues reckon that 15 Ma ago their sampling site was more or less at the same elevation as today, around 4.5 km above sea level. If true, they have established that the south part of the Plateau was already in existence during the Middle Miocene. Being so convoluted, despite its apparent precision, the leaf analysis method does need independent confirmation. There is a much easier and arguably more reliable method, based on the change in the size of bubbles formed by gas escaping from lavas, according to atmospheric pressure (see <u>Cunning means of estimating</u> uplift November 2002). There are lavas in southern Tibet that date from Cretaceous times, including some about a million years younger than the plant remains.

## Precambrian warmth and methane (February 2003)

Methane is a more efficient "greenhouse" gas than CO<sub>2</sub>, but it soon oxidises in the presence of oxygen. During the Phanerozoic there have been several massive releases of methane,

probably from gas hydrates in deep-ocean sediments, which produced warming spikes that decayed away quickly in geological terms. Before there was much, if any, oxygen in the atmosphere, methane could linger and add to the retention of heat by carbon dioxide and water in the atmosphere. One of the longest running disputes in environmental geochemistry concerns when oxygen levels became significant in the Precambrian, and what they were compared with later times. Whether the Earth was warm or cold has a bearing on this. Cosmological theory suggests that stars similar to the Sun progressively grow more energetic with time. Without some kind of greenhouse effect, the Earth would have been condemned to frigidity from its outset. Even today, with a more radiant Sun, only atmospheric retention of solar heat keeps overall temperature from being well below freezing. The further back in time, the greater the "greenhouse" effect would have to have been to stave off complete ice cover and a runaway "icehouse". Methane almost certainly played a part in this once methane generating organisms evolved, up to about 2200 Ma, when there are signs (continental redbeds and soils rich in iron oxides) that atmospheric oxygen was appreciable. However, warmth prevailed for about 1.5 billion years thereafter, until the plunges into frigid conditions of the so-called "Snowball Earth" period from about 700 to 550 Ma. Somehow, the greenhouse effect lingered.

Alexander Pavlov of the University of Colorado, and colleagues from Pennsylvania State University have addressed the implications of this continued warmth in terms of maximum oxygen levels needed to avoid complete oxidation of methane releases (Pavlov, A.A. et al. 2003. Methane-rich Proterozoic atmosphere? Geology, v. 31, p. 87-90; DOI: 10.1130/0091-7613(2003)031<0087:MRPA>2.0.CO;2). Today, more than 90% of all methane production beneath the ocean floor is consumed by bacteria, depending on the amount of dissolved oxygen and sulphate ions (for aerobic and anaerobic methanotrophs). There is plenty of evidence that deep Precambrian ocean water was anoxic, so a great deal more methane would have emerged from them. That it was also poor in sulphate ions is shown by their low levels in solid solution with carbonates and Proterozoic sulphur isotopes in marine sediments. The authors argue that this signifies low atmospheric oxygen levels, around 5 to 18 percent of modern concentrations. The scene may have been set for an excess of methane production over its oxidation, thereby keeping the "greenhouse" warming above the levels when glaciation would have been widespread.. If so, something completely upset this balancing act in the Neoproterozoic, to drive down temperatures several times - the "Snowball Earth" events. The trigger may have been a boost in oxygen production and retention in the atmosphere.

# El Niño in the Eocene (February 2003)

The oceanographic-climatic phenomenon in the equatorial Pacific, known as the El Niño-Southern Oscillation (ENSO), now seems to be major force in driving climate shifts far afield, such as the current drought in the Horn of Africa. Its cyclicity relieves the suffering brought by El Niño events, yet the processes may well be highly unstable. Some believe that it is only a matter of time before ENSO reverts to a permanent El Niño condition, with disastrous consequences. Such a stabilisation in the past may have resulted in warming at high latitudes that permitted lush vegetation in near-polar regions, during the Cretaceous and the Eocene. The Eocene was much warmer than now, as a result of a massive release of methane from seafloor sediments around 55 Ma. So it makes sense to look at its climate record to check for a permanent El Niño. Matthew Huber and Rodrigo Caballero of the

University of Copenhagen have compared climate records from annually layered lake sediments from the Eocene of Germany and Wyoming in the western USA with climate models to test the hypothesis (Huber, M. & Caballero, R. 2003. <u>Eocene El Niño: Evidence for robust tropical dynamics in the "hothouse"</u>. *Science*, v. **299**, p. 877-881; DOI: 10.1126/science.1078766). The climate data from the lake sediments (thickness variations in annual layers) show clear signs of a roughly 5-year cycle of climate change, attributed to an Eocene ENSO. This tallies nicely with simulations for the Eocene continent-ocean set-up. Although the authors claim that their findings refute the hypothesis that global warming tends to shut down ENSO, which is a comforting thought, Eocene ocean and air circulation was not the same as now by any means. There have been interglacial periods during the Pliocene to present climate system in which temperatures exceeded those of the Holocene. Surely, annually layered sediments from those times will provide a better test.

## Antarctic melting and northern hemisphere deglaciation (March 2003)

There is a large body of opinion, supported by plenty of circumstantial evidence, that the end of the last glacial maximum around 20 ka was controlled by processes that operated in the North Atlantic and its seaboard. A favoured mechanism is the re-establishment of thermohaline circulation involving North Atlantic deep water that dragged surface water northwards from the tropics, to set up the Gulf Stream. Temporary shut-down of thermohaline flux, probably by massive release of freshwater to the North Atlantic from melting of ice sheets, is widely understood to have triggered the sudden reversal to frigid conditions in the Younger Dryas around 11.5 ka. The largest warming pulse in the northern hemisphere, between 14.6 to 14.0 ka, is recorded by a sudden increase in  $\delta^{18}$ O of ice in the Greenland cores, and is known as the Bølling-Allerød warm interval. Around that time, sea level rose by 20 m in a few hundred years, and that involved production of fresh glacial meltwater at a rate equivalent to the continual flow of five rivers the size of the Amazon. Such rapid sea-level rise drowned coastlines and in some areas killed coral reefs. On such drowned reef in the Caribbean gave a date of 14.2 ka, which since 1989 has been the only indicator of precise timing for the massive influx of meltwater to the oceans. The date is within the Bølling-Allerød, hence the link between warming and events around the North Atlantic. That central hypothesis is now under threat, following the dating of drowned coral reefs on the Sunda Shelf at 14.7 ka, and a re-evaluation of the Caribbean data. (Weaver, A.J. et al. 2003. Meltwater pulse 1A from Antarctica as a trigger of the Bølling-Allerød warm interval. Science, v. **299**, p. 1709-1713; DOI: 10.1126/science.1081002).

Using the revised ages and climate modelling, Andrew Weaver and colleagues from the Universities of Victoria and Toronto, Canada and Oregon State University see the massive ice-melting as the precursor to the Bølling-Allerød warm interval and deglaciation of lands around the North Atlantic. A more plausible source of freshwater influx is a major melting event in Antarctica, so warming in the south may well have driven that of the northern hemisphere.

**See also:** Kerr, R.A. 2003. Who pushed whom out of the last ice age. *Science*, v. **299**, p. 1645; DOI: 10.1126/science.299.5613.1645.

#### No glacial refugia in the Amazon Basin? (April 2003)

Tropical rainforest in Africa and South America is the most diverse biome on the planet, both as regards plants and animals. One view of how such luxuriance arose is that the forests have blanketed the humid tropics for as long as 50 or 60 million years, and the fact that they encompass a huge variety of environments created by different levels in the dominant and diverse vegetation. Thousands of niches and the interactions between organisms that exploit them during lengthy stasis inevitably drives rapid evolution towards all kinds of specialisation. The other view is that rainforests are by no means static over millions of years, but climate shifts have caused them to retreat and advance, perhaps hundreds of times during the Cenozoic. Amazonia in particular shows surprising variation in diversity, some patches being far more biologically rich than others, and having regionally distinct assemblages of plants and animals. This theory suggests that climatic stress, probably drying associated with globally cool episodes, resulted in rainforest shrinking to "refugia". In them, populations of plants and animals shrank, thereby reducing the gene pool and giving greater chance for evolution by natural selection; different in different refuge areas.

Tropical soils are continually reworked and their highly oxidising nature destroys organic remains. So no record of its development exists in rainforest. However, wind and rivers transport spores, pollen and other biomarkers to seafloor sediments, where a complete record of fluctuations in biomass and diversity becomes preserved. A test of the popular refugia hypothesis is therefore to analyse organic matter in continuous cores taken from offshore sediment. Known fluctuations in global climate, from the oxygen isotope record should be matched by changes in the record of terrestrial biomarkers carried to the sea. Cores from the deep-sea sediment fan off the mouth of the Amazon potentially provide such a test (Kastner, T.P. & Goñi, M.A. 2003. Constancy in the vegetation of the Amazon Basin during the late Pleistocene: Evidence from the organic matter composition of Amazon deep sea fan sediments. *Geology*, v. **31**, p. 291-294; DOI: 10.1130/0091-7613(2003)031<0291:CITVOT>2.0.CO;2).

Kastner and Goñi, from the University of South Carolina, examined phenols and organic acids in the cores, which can discriminate between grassy plants and trees that would have dominated savannah and rainforest, whose relative cover of the Amazon basin should have changed, according to the refugia hypothesis, as climate shifted from globally cool-dry to warm-humid.. Although their record only spans the last glacial cycle since 70 ka, they detected no significant change in the proportion of grasses and trees in the Amazon catchment. Moreover, the biomarkers remained similar to those carried by the Amazon today, right through the last glacial maximum, when drying of the tropics would have been most likely to have driven a shrinkage of rainforest area. It seems unlikely that forest refugia developed during one of the most extreme climate shifts in the last 55 Ma. Global climate fluctuations were considerably less before 1 million years ago, when the current round of 100 ka cycles began. So there is little reason to doubt that the Amazon rainforest has had a more or less constant area for much of the Cenozoic. The same cannot be said for those in Africa and SE Asia, partly because there are no useful data from offshore sediments, but also because those regions have experienced changing topography due to major tectonic activity, whereas eastern South America has remained stable. To conclude, as the authors do, that the data signify no great fluctuation in rainfall is not so certain.

## The gas-hydrate "gun" (June 2013)

As fears of anthropogenic climate warming have risen, so more geoscientists have looked in detail at the stratigraphic record for signs of past warming, and funds have become more targeted towards palaeoclimatology. One of the most important discoveries was that the end of the Palaeocene, about 55 Ma ago, was a time of sudden global warming during the overall cooling that has characterised the Cenozoic. The first sign that something strange had happened then came from using the oxygen isotope geothermometer on plankton tests from marine drill core that passed through the boundary. There seemed to have been a 7º C jump in surface seawater temperature. An explanation for the thermal spike arose after carbon isotopes revealed a coincident spike in the lighter <sup>12</sup>C. Periods of low primary biological production can impose such anomalies, because photosynthesis selectively binds light carbon in carbohydrate. However, some of that light carbon ends up buried in seafloor sediments, so another explanation for a negative excursion in  $\delta^{13}$ C is that organic carbon has somehow been released from sedimentary storage to the atmosphere. So, either there was a sterile ocean or a massive release of organic carbon at the Palaeocene/Eocene boundary. Some kind of erosion to achieve the second possibility could not have led to such a speedy shift in carbon isotopes. The accepted explanation, suggested in 1995, stemmed from organic carbon that had been metabolised by methanogen bacteria in anaerobic sea-floor sediments to form methane. Given low enough sea-bottom temperatures and sufficient pressure, methane can crystallise with water to form an icy substance, known as gas-hydrate or clathrate, in sea-floor sediments.



Gas hydrate in fresh drill core. See also a movie

Being an unstable compound, gas hydrate can break down rapidly if seafloor temperature rises or sea-level falls. And, of course, the methane can rush to the surface as bubbles. Being 4 times more efficient than carbon dioxide at trapping thermal radiation emitted by the Earth's surface, methane releases are excellent explanations for sudden warmings in the stratigraphic record. And there is a great deal of methane locked as gas hydrate beneath the sea floor, about 2 teratonnes ( $2 \times 10^{12}$  t). Quirin Schiermeier reviews the basic concept (Scheiermeier, Q. 2003. Rapid climate change: Gas leak! *Nature*, v. **423**, p. 681-682; DOI: 10.1038/423681a), but poses the question of how methane-induced warming is reversed.

Methane is quickly oxidised to  $CO_2$  in the atmosphere, so lessening its warming effect. So a "spike" that lasts thousands of years has to be fed by continual releases. Since warming drives gas hydrate breakdown, something must intervene to stop the releases before the warming becomes a "runaway greenhouse". One view, and probably the correct one, is that warmth and more  $CO_2$  drives up biological activity so that the increased atmospheric carbon is "pumped" down by living processes, back to sedimentary burial. If sufficient nutrients are available, there is no way of stopping this negative feedback until a balance is restored. Schiermeier reports that new ocean drilling plans to test the hypothesis that the Palaeocene/Eocene warming accelerated continental erosion, which was able to wash the crucial nutrients phosphorus and iron into the oceans. Experiments have shown that increased iron in ocean-surface water far from land – now pretty sterile because it is iron-deficient – sparks up photosynthetic plankton. That is one possible way of artificially drawing down anthropogenic  $CO_2$ . The problem is, if such a process was involved in cooling the Eocene Earth, it took about 100 thousand years.

# Red Sea record links to northern hemisphere climate (June 2013)

In his forthcoming book, *Out of Eden: the Peopling of the World* (Constable and Robinson, July 2003), Stephen Oppenheimer offers the novel suggestion that fully modern humans left Africa by island hopping on log rafts across the Straits of Bab el Mandab, which connects the Red Sea to the Indian Ocean. The rationale to his suggestion is that sea-level falls during major glaciations would have partially exposed the shelf that lies beneath the Straits, presenting a route to SW Arabia across only 18 km of island-dotted sea. As today, it would have been impossible to trek across the deserts of the Middle East after a northward African migration along the Nile, without chains of wells. His thesis then sees humans migrating along coasts eventually to reach east Asia at about 70 ka. Precisely when the Straits of Bab el Mandab became shallow enough would have been determined by global climatic conditions, for only glacial maxima result in sufficient sea-level falls for such island hopping to be possible.

The shallowing of the shelf across the southern outlet of the Red Sea would have had a profound impact on seawater circulation. Already having restricted connection to the world's oceans, Red Sea water has elevated <sup>18</sup>O levels, because evaporation from it favours loss of lighter <sup>16</sup>O. With more restricted circulation, evaporation would have driven this up further. Geoscientists from the Universities of Southampton, Tuebingen and Göttingen, and the Geological Survey of Israel analysed the variation in oxygen isotopes of foraminifera from a Red Sea core to quantify ups and downs in sea level in more detail than possible from open-ocean cores, which have uncertainties of about ±30m) (Siddall, M. and 6 others 2003. Sea-level fluctuations during the last glacial cycle. *Nature*, v. **423**, p. 853-858; doi: 10.1038/nature01690). The method that they used models the effects on Red Sea oxygen isotopes of evaporation and changed circulation to estimate how the depth of the Straits of Bab el Mandab changed. They claim a precision of  $\pm 12$ m. Through the period from 70 to 20 ka, leading up to the last glacial maximum, their sea-level record tallies nicely with climate records from both Antarctic and Greenland ice cores, including shifts linked to the shortlived Heinrich and Dansgaard-Oeschger cycles. During the last glacial maximum(18-20 ka), sea-level fell by almost 120 m, so that the Straits of Bab el Mandab were on average only 15 m deep. The first human Exodus out of Africa to populate Eurasia would have been

between 120 to 130 ka, as suggested by Oppenheimer, when sea level probably fell a little further. However, at about 65 ka, sea level dropped to about 100 m below modern levels, perhaps presenting another window of opportunity.

#### Broecker reviews climate triggers (June 2013)

Wallace Broecker, of the Lamont-Doherty Earth Observatory at Columbia University, was the first to quantify in 1975 the 19<sup>th</sup> century prediction of Svante Arrhenius that increasing atmospheric carbon dioxide would drive up global temperatures. Broecker's early work lies at the centre of concern about global warming, and his subsequent contributions are enmeshed with the entire study of past climate change. A review by him of current ideas on palaeoclimates of the recent past is therefore compulsory reading, for all geoscientists (Broecker, W.S. 2003. Does the trigger for abrupt climate change reside in the ocean or in the atmosphere? Science, v. 300, p. 1519-1522; DOI: 10.1126/science.1083797). As well as the astronomically connected cyclicity that is apparent in all kinds of climate record through the Pleistocene, those records are punctuated by sudden, short-lived phenomena, whose magnitudes and pace are sufficiently dramatic to focus attention on processes that are probably entirely terrestrial. Foremost among these during the last glacial interglacial cycle are the astonishing coolings of Heinrich's iceberg armada events and the possibly catastrophic (in a human as well as an ecological sense) Younger Dryas, which reversed warming from the last Glacial Maximum, and the equally sudden warmings associated with Dansgaard-Oeschger events. Broecker's review focuses on the two mechanisms that have been suggested to underlie these overturns. One links such changes to shifts in wholeocean water circulation, especially the ons and offs of deep-water circulation beneath the North Atlantic, the other to perturbations of the way in which atmosphere and ocean interact in the tropics.

An entirely plausible scenario for climate-driving changes in North Atlantic water circulation is flushes of freshwater from the surrounding continents, so that formation of sea ice leaves residual water that is not saline or dense enough to sink and drag in water from lower latitudes. The problem is that the complete thermohaline cycle, which impacts on global atmospheric circulation, has a period longer than the changes that might be induced by its perturbation in the North Atlantic. Tropical atmosphere-ocean dynamics are the largest elements in global climate, in terms of the energy and mass that are shifted, so they are a natural candidate for a driving mechanism. Tropical climate shifts abruptly today in wellknown ways, most important being the El Niño-La Niña cycle. There is no ponderous underlying dynamic that would damp down connections between cause and global effect, and prevent sudden climate change. Yet, some kind of "flywheel" is essential to keep longterm cyclicity going and lock sudden changes into century to millennium-long climate "states", which should rapidly decay if effect rebounded on cause, as it does in the case of El Niño-La Niña. Broecker covers all the critical evidence that has borne on both hypotheses up to now. His conclusion is interesting. Both hypotheses are very much model led, and in need of as much empirical support as can be had. Yet, and here is the nub, the crucial data are those bearing on correlating times of events that are recognised all over the place. Time resolution is of the greatest importance, since climate transitions are fast; faster in fact than we can presently resolve before historical times. It is entirely likely that suitable resolution of times past may be absolutely impossible. Both hypotheses have a lot of empirical and theoretical support. So, what is the problem of combining them in a cunning way? Partly,

that may be because reductionism (controlling a few variables and looking for developments in another simple set) still plagues science. That is odd in climatology, where all motions and energy changes palpably relate to one another, with no control of a rational kind. Reductionism demands ever more staggering computing power and speed, to "keep all the eggs in the air". There is always the feeling, as Jimmy "Shnozzle" Durante observed in his musical monologue, *The Man Who Found The Lost Chord*, that if you find a hitherto overlooked connection, then everything goes well; if you can remember it! Broecker suggests that the missing connection must "transmit" from deep ocean water to tropical atmosphere.

## Iron isotopes and ocean evolution (July 2003)

The main driver for biological activity in the oceans far from land is the availability of iron, and this helps control the burial of organic carbon and hence aspects of global climate. At low Fe concentrations, as they have been since the oxygenation of the surface environment from 2 billion years ago, iron is cycled in the marine environment in a matter of a few hundred years. So, ocean water responds very quickly, in geological terms, to changes in the source of any dissolved iron. There are two main sources, discharge of hydrothermal fluids from the oceanic lithosphere and delivery of river water and dust derived from the continents. Of the last, riverine sources probably end up in near-shore sediments and only dust contributes significantly to deep ocean water. The slowly growing nodules and crusts, composed mainly of iron and manganese compounds, on the ocean floor can chart variations in the relative proportions of these sources, because their growth produces zonation. Measurements of  $\delta^{56}$ Fe in various materials show that the two sources are different in isotopic composition (Beard, B.L. et al. 2003. Iron isotope constrains on Fe cycling and mass balance in oxygenated Earth oceans. Geology, v. 31, p. 629-632; DOI: 10.1130/0091-7613(2003)031<0629:IICOFC>2.0.CO;2). While continent derived materials exude iron that is essentially the same as that in terrestrial volcanic rocks ( $\delta^{56}$ Fe ~0.0%), ocean-floor hydrothermal activity is significantly depleted in <sup>56</sup>Fe (‰<sup>56</sup>Fe ~ -0.38‰). From 6 Ma to 1.7 Ma iron-manganese crusts record iron with a dominant hydrothermal origin, but during the glaciation-dominated period since 1.7 Ma the contribution of continent-derived dusts becomes overwhelming – cooling forces drying on a global scale. Because hydrothermal contributions probably stay much the same over very long periods, because of the sluggishness of plate tectonics, iron isotopes in deep marine sediments, such as Fe-Mn crusts, may be important tracers for glacial events in the distant past, such as the glaciations during the Neoproterozoic and Palaeozoic. Interestingly, the largest iron-rich deposits on the planet, the BIFs that peaked during Archaean and Palaeoproterozoic times, record far larger excursions in iron isotopes than any other. The very low  $\delta^{56}$ Fe values of some BIFs (down to - 2.4%) probably signify the dominance of sea-floor sources, although a non-oxidising atmosphere would have mobilised dissolved iron from the continents too, which explains the range in BIFs up to +1.0%.

## High- and low-latitude climate changes almost match (September 2003)

Ten years ago the records of climate proxies from the Greenland ice sheet set new benchmarks for understanding how climate has varied over the last 100 thousand years – annual ice layers allowed division of that data to as fine as decades. Variations in the ice

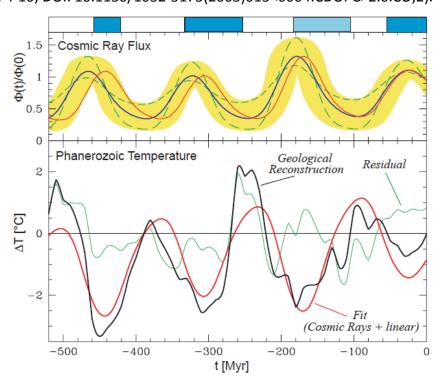
cores helped explain many of the variations found in more blurred data from sea-floor sediment cores in the Northern Hemisphere. Variations could be correlated with changes in the formation of North Atlantic deep water at high latitudes and the destabilisation of North American and Scandinavian glaciers. The whole hemisphere behaved in concert, through long-distance connections in climatic processes, but high-latitude processes seemed to dominate. Development of <sup>234</sup>U/<sup>230</sup>Th dating extended high precision to carbonates that have been precipitated from groundwater to form stalagmites or speleothem. The latest results from speleothem, collected on the Indian Ocean island of Socotra, cover 14 thousand years between 56 and 42 ka, and resolve down to only 8 year intervals (Burns, S.J. et al. 2003. Indian Ocean climate and an absolute chronology over Dansgaard/Oeschger events 9 to 13. Science, v. 301, p. 1365-1367; DOI: 10.1126/science.1086227). They show variations in rainfall on the island, though the  $\delta^{18}$ O proxy, and thus changes in the strength of the Indian Ocean monsoon. In terms of shape, the stalagmite record closely resembles  $\delta^{18}$ O changes in the Greenland ice cores, although the two have opposite senses, because the Greenland proxy is for air temperature above the ice cap. During the frigid Heinrich events that saw massive southward waves of icebergs, rainfall over Socotra was low. It became higher as high-latitude conditions warmed in Dansgaard-Oeschger events. The fine speleothem resolution shows a dramatic change-over that took only 25 years or so. The explanation is that warmer conditions increased equatorial evaporation from the oceans. But water vapour is the dominant "greenhouse" gas, and a wetter atmosphere would become warmer. So the question of whether low- or high latitudes drove the changes is still an open one. If North Atlantic events were the driver, then the tropical processes would greatly amplify their effects. One big problem emerges from the joint research by US, Swiss and Yemeni scientists. The highly reliable U/Th dating gives ages for each event that are about 3000 years older than those interpreted from the ice cores. The authors are convinced that the ice-core ages need revision, yet there are discrepancies with the eventages from other similarly dated speleothems.

Commenting on the paper, Frank Sirocko of Johannes Gutenberg University of Mainz in Germany (Sirocko, F. 2003. What drove past teleconnections. Science, v. 301, p. 1336-1337; DOI:10.1126/science.1088626) makes the point that maybe the quality and age of ice core records lie behind the widely accepted view that high-latitude process drive climate. He presents an excellent global image of modern sea-surface temperatures that show the main oceanic shifts of energy - the leakage of cold circum-Antarctic waters northwards, the westward movement of equatorial warm waters to which the El Niño - Southern Oscillation (ENSO) is due, and the unique movement of warm water to Arctic regions in the North Atlantic that is connected to deep water formation. To that he adds the major effect of continental winter snow cover in central Eurasia, that affects albedo and the size of the winter high-pressure zone there. Is there a teleconnection between that and events in the North Atlantic? Nobody knows, because there are no data to compare, yet. Another uncharted but likely linkage is between the ENSO and processes in the circum-Antarctic current. Using currently accepted dating of ice cores, records from those in the Antarctic show air temperature changes that precede those from Greenland by several thousand years. In that respect, the Socotra record possibly has a link with the South Polar climate. Until the issue of dating is sorted out, it will always be difficult to make concrete statements about global climate change.

Interestingly, in the same issue of *Science*, sea-floor data (between 9 and 16 ka) from the Cariaco Basin off Venezuela, at about the same latitude as Socotra, mimic the Greenland records to within 30 to 90 years (Lea, D.W. *et al*, 2003. Synchroneity of tropical and high-latitude Atlantic temperatures over the last glacial termination. *Science*, v. **301**, p. 1361-1364).

## "Greenhouse" controls challenged (September 2003)

There's data gathering and there's theorising. In palaeoclimate studies the two come into conflict. Theory suggests that CO<sub>2</sub> is likely to be the principal driver for climatic ups and downs, probably on all time scales. Atmospheric CO<sub>2</sub> estimates from the past are based on proxies of different kind, and the various models that they support do not tally vary well. Worst of all they do not fit climate records through the Phanerozoic at all well, except in the crudest possible way. Only the long-lived Carboniferous to Permian "icehouse" and Tertiary cooling tally, and then only in Berner's GEOCARB III model. One of the best records of major climate shifts, aside from continental tillites, are marine sediments that contain ice-rafted debris, in particular the palaeolatitudes to which they extend. They record four major cooling episodes: Late Ordovician; Devonian to Late Permian; Late Jurassic to Mid Cretaceous; and those since about 35 Ma ago. The oxygen isotope record from Phanerozoic fossils, partly correlated with ocean temperatures also suggest 4 global coolings in the last 545 Ma. Either the CO<sub>2</sub> modelling needs more detail, or the whole issue of the "greenhouse" effect is under question. That is the conclusion of a study by Nir Shaviv of the Hebrew University of Jerusalem, and Ján Veiser of the Ruhr University and The University of Ottawa (Shaviv, N.J. & Veiser, J. 2003. Celestial driver of Phanerozoic climate? GSA Today, Huly 2003, p. 4-10; DOI: 10.1130/1052-5173(2003)013<0004:CDOPC>2.0.CO;2).



Variations in cosmic ray flux and tropical temperature during the Phanerozoic Eon show a significant match. (Credit: Shaviv & Veiser 2003; Fig. 2)

Veiser has been analysing the chemistry of carbonates, especially their oxygen isotopes, throughout his 30 year career, and has amassed more data than any other geochemist on carbonate-related issues. The two have worked together because their interests fit together extremely well. Shaviv has reconstructed the variation of cosmic ray flux from studies of the exposure of iron meteorites to them, blended with analysis of how the Solar System moves through the spiral arms of our galaxy. Cosmic rays are known to affect the Earth's cloudiness and therefore albedo. Greater cosmic ray flux should increase the amount of solar energy reflected away by the Earth, thereby causing global cooling. The degree of fit between the cosmic ray flux and palaeoclimatic records is so good that up to 2/3 of climate variation may be connected with the Earth's celestial position. That is, as it passes through the star-rich spiral arms cosmic rays intensities go up. This happens every 140 Ma or so, which fits very well with the 4 icehouse periods during the Phanerozoic. They even suggest that the climate-CO<sub>2</sub> relationship may be the opposite of that generally agreed; climate might drive carbon dioxide levels. A secondary role for "greenhouse" gases wreaks havoc on attempts at modelling climate change feared to result from increasing anthropogenic releases.

Shaviv and Veiser's work comes at a particularly awkward time for climate modellers, who have just initiated a programme for running huge simulations by corralling the combined computing power of millions of home PC users, similar to the approach pioneered by the SETI Institute (Allen, M.R. Possible or probable. *Nature*, v. **425**, p. 242; DOI: 10.1038/425242a). Perhaps the view of Phillip Stott, that climate modelling is a complete waste of time (Stott, P. 2003. You can't control the climate. *New Scientist*, 20 September 2003, p. 25) might sink in as a result of the possible link between cosmic ray flux and climates of the past. Stott believes that acting on the output of such models might perhaps even be dangerous, since we clearly do not understand short-term climate change well enough.

#### Precambrian CO<sub>2</sub> levels (September 2003)

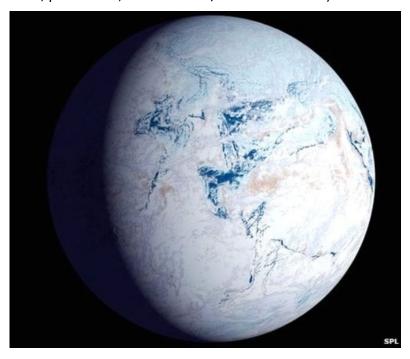
Whether or not fluctuations in the "greenhouse" effect drive climate change, the fact remains that CO<sub>2</sub>, methane and water vapour all act to retain solar heat in the Earth system. Were it nor for their presence in the atmosphere, the Earth would be about 33 degrees colder than it is. It would be covered by ice. Theoretical modelling of how stars evolve suggests that the Sun had progressive less energy output going back in Earth's history. Only gaseous heat retention could have prevented a sterile, frigid planet. Yet periods of cooling sufficient to hold large amounts of water in surface ice have occurred only a few times, 4 in the Phanerozoic, a flurry of so-called "Snowball" epochs in the Neoproterozoic and the earliest known glaciation around 2200 Ma ago. The earliest coincided with the first evidence for free oxygen in the atmosphere, and may have been caused by that. Methane, a more powerful "greenhouse" gas than water or carbon dioxide and abundantly produced by anaerobic decay, is easily oxidised. In later time, it has been ephemeral in the atmosphere, unless continuously released, for instance by destabilisation of gas hydrate in sea-floor sediments. Warming by CO<sub>2</sub> has undoubtedly kept total frigidity at bay since then. The problem is charting just how much was in the air, because most estimates have been based on studies of palaeosols that give odd and very imprecise results for the early Palaeozoic (see "Greenhouse" controls challenged above).

Photosynthetic organisms derived their carbon from CO<sub>2</sub>, either in the air or dissolved in water through equilibration with the atmosphere. The extraction favours lighter <sup>12</sup>C, so biological activity results in their products being depleted in the heavier <sup>13</sup>C by about 25 parts per thousand (%) relative to carbon in air and water. If organic carbon becomes buried, the remaining carbon in the surface environment gets richer in <sup>13</sup>C, and that signature becomes fixed in contemporaneous carbonates, both organic and inorganic. It is therefore possible to use the two carbon-isotope signatures to estimate the reservoir of CO<sub>2</sub>; its proportion in contemporary air. However, the degree of fractionation depends on the specific carbon metabolism of different organisms, yet most organic carbon in sediments is a mixed product of widely differing life styles. That severely blurs estimates of atmospheric carbon dioxide content. What is needed are data from a single source with known metabolism. Acritarchs are fossil remains of single-celled marine eukaryotes that were, and still are, marine photosynthesisers. They are made of degraded hydrocarbons. Advanced ion-microprobe resolution is now sufficient to produce carbon-isotope measurements of individual fossils (about 200 micrometres across). Sediments from northern China, roughly 1400 Ma old, contain abundant little-altered acritarchs and carbon isotope data from them give good estimates of atmospheric CO<sub>2</sub> levels, that are independent of other methods (Kauffman, A.J. & Xiao, S. 2003. High CO<sub>2</sub> levels in the Proterozoic atmosphere estimated from analyses of individual microfossils. Nature, v. 425, p. 279-282; DOI: 10.1038/nature01902). The estimates suggest between 10 to 200 times higher contents than today, but just about sufficient to keep the Earth above the limit of glacial temperatures when solar luminosity was about 88% of the present. Acritarchs are present throughout the Neoproterozoic, and it should prove possible to examine the critical periods of "Snowball" conditions using this method.

## Geochemical switch for Snowball conditions (November 2003)

Whether or not you believe that the Earth was totally encased in ice up to four times during the Neoproterozoic Era, there is convincing evidence that ice sheets did extend to the tropics during such "Snowball" episodes. How such extremely cold episodes came to prevail for several million years has been the subject of debate for 5 years, since Harland's notion of global glaciations was resurrected by palaeomagnetic evidence for the low latitudes of Neoproterozoic glaciogenic rocks. Ice extending almost to the Equator, even if just on the continents, would have driven down global temperatures simply because it would have reflected away solar radiation. Increased albedo helps explain why frigid conditions lingered, but some other cooling mechanism must first have encouraged the widespread formation of ice sheets. Essentially, the supply of the "greenhouse" gas CO<sub>2</sub> by volcanic activity must have been outstripped by burial or solution of carbon in some form. The two usually identified candidates are increased deposition of carbonate sediments and the accumulation of unoxidised organic carbon in sea-floor muds. It is the first of these that dominates climate control today, by the accumulation of carbonate shells of marine plankton, and that has probably prevailed since foraminifera and coccolithophores began to proliferate in the Mesozoic. No shelled organisms existed during the Precambrian, so a major factor in damping down climate fluctuations was missing before the start of the Phanerozoic. This crucial difference between the modern and Precambrian world focussed the attention of Andy Ridgwell, Martin Kennedy (University of California) and Ken Caldeira (Lawrence Livermore National Laboratory) in seeking an explanation for "Snowball" events

(Ridgwell, A.J. *et al.* 2003. <u>Carbonate deposition, climate stability and Neoproterozoic Ice</u> Ages. *Science*, v. **302**, p. 859-862; DOI: 10.1126/science.1088342).



Artistic impression of Snowball Earth

Carbonate sediments are plentiful in the Precambrian record. Some formed as a result of organic action (stromatolitic limestones) and others show evidence for direct, inorganic precipitation of carbonates from sea water. The latter indicate sea water in which calcium and carbonate/bicarbonate ions exceeded the solubility of calcite and the ability of organic activity to remove calcite from solution. Evidence for such extreme oversaturation is rare, but the cap carbonates that overlie Neoproterozoic glaciogenic rocks are important examples. The key area of carbonate deposition has always been on shallow continental shelves, the main secreters of carbonates during the Precambrian having been blue-green bacteria that can photosynthesise only in shallow water. Falls in sea-level or a reduction in the area of shelves during the Phanerozoic reduced this sink for CO<sub>2</sub> in the build-ups of coral and shelly limestones, but plankton of the open oceans continued to accumulate on the deep sea floor.

Because calcite can be dissolved at depth, the deepest sea floor does not contain much carbonate. However, a fall in sea level, increases the area suitable for deep-water burial of shelly material, because the carbonate compensation depth or lysocline also falls. In the absence of shelly plankton, this modern balancing mechanism for ocean chemistry did not exist during the Precambrian. Superficially, it might seem that a reduction in the area of shelf deposition of carbonates, brought on by a sea-level fall, would allow  $CO_2$  to build up in the atmosphere, driving towards warmer conditions. However the way in which atmospheric carbon dioxide is related to dissolved carbonate  $(CO_3^{2-})$  and bicarbonate  $(HCO_3^{-})$  ions tells a very different story. This is the equilibrium:  $CO_2 + CO_3^{2-} + H_2O = 2HCO_3^{-}$ . Less carbonate accumulation on reduced continental shelves would drive up the carbonate-ion concentration of sea water, and also its pH. So, according to Le Chatelier's Principle, the equilibrium proceeds to the right and adds to the more soluble bicarbonate ions in sea water. This consumes  $CO_2$ , and drives down the "greenhouse" effect. Ridgwell and

colleagues developed a model around this equilibrium, and applied it to conditions of falling sea level when carbonates were only deposited on continental shelves. Their results show that decreased shelf-carbonate burial during a period of sea-level fall would rapidly drive down the warming effect of atmospheric carbon dioxide. Combined with the lower solar energy output during the Neoproterozoic, that would be sufficient to create protracted periods of frigidity. Alkalinity of the oceans would increase through periods of glaciation, so that once sea-level rose, massive carbonate precipitation would form cap carbonates on the newly inundated shelves, thereby reducing the oceanic drawdown of CO<sub>2</sub>.

Ridgwell *et al*'s model is not easy to grasp, and relies on its initiation by falling sea-level. Either that resulted from build up of continental glaciers because of some other climatic mechanism, or internal processes increased the volume of the ocean basins. An example of the last is a decrease in sea-floor spreading, when cooling of the lithosphere increases it density so that it sags down. Periods of accelerated creation of oceanic lithosphere displace sea water upwards, and perhaps that might explain an increase in shelf areas, which would allow warming according to the new model. The model also needs special pleading to account for the 1 billion-year absence of glaciation before the period of Snowball events. The authors suggest that it could have been prevented by much wider shelves during earlier times, but without quoting evidence.

## Continental erosion and climate (November 2003)

Maureen Raymo suggested in 1988 that long term climate change was modulated by the rise of mountain chains and their erosion and weathering. This is because chemical weathering of silicate minerals is a net consumer of atmospheric carbon dioxide. Raymo's hypothesis, based on T.C. Chamberlin's theory of glaciation, has set climatically concerned geochemists to analysing the trace element content of river water in many mountainous regions, because those such as strontium are proxies for the amount of weathering going on today. Others have looked at the flux of elements into seawater through the Phanerozoic in particular, by analysing marine carbonates, to see if the ups and down's of water composition through time match the record of climate change. These time series do suggest some matching, but not precise enough for all to agree with the hypothesis. Measurements of river-water composition have also met set-backs. Much of the weathering flux from mountains seems to stem from dissolution of carbonate rocks, and that does not lead to long-term loss of CO<sub>2</sub> from the atmosphere.



New Zealand's Southern Alps

In a bid to resolve the contributions of carbonates and silicates, Andrew Jacobson and Joel Blum of the University of Michigan have studied the flux from part of the Alps of New Zealand's South Island (Jacobson, A.D. & Blum, J.D. 2003. Relationship between mechanical erosion and atmospheric consumption in the New Zealand Southern Alps. Geology, v. 31, p. 865-868; DOI: 10.1130/G19662.1). Their area is a good choice because the New Zealand Alps are actively rising, precipitous and drenched with continual heavy rain and snowfall. Moreover, they offer something that the Andes and Himalaya do not; the rocks are pretty uniform. What they find will not please Raymo's followers. As in many mountain ranges, mechanical erosion favours carbonate weathering over that of the CO<sub>2</sub> sequestering alteration of silicates. With a low ratio of silicate to carbonate weathering, mountain building in New Zealand does draw down carbon dioxide, but only by a factor of about 2. They conclude that more stable areas with lower relief are more likely to affect climate. Although chemical weathering in them is lower than in mountains, that of silicates is far higher than for carbonates. Moreover, active mountain ranges are minuscule compared with the extent of more subdued land. It seems likely from Jacobson and Blum's findings that the major control of weathering over climate depends to a large degree on where continents are located relative to warm, humid climatic zones. For much of the early Cenozoic, the dominantly crystalline Precambrian shields of India, Africa, Australia and South America straddled the Equator, and witnessed intense weathering. Maybe that relationship helped draw down carbon dioxide, and gradually cooled the planet from the hot and humid climate of the late Mesozoic.