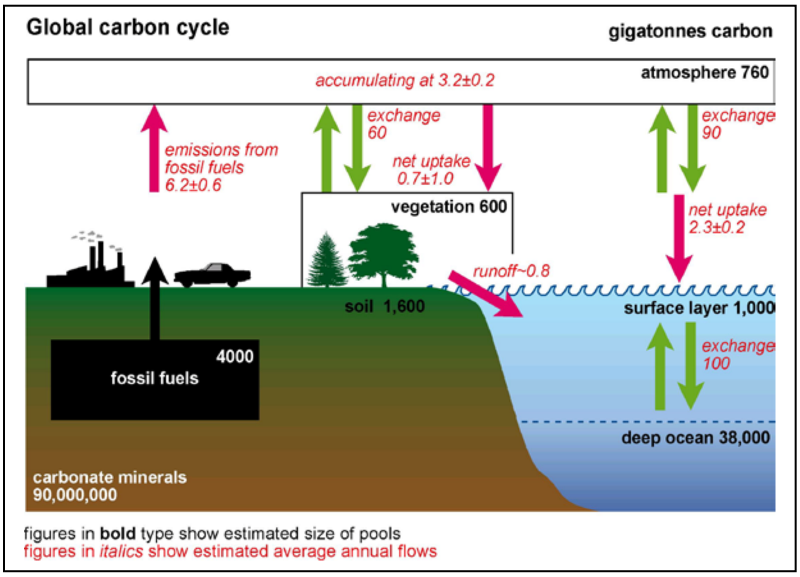
British
Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Geological Controls on Carbon Budgets

The global role of sediments as a sink and store for carbon: a literature review.

Coastal Geology and Global Change Impacts Programme

Internal Report IR/03/135



BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/03/135

Geological Controls on Carbon Budgets

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The global carbon budget (BGS)

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Foreword

This report is the result of a study by the British Geological Survey (BGS) as a contribution to the 'Carbon Dynamics Project' that forms a part of the 'Coastal and Global Climate Change Programme'. It is a review of the present state of knowledge on the Earth's carbon cycle based on peer reviewed published literature and Internet data. It has been formulated and written to identify the potential contribution the British Geological Survey can make to the NERC science programme in the context of the NERC publication 'Science for a Sustainable Future', and as a contribution to deliberations now taking place (March 2004) on the next BGS five year programme (2005-2010).

The Carbon Dynamics Project is a scoping study with the overall objectives of:

1. preparing a review of the long term role of sediment storage in the carbon cycle,
2. reviewing the carbon flux between sediments, the sea and the atmosphere over geological timescales,
3. estimating the volume of the long term carbon store,
4. providing data to calibrate models of the NERC Earth Science Modelling Initiative (NESMI),
5. providing a BGS context for contributing to the NERC Quantifying and Understanding the Earth System (QUEST) Initiative,
6. providing a discussion document for the new BGS five year plan (2005-2010), and
7. providing a foundation for BGS publications on the Public Understanding of Science (PUS).

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BGS staff contributions are as follows:

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Carbon distribution in sediments:

Organic carbon: Chris Vane and Keith Bateman

Carbonate reefs and carbonate rich sediments: Andy Butcher, Dave Tappin, Graham Lott, Bernard Humphreys, Anna Jarrow and Kathryn Rowlands,

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Diagenetic and Chemical factors and carbonate fluxes: Barry Rawlins, Chris Vane, Bernard Humphreys, Graham Lott, Keith Bateman and Chris Rochelle.

Release of stored CO_2 from sediments: Barry Rawlins, Dave Tappin.

Impacts of climate change: Barry Rawlings and Bernard Humphreys.

Theoretical and experimental factors: Keith Bateman, Chris Rochelle and Chris Vane.

Recommendations: All

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SUMMARY

BACKGROUND

The context of the BGS Science Programme is provided by funding from NERC and through the scientific initiatives identified in the NERC Science Plan for 2002-2007, ‘Science for a Sustainable Future’. Of the three major NERC scientific themes identified, two, ‘Climate Change’ and ‘Earth’s Life–Support Systems’, directly involve assessment of carbon cycling and global warming and to which this report directly contributes. The third main element, ‘Sustainable Economies’ is also relevant because of the impact of fossil fuel burning on global warming.

This report presents a review of the geological aspects of carbon cycling, identifying the potential contribution that can be made by geological research undertaken at BGS. It is does not cover every aspect of the carbon cycle, as it is focussed on the geological factors of carbon cycling and storage. However, it does present a comprehensive overview that shows the Earth’s carbon budget to intrude into all aspects of Earth Science pertaining to Climate Change, from the main climate drivers and amplifiers (such as Greenhouse Gases) to possible artificial sequestration mechanisms that may be used to address the impact of rising CO_2 levels due to anthropogenic greenhouse gas emissions. The report deals only with the natural processes of carbon cycling and the anthropogenic impact upon these. It does not specifically address downstream issues of artificial carbon sequestration except where appropriate and then only in a broad thematic sense, for example in iron seeding of the ocean.

A fundamental conclusion of the report is that the BGS Programme can make significant contributions to research on climate drivers and feedbacks, based on existing projects. However, the present organisation of these projects in the context of carbon cycling and climate change is dislocated. Additionally, BGS science is mainly focussed within the UK and climate research is global. To make a significant contribution a less parochial perspective is required. Notwithstanding, there are science themes that BGS has already developed that contribute to our understanding of carbon cycling, notably in the Marine and Coastal Programmes, Hazards and CO_2 sequestration. The intimate linkages between the different aspects of carbon cycling, involve the atmosphere, biosphere, land and ocean, therefore an ‘Earth System Approach’ is required to obtain maximum benefit from the results of the individual projects. Within BGS at present this holistic approach is lacking.

THE CARBON CYCLE

Earth carbon over the long term is stored mainly in rock and sediment. Over short timescales only a small fraction resides in mobile superficial reservoirs, such as the atmosphere, oceans, soil and biota. Sedimentary carbonates and kerogen are the largest carbon reservoirs, followed by methane hydrate, marine dissolved inorganic carbon, soils, surface sediments and the atmosphere. The living biomass reservoir is somewhat smaller than the atmospheric carbon reservoir, with which it actively exchanges through photosynthesis and respiration. The total sediment store of carbon has been estimated at 90×10^6 gigatonnes of carbon (Gt C), of which the largest three sinks are limestone (60×10^6 Gt C), kerogen (15×10^6 Gt C) and methane hydrate (500-2,500 Gt C). The size of the hydrate sink has recently been downgraded from the 1990’s estimate of 10×10^3 Gt because of better constraints provided from Ocean Drilling.

The short-term carbon cycle is dominated by exchanges between the biosphere, atmosphere, ocean and soil on time sales ranging from days to hundreds of years. The long-term Phanerozic carbon cycle between rocks, the atmosphere and the oceans operates over thousands to hundreds of millions of years. Three dominant slow processes control steady-state carbon flux: mantle degassing, chemical weathering of silicate minerals and burial and weathering of organic carbon. Secondary controls are due to interactions operating through plate tectonic processes and include; crustal mobility, metamorphism of carbonate, marine carbonate accumulation and carbonate turnover in subduction zones, ocean basin evolution and mountain building and decay. Over the long-term evolution of the Earth major influences on carbon budgets include biological changes such as the rise and diversification of land plants between 425 and 370 Million years BP.

In the Precambrian, the carbon cycle was very different to that of the Phanerozoic. The Earth, after its formation passed through gaseous and molten phases before solidification formed the crust. Continued outgassing created the proto-atmosphere and, once life had evolved, in a proto-biosphere in which a non-linear, non-steady-state carbon cycle prevailed. In the late Precambrian, in the Neoproterozoic, a period of extreme climates, the so-called ‘Snowball Earth’, terminated this phase of Earth evolution. During the Phanerozoic, the carbon cycle evolved in a variety of environments recognisable as broadly similar to those of today.

THE IMPORTANCE OF CARBON

The primary motivation for understanding the carbon cycle is because atmospheric CO_2 is a primary control on climate. This is particularly seen in the dramatic rise of anthropogenic CO_2 over the past 200 years, a rise that is now generally recognised as the primary driving agent of recent global warming. The simplest approach to solving the anthropogenic impact on climate change is to reduce anthropogenic CO_2 emissions. However, because of the lack of political commitment, this is not taking place sufficiently rapidly to address the impact on the climate from the rising levels of atmospheric CO_2 that are predicted to take place over the next hundred years. Finding a solution to increasing atmospheric CO_2 levels has devolved down to science, with the priorities to identify how climate operates and what practicable artificial mechanisms there are of atmospheric CO_2 sequestration to absorb the excess CO_2 created by man’s activities.

On the large scale the atmosphere/land carbon flux is reasonably well established and at present political considerations dictate that sequestration on land is the priority. However, there are fluxes that are still not well understood or are at an early stage of understanding (Figure 20). Recent research in the Amazon Basin indicates that the vegetation/atmosphere exchange is not behaving as modelled. The atmosphere/soil exchange requires additional study. The ocean carbon sink is recognised as larger than that on land, yet there are major uncertainties regarding the carbon flux between the land and the sea and within the ocean itself. The atmosphere/ocean flux as well the carbon exchange between the surface and deep ocean layers is poorly known. Thus a major imperative is to more fully understand the ocean’s role in the carbon cycle, identifying the physical and biological aspects, as well the natural processes that may be available for longer-term carbon storage, such as Fe seeding to enhance phytoplankton take-up.

THE GEOLOGICAL CONTEXT

Climate modellers are the main contributors to climate research, especially over shorter timescales. However, although there are increasingly accurate models of recent palaeoclimates present models cannot reproduce the extreme climates known to have occurred in the past; for example the late Cretaceous warm period. The atmospheric carbon dioxide levels we are now predicting for the future may result in extreme climates that have not been experienced for 10's of millions of years. Over these longer timescales insight into mechanisms and controls on extreme climates can only be provided by research into the rocks and sediment that hold the record of the past. The geological record provides longer-term background climate data critical to understanding these extremes.

The report presents the main processes controlling the carbon cycle in the context of the importance of CO_2 on climate change, particularly 'Greenhouse warming'. The recent history of climate change and the main climate drivers are described followed by their geological perspective. Based upon a consideration of both the Phanerozoic and Precambrian carbon fluxes, the main climate controls are considered in the context of our knowledge base. There is no doubt that as our knowledge of the longer-term record increases this knowledge will be incorporated into improved predictive models. The main contribution of geology is in providing a context for the improvement of understanding short-term effects of global warming and in an appreciation of what, unexpected, climate changes may lie ahead. If nothing else, 4,500 million years of Earth history demonstrates that anything may be possible.

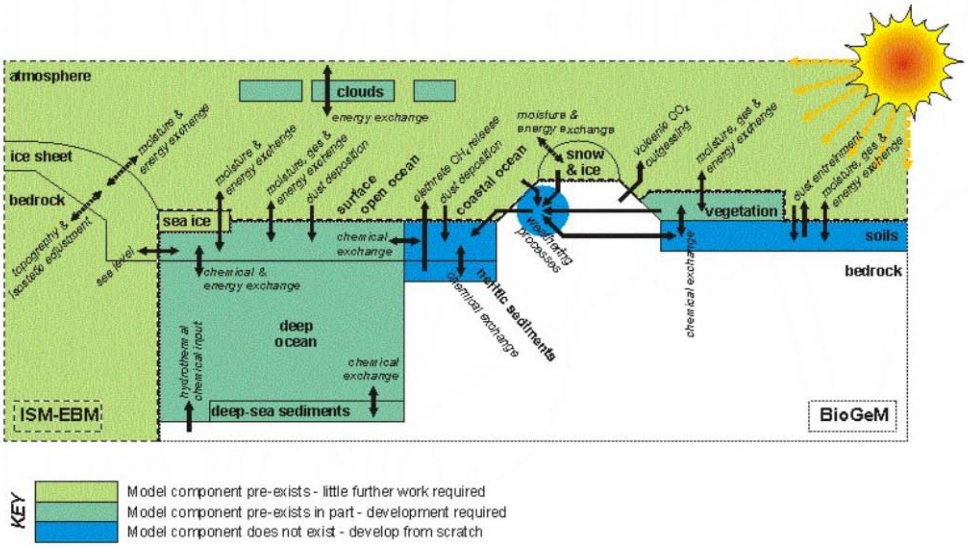


Figure Summary 1. Land/Ocean/Atmosphere model GENIE illustrating the levels of understanding of fluxes (Courtesy of A. Ridgwell, from John Shepherd, QUEST Meeting)**.**

Because of both the long term contribution to understanding the carbon cycle and hence the controls of carbon on climate and the inter-related nature of the active processes controlling the carbon flux, an 'Earth Systems Approach' is required to address the Earth's carbon budget and changes in this budget. The Earth System comprises the solid Earth and the land surface, the hydrosphere (oceans, rivers & lakes), the atmosphere, the cryosphere (sea-ice, glaciers and the ice caps) and the biosphere, encompassing both the terrestrial and marine environments. The Earth System components interact over a range of scales in both space and time. They exhibit a range of phenomena including the formation and movement of continents, opening and closing of ocean basins, formation and erosion of mountain ranges, waxing and waning of massive ice-sheets, inception and evolution of life and climate change on all time scales. All aspects of this system need to be studied if we are to fully understand the Earth's future climate.

THE BGS CONTRIBUTION

Notwithstanding the fact that climate underpins our interpretation of rock sequences, and that climate has been a major part of geological research for decades, the BGS has not developed a focussed programme of research on climate until during the past three years, a Climate Change component was added to the Coastal Programme. This does not mean that the BGS in the future cannot make a significant contribution to climate science. To the contrary, the BGS's substantial intellectual capacity, its comprehensive Earth Science database as well as its national and international programme of work provide a foundation for climate research over geological timescales. It is in this context that the recommendations as to the potential BGS programme are made. There are many, if not most, aspects of climate science that BGS can contribute to, although in many there are already individual scientists and/or institutions with an established reputation. The suggested avenues of research are in fields where we have an expertise and a track record. A potential, but not exhaustive, list of themes follows.

BGS RESEARCH THEMES

1. Continental Shelf Carbon Fluxes

Carbon fluxes from land to ocean, based on the BGS continental shelf mapping carried out over the past 40 years. A major knowledge gap is in the global carbon flux across the continental shelves in all parts of the world. Global models have addressed terrestrial and ocean flux to the atmosphere, in the latter instance mainly ignoring the role of continental shelves. Recent research indicates that continental shelves may not only be an important conduit to the deep ocean, but also a significant sink for carbon, particularly organic carbon from fluvial sources. Continental shelf sinks are especially important where sedimentation rates are high, for example in pro-delta settings, and where the shelf sediment is mud-rich. Sediment-starved shelves also play a significant role in the preservation of organic carbon.

2. Climate Proxies

Climate proxies are agents that provide surrogate data on temperature, such as from ice cores, and are mainly, on the hundred thousand year scale, confined to high latitudes. Other proxies include tree rings, pollen, coleoptera and corals, however all have their limitations. The main constraint on ice cores is their location, their data is critical to climate change assessment, but they are restricted to providing data for high latitudes and preclude detailed modelling or calibration in other areas. There is a requirement for new proxies that may be applied to other regions especially to alluvial environments. The use of lignin is constrained only by a lack of organic carbon and an oxidising environment. Its potential has yet to be fully explored. The stable isotopic analysis of waterbodies to provide a history of climate change has already been pioneered in the Sahel by BGS; the applications of this approach may be utilised in other areas.

3. Methane Hydrates

The investigation of methane hydrates contributes to our understanding of many aspects of the carbon cycle including carbon storage, as a potential fuel source and a driver of abrupt climate change. Methane is a major greenhouse gas and a contributor to global climate warming. There have been numerous field investigations into its presence and geographical extent and estimates made as to its global volume. There is a need for laboratory-based research on hydrate stability, which will contribute to understanding of its potential both as a fuel source and as a driver of and contributor to abrupt global warming. There is a requirement to resolve whether methane is a major driver of rapid climate change, the 'clathrate gun' hypothesis, which is based on the likelihood that there may have been large and rapid hydrate expulsions from the seabed that result in a change from glacial to interglacial conditions. Hydrate research will also add to our understanding of the potential threat from tsunamis as global temperature increases. The further study of the numerous submarine slumps on the northwest European continental margin, particularly mechanisms of failure and their ages is an associated theme.

4. Ocean Circulation

Carbon cycling in the deep ocean include fluxes between the deep and shallow ocean layers and controls on thermohaline circulation. It is poorly understood and operates over longer timescales than those on land. In the long term it is recognised that carbon sequestration in the ocean is a mechanism that could absorb the rising levels of anthropogenic atmospheric levels of CO_2. Carbon fluxes in the deep ocean are not as well understood as those on land. They are more complex and, unlike on land, include both biological and physical processes of carbon cycling. Thermohaline circulation plays a major role in distributing heat between the poles. It has been predicted that increased levels of atmospheric CO_2 of 700-800 ppmv could result in a collapse of the North Atlantic system leading to a reduction in heat transfer to the northern hemisphere. Additionally, phytoplankton are responsible for approximately 40% of the planet's total annual photosynthetic (primary) production. They play a major role in controlling the heat budget of the Earth during glacial/interglacial cycles through respiration of CO_2. The history of carbon change over geological times scales can be studied through the sedimentary sequences in cores of the sub seabed sediment. Over longer geological timescales changes in the morphology of the ocean basins also affects deep and intermediate water circulation that affects climate on a global scale.

5. Terrestrial Carbon

The effects of changing terrestrial sinks and sources in relationship to hydrological regime, base-level, climatic change and land-use changes. These include the likely controls of groundwater change, oxidation of organic soils and weathering of silicate and carbonate minerals.

6. Volcanism

The impact of volcanism is a recognised driver of climate change, as it is well established that outgassing of volatiles is one of the three major controls on climate. Recent research shows that over the short-term, weather may also be a control on levels of volcanic activity. For example, the eruption of Mount Pinatabu in the Philippines in 1991 followed a cyclone. More recently, in 2004, a major submarine eruption in Vanuatu ceased when a cyclone passed overhead. Over the longer term, major failure of volcanic edifices on intra-oceanic islands such as the Hawaiian chain has been linked to the climatic variation between glacial and interglacial cycles.

7. Biogeochemical Cycles

An improved understanding of the interactions of trace metals, nutrients and other key biogeochemical species (e.g. nitrates, phosphates and sulphates) with the carbon cycle is recognised as a requirement of biogeochemical modelling. Currently parameterisation of models is poor both in terrestrial and marine settings. The rates of processes driving or governing the carbon, water and other biogeochemical cycles under a range of human or natural pressures within key environments such as soils, the unsaturated zone, or mixing zones of estuaries, are currently very poorly understood.

8. Goundwater

The contribution of groundwater to the water cycle, and atmosphere to the carbon cycle, requires detailed analysis, not only in terms of its vital role in regulating terrestrial-atmospheric interactions (water vapour is the greatest contributor of radiative forcing) but in determining the health of wetlands, controlling rates of weathering, and transport of nutrients that impact upon other key biogeochemical cycles (see above).

BGS is very well placed to build and service models related to erosion and physical transport of materials, such as soils, coasts or submarine slopes. Work on the NESMI project has already demonstrated the value of such modelling to provide data for inorganic and organic climatic feedback models in temperate shelf sea settings. Determining past rates of flux, through detailed analysis of alluvial and colluvial records provides critical data for the calibration of Holocene climate change models that aim to discriminate between anthropogenic impact on, for example land-use change or contamination, and natural change, such as climatic variability and base-level change.

The remaining recommended projects are based upon the global experience of BGS including for example offshore studies of the UK shelf that latterly has encompassed large areas of the northwest European Shelf including collaborative EU projects such as ENAM, GITEC and COSTA.

9. Oceanic Thermohaline Circulation

Changes in oceanic thermohaline circulation (THC) are a consequence of temporal and spatial variations in solar insolation, which are driven by predictable and regular variations in the Earth’s orbit over time. This dictates the distribution and amount of heat energy in the oceans and is the primary driving mechanism in Quaternary climate change. It is the radiation that reaches the oceans and warms the waters, that produces a density gradient and strengthens THC. Orbital forcing also controls northern hemisphere ice volume. The release of freshwater into the oceans due to the melting of glaciers causes differences in salinity and water density, and this feedback mechanism also controls THC. The effects of a reduced THC in the Atlantic are predicted to be cooling of the European waters as heat transfer from the Equatorial regions declines. The record of past THC changes is contained in the ocean sub-seabed sediment column that can be interrogated, using palaeoecological, lithological and geochemical proxies, to determine past changes. Changes in THC can be abrupt, operating over tens to hundreds of years, and the feed back mechanisms controlling these rapid changes are not yet fully understood.

Other thematic programmes that will contribute to our understanding of climate change include the uses of isotope studies through the NERC Isotope Geoscience Laboratory (NIGL) and drilling using the new Integrated Ocean Drilling Program (IODP) ocean drilling initiative. In the latter instance combining the technical contribution to be made by BGS with an additional scientific input.

An important aspect of the BGS programme will be collaboration with other Natural Environment Research Council (NERC) institutes such as the British Antarctic Survey (BAS), the Centre of Ecology and Hydrology (CEH), Proudman Oceanographic Laboratory (POL) and Southampton Oceanography Centre (SOC).

1. INTRODUCTION

Recent reports on the increasing impact of global warming on the Earth's environment, including the extinction of a million animal species by the year ~2040, highlight the need for a better understanding of what drives climate change and the impact that man is making. A recent study published in the journal Nature,(Thomas *et al*., 2004) recognised that a quarter of all animals and plants living on land in six world regions could be forced into extinction over the next 30 years.

The creation in late March 2004 of an international taskforce chaired by former cabinet minister Stephen Byers indicates the priority of global warming to the government. Byers stated that climate change was the "overriding environmental challenge" of our age, and the task force participants are taking "a responsibility to future generations to hand to them a planet that is habitable and rich in life". "Climate change caused by greenhouse gas emissions from human activities threatens that objective".

The most direct approach to addressing the predicted rise in global temperatures is to reduce the main cause of the problem, the atmospheric greenhouse gases, particularly CO_2. Action on this would solve the problem, but it has to be undertaken immediately (IPCC Third Assessment Report, 2001). Through the Kyoto Protocol, signed in 1992, cuts in greenhouse gas emissions were agreed, but not all nations are committed to undertaking the necessary cutbacks, and the protocol at present has not been ratified. Notable amongst those nations not signatory to the convention are the major CO_2 emitting countries of the USA, Russia and China.

As an alternative to cutbacks, many nations are investigating methods of reducing atmospheric CO_2 levels through artificial methods of sequestration. However, because of the Protocol, these are mainly focussed on land sinks. Oceanic sinks, operating over longer timescales, could be the answer but further research into mechanisms of the natural ocean CO_2 fluxes are needed before the effects of artificial sequestration can be assessed (IPCC Third Assessment Report, 2001).

A major exclusion from the controls outlined in the Kyoto Protocol is the atmospheric pollution created by aircraft. CO_2 pollution from aircraft will constitute over 25% of the UK's CO_2 emissions by 2020. There has been a major environmental consequence from the recent massive expansion of air travel due to budget cost flights.

With the recognition that anthropogenic increases in atmospheric CO_2 is one of the major problems facing the human population of the Earth, and acknowledgement of the contribution geological research can make to understanding of the processes and impacts of climate change, it becomes apparent that an improved understanding of global carbon fluxes over geological timescales is required. Because of the intimate associations and interactions between the elements controlling climate, an understanding of the whole Earth system is required if we are to fully comprehend the extremely complicated inter-relationships of the carbon cycle. Thus an 'Earth Systems Approach' is needed if we are to take account of all aspects of carbon cycling on Earth, including: the solid Earth and the land surface, the hydrosphere (oceans, rivers

& lakes), the atmosphere, the cryosphere (sea-ice, glaciers and the ice caps) and the biosphere, both terrestrial and marine. We know the components of the Earth system and we recognise the range of scales in space and time over which they interact. We also appreciate the range of phenomena involved, including the formation and movement of continents, the opening and closing of ocean basins, the formation and erosion of mountain ranges, the waxing and waning of massive ice-sheets, the inception and evolution of life and climate change on all time scales.

Earth System Science provides a basis for, and a control on, the models necessary to predict the climate of the future. In this report we seek to outline the present knowledge base, the methodologies used to interpret the Earth's climate in the present and in the past and to identify what contribution the BGS can make.

2. CARBON AND CLIMATE CHANGE

2.1 CLIMATE BACKGROUND

Scientists have discovered that over the long-term, geological time scale a number of well -established global cycles are controlling the Earth's climate. For example over the past 2 million years, the glacial-interglacial cycle that resulted in alternations between periods of warmth (interglacials) and periods of cold (glacials). Until recently, climate over the human time scale was regarded as relatively stable, but a growing body of evidence indicates that global climate may change significantly over short periods and that the changes may be rapid, sometimes over decades if not years (Figure 1). Rapid climate change undoubtedly occurs naturally but rates of change are increasingly recognised as also attributable to human impact (Figure 2).

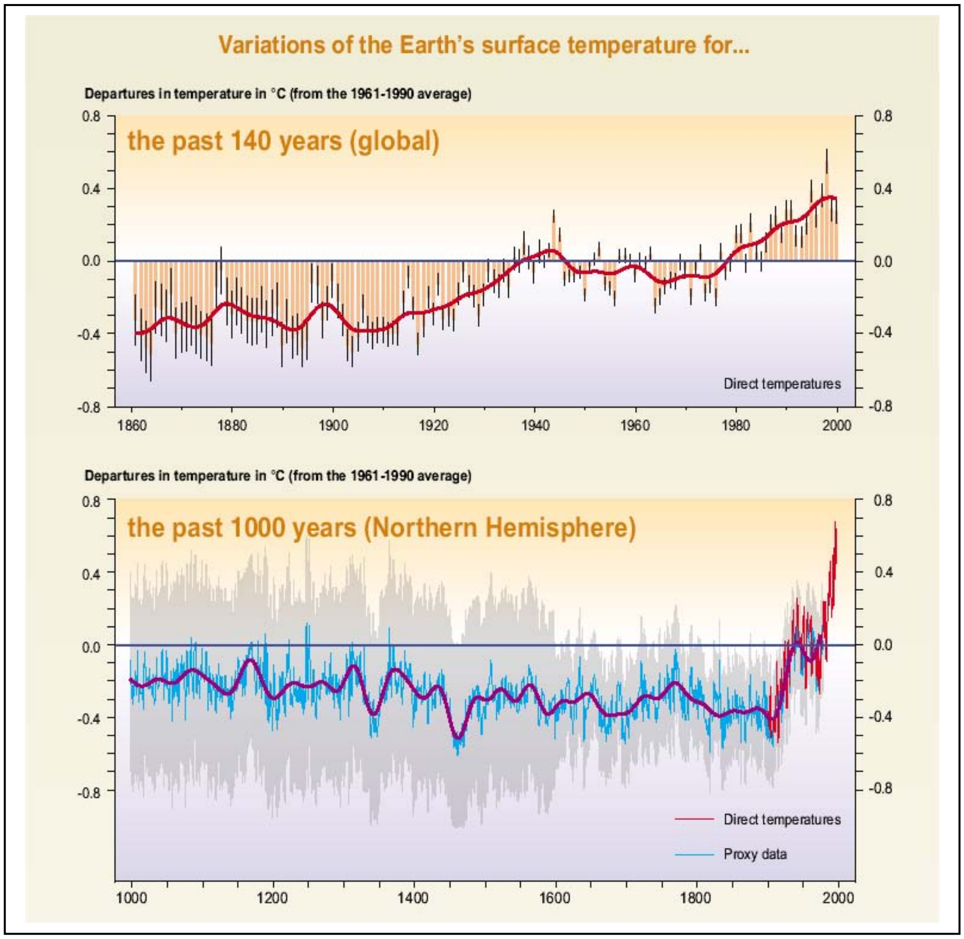


Figure 1. Temperature departures from 1961-1990 averages for (a) the past 140 and (b) the past 1000 years. (IPCC Third Assessment Report – 2001).

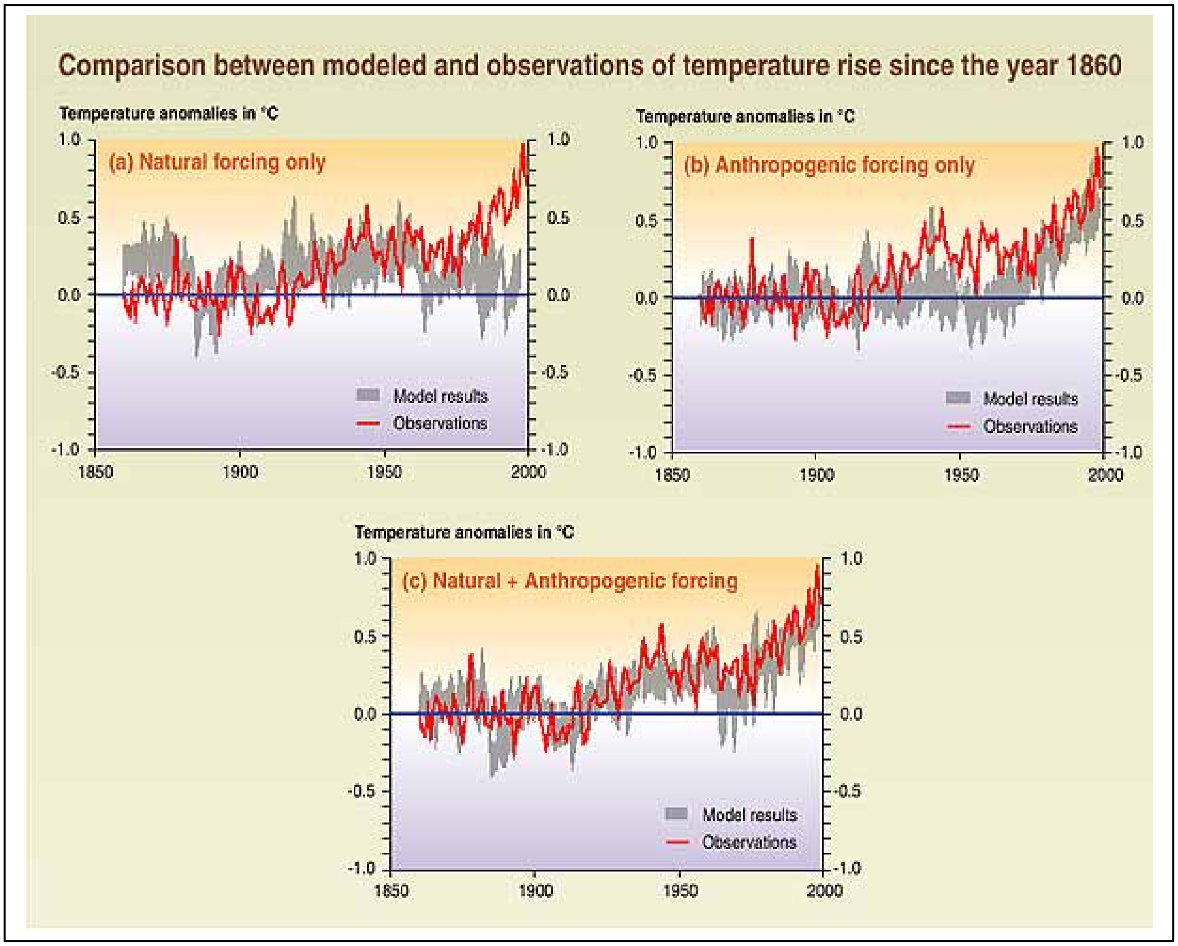


Figure 2. Simulated annual global mean surface temperatures to compare natural and anthropogenic factors (IPCC Third Assessment Report, 2001).

The dominant orbital controls on climate over the geological past have been recognised for a long time, initially by James Croll in 1875 (Croll, 1875). In the 1930's and 1940's Milutin Milankovitch elaborated Croll's theory by proposing that variations in northern hemisphere summer radiation at the 22 ka precession cycle and 41 ka obliquity cycle, drive northern ice sheets by summer ablation control of ice mass balance, and inferred that ice sheet responses should lag 5 ka behind summer radiation forcing. The 41 ka period drives ice-proximal signals such as Sea Surface Temperature (SST), North Atlantic Deep Water (NADW) and dust that produce a strong positive CO_2 feedback and further amplification of ice volume changes. The 22 ka period forces ice sheets, but also drives a fast and early response in CH_4 through changes in tropical monsoons and boreal wetlands and also through variations in CO_2 through southern hemisphere processes. In confirmation of Milankovitch's hypothesis, Hays *et al.* (1976) found that coherent changes in •^{18}O lag several thousand years behind the forcing at the two orbital cycles. Imbrie *et al*. (1984) determined that •^{18}O lags of 5 ka behind precession and 8 ka behind obliquity simultaneously satisfied a 17 ka time constant of ice response. These studies also detected a dominant • ^{18}O response at 100 ka that Milankovitch had not anticipated because direct solar forcing at that period is negligible. Because the 100 ka • ^{18}O signal is phased with orbital eccentricity, Hays *et al*. (1976) called it a “paced” response but left its origin unresolved. Most recently the 100 ka signal it has been attributed to effects resulting from a combination of precession and obliquity (Raymo, 1997; Ruddiman, 2003, 2004). After 0.9 ka, long term cooling allowed ice in the northern hemisphere to survive the weak precession peaks, that occur in clusters every 100 ka years, and that previously had led to melting. This resulted in enhanced positive CO_2 feedback at the 41 ka obliquity cycle, thereby amplifying the 100 ka cycle.

The most remarkable aspects of the external orbital forcing include the large distances involved, with an average Earth-Sun separation of 93 million miles, and exceptionally small annual variability of solar insolation values of 0.5°C driving the system. The large distances and small insolation values require large internal Earth feedbacks to drive the climate changes because, although insolation forcing acts as the trigger to climate change, it does not control their magnitude. The main greenhouse gases driving the feedbacks are recognized as CO_2 and CH_4 as well as H_2O and N_2O.

2.2 DATING

Direct measurement of climate change, such as by temperature, only dates back several hundred years to the mid-19th century, to investigate climate change before this time, climatic ‘proxies’ are used. Proxies are measurable parameters that provide quantitative data on variables such as temperature, rainfall or ice volume. Examples include tree rings, ice cores, pollen and corals (Table 1). Until the development of these new methodologies to accurately identify and chart climatic variables, the details of global climate change and the rate of change over longer time scales could not be elucidated.

Method	Information	Resolution (years)	Dating	Time Range (years)
Tree Rings	Temperature, Precipitation	Annual	Count rings, C14	500-700 (rarely up to 11 ka)
Pollen	Shift vegetation patterns, local climatic conditions	50	Based on dating of deposit biozones, indicator species	0-millions
Geomorphology	Numerous	Variable	Isotopes	Up to billions
Coleoptera	Temperature	Variable	Based on dating of deposit.	0- 2 million
Diatoms	Eutrophication, acidification, salinity changes, lake and sea level changes	Variable	Based on dating of deposit.	Dependant of preservation
Plant macrofossils	Shift vegetation patterns	Variable	ASM radiocarbon dating	Dependant on preservation
Mollusca	Temperature,	Variable	Based on dating	Dependant on

	moisture, local habitat		of deposit.	preservation
Foraminifera	Surface water temperature, sea level change and climatic conditions	Variable	Based on dating of deposit.	Dependant on preservation
Ostracod	Temperature, salinity - sea level change	Variable	Radiocarbon dating	Millions of years, but dependent on preservation
Mammal remains	Environment and temperature	Variable	Assemblages can be used for stratigraphic purposes – biostratigraphic markers	Millions of years
Stalactites	Temperature	Millenia???	Uranium isotope techniques	>0.25Ma
Lithological evidence	Numerous environmental conditions	Variable – day to millennia	Based on dating of deposit.	0 - billions
Ice cores	Ice volume, CO_2/CH_4, wind, temperature, sunspot cycles	Subseasonal to decadal. Highly accurate to 40 ka	Annual layers, correlation	0- 440 ka
Corals	Sea Surface Temperature, salinity, El Nino,	Week/month	Annual bands, isotopes	Continuous to 400
Marine sediments	Numerous	Seasonal to 1,000's years	Isotopes	180 million

Table 1. Comparison of 'proxy' methodologies used in reconstructing the past.

Using a combination of detailed direct temperature measurements made over the past 200 years, together with measurements of an indirect nature (proxies), an accurate knowledge of climate change has been deduced that now extends back into the geological past (Table 1). The most scientifically viable approach is a multi-proxy approach, investigating a number of proxies to build up a picture of the past climate. The order of accuracy varies and decreases with increasing age but, notwithstanding, we are now able to identify climate changes on a decadal level going back hundreds of thousands of years.

2.3 MANS IMPACT

One of the major controversies over the past decade has been the anthropomorphic effect on climate change, particularly on the increased rate of warming identified over the past 200 years (Figure 3). The record of direct temperature measurements is short lived, but using ice cores from Antarctica and Greenland there is a strong correlation between temperatures as recorded in oxygen and deuterium isotopes (^{18}O and D) from water molecules and CO_2 and CH_4 levels. The positive correlations show that changes in the greenhouse gas concentrations played a large role in amplifying the temperature changes. The ice core records from Antarctica show that atmospheric CO_2 has risen from pre-industrial levels of 280 parts per million volume (ppmv) to 370 ppmv today indicating significant warming over this period (IPCC, 2001). This rapid rate of warming has not been seen in the geological record over the previous 400 kyr. The rise is attributed to increased burning of fossil fuels together with changes in agricultural practices, including the clearing of forests and increased animal husbandry. The temperature increase is because of the so-called ‘greenhouse effect’ with atmospheric carbon trapping some of the radiation that would otherwise be lost to space. This entrapment causes the Earth's atmosphere to be warmer than it would otherwise be. It is due to changes in the global flux of radiation resulting from the increased atmospheric levels of greenhouse gases such as CO_2 and CH_4. The most recent Intergovernmental Panel on Climate Change (IPCC) report indicates that global average surface temperature has increased over the 20th century by about 0.6°C (IPCC, 2001). Over the next century

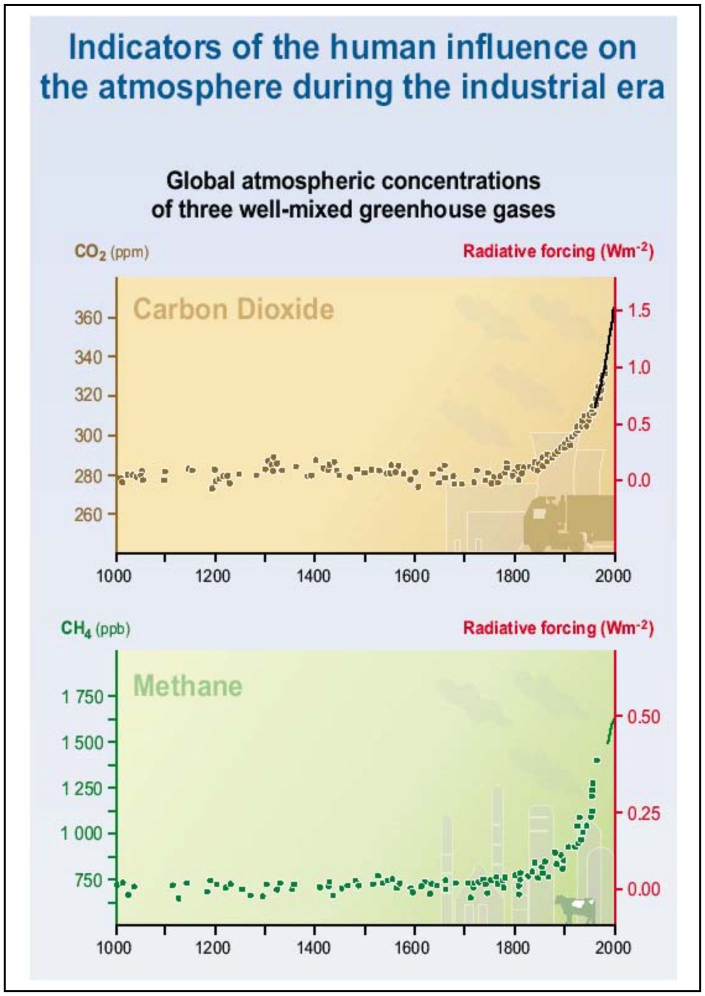


Figure 3. Atmospheric levels of carbon dioxide and methane over the past 1000 years (IPCC Third Assessment Report, 2001).

(to 2100) the IPCC estimates an increase in CO_2 levels to between 500 and 1000 ppmv and an associated temperature rise of between 1.5 and 5.5°C. Sea level is estimated to rise by between 0.1 and 0.9 m. The uncertainties in the estimates reflect in part the incomplete understanding of the carbon cycle.

Although CO_2 levels have risen abruptly over the past 200 years because of anthropogenic input, evidence from the CH_4 levels in ice cores suggest that human influence on global climate may extend back even further to 5000 yrs BP (Ruddiman and Thomson, 2001). Whereas CO_2 is a major climate driver, its impact is slower than that of CH_4 and its influence extends over longer timescales. The rapid climate changes that take place at the termination of cold periods require a rapidly operating driver and the primary suspect is CH_4. Two possible sources of the CH_4 are wetland regions or gas hydrates buried on the continental shelves. Ruddiman and Thomson (2001) propose that global warming following on from the end of the last cold period was strongly influenced by CH_4 from the growth of agriculture, notably rice growing, as the global human population increased. An alternative interpretation is that the CH_4 increase at the end of the glacial period was due to rapid, if not catastrophic, methane expulsion from the continental shelves, supplemented later by methane released during the mid-Holocene age (7 ka BP) as the wetland areas expanded following the glacial retreat (Kennett *et al.*, 2002). However, consideration of the carbon budget over the period of the last deglaciation (18 to 8 ka) shows that, whereas methane release into the atmosphere made a 30 % contribution to the total CH_4 atmospheric budget, the remaining, larger, volume of methane release was from wetlands (Maslin and Thomas, 2003).

2.4 KYOTO PROTOCOL

An essential political context of research into global warming is the 1997 Kyoto Protocol that committed the developed nations to reducing their aggregate emissions of greenhouse gases by 2008-2012 by a figure of 5.2% below their emissions in 1990. Ratification of the Protocol has been delayed by disagreement about the extent to which carbon sinks, in the form of agreed land use, land-use change and forestry activities, could be used to meet emission reduction commitments. The use of forests and agricultural land to mitigate CO_2 emissions was recognised in the United Nations Framework Convention on Climate Change (UNFCCC) in 1992. The Kyoto Protocol in 1997 endorsed the notion not only that governments should employ policies to enhance the land carbon sink capacities of their territories but also that such mitigation could be set against requirements for reductions in emissions from fossil fuel consumption. (See Annex 1 for an overview of international agreements on climate change).

Although recognising that the oceans constitute a potential sink for CO_2, the Kyoto Protocol emphasized terrestrial (land) rather than oceanic sinks, largely because issues of ownership and sovereignty are very difficult to resolve in the latter case, but also because land carbon sinks are more easily manipulated and may also have added value through promoting clean development at community level in less developed countries. Additionally, land sinks operate over shorter (political) time scales and therefore, are more useful in sequestrating the rapidly rising atmospheric levels of CO_2. Ocean sinks, are recognized as potentially larger reservoirs, but they operate over longer time scales (thousands of years) and, although more useful over the longer term, the slower uptake rate makes them less attractive (IPCC, 2001). Proposals for increasing ocean uptake of CO_2 by fertilisation with nutrients including iron are extremely speculative and, contrary to previous studies (eg. Martin *et al*., 1994), recent modeling and observations indicate that carbon fixed in this way may rapidly be recycled (Ridgewell, 2000). More research is required to establish the main drivers of oceanic carbon fluxes.

3 WHY STUDY CARBON?

Carbon (C) is the fourth most abundant element in the Universe, after hydrogen (H), helium (He), and oxygen (O). It is ***the*** building block of life, and the element that anchors all organic substances, from fossil fuels to DNA. On the Earth, carbon cycles through the land, ocean, atmosphere, and the Earth's interior in a major biogeochemical cycle (the circulation of chemical components through the biosphere from or to the lithosphere, atmosphere, and hydrosphere).

One of the main reasons for studying Earth's global carbon cycle is to enable scientists to predict future levels of CO_2 in the atmosphere, because of its major contribution to global warming. Understanding how the global carbon cycle works is essential for us to predict how it, and the climate system, may behave in the future.

3.1 GREENHOUSE GASES

The contemporary interest in global climate change, both in the future and in the geologic past, has focused strongly on the importance of the role of atmospheric CO_2 concentration (PCO_2) in modulating the greenhouse effect. Water is the main greenhouse gas, but CO_2 is the only additional major non-anthropogenic, photochemically stable, polyatomic, tropospheric gas after H_2O, and there is a broad consensus that changes in PCO_2 are a major driver, if not an amplifier, of climate change, although this coupling of PCO_2 and temperature has recently been questioned (Van Der Burgh *et al*., 1993, Pagani *et al*., 1999b, Pearson and Palmer, 2000, Veizer *et al*., 2000 and Rothman, 2002). Atmospheric levels of CO_2 vary with climate, with low levels (<500 ppmv) during glacial periods and high (>1000 ppmv) during warm periods (for comparison, values today are 370 ppmv). After H_2O, CO_2 is the most important greenhouse gas because it has an atmospheric residence time of decades to thousands of years as well as numerous sources and sinks. Methane is the third most important greenhouse gas, with an atmospheric concentration of 1.8 ppmv and, by contrast to CO_2, a very short residence time of ~10 years. However, methane has 23 times the warming potential of CO_2.

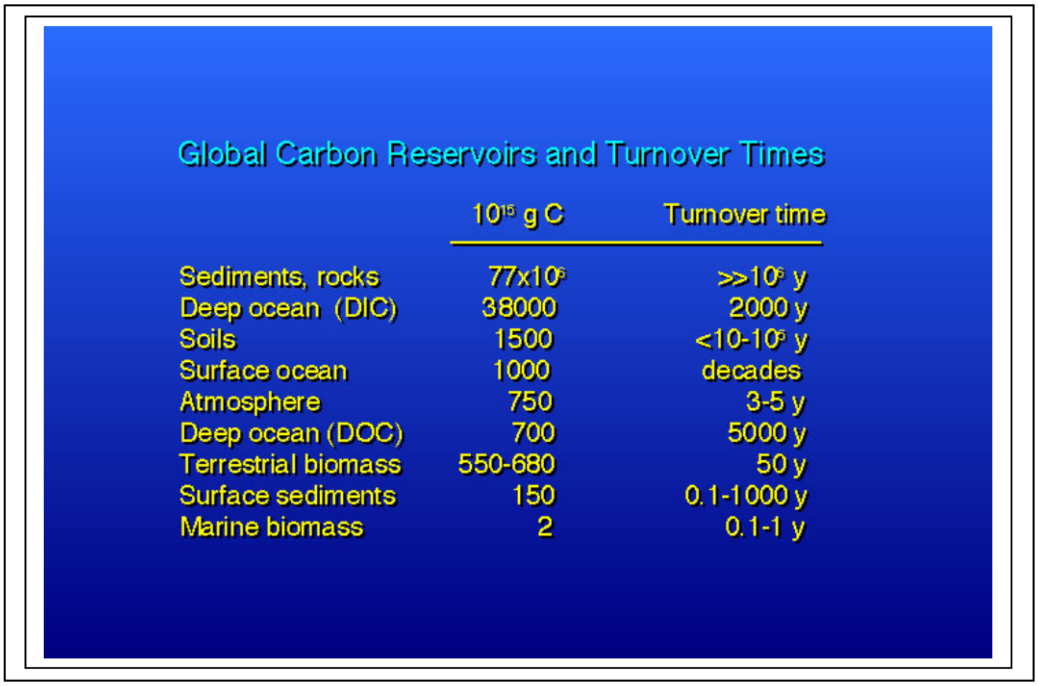
3.2 CARBON RESERVOIRS

The global carbon cycle can be considered in two parts, the exchange of carbon in the:

- Surficial reservoir, comprising the atmosphere, biosphere, oceans and soils, which operates on shorter time scales of days to hundreds of years, and in the
- Geological reservoir, where there is an exchange between rocks and the surficial reservoir, but where the carbon in the surficial reservoir is small by comparison and where processes operate over time scales of thousands to multimillions of years.

3.2.1 The surficial reservoir

In the surficial reservoir, carbon is continuously cycled between the ocean, land and atmosphere, where it occurs primarily as CO_2. On land, carbon occurs primarily in living biota and decaying organic matter. Photosynthesis takes CO_2 from the atmosphere and transfers it to vegetation, and respiration releases CO_2 back into the atmosphere. In the ocean, the main form of carbon is dissolved CO_2 and small creatures, such as plankton. The largest reservoir is the deep ocean, which contains close to 40,000 Gt C, compared to around 2,000 Gt C on land, 750 Gt C in the atmosphere and 1000 Gt C in the upper ocean (Figure 4). The atmosphere, biota, soils and the upper ocean are strongly linked, however, turnover times vary. The atmosphere/terrestrial flux operates over timescales of days to years. By contrast the exchange of CO_2 between the ocean and the atmosphere takes place over years with the exchange between the deep and shallow ocean over hundreds to thousands of years.



Global Carbon Reservoirs and Turnover Times

	10^{15} g C	Turnover time
Sediments, rocks	77×10^6	$>>10^6$ y
Deep ocean (DIC)	38000	2000 y
Soils	1500	$<10\text{-}10^5$ y
Surface ocean	1000	decades
Atmosphere	750	3-5 y
Deep ocean (DOC)	700	5000 y
Terrestrial biomass	550-680	50 y
Surface sediments	150	0.1-1000 y
Marine biomass	2	0.1-1 y

Figure 4. Carbon reservoirs and turnover times

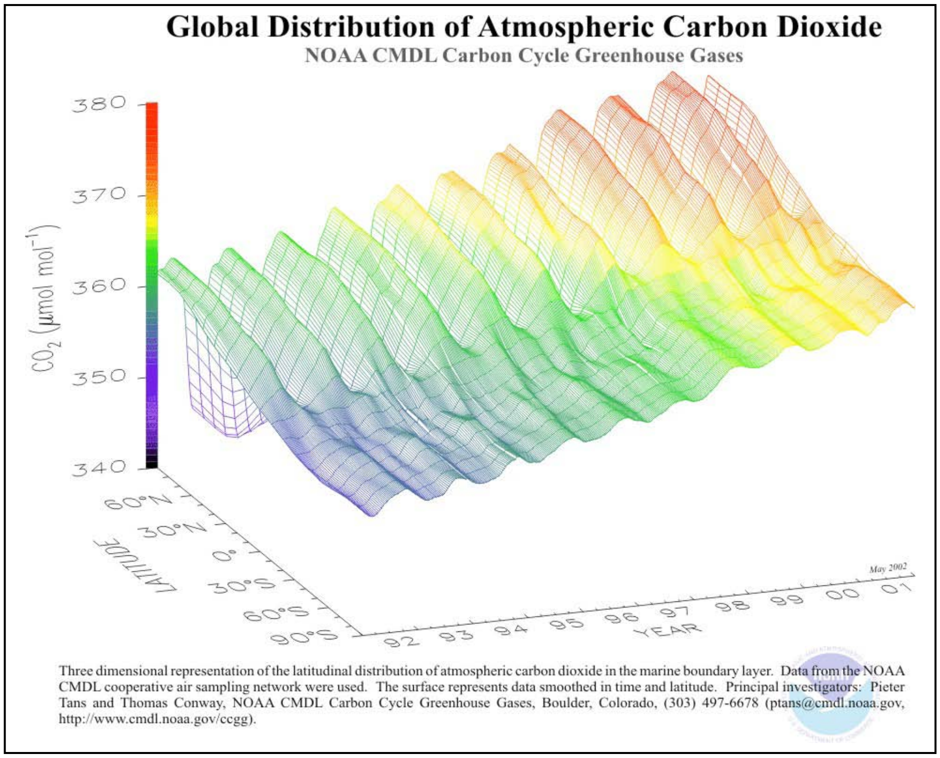
(http://www.ess.uci.edu/~reeburgh/figures.html)

The ocean takes up CO_2 where it is cold, at higher latitudes, and releases it where it is warm near the tropics. Although natural transfers of CO_2 are approximately 20 times greater than those due to human activity, they are in near balance, with the magnitude of carbon sources closely matching those of the sinks. The additional carbon resulting from human activity is now recognised as the cause of atmospheric CO_2 rises over the last 200 years.

Changes in climate have a significant effect on the carbon cycle, although relationships are complex. Increases in the concentration of atmospheric CO_2 increase plant photosynthesis and the amount of carbon stored in vegetation. However, increases in temperature also lead to increases in plant and soil respiration rates, which tend to reduce the size of the terrestrial carbon store. In some regions, the changes in climate (such as decreased rainfall) can also reduce plant photosynthesis and reduce the ability of vegetation to sequester carbon.

3.2.1.1 Man's Impact

For several thousand years before the Industrial Era, which started in the mid 18th century, average atmospheric CO_2 concentration was 280 ± 10 ppmv. Since this time levels of CO_2 have risen continuously, every single year, reaching 367 ppm in 1999, with the increase caused by anthropogenic emissions. 80% of this increase has taken place since 1900. Worldwide, humans release about 7-8 Gt of carbon annually, three-quarters from fossil fuel burning, the remainder from land use change (IPCC, 2001). Approximately 3 Gt C remains in the atmosphere and approximately 2 Gt C are absorbed into the ocean (IPCC, 2001). The remaining approximately 1.5 to 2 Gt C, are absorbed terrestrially (by the so-called 'missing sink'). There are significant latitudinal variations in the terrestrial sinks, with the main locations north of 30°N (1980 to 1989 ranges from −2.3 to −0.6 Gt C/yr) and in the tropics (1980 to 1989 ranges between −1.0 to +1.5 Gt C/yr). These latitudinal variations are reflected in the direct measurement of atmospheric CO_2 (Figure 5).



Global Distribution of Atmospheric Carbon Dioxide

NOAA CMDL Carbon Cycle Greenhouse Gases

Three dimensional representation of the latitudinal distribution of atmospheric carbon dioxide in the marine boundary layer. Data from the NOAA CMDL cooperative air sampling network were used. The surface represents data smoothed in time and latitude. Principal investigators: Pieter Tans and Thomas Conway, NOAA CMDL Carbon Cycle Greenhouse Gases, Boulder, Colorado, (303) 497-6678 (ptans@cmdl.noaa.gov, http://www.cmdl.noaa.gov/ccgg).

Figure 5. Measured latitudinal variation of atmospheric CO_2 between 1992 and 2001

(National Oceanic and Atmospheric Administration (NOAA), Climate Monitoring and Diagnostics Laboratory (CMDL), Carbon Cycle Greenhouse Gases).

The ability to predict atmospheric CO_2 levels is essential if we are to discover by how much global temperatures will continue to rise in the near future and how this rise will impact, not only on other aspects of Earth's climate, but on life itself. CO_2 emissions from fossil fuel burning are virtually certain to be the dominant factor determining CO_2 concentrations during the 21st century (IPCC, 2001). If all of the carbon so far released by land-use changes could be restored to the terrestrial biosphere, CO_2 at the end of the century would be 40 to 70 ppmv less than it would be if no such intervention had occurred. By comparison, global deforestation would add two to four times more CO_2 to the atmosphere than reforestation of all cleared areas would subtract. Within the ocean there is sufficient capacity to incorporate 70 to 80% of foreseeable anthropogenic CO_2 emissions to the atmosphere, but this process takes centuries due to the slow rate of ocean mixing. CO_2 stabilisation at 450, 650 or 1,000 ppmv would require global anthropogenic CO_2 emissions to drop below 1990 levels, within a few decades, about a century, or about two centuries respectively, and continue to steadily decrease thereafter. Significantly, many predictions of future climate warming are based on a doubling of atmospheric CO_2, yet if all the solid (coal) hydrocarbon store is utilized the atmospheric CO_2 increase would be three times this volume. Only 5% of the Earth's hydrocarbons have been used so far, enormous reserves lie untouched (Table 2). If all these hydrocarbons were consumed the temperature would rise much more than the 1-2°C at present predicted for the end of the 21^{st} century. This would mean a rise in temperature of 3° to 6°C. A temperature rise of this magnitude would result in a globally warm climate similar to that experience in the Late Cretaceous, the warmest period during the past 200 million years.

Fossil Fuel reservoirs	
Reservoir	Size (Gt)
Coal	4,000
Oil	500
Natural Gas	500
Total	5,000

Table 2. Global Fossil Fuel Reservoirs

3.2.1.2 The Problems and the Questions

Already we can identify some effects the rapid rise in volume of greenhouse gases are having on global climate change. For example, rising temperatures and associated rising levels of bacteria, pollution and increased atmospheric dust levels are combining to kill off the coral reefs. By 2050 the Great Barrier Reef will be destroyed by global warming (http://news.bbc.co.uk/2/hi/asia-pacific/3509383.stm). In the longer term, as the world warms, we know that the relationship between the present carbon sinks and sources will change. Present day net sinks may well become net sources of CO_2.

There are conceptual answers to some questions. For example, although the atmosphere/ocean chemical flux is complex, we know that warming reduces the solubility of CO_2 and therefore reduces its uptake by the ocean. A rise in global temperature will also result in an increase in the vertical stratification in the ocean, resulting in reduced outgassing of upwelled CO_2, reduced CO_2 uptake because of reduced transport of excess carbon to the deep ocean and changes in biological productivity (IPCC, 2001). On short time-scales, warming will increase the rate of heterotrophic respiration on land, but the extent to which this effect will alter land-atmosphere fluxes over longer timescales is not yet clear.

Recent reports from the Amazon basin, that accounts for more than half of the world's remaining rainforests, indicate that increased levels of CO_2 are resulting in signs that the forests may become less able to absorb the increasing CO_2 emissions. A 20-year study in pristine areas reveals trees have been growing and dying faster than before. In "control" areas, where there was no human activity such as logging or burning, bigger, quicker-growing species were flourishing at the expense of the smaller ones living below the forest canopy. The increased growth is attributed to the rising levels of CO_2 from anthropogenic activities. Increases in forest carbon storage may be slowed by the tendency of canopy and emergent trees to produce wood of a reduced density as their size and growth rate increases, and by the decline of densely wooded sub-canopy trees (http://news.bbc.co.uk/2/hi/americas/3499500.stm).

Regional warming and changes in precipitation patterns and cloudiness are also likely to bring about changes in terrestrial ecosystem structure, geographic distribution and primary production. The interior of continents will become drier, there will be increased storminess and, in the lower latitudes, increased cyclone frequency. Again, the problems of addressing rising CO_2 levels is shown in a recent report which suggests that combating rising CO_2 levels by increasing terrestrial sequestration using vegetation may reduce the input of dust to the ocean that fertilises plankton, another important sink of CO_2 (Maslin, 2002).

3.2.1.3 The Politics

Politically, there are strong pressures to better understand the effects of global warming and how to address these in reducing the increasing CO_2 content of the atmosphere. Under the Kyoto Protocol (Appendix 1), many nations would like to count their terrestrial carbon sinks against their CO_2 emissions. The recent Royal Society Report on ‘The role of carbon sinks in mitigating climate change’ (2001) concluded that:

“…. terrestrial vegetation and soils are absorbing around 40% of current human CO_2 emissions. The magnitude of this ‘natural’ land carbon sink (which is currently being stimulated by recovery from natural disturbance and fertilisation from atmospheric CO_2 and nitrogen) is estimated approximately at 3.2+1.6 Gt C/yr although there is considerable uncertainty associated with this estimate. Using figures published by the IPCC (IPCC, 2001), we estimate that changes in agricultural and forestry practices and slowing deforestation could enhance this by a maximum of 2 Gt C/yr by the year 2050. Managed land carbon sinks could therefore potentially meet 25% of the reductions in CO_2 projected to be required globally by 2050 to avoid large increases in temperature. However this would require considerable political will but there is little potential for increasing the land carbon sink thereafter.”

While the reductions in carbon emissions, agreed under the Kyoto Protocol, are not fully implemented, atmospheric CO_2 levels will inevitably continue to rise. Without serious attempts to reduce CO_2 output it is probable, based on present evidence, that the adjustment of the natural carbon cycle to the anthropogenic inputs of fossil fuel carbon will take many tens of thousands of years (IPCC, 2001).

"In conclusion, *anthropogenic CO_2 emissions are virtually certain to be the dominant factor determining CO_2 concentrations throughout the 21st century.* The importance of anthropogenic emissions is underlined by the expectation that the proportion of CO_2 emissions taken up by both ocean and land will decline at high atmospheric CO_2 concentrations (even if absolute uptake by the ocean continues to rise). There is considerable uncertainty in projections of future CO_2 concentration, because of uncertainty about the effects of climate change on the processes determining ocean and land uptake of CO_2. These uncertainties do not negate the main finding that anthropogenic emissions will be the main control" (IPCC, 2001). Without an immediate and significant reduction in anthropogenic CO_2 output major effects of warming will be experienced within 50 years (IPCC, 2001).

3.3 THE GEOLOGICAL PERSPECTIVE

The shorter-term carbon cycle processes are becoming increasingly better understood, with direct measurement of the variables that control climate, such as atmospheric levels of H_2O, CO_2 and CH_4 (Figure 4). This data has contributed to a better understanding of climate change and especially the carbon cycle, mainly through significant effort made to construct Global Circulation Models (GCM's) which, as computing power has increased, have become more sophisticated. A great deal of work on climate change has been undertaken by climatologists, because our main interest is on the shorter-term changes that will impact on humans, and also because these changes are simpler to model and understand. Notwithstanding, the longer-term geological changes in the carbon budget are critical to our understanding of what might happen in the future. This is because our recent records do not extend back in time far enough to provide evidence on these possible variations.

Research has proved that, as our knowledge has increased and we extend our understanding farther back in time, a geological perspective becomes more relevant and increases in importance. This is because in the geological past there have been climate changes, particularly related to changes in the carbon budget, that we cannot identify as taking place over the past hundred's of years. Additionally, the GCM's require validation, and longer-term assessments of climate behaviour provide controls on the models not otherwise available. Although the natural carbon budget operates as a closed system, over geological time sales the proportions of the individual elements change considerably, with associated climatic effects.

The major questions requiring answers are:

1. How concentrations of greenhouse gasses, or other factors that fix climate, have varied in the past?
2. How has the surface temperature responded?

3. Are there natural controls that limit the range through which climate varies naturally, and if so what are they?
4. What processes trigger the rapid climate changes identified in the Quaternary record?
5. How will increased atmospheric CO_2 alter the balance between terrestrial and oceanic reservoirs?
6. How well known are the factors affecting CO_2 uptake and what will be their responses to future global climate change?
7. In the longer term, how can geological research improve our understanding of the short-term climate changes, by placing these in a longer-term perspective?

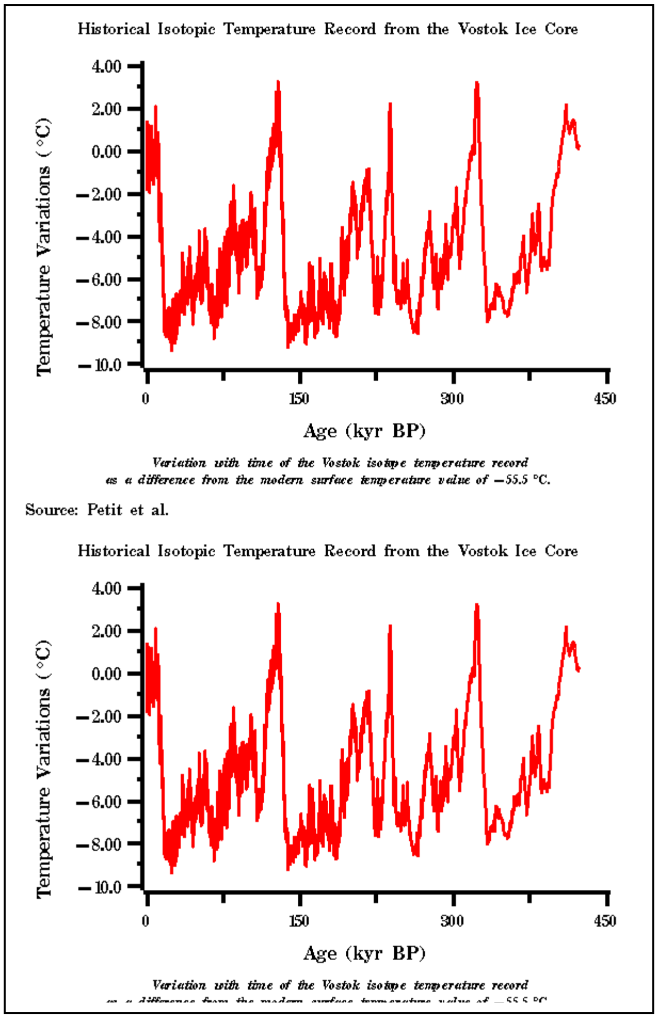


Figure 6. Ice core data on temperature and CO_2 variation over the past 450,000 years (From Petit *et al*. 1999).

To answer these questions we have to understand more fully past climate changes, over geological timescales. We know already, by study of past climates, that there are aspects of present climate conditions that are unique. At no other time has there been an association of high atmospheric levels of CO_2, polar ice caps and a non-equilibrium climate, with a great potential for rapid climate changes. Fortunately, climate data is available over a range of timescales up to multimillions of years and this allows a better appreciation of what has happened in the past, an appreciation that may guide us as to what may happen in the future. Over shorter timescales the surficial reservoir of carbon fluxes may be identified and modeled through the use of direct measurement of greenhouse atmospheric gases (Figure 5) supplemented by proxy measurements such as those, providing information on the past 420 ka years, from ice-cores (Figure 6).

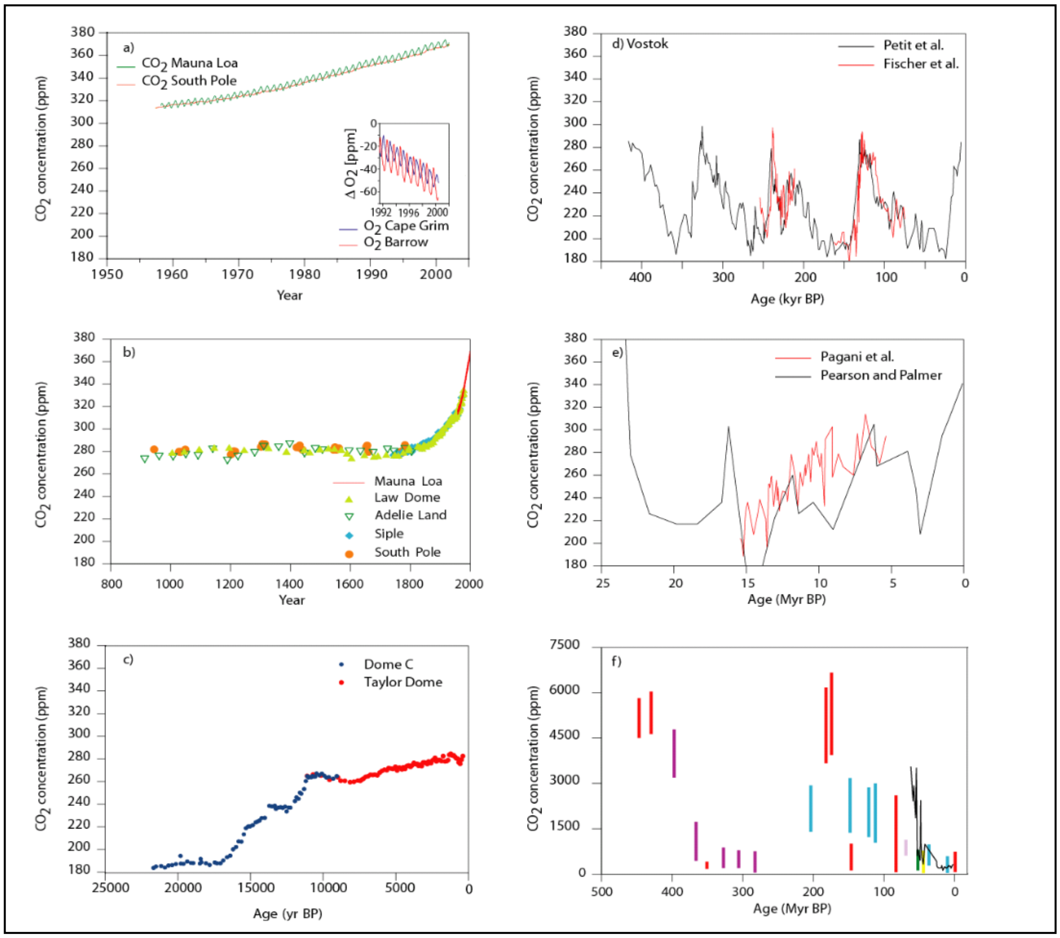


Figure 7. Variations in atmospheric CO_2 concentration on various time-scales.

(a) Direct measurements of atmospheric CO_2 concentration (Keeling and Whorf, 2000), and O_2 from 1990 onwards (Battle *et al.*, 2000). O_2 concentration is expressed as the change from an arbitrary standard. (b) CO_2 concentration in Antarctic ice cores for the past millenium (Siegenthaler *et al.*, 1988; Neftel *et al.*, 1994; Barnola *et al.*, 1995; Etheridge *et al.*, 1996). Recent atmospheric measurements at Mauna Loa (Keeling and Whorf, 2000) are shown for comparison. (c) CO_2 concentration in the Taylor Dome Antarctic ice core (Indermühle *et al.*, 1999). (d) CO_2 concentration in the Vostok Antarctic ice core (Petit *et al.*, 1999; Fischer *et al.*, 1999). (e) Geochemically inferred CO_2 concentrations, from Pagani *et al.* (1999a) and Pearson and Palmer (2000). (f) Geochemically inferred CO_2 concentrations: coloured bars represent different published studies cited by Berner (1997). The data from Pearson and Palmer (2000) are shown by a black line. (BP = before present.)

Over longer geological timescales measurements of the surficial reservoir are impossible because of its relatively small volume compared to that held in rocks. Thus proxies have to be used. Because well-known geological processes regulate the volume of atmospheric CO_2 on multimillion-year timescales, these processes can be modelled and atmospheric levels of CO_2 roughly quantified (Figure 7).

Carbon is recognised as a major contributory element to climate change as a major greenhouse gas, either as a driver or an amplifier of global climate change. This report attempts to provide an overview of the relative importance of carbon sinks in marine and terrestrial environments on a geological timescale, and highlights where major uncertainties remain. It is also framed to articulate the importance of the contribution of geological research to climate studies. Additionally, a primary purpose of the report is to identify where BGS may contribute geological and geochemical expertise to provide assistance in solving the outstanding questions of how climate changes, the major climate drivers of climate change and how we may better understand them.

4 GLOBAL CARBON CYCLE

4.1 OVERVIEW OF THE CARBON CYCLE

There is a general consensus on the relative importance of carbon sources and sinks, and a representative version of the interpreted details of global carbon cycle is shown in Figure 8.

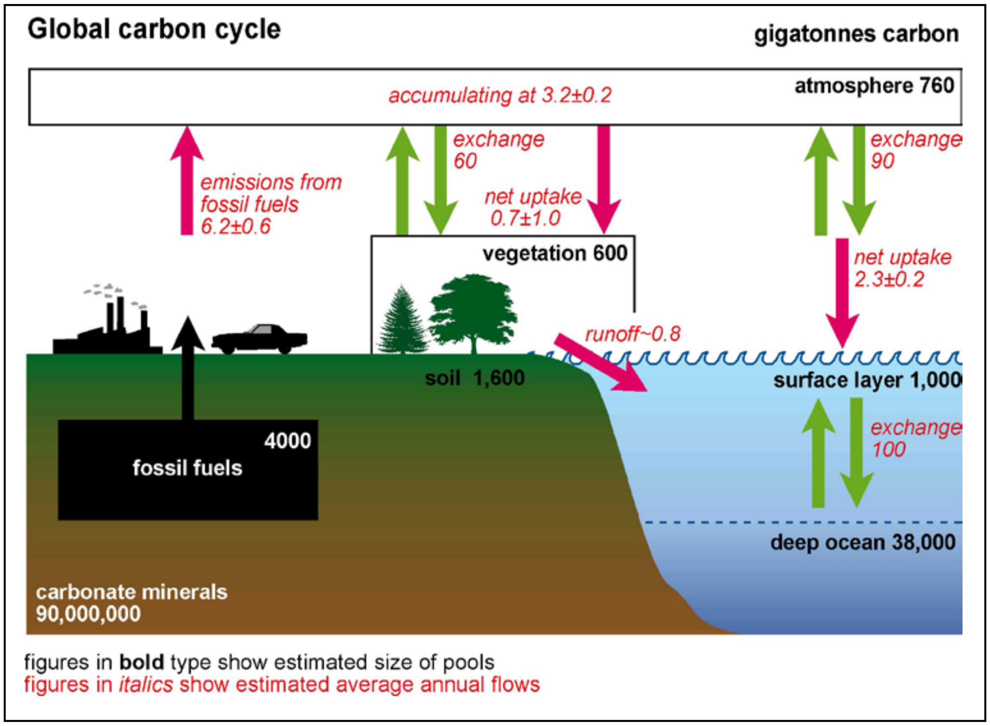


Figure 8. Short timescale Carbon cycle (British Geological Survey).

The largest fluxes of carbon occur between the oceans and the atmosphere (90 Gt C/yr), land plants and the atmosphere (60 Gt C/yr) and between marine biota and oceanic waters (45 Gt C/yr) (IPCC, 2001; Liu *et al.* 2000). However, ultimately it is the sinks that remove carbon from the cycle, either temporarily or permanently, and work towards stabilisation of the carbon cycle. Land and marine biota act as natural regulators, responding in their abundance to the atmospheric CO_2. The natural system is in equilibrium. Due to anthropogenic impacts, particularly fossil fuel burning, the natural regulation of the carbon cycle have been disturbed. If land-use changes continue at present rates, some existing terrestrial sinks will disappear, exacerbating current imbalances in the carbon cycle.

To understand how the changing global environment may control the carbon cycle it is necessary to consider the fluxes and the processes that govern them. The basic carbon cycle operates as follows (IPCC, 2001).

4.1.1 The terrestrial carbon cycle

Atmospheric CO_2 is utilised by plants through photosynthesis (Appendix 2) and the carbon they absorb is used within the plant to make up its roots, wood and leaves (autotrophic respiration). Some of this carbon is then lost - either when the leaves drop, or when the plant dies - and becomes soil carbon. Microbes within the soil breakdown this carbon and release it back to the atmosphere as respiration, in the form of CO_2 (heterotrophy). This is the terrestrial carbon cycle on a small scale (i.e. on the scale of individual plants).

On a larger scale (i.e. across geographical regions), the distribution of vegetation is important in the carbon cycle. Different plant types store different amounts of carbon, but they grow at different speeds and favour different conditions. For example trees can store more carbon than grass (per unit area of land covered), but they take a lot longer to grow. So if a previously barren area of land becomes fertile, then grasses will grow first, but trees may take over later. The local climatic conditions, and how they change over time, determine which type of plant dominates in any given location.

Human activity also changes the land use, and hence the carbon stored by the biosphere. Cutting down trees removes a potentially large sink of CO_2 and if the wood is burnt, or left to decay, then the carbon is released back to the atmosphere. Disturbance of vegetation also affects the soil, and deforestation can result in large amounts of carbon being lost from the soil. This has an impact on the fertility of the ground and may affect future vegetation growth in the area. Such changes in land use (predominantly in the tropical forests) accounted for the most significant part of anthropogenic CO_2 release during the 19th Century. It was not until about 1950 that fossil fuel emissions became significantly larger than the source from land use change. Present day emissions due to anthropogenic land use change amount to around 1.7 Gt C/yr.

4.1.2 The oceanic carbon cycle

CO_2 from the atmosphere dissolves in the ocean surface waters and undergoes rapid chemical reactions with the water with only a small fraction (1%) remaining as CO_2, the rest disassociating into the bicarbonate (91%) and carbonate (8%) ions. The CO_2 and the associated chemical forms are collectively known as dissolved inorganic carbon (DIC). This chemical partitioning of DIC ('buffering') affects the air–sea transfer of CO_2, as only the unreacted CO_2 fraction in the seawater takes part in ocean–atmosphere interaction.

Exchange of CO_2 between the ocean and the atmosphere operates on a time-scale of several hundred years. The CO_2 only exchanges with the atmosphere until the partial pressure in surface water and air are equal. With an increase in atmospheric CO_2 there is an increase in dissolved CO_2, with most of the added CO_2 converting to HCO_3. However, because CO_2 reacts with ionic CO_3 to form ionic HCO_3, the reduction of CO_3 available to react with atmospheric CO_2 results in a reduced uptake of CO_2. Thus as levels of atmospheric CO_2 rise there is a decrease in ocean CO_2 uptake. Other factors affecting CO_2 uptake include seawater temperature, salinity and alkalinity. The latter is primarily controlled by $CaCO_3$ formation in shells and corals and dissolution.

Ocean currents transport DIC as part of a global system. Near the poles, cold dense waters sink and subsequently spread through the ocean basins, returning to the surface hundreds of years later. As more CO_2 can dissolve in cold water than in warm, the cold dense waters sinking at high latitudes are rich in carbon and are able to move large quantities of carbon from the surface to deep waters. This mechanism is known as the 'solubility pump'. We know that temperate and polar oceans are the major sinks of atmospheric CO_2 whereas equatorial oceans are major sources. The Atlantic Ocean provides 60% of global CO_2 uptake, with the Indian and Southern oceans uptake both 20%. The Pacific Ocean is neutral, because its equatorial source flux is balanced by its temperate sink flux.

As well as being transported around the ocean, DIC is also utilised by ocean biology. Drifting microscopic oceanic plants known as phytoplankton grow in the surface waters. As with land-based plants, phytoplankton utilise CO_2 during growth and convert it to complex organic forms. The phytoplankton are eaten by drifting oceanic animals known as zooplankton, which themselves are preyed upon by other zooplankton, fish or even whales. During these biological processes, some of the carbon taken in during growth of the phytoplankton is converted back to DIC. If, between the carbon uptake by phytoplankton and the subsequent return of the carbon to DIC, the biological material has been transported to depth, for example by the sinking of large biologically formed particles, there is a net transfer of carbon from the surface to depth. This process is termed the 'biological pump'. The carbon can also sink as skeletal structures of the biology, a process that is known as the 'carbonate pump'.

Dissolution in the ocean provides a large sink for anthropogenic CO_2. Unlike the land, the processes of uptake are mainly physically and chemically controlled. Uptake of anthropogenic CO_2 is strongest in regions of ‘old’ ocean waters, exposed after long periods in the ocean interior. Re-equilibration of the older waters with the present atmosphere takes about a year, during which time CO_2 levels increase. Uptake of CO_2 is limited by the rate at which the older waters mix with the present atmosphere. Thus the rate of exposure of the older waters is critical in the process. In principle there is sufficient ocean capacity to take 70-80% of anthropogenic CO_2. However, because rates of mixing are slow, this will take hundreds of years. Chemical neutralisation of CO_2 through reaction with $CaCO_3$ in deep-ocean sediments has the potential to uptake another 9-15% of CO_2, reducing the airborne fraction of cumulative emissions by about a factor of 2. However, the response time of the deep ocean sediments is again slow and in the order of 5000 years.

4.2 LAND-OCEAN CARBON TRANSPORT

0.8 Gt of carbon is annually exported from the land to the sea via rivers (Figure 6; IPCC, 2001; Liu *et al*., 2000). Of this, half is dissolved inorganic (DIC) and half dissolved organic (DOC) (Meybeck 1982, 1993; Sarmiento and Sundquist 1992). Of the DIC input, half is from the atmosphere and half from weathered carbonates. 80% of the carbon flux to the ocean from land is derived from the tropical and temperate climate zones.

The 0.4 Gt of natural DIC transport from rivers to the ocean is part of a large-scale cycling of carbon between the land and the open ocean associated with dissolution and precipitation of carbonate minerals. This cycle drives net outgassing from the ocean of the order 0.6 Pg C/yr globally. Half of the 0.4 Gt C is returned to the atmosphere during $CaCO_3$ production by marine organisms and half is buried in deep-sea sediments, which later form carbonate rocks. The 0.4 Gt C of DOC transported from land is derived from plants etc, and mostly deposited and/or respired and outgassed close to land, mainly within estuaries (Smith and Hollibaugh, 1993). Additional fluxes due to human activity (mainly organic carbon) have been estimated to be about 0.1 Pg C/yr (Meybeck, 1993).

4.2.1 The role of continental shelves

The role of continental shelves in the carbon cycle is poorly understood. Because the ocean is a major sink of anthropogenic CO_2, a better understanding of the continental shelves rate of uptake of anthropogenic CO_2 is required if we are to improve our predictions on future climatic effects of anthropogenic CO_2 levels in the atmosphere. The shelves form an important link between the land and sea global carbon cycle. They are regions of active physical and biogeochemical processes that transport, transform and bury carbon, thus they are not only a pathway between the land and ocean, but also a sink of CO_2. To identify carbon fluxes across continental shelves has proved elusive. A major problem is that the net air-to-sea CO_2 flux is small (about 2 Gt C/yr) compared to the intake and release of CO_2 at the sea surface (each about 90 Gt C/yr). A general thesis is that carbon burial rates on continental shelves of the temperate and polar regions are slow, whereas carbon burial rates in wet tropical parts of the world are expected to be very fast. To investigate this hypothesis, further research is required to increase our understanding of the different burial rates.

We do know what happens to ~0.8 Gt C/yr of fluvial carbon discharged from the land to the sea varies with location, but that generally it is subject to active cross-shelf transport and biogeochemical processes that influence the carbon cycle of the ocean as a whole (Figure 9; Liu *et al*., 2000). In the North Sea, sediment studies suggest that the organic carbon is exported out of the area. In the East China Sea (ECS), the continental shelf acts as a carbon sink (Chen and Wang, 1999). Evidence from the Fly River delta in the tropical area of Papua New Guinea, indicates that the carbon deposited on the shelf may be returned to the atmosphere (http://www.aims.gov.au).

Before the Industrial Revolution the ocean/atmosphere carbon flux was assumed to be in steady state. However, due to the external fluvial input of organic carbon (~0.8 Gt C/yr) the global ocean would have consumed more organic carbon than it produces thus CO_2

would have been outgassed to maintain the equilibrium (Smith and Mackenzie, 1987). The ocean was thus a net source of CO_2. Since the Industrial Revolution, the increase in atmospheric CO_2 from anthropogenic sources has shifted the system away from steady state making the ocean a net sink, with the consequence that the carbon content of the ocean is presently increasing with time.

The oceanic rate of uptake of anthropogenic CO_2 can be defined as the increased rate of the oceanic carbon pool, which equals the net carbon influx to the ocean (0.8 Gt C/yr from rivers). The burial rate of carbon in marine sediments is estimated at 0.2 Gt C/yr, the rest, about 0.6 Gt C/yr, must have been outgassed by the ocean before the Industrial Revolution (Sarmiento and Sundquist, 1992). This flux offsets the downward flux of CO_2 and makes the net atmosphere/ocean transfer smaller than the anthropogenic CO_2 invasion rate as illustrated in Fig. 9.

Therefore, the oceanic uptake rate of anthropogenic CO_2 equals the net atmosphere/ocean flux of CO_2 plus the 0.6 Gt C/yr from the continental margins. This explains the rather modest value of the net air-to-sea CO_2 flux of 1.4 Gt C/yr based on earlier observations as compared to the model predicted oceanic uptake of anthropogenic CO_2 at 2 Gt C/yr

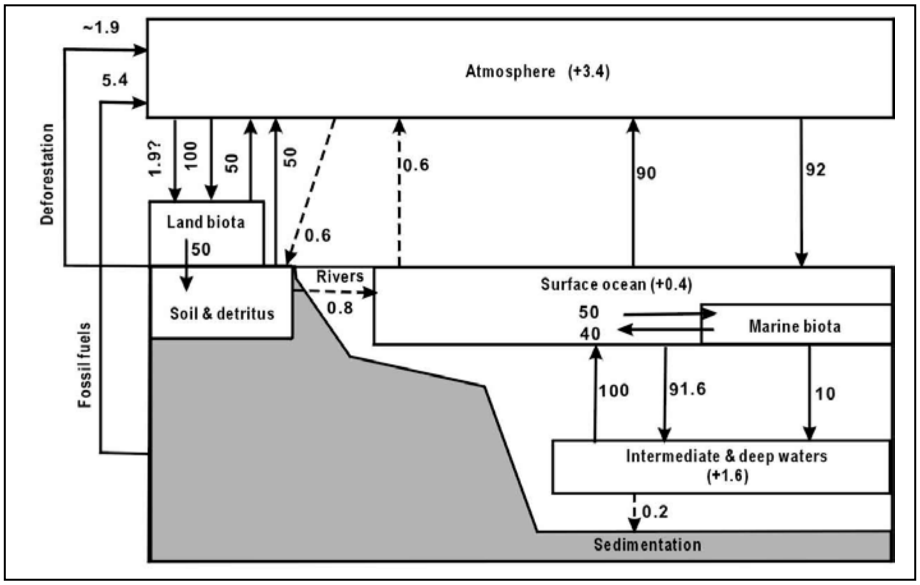


Figure 9. Global carbon cycle 1980-1989 (after Siegenthaler and Sarmiento, 1993. The carbon fluxes are in units of Gt C/yr).

The oceanic uptake of anthropogenic CO_2 is 2 Gt C/yr, but the net air-to-sea CO_2 transfer is offset by 0.6 Gt C/yr that represents outgassing of the riverine carbon (indicated by dashed arrows). However, if all of the remobilized riverine carbon is outgassed in continental margins, then there will be no offset for the CO_2 flux in the open ocean. The latter estimate was accepted by the IPCC 1995 assessment of the global carbon budget (Fig. 9). However, recently revised atmosphere/ocean CO_2 fluxes are as high as 2.2 Gt C/yr (Takahashi *et al.*, 1999). Thus if amended by the terrestrial input, the uptake rate of anthropogenic CO_2 would be as high as 2.8 Gt C/yr, significantly higher than previous model prediction.

One explanation for this discrepancy between models and observations is that the coarsely gridded ΔPCO_2 data set misses most, if not all, of the continental margins, and, therefore, it represents the atmosphere/ocean CO_2 exchange only for the interior ocean. The river-discharged carbon fluxes may be mostly outgassed on continental margins with little influence on the carbon budget in the interior ocean. If this is the case, continental margins would be a net source of CO_2 with an average flux of 17 gC m^{-2} /yr. Furthermore, the cross-shelf export of carbon to the open ocean must be so small that its effect on the carbon budget of the ocean interior would be negligible. Recent observations contradict both of these conclusions.

3.2.2 Recent observations of continental margin carbon fluxes

Over the past ten years, a number of continental margin studies from different areas have focused on carbon fluxes, biology, physics and/or sedimentology (Figure 10; Liu *et al*., 2000).

On several continental margins, including the North, Baltic and East China seas, all of which have significant terrestrial carbon input, contrary to accepted understanding that these margins are CO_2 sources, the studies reveal them all to be net CO_2 sinks. The East China Sea (ECS) receives a large volume of carbon from two of the world’s largest rivers, the Changjiang (the Yangtze River) and the Huanghe (the Yellow River). It is a net carbon sink with an estimated mean sink as large as -35 gC/m^2 /yr (Tsunogai *et al*., 1999). In the North Sea, a mean sink of -16 gC/m^2 /yr occurs in summer (Kempe and & Pegler, 1991).

Continental shelf waters have limited storage capacity for absorbed atmospheric CO_2 and river-discharged carbon because of their limited volume. All but a small fraction of the received carbon must either be exported to the ocean or buried in sediments. In the Mid Atlantic Bight, export flux of particulate organic carbon (POC) from the shelf to the ocean is considered to be small and less than 5% of total primary production (Liu et al., 2000). This conclusion, based on the concept that a major fraction of the primary production on the shelf could be exported, has been now been questioned because recent observations indicate that the area may well be a CO_2 sink (M. DeGrandpre, in Liu *et al*., 2000).

The mechanism of the continental shelf serving as a CO_2 sink has been termed the ‘continental shelf pump’ (Tsunogai *et al*., 1999). In the ECS the shelf pump has an estimated capacity of 20 to 30 Mt C/yr, controlled in summer by active biological carbon uptake and in winter by the high solubility of CO_2. The estimated organic carbon burial rate in the ECS shelf sediments is no more than 10 Mt C/yr (Chen and Wang, 1999; S. Gao, unpublished data). Thus carbon burial cannot possibly store all of the absorbed CO_2 nor the riverine input, and a large fraction is exported off the shelf as POC, DOC and/or DIC. Advective export of POC has been observed in association with a cyclonic eddy at the shelf edge northeast of Taiwan (Liu *et al*., 2000).

Studies from other areas show that the shelf pump is driven by a combination of physical and biogeochemical processes that are still not fully understood. Near Cape Hatteras, on the eastern margin of the North Atlantic, there is a strong off-shelf export of carbon (Liu *et al*., 2000). On the western margin of the Atlantic, in the northern Gulf of Biscay, there is a 15% export of carbon from the shelf (R. Wollast and L. Chou, personal communication).

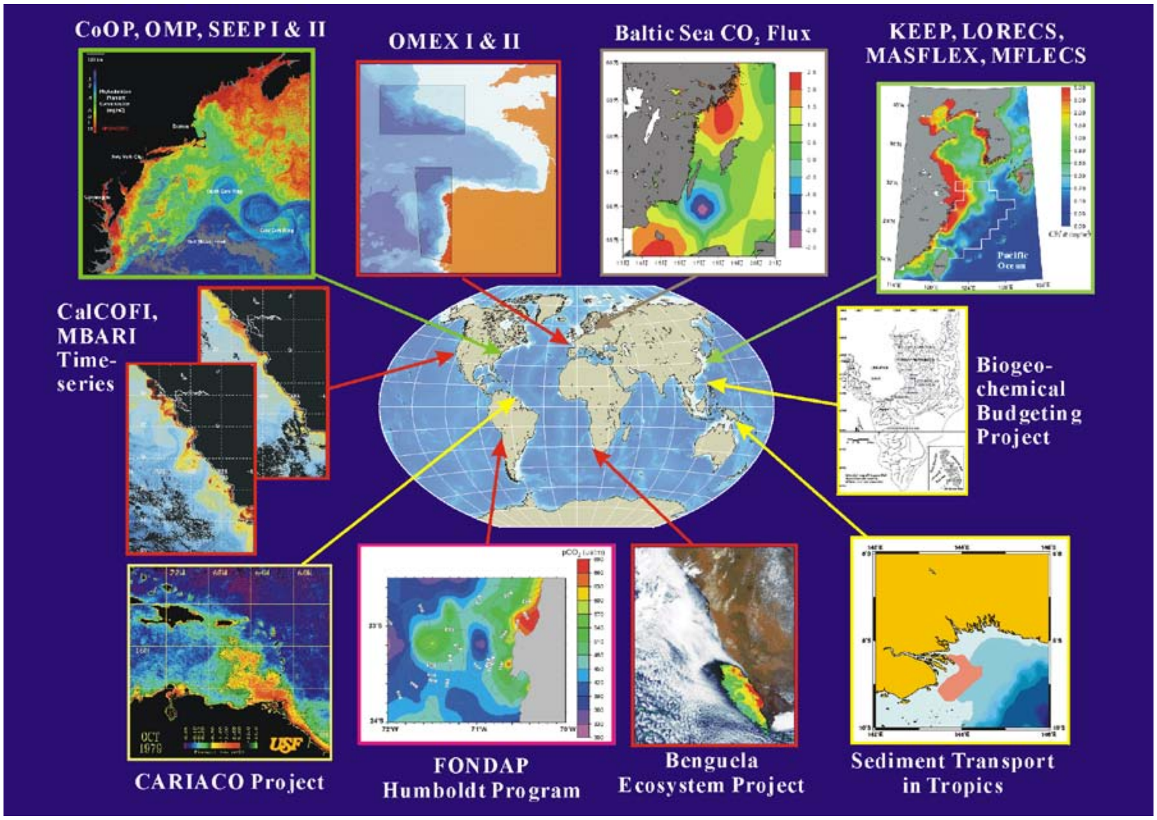


Figure 10. Examples of continental margin biogeochemical studies

(From Liu *et al*., 2000). Clockwise from upper left corner: 1. Mid Atlantic Bight: Shelf Edge Exchange Processes-I & II (CZCS pigment image from NASA); 2. Bay of Biscay & Iberian Coast: Ocean Margin Exchange-I & II (Bathymetry); 3. North Sea: (PCO$_2$ map, Kempe and Pegler, 1991); 4. East China Sea (ECS): Kuroshio Edge Exchange Processes, Longterm Observation & Research of ECS, Marginal Sea Flux Experiment, Mass Flux in the ECS (Chl distribution on the ECS shelf from G.C. Gong with CZCS pigment image for summer as the background); 5. Biogeochemical Budgeting Modeling Project of LOICZ (Lingayen Gulf, Philippines: one of the study sites); 6. Sediment transport in tropical coasts (Gulf of Papua, bathymetry, Nittrouer et al., 1995); 7. Benguela Ecosystem Project of South Africa (SeaWiFS pigment image from NASA); 8. FONDAP-Humboldt Program (PCO$_2$ flux map off Chilean coast at 23$_o$S, July 1997; N. Lefevre et al., unpublished data); 9. Cariaco Basin area: Carbon Retention In A Colored Ocean (CZCS image from F. Muller-Karger); 10. California Current system: Coastal Transition Zone, California Cooperative Oceanic Fisheries Investigation (SeaWIFS images during normal and El Nino conditions, from MBARI).

On polar margins and on tropical coasts there are effective, but different, export processes taking place. In the Arctic, ice formation and melting produces algal habitats that alternately stabilise and destabilise the water column. The coupling between the biological and ice cycles provides an effective carbon pathway to the deeper interior of the ocean that is particularly vulnerable to change (Walsh, 1989). Off the high latitude Mackenzie River the coastal zone in summer is ice-free and the water column stratified, productivity is high and organic carbon is deposited on the shelf (Figure 11). In winter, sea ice formation produces brine, which can sink from the surface down the continental slope. The brine not only carries anthropogenic CO_2 but also sweeps re-suspended organic matter and regeneration products into the deep ocean basin. The Arctic, by means of brine export and sinking of algal mats from the ice, potentially contains some of the most efficient shelf export regions in the world.

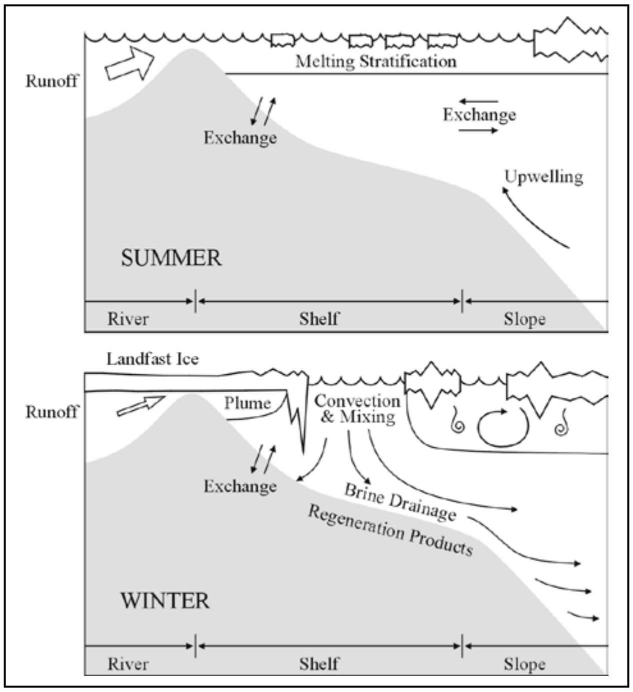


Figure 11. Summer and Winter exchange across the coastal zone off the Mackenzie River.

In contrast other margins are sources of CO_2. Many coastal embayments and lagoons export more phosphate (an essential nutrient for marine primary producers) than they receive, suggesting these systems to be either net heterotrophic or respiring CO_2 (Stephen Smith and Fred Wulff in Lieu et al., 2000). In the nearshore, a fraction of the riverine carbon is remobilized and released to the atmosphere. However, the calculated budgets also show quite a few net autotrophic systems. Systems with sluggish water exchange processes may well be more likely to be CO_2 sources.

The eastern boundary current systems represent another type of coastal CO_2 source. The west coast of the Iberian Peninsula is a weak net source of CO_2 because of upwelling of the Eastern North Atlantic Central Water, rather than by the terrestrial input of carbon. Off both Oregon and Chile there is strong outgassing of CO_2 during powerful upwelling events. These systems are complicated by the juxtaposition of strong sources and sinks of atmospheric CO_2, which are associated with both poor- and well-developed phytoplankton communities. Recent findings suggest that iron supply from shelf sediments may play a role in regulating the growth of phytoplankton (Lieu et al., 2000).

Many tropical watersheds, such as the Amazon and Papua New Guinea (PNG), discharge a high volume of water and sediments to the ocean due to frequent floods caused by torrential rains. More than half of the total runoff and land-derived sediments are discharged to the oceans from tropical coasts, especially the Indo-Pacific Archipelago (Nittrouer et al., 1995). Because these tropical regions deliver large amounts soils rich in organic matter to the coastal ocean, it was thought that burial of this terrestrial and associated marine organic matter on continental shelves would be an important site of removal of fossil fuel CO_2 in the global inventory. Recent evidence indicates that this is not true as they are not sites of large carbon sequestration. The narrow shelves and weak Coriolis force favour cross shelf transport of sediments, which carry a significant amount of carbon, to the deep ocean.

Because of high rainfall, high mountain ranges, and tectonically active landmass, the island of Papua New Guinea (Figure 12) contributes more water, solutes and sediment to the coastal ocean than the Amazon River. As a consequence, the continental shelf of the Gulf of Papua is a source of CO_2 to the atmosphere, and it was expected that carbon burial rates here would be rapid. In fact, although carbon burial rates are high, the decomposition rate of terrestrial and marine organic matter is even greater. Measurements suggest that most of the organic carbon being delivered to the continental shelf of the Gulf of Papua by rivers and by estuarine productivity is being oxidised and returned to the atmosphere, because the decomposition rate of organic matter is equal to, or greater than, the measured supply rate of organic matter from rivers and plant growth. To balance the budget, there has to be an import of more organic matter from the Coral Sea. Thus there is more CO_2 being released from the sea to the atmosphere, than is being buried in the mud and the region is a net source of CO_2 to the atmosphere, even if large amounts of organic matter are being buried in the mud today. Wet tropical continental shelves are good incinerators of organic matter because they are warm, have a high and steady nutrient supply, and have many kinds of microorganisms that decompose organic matter in the water and deep in the mud.

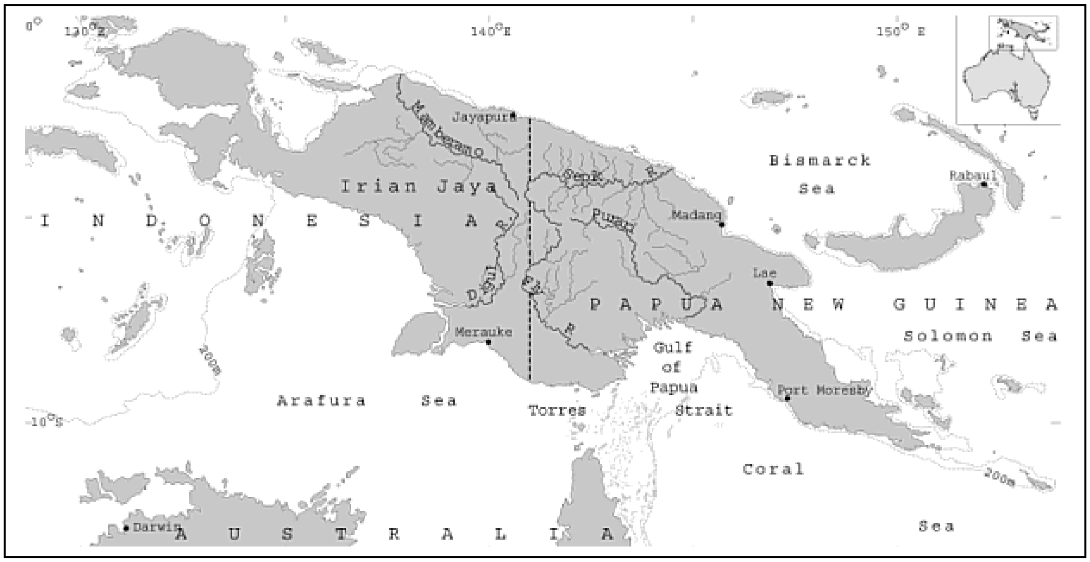


Figure 12. Map of Papua New Guinea, study area of the Gulf of Papua

In summary, riverine carbon fluxes, in addition to those from the atmosphere, do not necessarily result in the adjacent continental margins being a CO_2 source. Instead, especially in arctic or temperate areas, the margins may serve as a net CO_2 sink and also export a significant fraction of locally produced and river discharged organic carbon to the open ocean. The shelf biological pump is driven by both the riverine nutrients as well as upwelled nutrients from off-shelf. Shelf released iron is also an important, but poorly quantified, micronutrient. The export of shelf primary production accounts for 7-27% of the global biological pump (Liu *et al*., 2000).

The effect of continental margin carbon fluxes on the global ocean carbon budget is illustrated in Figure 13. It is based on the following precepts. Continental margins as a whole serve as a weak CO_2 sink (0.1 Gt C/yr), the storage of anthropogenic CO_2 on margins (0.05 in parentheses) is proportional to their seawater volume, three-quarters of carbon burial takes place on the shelf, half of carbon that can be remobilized from the river run-off is released to the atmosphere from the margins, and the export of shelf primary production accounts for 20% of the global biological pump (2 Gt C/yr from margins to intermediate and deep waters) which is compensated by upwelling of dissolved inorganic carbon of equal strength

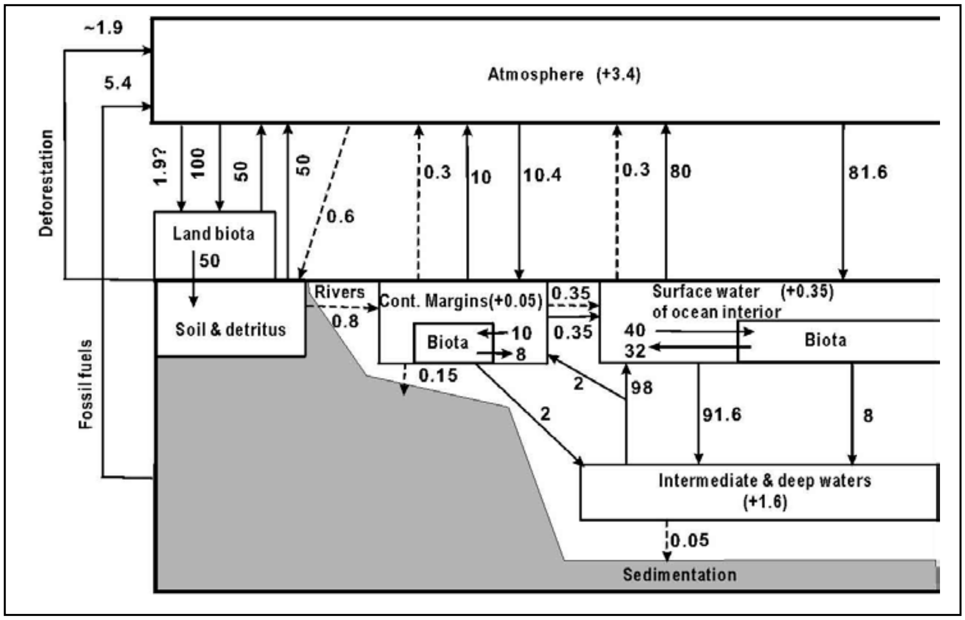


Figure 13. Modified global carbon cycle, allowing for continental margin carbon fluxes.

The net exchanges between the ocean and other reservoirs remain the same as those in Fig. 9. It is assumed that continental margins are a net sink of CO_2 (0.1 Gt C/yr), the shelf export accounts for 20% of oceanic biological pump and about half of the riverine carbon flux gets exported out of the shelf.

. On this basis the net air-to-sea CO_2 flux in the open ocean would be 1.3 Gt C/yr. In these calculations it also assumed that the net oceanic uptake of anthropogenic CO_2 and the total physical and biological pumps remain the same as those illustrated in Fig. 6.

However, if the net air-to-sea CO_2 flux in the open ocean is as large as the current estimate of 2.2 Gt C/yr, the actual uptake rate of anthropogenic CO_2 would be 2.9 Gt C/yr with the increase due to the net input of terrestrial carbon (0.6 Gt C/yr) and net CO_2 uptake on the margins (0.1 Gt C/yr).

5 CARBON FLUXES OVER GEOLOGICAL TIME SCALES

5.1 PROCESSES CONTROLLING GEOLOGICAL CARBON FLUXES

Over multi-million year timescales the carbon cycle is controlled mainly by chemical weathering, volcanic and metamorphic mantle degassing and the burial of organic carbon (Berner, 1993, 1997; Berner and Kothavala, 2001; Royer *et al*., 2004; Walker, 1977; Wallman 2001; and Holland, 1978). Degassing involves a subduction-related component and metamorphic breakdown of carbonates in active orogenies in oceanic and continental arcs (e.g. the Southwest Pacific and the Western Americas). Outgassing from weathering of carbonates may in part be controlled by tectonics such as mountain uplift, and due to collision driven by plate tectonics (Edmond, 1992). Outgassing due to subduction of carbonate is determined by a number of processes that control both the origin of carbonate in the ocean, its preservation and ultimate destruction at convergent margins. These processes include: eustatic sea level, the Carbonate Compensation Depth (CCD), seabed configuration and morphology, ocean chemistry and circulation, sediment burial preservation, the location of subduction zones, and ultimately the configuration of continents.

The initiation and rise of terrestrial vegetation has dramatically enhanced the rate of silicate weathering, which consumes CO_2 while releasing base cations that end up in the ocean. Subsequent deep-sea burial of Ca and Mg (as carbonates, for example $CaCO_3$) in the shells of marine organisms removes CO_2. The net effect of slight imbalances in the carbon cycle over tens to hundreds of millions of years has been to reduce atmospheric CO_2. The rates of these processes are extremely slow hence they are of limited relevance to the atmospheric CO_2 response to emissions over the next hundred years.

The dominant CO_2 consuming weathering reaction is the degradation of the high temperature aluminosilicate minerals in igneous and metamorphic rocks to residual clays, dissolved cations and silica. A balance between weathering uptake and metamorphic release of CO_2 is mediated by the precipitation of $CaCO_3$. Spreading of the seafloor into subduction zones delivers the sedimentary calcite for metamorphic CO_2 regeneration through the so-called Urey reaction (Urey, 1952) and the release of CO_2 ultimately to be consumed in weathering reactions:

$$CaCO_3 + SiO_2 \bullet \quad CaSiO_3 + CO_2$$

The above reaction is schematic, where SiO_2 represents degraded fluvial and aeolian cation-poor clays, products of continental weathering, or biogenic, opaline shells, or tests of diatoms and radiolarians in the sedimentary section. Reaction rates become significant in water-saturated thermal regimes (• 150°C), the upper bound of the oil maturation window (Bird *et al*., 1984 and Hunt, 1995).

Although the dominant controls on the carbon cycle over geological time scales are recognized, and the control of CO_2 on climate generally accepted there are some inconsistencies. For example during the mid-Mesozoic (120-220 Myr) at which time oxygen isotopes indicate cold temperatures whereas other data indicates CO_2 levels to be high. The inconsistencies are as much to with our knowledge base as our understanding of the proxy methods we use to measure CO_2 levels.

5.2 MEASURING CARBON FLUXES

Most treatments of the Phanerozoic evolution of the CO_2 content of the atmosphere (PCO_2) assume a steady state closed system. Release of CO_2 by mantle degassing and by biogenic precipitation of carbonates and their metamorphism in subduction zones balances the consumption by continental aluminosilicate weathering. Small perturbations in this balance bring about changes in PCO_2, but given the small size of the atmospheric CO_2 reservoir relative to the rate of fixation by weathering, mechanisms that maintain this apparently precarious balance dominate current thinking.

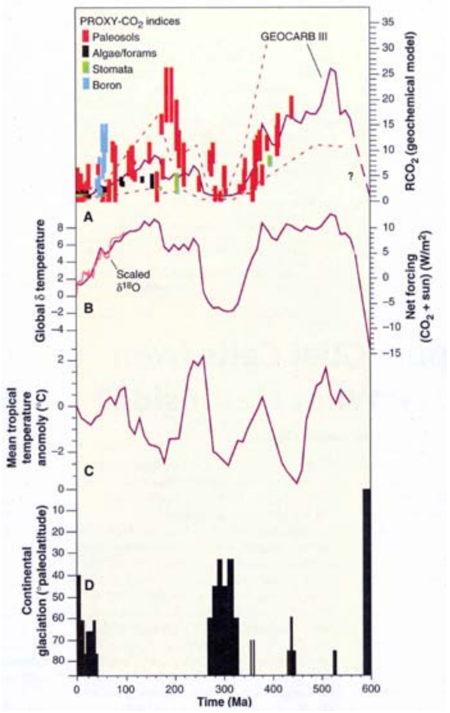


Figure 14. Comparison of methodologies to estimate CO_2 levels over the Phanerozoic (from Crowley and Berner, 2001). (A) Comparison of CO_2 concentrations from the GEOCARB III model with a combination of proxy- CO_2 evidence (vertical bars). Dashed lines: estimates of uncertainty in the geochemical model values. Solid lines: conjectured extension into the late Neoproterozoic (590-600Myr). R CO_2, ratio of CO_2 levels with respect to the present (300ppm). (B) Radiative forcing for CO_2 calculated and corrected for luminosity after adjusting for an assumed 30% planetry albedo. Deep-sea oxygen isotope data over the past 100Myr have been scaled to global temperature variations. (C) Oxygen isotope-based low latitude palaeotemperatures. (D) Glaciological data for continental-scale ice sheets. The duration of the late Neoproterozoic glaciation is subject to debate

Atmospheric CO_2 concentration has varied on all time-scales during the Earth's history (Figs. 7 and 14) and its measurement has been based on direct readings for approximately the last 50 years. Accurate proxies such as ice cores have been used to investigate CO_2 concentration during the Quaternary, back to 420,000 years (Figures 6 and 7). For the earlier Phanerozoic, CO_2 levels have been identified using mass-balance models, such as GEOCARB (Berner, 1989, 1993, 1994, 1997), based on our knowledge of Earth processes and by proxies (Figure 14), of which four are recognised as most reliable: • ^{13}C in paleosols (Cerling, 1991; Yapp and Poths, 1992), • ^{13}C of phytoplankton (Freeman and Hayes, 1992; Pagani *et al.*, 1999b), the stomatal distribution in the leaves of C_3 plants (Van de Burgh et al., 1993; McElwain and Chaloner, 1995) and the • ^{11}B of planktonic foraminifera (Pearson and Palmer, 2000). Other lines of evidence used to investigate Holocene CO_2 variations, include species of plant macrofossils in peat deposits (White *et al*., 1994) and stomatal density in macrofossils (Beerling *et al.*, 1992).

In simple models, such as GEOCARB, the modelling is based on quantifying the uptake of CO_2 during the weathering of Ca and Mg silicates and its release during the weathering of sedimentary organic matter (eg. Royer *et al*., 2004). The models assume a number of conditions that include the burial of carbonates and organic matter in sediments and the fluxes of CO_2 to the atmosphere and oceans from the thermal decomposition of carbonates and organic matter at depth. Also addressed are the variations in weathering fluxes due to changes in global temperature, continent area, location and relief, and land plant colonisation.

Allowances have to be made for changes in solar radiation due to the slow stellar evolution of the sun, and the CO_2 greenhouse effect in Global Circulation Model (GCM) calculations of global mean sea surface temperature and river runoff. Volcanic degassing is identified from the abundance of volcanic rocks, sea floor spreading rates and the carbonate content of subducted crust. Controls on geochemical models are provided by proxies, that include the • ^{13}C isotope of pedogenic carbonates and phytoplankton, stomatal density and • ^{11}B isotope of marine carbonate (Royer *et al*., 2001; 2004). Thus by the use of direct and proxy measurements of greenhouse gasses over millions of years we arrive at measurements of atmospheric CO_2 levels, that we use as proxies for temperature, that stretches back over the Phanerozoic (Figure 7).

Review of a combination of mass-balance modelling and critical evaluation of the four main proxies (Royer *et al*., 2001) shows that over timescales of millions of years the proxies each have a different temporal extent and resolution that, in combination with mass-balance modelling, provides an order of magnitude accuracy of temporal atmospheric CO_2 variability of the order of 5-10 Myr. The use of the combination of long-term carbon cycle models and proxies form a hierarchical series with the former providing an overarching set of predictions within which the latter reside. Palaeosol proxies can be used as far back as the Devonian, and provide coverage of the order of thousands to ten's of thousands of years, the minimum period in which soil carbonate can form. Paleosols provide the longest temporal record for comparison with mass-balance model results. The two ocean proxies, the isotopes of carbon and boron, are limited by the resolution of marine records that depend upon burial rate, biological productivity and intensity of bioturbation. The temporal resolution for organic carbon in pelagic sediments is again thousands to ten's of thousands of years (Kennet, 1982). The use of calcareous marine plankton is limited by their evolution at 140 Myrs. The application of stomata extends back to the Devonian and the rise of vascular plants between 380 to 350 Myr. The terrestrial based stomata leaf record offers the best temporal resolution, with pre-Quaternary leaf response time ranging between months to 100's of years. Thus the sequence of temporal sensitivity is mass-balance < palaeosols = marine phytoplankton < stomata.

Checks on the models created from mass balance and proxy studies are made through comparison with directly derived evidence on glaciations such as tillites, rock striations, etc. The identification of the atmospheric levels of CO_2 from the proxies is dependent upon knowledge of the controlling environments, such as the ph or temperature of seawater. Recent challenges to the GEOCARB models based on re-interpreted • ^{13}C of phytoplankton (Shaviv and Veizer, 2003; Veizer *et al*., 2000) and a proposed alternative forcing climate mechanism of cosmic ray flux have proved unfounded and the GEOCARB model remains robust (Royer *et al*., 2004).

5.3 ISOTOPIC CARBON AND STRONTIUM

Ancient atmospheric carbon dioxide levels are reflected in the isotopic content of organic carbon (Hayes *et. al*., 1999) and, less directly, strontium (Veizer *et al.*, 1999) in marine sedimentary rocks. The former because photosynthetic carbon isotope fractionation (•$_{toc}$) is sensitive to CO_2 levels, and the latter because weathering and degassing are associated with extreme values of the abundance ratio 87Sr/86Sr. The use of the isotopic content of organic carbon (Hayes *et. al*., 1999) and strontium (Veizer *et al*., 1999) in marine sedimentary rocks to estimate past CO_2 levels (Freeman and Hayes, 1992, Francois and Walker, 1992 and Berner, 1994) is hindered by the signals' additional relationship to various tectonic (Edmond, 1992 and Richter *et. al*., 1992) and biological (Hayes, 1993) effects. Moreover, the strontium signal has proven especially difficult to parse (Derry and France-Lanord, 1996, Quade *et. al.*, 1997, Sharma *et al*., 1999 and Basu *et. al*., 2001).

Resolution of the ambiguities in the isotopic signals of carbon and strontium (Rothman, 2002) shows that the last 500 million years of the strontium signal, after transformation to remove the effects of recycled sediment (Garrels and Mackenzie, 1971 and Brass, 1976), correlate significantly with the record of isotopic fractionation between inorganic and organic carbon (Figs 15 and 16; Hayes *et al*., 1999). The result is based on the theoretical deduction that the two records are linked by a common dependence on rates of continental weathering and magmatic activity. Because CO_2 levels fall with the former and rise with the latter an appropriate average of the two records should reflect the long-term fluctuations of the partial pressure of atmospheric CO_2. The CO_2 signal derived from this analysis represents fluctuations at time scales greater than about 10 Myr, although comparison with the geologic record of climatic variations (Frakes *et al*., 1992) reveals no obvious correspondence.

Rothman (2002) estimates the CO_2 signal and produces the variation in pCO_2 over the Phanerozoic (Fig 17) that shows CO_2 levels to have mostly decreased for the last 175 Myr. Prior to this time they have fluctuated from about two to four times modern levels

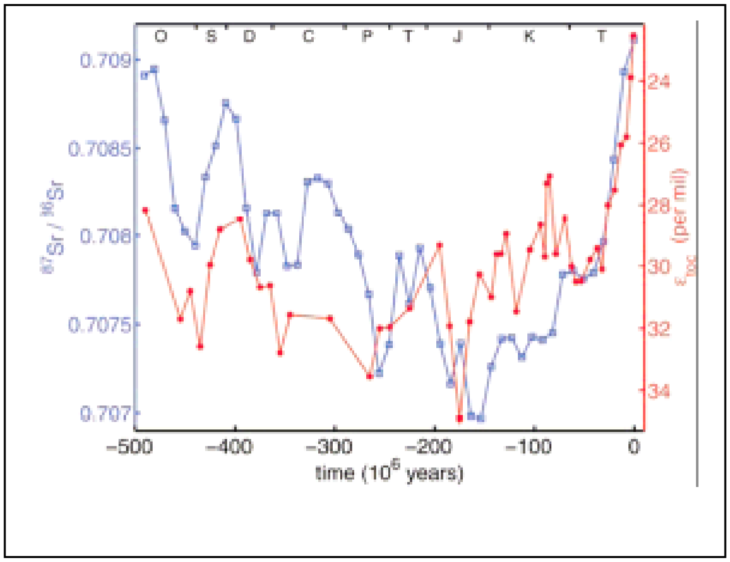


Figure 15. Data for $\bullet_{toc}$ (red filled circles) (Hayes *et. al.*, 1999) and $^{87}Sr/^{86}Sr$ (blue open squares) (Veizer *et. al.*, 1999). The time scale for $\bullet_{toc}$ has been revised from the original to match the scheme (Harland *et. al.*, 1990) used for the strontium data. The capital letters correspond to the geologic periods: Ordovician, Silurian, Devonian, Carboniferous, Permian, Triassic, Jurassic, Cretaceous, and Tertiary.

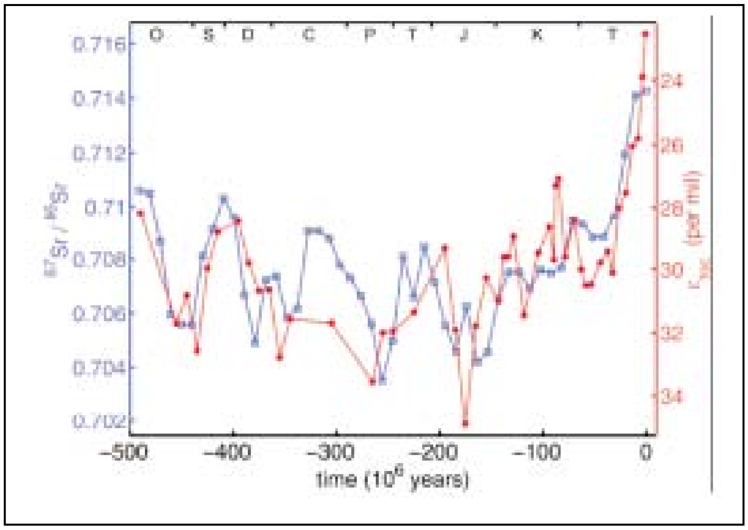


Figure. 16. The function *g* (blue squares) obtained by removing the memory flux from the $^{87}Sr/^{86}Sr$ data of Fig. 8, along with $\bullet_{toc}$ (red circles).

In Figure 16, note that the range of the $^{87}Sr/^{86}Sr$ curve is approximately five times greater than in Fig. 15. The data are plotted such that the mean of both time series lies on the same horizontal line and their rms fluctuations have the same vertical extent.

with a dominant period of about 100 Myr. The decline for the last 175 Myr is also present in several previous *p*CO_2 reconstructions (Berner, 1994; Rothman, 2001; Budyko *et. al*., 1987; and Ekart *et. al*., 1999), and the entire curve is similar to a previous estimate derived from the geologic record of carbonate formation (Budyko *et. al*., 1987).

Using a variety of sedimentological criteria, Frakes *et al.* (1992) conclude that Earth's climate has cycled several times between warm and cool modes for the last ~600 Myr. Oxygen isotopes in calcite and aragonite shells, appears to confirm the existence of these long-period (~135 Myr) climatic fluctuations (Veizer *et al*. 2000). Figure 17 shows some correspondence between low levels of CO_2 (cooling) and cool periods (the grey bars at the top of the figure), with the most recent cool period corresponding to relatively low CO_2 levels, as expected (Crowley and Berner, 2001). However, over the remainder of the record the correlation is not as strong as might be expected considering the assumed dominant control of CO_2 on long-term climate change, in part because the apparent 100 Myr cycle of the *p*CO_2 record does not match the longer climatic cycle. The lack of correlation remains if the change in average global surface temperature resulting from changes in *p*CO_2 and the solar constant using energy-balance arguments is also calculated (Berner, 1994 and Budyko *et. al*., 1987).

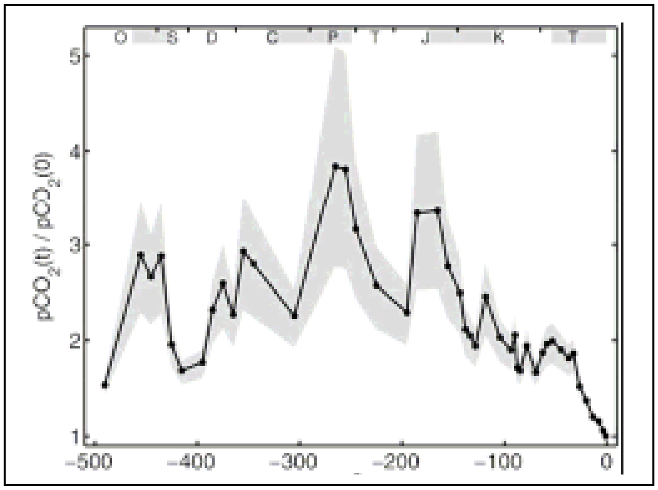


Figure. 17. Fluctuations of *p*CO2 for the last 500 My, normalized by the estimate of *p*CO2. The lower and upper limits of the gray area are bounds of accuracy. The gray bars at the top correspond to periods when Earth's climate was relatively cool; the white spaces between them correspond to warm modes (Frakes *et. al.*, 1992).

The paleo-CO_2 results of Rothman (2002) and also Berner and Streif (2001) are not based on carbon cycle modeling, but are an extension of the • ^{13}C plankton CO_2 proxy. These authors apply • ^{13}C, the difference between the • ^{13}C of bulk organic matter and carbonates (Hayes *et al*., 1999) to directly calculate palaeo-CO_2. However, bulk organic matter can include non-photosynthetic compounds as well as terrestrial material derived from rivers. The original method was based strictly on marine photosynthetic compounds (Freeman and Hayes, 1992; cf. Royer *et al*., 2001). In addition, changes in • ^{13}C over time can be due to changes in seawater temperature (Rau *et al*., 1989) or O_2 concentrations (Beerling *et al*., 2002), not only atmospheric CO_2.

Notwithstanding, the constraints of the method, one of the principal contributions of the Rothman (2002) study is to relate the weak correlation between strontium and carbon isotopic signals (Fig. 15) with their shared dependence on global weathering rates and magmatic activity, and then deduce the primary processes driving the signals' fluctuations. Correction for the effects of sedimentary recycling enhances the correlation (Fig. 16) and indicates a strong, shared signal, and strengthens this conclusion. Secondly, any quantity with a similar joint dependence on weathering and magmatic processes may be expected to display similar fluctuations. CO_2 levels fluctuate roughly synchronously, but with opposite sign, with those of strontium and carbon isotopic signals, which in turn depend on weathering and magmatism. This doesn't mean that $p$$CO_2$ does not exert dominant control on Earth's climate at time scales greater than about 10 Myr, but it does raise the issue of cause and effect. Degassing and silicate weathering were undoubtedly the primary controls on the carbon cycle for the last 500 Myr. But there are other influences that have to be considered, including the origin and diversification of land plants (Rothman, 2001), continental collisions (Edmond, 1992), or a complex combination of tectonic, biological, and geochemical processes (Berner, 1994). There is no doubt that the carbon cycle is complex.

5.4 TECTONICS

Global climate changes during the Cainozoic may be related to plate tectonic changes that disrupted the stability of the climate system, including the rearranging of continental positions, building mountain ranges and opening and closing ocean basins. One of the problems is linking climate change, which can be dated fairly accurately, with tectonics, which cannot. However longer-term changes over 10 Myr can probably be identified, such as the linkage between the Miocene and Pliocene glaciations with uplift of the Tibetan Plateau (Ruddiman *et al*., 1989; Raymo and Ruddiman, 1992).

Tectonic effects, notably mountain building, on the CO_2 record are considered by Edmonds (1992) again through the use of the Sr isotope record. Noting the variation in the ratio of $^{87}Sr/^{86}Sr$ over the Phanerozoic, Edmond (1992) correlates the highs in the early Phanerozoic and Tertiary with major episodes of mountain building. The study predates Rothman (2002), and requires recalculation based on the removal of the recycling effect of Sr. Notwithstanding, it demonstrates the relation of the $^{87}Sr/^{86}Sr$ ratio to carbon and shows that the effects of major orogeny on carbon fluxes and hence on climate. The Mesozoic-Cenozoic cooling trend is attributable to the closure of Tethys Ocean and subsequent uplift of the Himalayas and the Tibetan Plateau.

Most recently a quite different association of climate change and tectonics has been proposed for uplift of the Andes (Lamb and Davis, 2003). Rather than mountain uplift controlling climate the reverse has been proposed. Different mountain elevations along the mountain chain have been correlated with varying rainfall. Where the rainfall is greatest, sediment eroded from the mountains has been transported into the subduction zone offshore the Andes, where it lubricates the underthusting and decouples the plates.

In this area the mountains are at their lowest elevation. In the central region of Peru, Bolivia and Northern Chile, the mountains attain their greatest elevation and here a drier climate results in little sediment transport into the subduction zone. The sediment thickness on the oceanic less than to the north and south and the rougher plate topography results in a greater plate coupling resulting in higher mountains.

5.5 MANTLE DEGASSING

During the Precambrian the Earth developed the present atmosphere as we know it today mainly by cooling of a molten protoearth and volcanic outgassing of CO_2 and H_2O. During subsequent Phanerozoic modification of the earth's surface through plate tectonics and mantle outgassing continued, with increased and decreased phases dependent on the plate configuration and subduction processes. During periods such as the mid-Cretaceous the climate was one of warmest of the Phanerozoic, attributable to high CO_2 levels resulting from high rates of mantle degassing caused by increased mantle plume activities and high rates of seafloor spreading, that were twice those of the present.

5.6 THE DEEP OCEAN

Carbon fluxes in the ocean are not as well understood as those on land and, unlike their terrestrial counterparts, the fluxes are determined by both physical and biological processes operating over longer timescales. They are a significant influence on the short-term global carbon budget. Phytoplankton are responsible for approximately 40% of the planet's total annual photosynthetic (primary) production. There is exchange between the shallow and deep ocean, in which ocean layering, due to salinity and temperature variation, plays a significant role.

In the long term it is recognised that carbon sequestration in the ocean is a mechanism that could absorb all the predicted anthropogenic atmospheric CO_2 (IPCC, 2001). Thermohaline circulation, driven by temperature and salinity differences, plays a major role in CO_2 fluxes as it redistributes heat between high and low latitudes. It plays a major role in controlling the heat budget of the Earth during glacial/interglacial cycles through different levels of absorption of CO_2. Increased levels of atmospheric CO_2 of 700-800 ppmv have been predicted to result in a collapse of the THC system leading to a reduction in heat transfer to the northern hemisphere in the Atlantic, with potentially catastrophic cooling (Broecker, 2001).

The history of carbon change in the ocean over geological times scales can be studied through the sedimentary sequences in cores of the sub seabed sediment. Over longer geological timescales changes in the morphology of the ocean basins may also affects deep and intermediate water circulation that affects climate on a global scale (Wright and Miller, 1996).

5.6.1 Thermohaline Circulation

The global thermohaline circulation (THC) comprises cooling-induced deep convection and sinking at high latitudes, upwelling at lower latitudes, and the horizontal currents feeding the vertical flows. In the North Atlantic, where most of the deep sinking occurs (Gordon, 1986), the THC is responsible for the unusually strong northward heat transport. Together with the equatorward (up-gradient) heat transport in the South Atlantic (Macdonald and Wunsch, 1996), this northward heat transport leads to the relative mildness of western European climate. Although recognized as an important control on climate, the lack of a complete understanding of how THC contributes to rapid climate change poses major scientific challenges and provides a powerful focus for climate research (Marotzke, 2000).

The most conspicuous feature of the observed global THC is its geographic asymmetry: whereas water sinks in the North Atlantic to depths between 1 and 4 km, no such deep sinking occurs in the North Pacific (Warren, 1983). The reason for this difference lies in the different surface salt concentrations; the North Pacific is so low in surface salinity that not even water cooled to the freezing point becomes dense enough for deep sinking. However, the difference in surface salinity is in part a consequence of the presence and absence, respectively, of a vigorous THC in the North Atlantic and the North Pacific. Thus, high surface salinities at high latitudes can maintain themselves through the THC they help to induce. Model studies, ranging in complexity, have confirmed that such a THC collapse is in principle consistent with the physical laws governing the ocean (Bryan, 1986). The associated reduction in the North Atlantic heat transport would lead to a cooling of western European climate, which might have triggered the onset of ice ages and temporary cold spells such as the Younger Dryas.

Changes in the THC contribute to the abrupt climate changes of the Quaternary, although the relationships are not fully understood (Stocker, 2000; Clark *et al.*, 2002). These rapid transitions from cold to warmer “interstadial” phases, not associated with Milankovitch radiation variations, are termed Dansgaard-Oeschger (D-O) oscillations, visible on Figure 18. They are recorded in the •^{18}O records from ocean sediment cores and correlate with abrupt climate changes in Greenland ice cores (Grootes *et. al*., 1993). These D-O events appear to be superimposed onto a longer, gradual cooling and rapid warming cycles, called Bond Cycles. The current hypothesis on this cycle is the Binge/Perge Model (Alley et al., 1994). At the coolest point in the longer-term cycle, when the ice sheets are at their largest, the glacial bed thaws due to pressure from the overlying ice and forms a decollement, allowing rapid ice flow. This effect produces episodically, ice streams and discharge of icebergs into the Atlantic, termed Heinrich events (Heinrich, 1988), with the ice rafted debris (IRD) laid down in the North Atlantic, termed Heinrich layers (Figure 18) that are found in sediment cores, providing a detailed record of events.

The ice streams and icebergs cause a significant decrease in the seawater salinity and sea surface temperature. This in turn causes thinning of the Arctic ice sheet, allowing the base to refreeze, bringing to an end this period of rapid temperature change. The rapid warming brings to a Bond Cycle (the long term cooling cycles shown on Figure 18) back to a warm temperature peak. The importance of these events to carbon fluxes is in their effect on the overturning strength of the THC through changes in North Atlantic Deep

Water (NADW) that leads to a reduction in the transport of inorganic carbon from the surface to the deep ocean. Changes in sea ice cover corresponding to changes in poleward transport heat transport from the equatorial regions affects CO_2 uptake at high latitudes. Changes in Sea Surface Temperatures (SST's) Salinities (SSS's) and alkalinity affect CO_2 solubility and uptake in both hemispheres. This impacts upon the global climate cycle. The calculated changes in atmospheric CO2 with the change to warm period is calculated at between 10 and 40 ppmv, changes that agree with ice core records (Ewen *et. al.*, 2004).

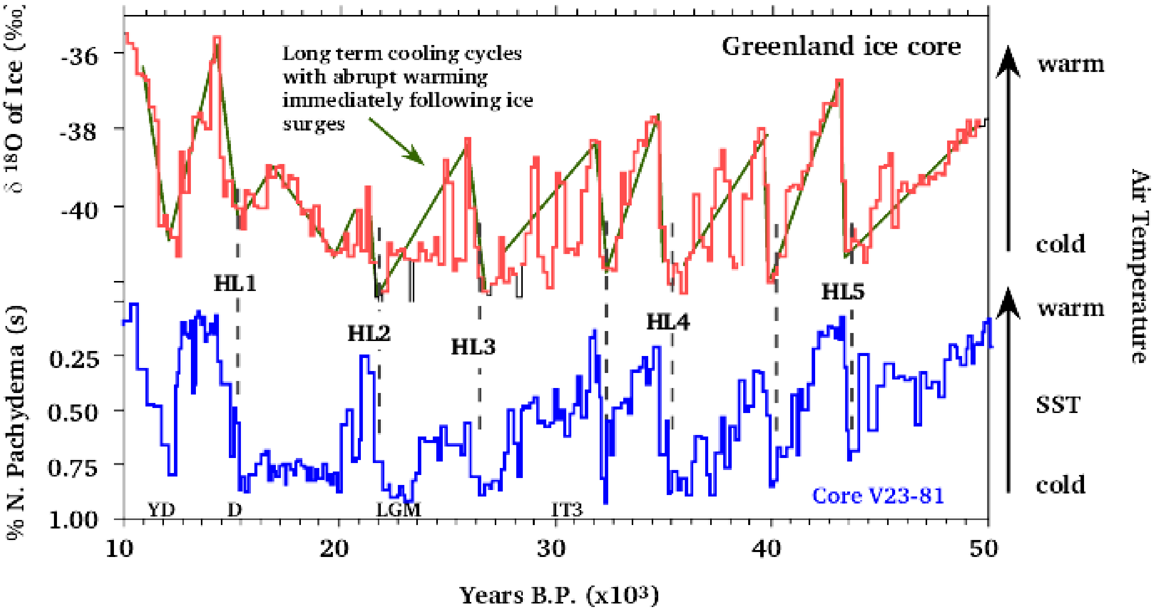


Figure 18. Comparison of GRIP with North Atlantic polar foraminifera

Comparison of a Greenland ice core oxygen isotope record (GRIP) with the relative abundance of a polar foraminifera (N. pachyderma) in the North Atlantic sediment core V23-81 for the period 10 to 50 kyr B.P., illustrating the close coupling of abrupt climatic change in the glacial atmosphere and ocean (YD: Younger Dryas; D: Deglaciation; LGM: Last Glacial Maximum; IT3: Interstadial 3; HL: Heinrich Layer) (after Bond et al., 1993). (http://www.ngdc.noaa.gov/paleo/reports/interx/2_4_2.html)

A further impact of changing THC is upon oceanic circulation at shallower depths, specifically upon intermediate water depth currents, because it here at depths of 400 to 1000 m that hydrate, beneath the seabed, has the potential to become unstable. The 'clathrate gun' hypothesis, that proposes a massive release of submarine methane hydrate triggering abrupt climate warming (Kennett *et al*., 2002), requires a phase change from solid to gas to be caused either by a decrease in pressure from sea level change and/or an increase in temperature. Sea level changes at stadial and glacial terminations are too slow to have caused rapid methane hydrate disassociation, thus the alternative mechanism is by rapid temperature change in the upper intermediate waters. There is evidence for temperature changes of between 2 and 4°C from all the ocean basins (eg. Marchitto *et. al.*, 1998), with the increase in temperature during warming intervals at low sea levels (Kennett *et al.*, 2002). The interpretation is that this is evidence to support the theory of hydrate destabilization resulting in burst of methane into the atmosphere (Kennett *et al*., 2002).

5.6.2 The role of Phytoplankton

Phytoplankton are responsible for approximately 40% of the planet's total annual photosynthetic (primary) production, a major contribution to global primary production considering their small fraction of the total global photosynthetic biomass. They are part of a very dynamic ecosystem where time scales of environmental forcing are on the order of days.

Phytoplankton exert a major influence on climate and, like plants, they respire CO_2 in photosynthesis. The larger the phytoplankton population, the more CO_2 gets absorbed from the atmosphere thereby lowering the average temperature. The rates of respiration are rapid and phytoplankton can double their numbers on a daily basis. They respond very rapidly to changes in their environment. Large populations, sustained over long periods, have the potential to significantly lower atmospheric CO_2 levels and temperatures.

Phytoplankton growth is regulated by light and nutrients, thus they are confined in the open ocean to the photic zone where light penetrates to a depth of ~200 m. Nitrogen (N) and phosphorus (P) provide the main inorganic nutrient supply and as phytoplankton grow the surface waters become depleted in these elements. Phytoplankton contribute to the carbon budget both directly and indirectly. Most are eaten in the water column and the nutrients comprising their biomass are regenerated at the surface and become available for another round of production. Some of the primary production finds its way to the deep sea, either through the settling of dead cells and faecal matter or through advection in the course of global circulation patterns (THC). Most of the organic carbon, which ends up in the deep sea, is assimilated by bacteria, which regenerate it (and N and P) into inorganic forms. This collective action is the ‘biological pump’ that operates over hundreds of years. It results in a sharp concentration gradient of nutrients with depth. The gradient is larger in the Pacific than the Atlantic because deep ocean currents flow from the Atlantic to the Pacific, collecting as they travel the rain of nutrient-rich particles from the productive surface waters above.

The biochemical pump, comprised of phytoplankton cells, their animal predators, and the bacteria that assimilate their waste, plays a central role in the global carbon cycle. The biological pump delivers carbon from the atmosphere to the deep sea, where it is concentrated and sequestered for centuries. Superimposed on the biochemical pump is a ‘solubility pump’, the driving force of which is the THC, which concentrates dissolved inorganic carbon (CO_2 plus bicarbonate and carbonate ions) in the deep ocean. Estimates of the relative importance of the two pumps vary widely, but it is likely that 75% of the difference in dissolved inorganic carbon concentration between the surface and deep oceans is due to the biological pump (Sarmiento and Bender, 1994). If there were no biological pump and the dynamics of the oceanic carbon cycle were driven solely by physical and chemical processes, the amount of carbon released from the deep ocean as it equilibrated with the atmosphere would more than double the CO_2 concentration in the atmosphere.

Although there are many cyclic processes in the ocean surface waters that are coupled to the biological pump, the net flux of biologically produced materials is one way of cycling between surface and deep ocean waters. Nutrients have to be recycled back to the surface waters to resupply phytoplankton on the time scales relevant to anthropogenic change and this takes place through three mechanisms:

- Upwelling of the nutrient-rich deep water (e.g., along the western coasts of continents),
- Diffusion across the thermocline (e.g., the central ocean gyres), and
- Seasonal, wind-driven deep mixing, which erodes the thermocline and entrains the deep water to the surface (e.g., the North Atlantic).

Fuelling of the phytoplankton pump by N and P generates more organic carbon through photosynthesis as well as CO_2 from the deep water. Inorganic N and P are delivered to the surface waters in the Redfield Ratios of C:N:P = 106:16:1 (Redfield, 1934, 1958) together with CO_2 in excess, are converted to organic compounds (i.e., biomass) in the Redfield proportions of C:N:P, are recycled in the surface waters many times in those proportions, and ultimately are re-pumped to the deep sea in the same proportions. Thus, on a global scale, any changes in upwelling and the supply of nutrients to the surface waters will not influence the biological pump's role in the annual atmospheric carbon budget, so long as the supply and assimilation of N, P, and C are tightly coupled.

However, in some areas of the world's oceans the supply and assimilation of N, P and C are not tightly coupled, even on an annual average, because N and P do not appear to be limiting phytoplankton growth. These are the so-called ‘high-nutrient, low-chlorophyll’ (HNLC) waters of the subarctic Pacific, the Southern ocean around Antarctica, and the equatorial Pacific (Cullen, 1991). Here the biological pump is inefficient: the phytoplankton standing stocks are not large enough to assimilate the N and P in the surface waters fast enough to deplete them at any time throughout the year. These regions, particularly the Southern Ocean, are of major interest to paleooceanographers because they could have played a role in past climate change (Sarmiento and Togweiler, 1984). The cold surface waters of the Southern ocean steadily sink to the abyss as part of the global ocean circulation and, in today's ocean, carry with them a large reservoir of unused nutrients, a potential carbon sink of some magnitude.

There has been a great deal of uncertainty regarding the HNLC regions and why they occur, what factors are responsible for the inefficiency of the biological pump in these regions and why can't the phytoplankton use up the nutrients as they do so effectively in the other regions of the world's oceans? Of the hypotheses proposed for the origin of the HNLC regions, which primarily involve light limitation or control by zooplankton grazing (Cullen, 1991), the most provocative is that the supply of iron to these regions regulates primary productivity (Gran, 1931; Hart, 1934; Harvey, 1938). Iron in today's oxygenated oceans is extreme insoluble. In areas where it was not readily replenished from the land it must be in very short supply. Its potential as a limiting factor is predicated upon the early Precambrian evolution of the biochemical pathways that drive phytoplankton physiology, when the ocean and atmosphere were anoxic. Because of its high solubility under these reduced (oxygen free) conditions, iron was extremely abundant relative to other trace nutrients and biochemical pathways were not under evolutionary pressure to be efficient with respect to iron. When oxygenic photosynthesis evolved around 3 billion years ago, iron was rapidly oxidized, becoming significantly less available to the biota.

Experiments on the limiting effect of iron on phytoplankton productivity demonstrate that iron plays a major regulatory role (Martin, 1992). The primary source of iron to the oceans is from the land, either via atmospheric dust deposition in offshore areas, or by direct deposition from rivers. Dissolved iron concentrations in offshore areas are extremely low (Martin and Gordon, 1988). In the Southern Ocean, based on Redfield ratios for C:N:P, the amount of oceanic iron was one-tenth that required to allow the phytoplankton to assimilate the ambient nitrate in the surface waters. In addition, atmospheric dust deposition in the two major HNLC areas, the Antarctic and equatorial Pacific oceans, is the lowest in the world (Prospero, 1981; Uematsu, 1987). Conversely, in the equatorial North Atlantic, which receives large amounts of dust from the Saharan desert (Prospero, 1981), iron concentrations are sufficient for the complete assimilation of available nitrates and phosphates.

Laboratory experiments prove that the phytoplankton biomass in iron seeded surface waters from the HNLC regions, was always higher than in the control bottles with nitrates and were always more depleted in the iron-enriched bottles. One particular group of species, the pennate diatoms, were stimulated more than others, proving that not all phytoplankton species are equally iron limited (Hudson and Morel, 1990). To confirm the laboratory results, a more realistic experiment in the ocean was set up to enrich a patch of the ocean with iron to see how the phytoplankton would respond when the food web was intact. This proved successful and iron seeding accelerated phytoplankton growth (Coale *et al*., 1996).

The amount of iron reaching the oceans has far reaching ramifications on climate change. From the composition of materials trapped in ice cores from Antarctica, including the CO_2 content of ancient air, the chemistry of the oceans and atmosphere of past eras can be deduced. During the last glacial maximum, 18,000 years B.P., atmospheric CO_2 levels in the atmosphere were 200 ppmv, far less than pre-industrial levels of 280 ppmv, and previous interglacial atmospheres (Raynaud *et al*. 1993) which had similar concentrations. Knowing that the deep ocean CO_2 reservoir plays a major role in glacial/interglacial transitions in atmospheric CO_2, one key element may be changes in primary productivity in the Southern Ocean (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984).

The Southern Ocean today receives one of the lowest dust inputs in the world, but this has not always been the situation (Martin, 1990a, 1992). During the last glacial maximum arid land regions were 5 times larger than today, and 50 times today's values of wind-borne iron was deposited on waters around the Antarctic continent (Petit *et al*., 1981; De Angelis *et al*., 1987). Support for an iron control from wind-blown terrestrial dust is gained from ice core evidence that indicates that around Termination II only changes in dust deposition appear to precede the observed rise in global CO_2 (Broecker and Henderson, 1998). Furthermore, the observed relative timing between these two signals is consistent with recent carbon cycle model results (Watson *et al*., 2000).

However, recent research on iron fertilisation in the Southern Ocean suggests that despite the strong response in biomass to iron addition, export of particulate organic matter

(POM) was virtually unaltered. The response was not entirely unexpected because the much colder temperatures in this part of the ocean are likely to slow the response of phytoplankton to any relief of nutrient limitation. If the grazing response was similarly suppressed then the bloom succession will have been stretched out in time and final export delayed. However, complicating this intuitive explanation is the apparent persistence of the bloom for several months after the end of the experiment, based on remotely sensed elevated surface chlorophyll concentrations. This implies that losses of iron must have been relatively restricted over this entire period and any export therefore modest. The results have to be interpreted with care because seasonal constraints may have limited POM export and the timescales may have been too short. The whole of the Southern Ocean during the LGM receiving an enhanced aeolian iron supply, persisting for thousands of years, might produce a very different export response from the temporal and spatially limited experimental conditions of the recent experiment.

The evidence suggests that increased supplies of iron to the Southern Ocean (where nitrates and phosphates are present in excess) during the last glacial maximum may have stimulated the biological pump and contributed to the draw down of atmospheric CO_2 to 200 ppm (Martin, 1990a). Consideration of the relationship between iron concentrations in Antarctic ice cores and the corresponding atmospheric CO_2 concentrations shows that there is strong relationship. It is also possible that changes in CO_2 concentration may have played a role in the changing temperatures during the interglacial/glacial transition (Shafter, 1989).

5.6.3 Ocean seabed configuration

Seabed morphology is recognized as exerting a significant control on deep-sea carbonate production, transport and sedimentation (Edmond and Huh, 2003). However, it also has a major influence on deep-sea bottom waters (Wright and Miller, 1996). In the North Atlantic there is a correlation between the flux of the North Atlantic Deep Water (NADW) and the elevation of the Greenland-Scotland Ridge that also correlates with the advent of cooling during the middle Miocene and middle Pliocene and the climatic optima of the late early Miocene and early Pliocene. The periods of cooling correspond to reduced NADW (or Northern Component Water -NCW) across the Ridge, and climatic warming to stronger flow. The fundamental control on the elevation of the Ridge was waxing and waning of the Icelandic Hotspot. This evidence demonstrates the linkages between long period mantle events (plume evolution), seabed morphology, ocean current flow and climate. It shows how complex the drivers and amplifiers of climate can be.

5.7 THE NEOPROTEROZOIC

Over the past 500 million years ago the Earth's atmospheric composition has remained almost constant (78% Nitrogen, 21% oxygen and 1% other gases including the important greenhouse gases CO_2, CH_4 and H_2O). Most recently, because of anthropogenic impacts on increasing CO_2 levels, this has changed. Before 500 Myr in the Precambrian, the atmosphere was of a different composition, probably mainly CO_2 and H_2O, gases emitted from volcanoes. With the explosion of life at the beginning of the Phanerozoic and the beginning of major photosynthetic production of oxygen, the composition of the atmosphere evolved, more or less, to its present composition.

In the Neoproterozoic (1,000–543 Myr) there are unusually large fluctuations of the carbon-isotopic record that imply strong perturbations to the Earth's carbon cycle (Rothman, 2002). Examination of records of both the isotopic content of carbonate carbon and the fractionation between carbonate and marine organic carbon indicates that these records are inconsistent with conventional steady-state models of the carbon cycle, that are characteristic of the Phanerozoic. They can be understood as deriving from the nonsteady dynamics of two reactive pools of carbon one, as now, oceanic and atmospheric CO_2, and the other, probably, a reservoir of oceanic organic carbon.

The isotopic data indicate that the oceanic organic carbon reservoir was large and that its average properties changed slowly. Fluctuations in its size would have led to major variations in the isotopic record. Moreover, even if the size of the organic reservoir had been perfectly constant, changes in the fractionation associated with organic production would have led to isotopic fluctuations much greater than those predicted by steady-state theory. The lack of a steady state is due to the large size of the oceanic reservoir of organic carbon. A significant intra-Neoproterozoic negative carbon-isotopic excursion resulted from increased remineralization of the oceanic carbon reservoir. The terminal event, at the Proterozoic-Cambrian boundary, signals the final diminution of the reservoir, a process that was probably initiated by evolutionary biological innovations that increased export of organic matter to the deep sea. The study has implications for climatic changes, particularly 'Snowball' Earth.

We know that the Earth experienced extreme climates during the Phanerozoic that, by comparison, makes the most recent Quaternary alternations of cold/warm periods look insignificant. The influence of CO_2 has been recognized in both. During the Quaternary, up to 30% of the Earth's surface was ice covered. Near the end of the Neoproterozoic (1000-543 million years ago) an extreme series of climate coolings, termed 'Snowball' Earth, are believed to have led to a complete ice cover of the planet (Appendix 3). The hypothesis is as interesting as much for the development of ideas as the hypothesis itself. Development of the hypothesis demonstrates the contribution that geology can make to the understanding of climate change. It also shows how advances in technology have allowed a far greater insight into Earth evolution: scientific thought going hand-in-hand with the development of scientific ideas.

An intense Neoproterozoic glaciation was first postulated in 1964 (Harland and Rudwick, 1964) based on the study of glacial deposits that were formed at low elevations in equatorial regions. Glaciers at 4-5000 metres altitude are located in these areas at present, but not at sea level. At the same time, early climate models indicated that the ice-albedo feedback created if the Earth cooled sufficiently to allow ice to form at low latitudes, would result, once the ice had advanced beyond a critical latitude (30° N and S, equivalent to half the Earth's surface area), in a positive feedback so intense that temperatures would plummet and a frozen planet would result (Budyko, 1969). Only the small amount of heat escaping from the Earth's interior prevented the oceans from freezing completely. In the late 1970's with the discovery of organisms inhabiting areas close to deep-sea hydrothermal vents and, even later, in the extremely cold, dry valleys of

Antarctica, the theory gained additional support. Up until these discoveries a major objection to a completely frozen Earth was how life survived during these cold periods, although it was known that microscopic organisms survived through them. Another major objection was how climate changed from cold to warm conditions, which was answered by plate tectonics and the acceptance of the association between the mobility of the Earth's surface and the weathering and volcanic cycles that control the CO_2 fluxes that we now recognize as dominating climate change (discussed above).

The term 'Snowball' Earth was coined in the late 1980's by Joe Kirschvink who, whilst investigating the control of CO_2 on global climate, realized that without liquid water on the continents there would be no weathering, a situation that would result in such high levels atmospheric CO_2 that greenhouse warming would result, offset the ice albedo control of glaciation and terminate the extremely cold conditions (Kirschvink, 1992). Solar luminosity 600-700 million years ago was about 6% lower than today due to stellar evolution, so to overcome the albedo of Snowball Earth, a concentration of CO_2 about 350 times greater than that today would be required (Caldeira and Kasting. 1992).

The theories about Snowball Earth have been supported by more recent palaeomagnetic studies on Neoproterozoic glacial deposits (overcoming such problems as remagnetisation through water percolation) that prove their origin at low elevations at low latitudes. Alternative explanations, such as a higher angle of the Earth's obliquity (the difference between the tilt of the Earth's spin axis and the Earth's ecliptic plane) are not practicable. A 54° angle of obliquity (compared with 23.5° today) would result in a greater seasonality of climate that would not allow the growth of glaciers necessary to create global arctic conditions. Summer insolation is the key to the growth and retreat of glaciers. Another objection to the hypothesis is that it would require a giant impact, is incompatible with the accepted orbit of the moon.

Additional data from the stratigraphy of the Neoproterozoic sequences, interbedded diamictites, banded iron formations and marine carbonates provide supporting evidence for the fluctuations between cold and warm periods. Banded ironstones, intimately associated with the glacial deposits, are the result of changes in the oxidation potential of the oceans as intensely cold glacial conditions alternated with warm periods. During the glaciations the thick ice cover of the oceans led to the creation of anoxic conditions allowing iron in its reduced form to stay in solution. With climatic amelioration, the oceans were exposed to the atmosphere, and with increased circulation and oxygenation the iron was oxidised to its more insoluble form and precipitated from solution. Climatic amelioration also resulted in increased CO_2 content of the atmosphere and, with the exposure of glacially derived rock flour, increased weathering and an increased input of bicarbonate and carbonate that transported to the acidic surface waters of the ocean was precipitated and deposited as limestone.

5.8 THE PAST 60 MILLION YEARS

There is no doubt, given the fossil and isotopic records, that there has been a steady deterioration in Earth surface temperatures over the last 60 Myr, from the essentially global tropical conditions of the early Tertiary, with ocean bottom water temperatures of

~12°C to the present ice age conditions (Zachos *et al*, 2001). Under the contemporary Earth surface environment, CO_2 is close to being a limiting nutrient for terrestrial vegetation, especially C3 plants, such as trees and shrubs. Strongly enhanced growth is observed in greenhouse experiments with artificially increased PCO_2 (Korner and Arnone, 1992), and greatly reduced growth results at PCO_2 9150 ppmV (c.f. the preindustrial interglacial value is V280 ppmV). C4 plants, mainly grasses, are much more resilient to both low PCO_2 (limit V20 ppmV) and low PH_2O. Between 8 and 5 Myr, a drastic change in the relative preponderance of C3 and C4 plants occurred in response to decreasing PCO_2 (Cerling *et al*., 1993). Consistent with this limitation, there are strong seasonal oscillations in atmospheric PCO_2, especially in the Northern Hemisphere where, at high latitudes, the total amplitude is about 5% of the average background value (Machta *et al*., 1977). For reasons not entirely understood, the Ice Age glacial maxima are accompanied by a 30% decrease in PCO_2 (Barnola *et al*., 1987 and Boyle, 1988). Thus, present day atmospheric PCO_2 levels are not only weakly buffered against the effects of short-term biospheric and climatic change, but appear to be close to the minimum value geologically.

5.9 BIOLOGICAL CONTROLS ON CARBON RESERVOIRS

The primary sources of atmospheric CO_2 are considered to be from direct input from mantle outgassing, probably with a subduction-related component, and metamorphic breakdown of carbonates in active orogenies in oceanic and continental arcs (e.g. the Southwest Pacific and the Western Americas). However, there are significant correlations between the diversity of marine animals and land plants from the concurrent measure of stable carbon isotope fractionation for approximately the last 400 million years (Rothman, 2001). The correlations are based on the assumption that increasing plant diversity led to increasing chemical weathering of rocks and therefore an increasing flux of carbon from the atmosphere to rocks and nutrients from the continents to the oceans. The CO_2 concentration dependence of photosynthetic carbon isotope fractionation then indicates that the diversification of land plants led to decreasing CO_2 levels, wheras the diversification of marine animals derived from increasing nutrient availability. Under the explicit assumption that global biodiversity grows with global biomass, the conservation of carbon shows that the long-term fluctuations of CO_2 levels were dominated by complementary changes in the biological and fluid reservoirs of carbon, while the much larger geological reservoir remained relatively constant in size. As a consequence, the palaeontological record of biodiversity provides an indirect estimate of the fluctuations of ancient CO_2 levels.

Surprising correlations exist between palaeontological records of biodiversity and the carbon isotope fractionation evident in the sedimentary record for the last 370 million years (the advent of vascular plants). Assuming that (i) chemical weathering rates increase with plant diversity; (ii) diversity grows with biomass at the global scale; and (iii) changes in phytoplankton physiology neither correlate with diversity nor fully compensate changes in CO_2 levels, we find that the correlations express complementary fluctuations in the size of the organic and inorganic carbon reservoirs within the biosphere, atmosphere, and hydrosphere. Consequently, CO_2 levels decrease as biodiversity increases. The implication is that fluctuations of CO_2 levels have been driven primarily by changes within the biosphere and only secondarily by purely geologic and geophysical processes. However, as with the relationship between $^{87}Sr/^{86}Sr$ and PCO_2 there are other factors that require consideration such as tectonically induced reductions of CO_2 levels that may lead to increased diversity in both continental and marine ecosystems. This demonstrates yet again that the drivers of climate change are complex and that further work is necessary to define their relative contributions. This additional research requires not only the study of other geochemical signals (Veizer *et al*., 1999) but also, improved palaeontological records.

6 GEOLOGICAL SINKS OF CARBON

6.1 CARBON RESERVOIRS.

Geological sinks of carbon are most important in the long-term context and the main carbon reservoirs are the sedimentary rocks (Figure 3). The National Oceanic and Atmospheric Administration (NOAA) of the US Department of Commerce has estimated that the sediment store of carbon totals 78 x 10^6 GtC (Table 1). The largest carbon reservoirs are sedimentary carbonates, stored as coral reefs and deep-water carbonates, and kerogen, followed by hydrates, marine dissolved inorganic carbon, soils, surface sediments, and the atmosphere. The oceanic reservoir contains almost 20 times more carbon than the continental ecosystem. The living biomass reservoir is somewhat smaller than the atmospheric carbon reservoir with which it actively exchanges through photosynthesis and respiration. The size of the hydrate sink is uncertain. The estimated size of the largest three sinks are as follows:

- Carbonates: 60 x 10^6 GtC
- Kerogen: 15 x 10^6 GtC
- Methane hydrates: 10 x 10^3 GtC

6.2 GEOLOGICAL SINKS - CARBONATES

Carbonate sinks are mainly of two types: shallow water/shelf reef carbonates and deep-water carbonates. Both are subject to similar and related controls and over geological time scales carbonate flux in the ocean is dependent on a number of factors, which include eustatic sea level, the Carbonate Compensation Depth (CCD), seabed configuration, ocean chemistry, ocean circulation, potential burial preservation, location of subduction zones and the global configuration of continents. These controls vary and interact in a complex manner. At higher sea levels the balance is in favour of more reefs, with less carbon available for carbonate deposition in the deep ocean. At present we are experiencing a period of low eustatic sealevel, hence there is a smaller volume of carbon bound up in shallow water carbonate reefs than during some previous periods of Earth history.

At present, the Atlantic and Indian oceans are major depocentres of $CaCO_3$, but in these basins rates of subduction are low (Edmond and Huh, 2003). The main subduction zones are located along the boundaries of the Pacific Ocean. However the locus of metamorphic regeneration of CO_2 is restricted to the trenches off Central America. This is because of global asymmetries in the age of crust being subducted, in the distribution of oceanic carbonate productivity, and in the carbonate compensation depth, coupled with the poor preservation of old carbonate sediments.

In considering the carbonate flux a critical temporal dividing line is at 140 Myr, when calcareous plankton evolved to produce a deep-water carbonate source. Prior to this time carbonate sedimentation was confined mainly to biogenic environments on shelves and oceanic islands, or by inorganic precipitation in the deep sea (cf the inorganic 'whitings' of the Caribbean). The CCD is a major controlling influence of carbonate sedimentation in the ocean, and is in part dependent on the depth of the ocean. There is a relationship between the depth of the CCD and the deposition of carbonate: with deeper CCD's there is older crust with carbonate deposited, with a shallower CCD there is more restricted carbonate deposition. There is also a decrease in the preservation of carbonate with age, due to dissolution and also to the effects of deep ocean currents.

At present it would appear that the combination of the depth evolution of the CCD, the distribution of oceanic productivity, and the rate of formation (depth) and age of subducting crust makes the west coast of Central and South America between 10°S and 20°N the locus of metamorphic recycling of CO_2 in the contemporary global subduction system. Here carbonates from the equatorial high productivity zone are being delivered to the subduction zone on timescales <15 Myr and with minimal penetration of the CCD.

Based on these considerations it appears that there is no causal relationship between the metamorphic release and weathering uptake of CO_2 and subsequent deposition of carbonate on timescales shorter than a complete cycle of opening and closure of a basin. The low present-day PCO_2 is maintained by a time lag between:

1. Mantle outgassing and metamorphic regeneration related to orogenic events in the geologic past, and
2. Consumption driven by recent mountain building in the Tethyan zone and in the Western Americas.

If this interpretation is correct, then at the present 'kinetic minimum' both the terrestrial biosphere and the weathering rates are CO_2 limited and atmospheric PCO_2 levels are controlled by weathering reactions, only at this limit. In epochs of tectonic stability outgassed CO_2 can accumulate in the atmosphere to very high concentrations with no obvious limit. Thus, if as in the past, the current 'Ice House' environments will continue for tens of millions of years, possibly until the closure of the Atlantic recycles the first deep carbonate depocentre since the destruction of the Tethys. Unless of course anthropogenic influence destabilize this natural cycle. A greater understanding of all these processes is required for the geochemical evolution of the Earth surface environment to be simulated.

6.2.1 Tropical Shelf Carbonates

The global area of reef is dependent upon eustatic sea level, with more reef area when sea level is high. At present coral reefs occupy a limited area of the globe - 600,000km^2- (Smith, 1978) with the only large reef area the Great Barrier Reef off north-west Australia. This is only just less than one tenth of one percent of the area of the world's oceans. In the geological past, during periods of higher eustatic sea level such as during the Carboniferous, Jurassic and Cretaceous there were wide shallow continental shelves and an associated larger reef area.

Tropical coral reefs are constructed of calcium carbonate ($CaCO_3$). However, in the process of carbonate production, reefs are not major sinks of CO_2. Carbonate reefs accumulate by a combination of skeletal growth around living organisms, and sedimentation and cementation of voids within and around the accumulating carbonate mass. When $CaCO_3$ is precipitated, CO_2 is generated rather than consumed (Arrhenius, 1896). During calcification, the water becomes more acid due to the removal of bicarbonate and carbonate ions, and this change in pH lowers the solubility of CO_2 (Broecker and Takahashi, 1966; Stumm and Morgan, 1981). The partial pressure of CO_2 increases and, in an open system, CO_2 escapes into the atmosphere. The reaction is:

$Ca^{2+} + 2HCO_3$ • $CaCO_3 + H_2O + CO_2$

In seawater, for each mole of $CaCO_3$ deposited, 0.6 moles of CO_2 are liberated (the 0.6 rule of CO_2 production; Ware *et al*. 1991). In the short term, over hours to days, biological processes on the reef may absorb some or all of this CO2. However, over extended periods (seasons or longer) coral reefs contribute to atmospheric CO_2. Estimated regional averages of gross CaCO3 reef production is 1.5 (±0.5) kg/m^2/yr (Smith and Kinsey, 1976; Smith, 1983; Buddemeier and Smith, 1988; Kinsey and Hopley, 1991). 1.5 (±0.5) kg/m^2 /yr corresponds to 180 (±60) g C/m^2/yr which based on the '0.6 rule' would release 108 (±36) g C/m^2/yr as CO_2. Much of this would be taken up by organic production (Smith and Veeh, 1989). Reef systems produce 36 g C/m^2/yr in net organic production that represents the maximum of CO_2 released by carbonate deposition that could be incorporated into organic production. Thus, assuming that all the net organic production offsets CO_2 production from calcification, reef carbonate production would release 108 (±36) – 36 = 72 (±36) g C/m^2/yr to the atmosphere (Ware *et al*., 1991). As the organic material buried in reefs is not oxidised, thereby producing CO_2 and that reef sediments contain 0.4% organic carbon by weight, which equals 6 (±2) g C/m^2/yr, 102 (±34) g C/m^2/yr may be released into the atmosphere by carbonate production. The total range of CO_2 released into the atmosphere is thus between 36 and 136 g C/m^2/y which, when multiplied by the total global reef area of 6 x 10^{11} m^2 yields 2.2 to 8.2 x 10^{13} g C/yr. Coral reefs are thus contributing between 0.02 and 0.08 Gt of carbon as CO_2 to the atmosphere each year, very small (0.4% to 1.4%) when compared to the anthropogenic volume of 5.7 Gt.

When referring to the release of CO_2 into the atmosphere from coral reefs, this is not strictly correct because the oceans are overall a CO_2 sink and it is not possible to differentiate between any source, anthropogenic or otherwise. It is preferable to state that over decadal timescales the carbonate precipitation on coral reefs results in a global absorption of CO_2 from the atmosphere to the ocean surface waters of between 0.02 and 0.08 GtC/yr as CO_2. Over geological timescales this process cannot continue indefinitely without replacement of the carbonate ions and restoration of the pH balance. This balance is restored by various feedback mechanisms associated with volcanism, metamorphism and weathering. As the total carbon store of the world's oceans is 38,000 Gt the imbalance over the short timescales of 100's years, of most interest to our management of the anthropogenic impact, is not important. It is understood on this basis that coral reefs are not major participants in the global CO_2 balance. Notwithstanding, the processes of carbonate precipitation in coral reefs and the resultant CO_2 production need to be understood. One consequence of global warming is an increase in coastal flooding and extensions of continental shelves; this could have a small positive impact on carbonate formation in the near future.

Notwithstanding the recognised ability of corals to withstand major changes in temperature and sea level during glacial/interglacial transitions, recent studies on the Great Barrier Reef indicate that because of increased global warming resulting in rising sea temperatures, the reef will be destroyed by the middle of this century (http://news.bbc.co.uk/2/hi/asia-pacific/3509383.stm).

6.2.2 Deep Sea Carbonates

Deposition of deep-sea carbonate has been described above. The total global deep-sea calcite productivity has been calculated from the average amount of calcite in marine cores divided by the rate of accumulation of the sediment. Values of the calcium carbonate accumulation rate (effectively the rate of fixation of carbon in shells and as cement) varies between different environments, but estimates have generally fallen in the range of 0.63 to approximately 2.0 Gt C/yr, with an average of ~1.0 Gt C/yr:

- 0.63 Gt C/yr (Morse & Mackenzie, 1990)
- 1.13 Gt C/yr (Wollast, 1994)
- 0.64 Gt C/yr (Milliman, 1993)
- 1-2 Gt C/yr (Shaffer, 1993)
- 1.2 Gt C/y (Archer & Maier-Reimer, 1994)

Diagenetic loss of carbonate during early burial and compaction of sediments, with bicarbonate loss occurring with expulsion of pore water, means that estimates of carbonate fixation in sediments should err on the lower side on a long-term basis. Over geological timescales there is an inverse relationship between deposition of carbonate in reefs and in the deep ocean with eustatic sea level.

6.2.3 Temperate Carbonates and Gas Hydrate Related Carbonates

In recent decades with the advent of improved sea floor surveying techniques, temperate and cold-water carbonates have been discovered and recognised as important natural carbon repositories. Mounds and chimneys of carbonate form on the deep sea floor in the vicinity of active methane expulsion vents, or near-surface gas hydrate occurrences. This methane-derived carbonate cementation is recorded from many sites, notably along convergent margins such as Cascadia and Papua New Guinea, and in other areas such as the Gulf of Mexico.

There is a clear trend of locations along the western Atlantic margin. The Sula Reef off Norway is the world's largest known cold water *Lophelia* reef. Recent evidence has been found of the micro-scale seepage of methane through the seafloor in the vicinity of coral mounds and bioherms off mid-Norway (Hovland & Thomsen, 1997; Hovland *et al.* 1998), indicating that carbonate-producing ahermatypic corals may indirectly sequester methane and possibly carbon dioxide during their growth cycle. The Darwin Mounds, located south of the Faero-Shetland Channel is another area of recently discovered carbonate precipitation.

Authigenic carbonates are found intercalated with massive gas hydrates at other continental margin settings (e.g. Bohrmann *et al*., 1988)

6.2.4 Deep Sea Carbonate Oozes

The accumulation of organic material in the deep marine environment at the present day has been identified and mapped mainly from ocean drilling during the Deep Sea Drilling Programme and succeeding programmes of the International Programme of Ocean Drilling (IPOD) and the Ocean Drilling Project (ODP). Berger (1976) has estimated that about half the deep-sea floor is covered by biogenically produced pelagic sediments, of which calcareous oozes, with concentrations of calcite varying from 10 to 90%, form approximately half again, iron- reddened clays contributing about 35% and siliceous oozes making up about 15% of the total coverage.

The carbon deposited in deep-sea sediments is derived from the ocean waters that are in quasi-equilibrium with the atmosphere. The main source of organic carbon compounds in the deep ocean is phytoplankton, their abundance controlled primarily by temperature, nutrient levels and light levels.

Much dissolution of carbonate occurs in marine waters before it becomes incorporated into sediment. No calcite reaches the very deepest waters (~4-5 km depth), below the calcite lysocline (Broecker & Peng, 1982). At great ocean depths the high pressures affect seawater chemistry such that waters become undersaturated with respect to carbonate, and calcite is forced into solution. It is therefore not surprising that following the death of phytoplankton, less than 0.2% of their calcite tests survive dissolution. However, organic matter adhering to the phytoplankton tests may increase the importance of this carbon sink (Appendix 2).

6.3 GEOLOGICAL SINKS - ORGANIC CARBON

Organic carbon (OC), mainly in the form kerogen, accounts for about 20% of the sedimentary carbon reservoir, with recycling taking place over geological time scales. In addition to the carbon in the geosphere there are a number of active (or surface) carbon pools in the biosphere and atmosphere. Forms of OC in the atmosphere include about 780 Gt carbon in CO_2 (Sieganthaler and Sarimiento, 1993).

On land the main reservoirs are vascular plant tissues (570 Gt) (85 % wood, 5 % leaves and 10 % ground vegetation), plant litter on the soil surface (0-100 cm) (70 Gt) and organic matter (OM) in soil (humus 1600 Gt) (Hedges, 1992). The OM in soils is cycled about every 1-1000 years (Kiem *et al*., 2000). In the marine environment there are two active organic carbon reservoirs, namely, surface marine sediments (150 Gt) and seawater dissolved organic carbon (DOC 700 Gt). Riverine DOM is not observed in marine sediments and therefore appears to be efficiently mineralized within the oceans. Overall about 95 % marine primary production and a minimum of 50 % terrestrial OM (TOM) is oxidized to CO_2, H_2O and nutrients (Hedges *et al*., 1997).

The global burial rate of TOC in the ocean is about 0.2 Gt/yr (Berner, 1989; Hedges and Kiel, 1995). Most sedimentary OM derived from terrestrial sources is deposited in either deltas or on continental shelves/slope. Some continental margins have been shown recently to be net CO_2 sinks (Liu *et al.*, 2001. 2002). An example is the East China Sea where large amounts of carbon, carried down the rivers Changjiang (Yangtze River) and Huanghe (Yellow River), are being laid down. Fluvial carbon fluxes comprise 12Tg C/yr in organic form and 20 Tg C/yr in dissolved inorganic form (Chen & Wang, 1999). The net carbon sink is, on average, 35 gC/m^2 /yr (Tsunogai *et al*., 1999).

Isotopic and biomarker measurements indicate that OM accumulating along coastal shelf /slope zone is of marine origin, because TOM is extensively and rapidly destroyed at sea. Although modern shelf environments represent only 7.6 % of the global marine area 80-90 % of marine organic carbon is buried in these sediments with mean TOC value of 1 wt % (Tyson and Pearson, 1991). In contrast modern deep marine environments constitute 92.4 % of the global marine area but contain sediments contain only 0.1-0.3 wt % OC (Tyson and Pearson, 1991).

Recent research on the carbon budget of continental shelves has highlighted the possibility of cross-shelf transport of sediments, which could carry significant amounts of carbon to the deep ocean (Liu *et al*. 2001, 2002). Two examples cited are the Indo-Pacific Archipelago where high tropical rainfall and discharge across narrow shelves may favour transport to the deep ocean, and the Arctic shelf where algal mats deposited on the shelf are re-suspended and transported by brines sinking down the continental slope (Melling, 1993). Cross shelf transport of carbon is also taking place in the North Sea (de Haas *et al.*, 1997).

The upper sedimentary layer of modern sediments (0-5 cm) accumulating in central regions of the Pacific and Atlantic and Indian Oceans has TOC values of <0.25 wt % . The importance of shelf sediments is attributed to high production and preservation of organic matter which are influenced by factors such as marine primary productivity, terrestrial influx, nutrient supply, upwelling, water oxicity, sedimentation rate as well as sediment particle size. Sediments rich in organic carbon (>2.00 wt %) are at present accumulating on the shelf and slope regions of SW African (Namibia) (>3-26 wt %), Peru (5-11 wt %) and the upper continental slope of the Indian Ocean from the Gulf of Aden to Andaman Islands (1-10 wt %) (Pedersen and Calvert, 1990). Contemporary sediments with high organic carbon contents have also been observed in the Baltic Sea (ca. 3 wt %), Gulf of California (ca. 0.5-2%) Red Sea as well as coastal Venezuela to Guiana (Demaison and Moore, 1980).

6.3.1 Reservoirs of organic carbon

The major organic form of carbon is kerogen, a macromolecular material, insoluble in common organic solvents. Kerogens are formed in part from a series of consecutive and random repolymerization and polycondensation reactions of extant plant and animal biomass. Biomacromolecules which are resistant to (bio)chemical degradation undergo selective preservation and are consequently enriched during the processes of sedimentation (Teegelaar *et al*., 1989). Kerogen is distributed at an average concentration of 1 wt % in shales and limestones. Global reservoirs of kerogen are estimated at 15 x 10^6 Gt making it the second largest pool of carbon on earth (Hedges and Oades, 1997). The thermal degradation of kerogen depends upon chemical composition and temperature /pressure yield either, oil, gas or both; these account for 0.05% of total sedimentary carbon.

6.4 GEOLOGICAL SINKS - GAS HYDRATES (CLATHRATES)

Gas hydrates or clathrates are naturally occurring solids composed of water molecules forming a rigid lattice of cages with most of the cages containing a molecule of gas, usually methane. Depending on their mode of formation, gas hydrates can occur as massive, bedded, nodular or disseminated forms. They are found where there is a combination of low temperatures and/or high pressure and sufficient organic carbon (Henriet and Mienert, 1998).

Estimates of the global volume of methane existing in hydrate form have varied widely, with some authors claiming that the quantity of carbon stored is at least as great as all other forms of carbon added together, including all known reserves of fossil fuels (Woodside, 2000). A ballpark figure of 10,000 Gt of carbon (2 x 10^{16} m^3) of methane gas stored in hydrates as determined by Kvenvolden (1993) is widely cited, although further study is required of their world-wide distribution and stability to confirm this figure. This figure represents approximately a third of the amount of carbon in the deep ocean dissolved inorganic carbon and almost 20 times that in the preindustrial atmospheric reservoir.

Gas hydrates are rare occurrences in deep-sea sediments, because they can only form where there is significant biogenic methane production, or where there is migration of thermogenic gases from deeper horizons.

7 CARBON RELEASE FROM SEDIMENT SINKS

7.1 DEGRADATION OF CARBONATE REEFS

Pollution and other human activities are leading to reef degradation in many tropical areas. A comprehensive review of the state of the World's coral reefs is presented in Appendix 4. A reduction in the amount of new reef growth equates to a reduction in carbon fixation as limestone.

There are increasing numbers of reports on reef destruction from around the world. A recent report concludes that 15% of the world's reefs are beyond repair and another 30% may also be lost over the next 30 years (Pew Centre). There are three major reasons for the decline, all related to global warming. Changes in sea water temperatures of 1° to 2° C is stifling the symbiotic algae that are essential for coral reef survival. Increasing levels of CO_2 dissolving in seawater are resulting in increased levels of acidity that stops the coral polyps from secreting their carbonate skeleton. The increased seawater temperatures are leading to over-fishing, disease and pollutants.

In the Philippines reef degradation has been extensive, in part due to the effect of fishermen using dynamite and cyanide to increase fishing catches, but also due to increased sediment loads being carried offshore due to deforestation. Up to 30% of the natural reefs around the Philippines have been destroyed, with a further 39% dying.

The Great Barrier Reef, the largest reef accumulation on Earth is in a serious state of decline, and it has recently been given until the middle of this century to survive (http://news.bbc.co.uk/2/hi/asia-pacific/3509383.stm). The prognosis is based upon the evidence that corals could not adapt quickly enough to a rise in sea temperatures of 2°C. Overfishing and water pollution are also to blame. It is predicted that the reef's demise will take place quickly and by the middle of the century less than 5% of the reef will remain alive.

In the Caribbean, reef areas are shrinking because of a doubling of the amount of dust carried westbound from the Sahara Desert. Desertification in North Africa is leading to increased wind-blown dust that contains a fungus that attacks the reefs, and also minerals such as iron and silicates that promote the growth of algae in the normally nutritionally poor waters of the Caribbean. This algae colonises the reef and suffocates it (Shinn *et al.*, 2000).

Another phenomenon affecting coral reefs is bleaching, attributed to the increasing affects of El Nino. The raised ocean temperatures due to the El Nino of 1997-1998 destroyed 16% of the world's reefs. The impact of sea-level rise associated with global warming on reefs is not considered a threat because the geological record demonstrates that most reefs can grow at rates that match sea-level change as long as other conditions favourable for growth are not compromised. In all likelihood carbonate precipitation would be able to keep up with a eustatic sea-level rise because rates of shallow neritic carbonate sedimentation are fast but intermittent (Wilson, 1975). Bearing in mind the geological record, for example the Carboniferous where high eustatic sea levels equate with a greater area of reef limestone, sea-level rise might be expected to encourage carbonate precipitation.

However, increased terrigenous input and pollution may be more serious threats to coral reefs. Increased disturbance of sediment, especially fines, is recognised as inhibiting reef growth as well as the effects of increased agitation of surface waters caused either by climate change or anthropogenic influences such as water sports and fishing.

As atmospheric CO_2 increases, the dissolved CO_2 content of surface seawater increases at a similar rate, but most of the added CO_2 ends up as $HCO_3{}^{-}$. Meanwhile, the $CO_3{}^{2-}$ content decreases, since the net effect of adding CO_2 is a reaction with $CO_3{}^{2-}$ to form $HCO_3{}^{-}$. There is therefore less available $CO_3{}^{2-}$ to react with further CO_2 additions, causing an increasing proportion of the added CO_2 to remain in its dissolved form. This restricts further uptake, so that the overall ability of surface seawater to take up CO_2 decreases at higher atmospheric CO_2 levels. The effect of this is large. For a 100 ppm increase in atmospheric CO_2 above today's level (i.e., from 370 to 470 ppm) the DIC concentration increase of surface sea water is already about 40% smaller than would have been caused by a similar 100 ppm increase relative to pre-industrial levels (i.e., from 280 to 380 ppm). The contemporary DIC increase is about 60% greater than would result if atmospheric CO_2 were to increase from 750 to 850 ppm. A recent study indicates that the net result of increasing CO_2 levels is an increase in the acidity of the ocean that could affect reef growth.

7.2 SUDDEN RELEASE OF GASES FROM METHANE HYDRATE

Methane is an important greenhouse gas, which is currently believed to account for 19% of enhanced greenhouse forcing (IPCC, 1995). It is important in the global carbon cycle because transport of this gas to the sediment surface is one of the major mechanisms by which buried carbon can be recycled into the upper biosphere . With gas there is always the possibility of escape to the earth's surface as a result of tectonic events (seeps) or natural flux through the sediments.

Hydrate is 14% less dense than water with a specific gravity of 0.85 g/m3 and will therefore rise to the sea surface if it is removed from the seabed. It will sublimate as it rises through warmer waters and decreasing hydrostatic pressures.

There is considerable speculation in the literature that global warming could lead to the sudden and explosive release of methane from methane hydrate, the 'Clathrate Gun Hypothesis' (Kennet et al., 2002). The permafrost in Arctic regions, which hosts methane hydrate, is thought to be particularly susceptible to the effects of global warming. In the Caspian Sea accidental releases of methane from hydrate during drilling for oil led to a "sea boiling" effect. It is a possibility that extensive destabilisation of gas hydrates might have occurred on continental slopes during sea-level lowering at the onset of glaciations (Kennet et al., 2002).

At the Palaeocene/Eocene boundary there is evidence for sudden, large-scale methane release that resulted in a major climatic amelioration (Norris & Rohl, 1999; Beerling *et* *al.* 2002). Analysis of atmospheric CO_2 and CH_4 concentrations in ice cores indicates catastrophic releases of gases at this time. Methane release from hydrates is also being invoked as a partial cause of the Permian mass extinction event (Benton & Twitchett, 2003; Benton, 2003a). Work by Wignall (2001) and Benton (2003b) have cited • ^{12}C enrichment of end-Permian sediments as evidence for hydrate release. The current consensus is that volcanic eruptions from the Siberian Traps initiated a global temperature rise in the order of 5°C. This led to higher seawater temperatures that in turn stimulated massive release of methane from hydrates and a further 4 to 5°C rise in global temperature. The combined volcanic and hydrate release processes raised global temperatures in the order of 10°C and led to the mass extinction of most life on Earth. These examples from the geological past provide evidence of catastrophic methane release that may have lessons for present-day life on Earth.

As stated above, the most recent theory regarding methane release is termed the 'Clathrate Gun Hypothesis' (Kennet *et al.*, 2002). Consideration of a significant body of evidence suggests that rapid release of methane may have precipitated rapid climate warming at the end of interstadials and interglacials. Although attractive in explaining some aspects of climate change, there are problems with identifying the trigger for such massive methane destabilisation and expulsion. The expulsion mechanism has to be rapid otherwise the methane would be dissolved in the sea water column on its passage to the atmosphere. Eustatic sea level change (rise) is not sufficiently rapid enough to effect the density changes in the subseabed methane hydrate to destabilise them. Changes in upper-intermediate water temperature and circulation has been proposed, but not proved. Additionally such catastrophic methane expulsion should be accompanied by evidence of extensive sediment failures on the continental shelf and margin. And it is on this basis that the hypothesis has been challenged (Maslin *et al.,* 2004). Dating of the slope failures along the Atlantic margin does not agree with the proposed periods of methane expulsion. However, the evidence of the timing of slide failure is limited.

7.3 INDUSTRIAL USE OF LIMESTONES

The production of cement releases CO_2 back into the atmosphere, however the increase in CO_2 levels is small at 0.2 Gt C/yr, 3% of total anthropogenic production. Cement production requires a source of calcium (usually limestone) and a source of silicon (such as clay or sand). The first important reaction to occur is the *calcining* of limestone (calcium carbonate) into lime (calcium oxide) and carbon dioxide, which occurs in the lower-temperature portions of the kiln, up to about 1650°F (900°C). Limestone, marl, and chalk are the most common sources of calcium in cement (converted into lime through calcination).

There are two very different sources of carbon dioxide emissions during cement production. Combustion of fossil fuels to operate the rotary kiln is the largest source: approximately $^{3}/_{4}$ tons of CO_2 per ton of cement. But the chemical process of calcining limestone into lime in the cement kiln also produces CO_2:

$CaCO_3$ ' $CaO + CO_2$

limestone ' lime + carbon dioxide.

This chemical process is responsible for roughly $^1/_2$ ton of CO_2 per ton of cement, according to researchers at Oak Ridge National Laboratory. Combining these two sources, for every ton of cement produced, 1.25 tons of CO_2 is released into the atmosphere. In the United States, cement production accounts for approximately 100 million tons of CO_2 emissions, or just under 2% of total human-generated CO_2. In 1991, worldwide cement production accounted for more than 1.6 billion tons of CO_2.

8 GEOLOGICAL RESERVOIRS FOR CARBON STORAGE

It is generally assumed that the adjustment of the natural carbon cycle to the anthropogenic inputs of fossil fuel carbon will take many tens of thousands of years. In the past 200 years there has been a net overall increase in atmospheric CO_2 concentrations equivalent to approximately 550 Gt CO_2. Any method that would aid disposal of CO_2 within sedimentary systems would help to mitigate against this long period of adjustment of the carbon cycle to these anthropogenic induced greenhouse gas emissions.

8.1 STORAGE OF CO_2 IN SEDIMENTARY RESERVOIRS

Carbon dioxide storage in sedimentary rocks could offer a rapid and relatively short-term fixation process for large point sources of CO_2. The effectiveness of the seal/cap rock to gas reservoirs is a potential problem. Tectonic activity could limit the effectiveness of this storage mechanism. The main positive aspect is that the amount of CO_2 that could potentially be stored is huge as the CO_2 is stored as a very dense gas. Secondly, the CO_2 could be released back into the atmosphere if and when atmospheric concentrations begin to fall.

Underground storage of CO_2 could in some circumstances lead to permanent fixation of carbon. Aqueous CO_2 is very reactive and reactions with the host rock could lead to the precipitation of pore-filling cements. Any method that allows the crystallisation of $CaCO_3$ is probably a more effective means of carbonate fixation in the longer-term.

Putting large amounts of chemically reactive aqueous CO_2 into reservoirs could have unforeseen and unhelpful effects, such as the corrosion of existing carbonates.

9 CONCLUSIONS

Most climate-related studies are focussed on the shorter term changes that impact over human timescales and are undertaken mainly by climatologists and increasingly sociologists, as the management of the anthropomorphic contribution to global CO_2 levels becomes ever more important. A fundamental aspect of these studies is the acquisition of data over decadal to century timescales and use of this data in constructing more sophisticated models of global climate (GCMs) that lead to improving our understanding of the main climate drivers and in predicting the future impacts due to global warming. Whereas these approaches allow the fundamental drivers and amplifiers of climate change to be identified their combined effects are still not fully understood. The primary forcing mechanisms of climate change are orbital controls on solar insolation, but the secondary forcing feedback mechanisms, such as the levels of greenhouse gasses, are internal to the Earth and of a geological nature because natural controls on atmospheric gases such as CO_2 include rock weathering and Earth outgassing, as well as the storage of carbon over various times scales.

A fundamental context to understanding climate change is the past climate record, and as our methodologies for deciphering this improve, there is an increasing level of knowledge of past climates that extends back into the Precambrian. The methodologies used to determine the climates are mainly of a geological/geochemical/geophysical nature. For the Precambrian Period, orders of accuracy are hundreds of millions of years and for most of the Phanerozoic they are ten’s of million of years. For the Tertiary, estimates of climate change are of the order of hundred’s of thousands of years and our knowledge of the Quaternary has advanced to the point where we can plot the locus of glacial and inter-glacial events with accuracies of decades. There is no doubt that based on this knowledge we are in uncharted territory. Thirty years ago we believed that we were heading into a new glacial period. When we consider the advances in scientific understanding of climate change made over the intervening period, it is not surprising. The new database, for the past 400 ka, acquired from ice-cores demonstrates the unanticipated perturbations due to the anthropogenic impact of unconstrained burning of fossil fuels, in association with land use changes potentially going back thousands if not tens of thousands of years (Figure 19). The result is a temperature rise not experienced for hundreds of thousands of years if not longer. It is here that the geological context begins to assume increasing importance, and the whole-earth study approach is most appropriate as the processes involved are intimately associated.

The Earth system comprises the solid Earth and the land surface, the hydrosphere (oceans, rivers & lakes), the atmosphere, the cryosphere (sea-ice, glaciers and the ice caps) and the biosphere – both terrestrial and marine. Its components interact over an enormous range of scales in both space and time. They exhibit a range of phenomena, including the formation and movement of continents, the opening and closing of ocean basins, the formation and erosion of mountain ranges, the waxing and waning of massive ice-sheets, the inception and evolution of life and climate change on all time

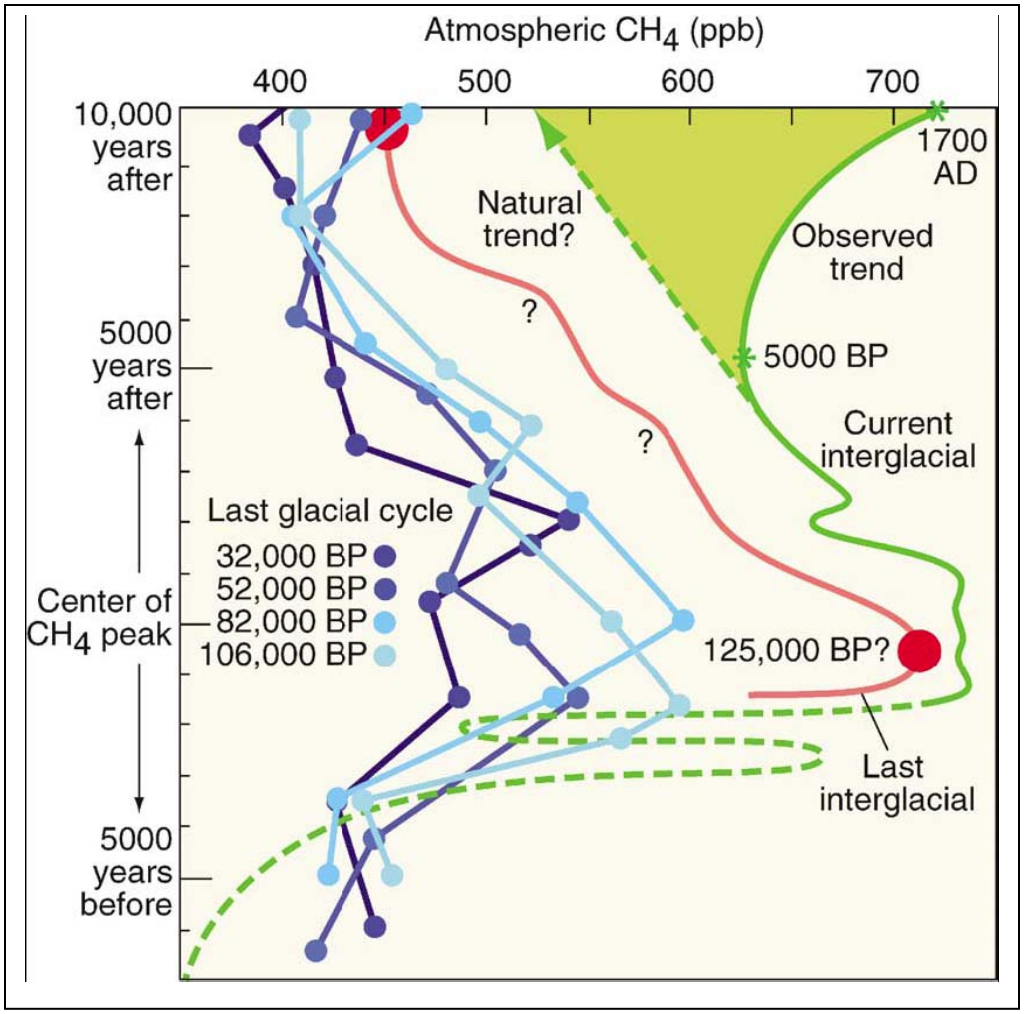


Figure 19. Atmospheric methane levels during the late Quaternary. Following the most recent natural (monsoon-driven) peak in atmospheric methane (far right), the level of atmospheric CH_4 initially followed a downward trend similar to previous peaks that had been driven by the same kind of orbital forcing (left), but methane concentrations after 5000 cal BP began a slow rise unprecedented in the earlier record. Dashed green line shows the hypothesized projection of the natural trend through recent centuries (From Ruddiman and Thomson, 2001).

The ‘present is the key to the past’ underpins geological philosophy, yet recent research shows that late in the Neoproterozoic the Earth experienced climates during ‘snowball’ Earth with ranges of temperature of over 100°C, never again repeated over the 500 million years of the Phanerozoic. This may prompt a review of what climate conditions await in the future. Previously unforeseen changes may lie ahead. One outstanding aspect of the study of ‘Snowball’ Earth is the non-steady state changes from cold to warm climate conditions that occurred rapidly. Another is that so far back in the past over 500 million years ago, we can now identify them with our sophisticated technologies. Rapidity of climate change is a characteristic of the Quaternary, during which, over tens to hundreds of thousands of years, not only does climate change but it does so with a rapidity previously unsuspected, and is taking place over human time-sales of tens to hundreds of years. It is likely that climate in the Precambrian operated as rapidly, it is just that at present we cannot measure it.

The contribution from Earth Science in identifying these past changes has been fundamental and has had a direct bearing on the understanding of climate change that is of immediate application. Traditionally studied geological concepts have important climate controls. A fundamental driver of climate change over geological time scales is the variation in atmospheric CO_2 that is regulated over million year time sales by geological processes, pre-eminent of which is silicate weathering through the Urey cycle, and Earth outgassing. The weathering cycle is controlled by tectonics with mountain building and decay primarily driven by plate tectonics, a recent study of the Andes suggests a circular cycle of tectonics driving climate that in turn drives tectonics. The recycling of material through subduction zones is also related not only to the location of these zones but to the type of sediment being subducted which, in turn, is dependent upon the depth of the ocean basins and their configuration, the latitudinal location of sedimentation, the rate of seafloor spreading and the depth of the CCD. Mantle outgassing is dependent upon plate tectonics driving movement of the crust, subduction and plume activity. The burial of carbon and its subsequent metamorphism at subduction zones is a further process contributing to the control of atmospheric CO_2 levels and climate impact. Without a comprehensive assessment of all the drivers and amplifiers of climate, the system will not be understood.

There are several other major insights that may be gained from this study. The major change on Earth at the end of the Precambrian delineates a major change in how climate processes take place: from non-linear to steady state, and from a cyclable carbon budget that was variable in proto-Earth to a later Phanerozoic carbon budget that operates as a closed system. With regard to the latter this was undoubtedly due to the combined influences of the physical (degassing) and biological evolution of the Earth because during this period the biosphere was undergoing fundamental evolutionary changes. Whether the late Neoproterozoic ‘Snowball’ Earth was a catalyst for the great biological take-off of the early Phanerozoic is a still controversial, but attractive, theory. Across the Precambrian/Phanerozoic boundary there is a major change in the biosphere fundamental to the evolution of the global carbon flux that impacts upon climate change, followed in the later Palaeozoic by the rise of vascular plants at approximately 300 Myr ago. The changes had major effects on carbon dioxide and oxygen production rates that consequentially impacted upon weathering.

Notwithstanding the actual drivers contributing directly to carbon cycling and climate change, the process of scientific progress is at least as important and reflects the changes in geological science over the past few decades. Here we refer to the human timescale and the development of ideas that eventually led to the ‘Snowball’ Earth theory. Originally postulated in the mid 1960’s the theory was based on putting together in a conceptual framework a series of apparently unrelated geological observations and climate models that, when compiled, provided a compelling case for a revolutionary new theory. It should be noted that the supporting science was not possible without technological progress going hand in hand with the development of these ideas.

Thus from observations and models compiled over hundreds of years, in fact since James Croll introduced the idea in the 17th century we now know that the main drivers of climate change are extraterrestrial and the main internal Earth control is the land/ocean/atmosphere system. Additionally, the internal Earth processes driving the atmospheric feedback mechanisms that result in global warming and cooling can be viewed as geological in nature. Thus geologists have ever increasingly contributed to research into climate and how it has changed over time scales longer than hundreds of years and how these changes have operated. The drivers of major non-linear changes in climate are more likely to be identified by examination of the long-term geological record rather than from the most recent past. Climate models require controls that can only be provided by observational and laboratory studies, mostly geologically based. Drivers and feedback mechanisms are increasingly recognised as complex and inter-related, not surprising considering their ultimate sources, both those extra-terrestrial and those within the Earth itself. Orbital controls operate over tens if not hundreds of thousands of years, at distances from source (the sun) of millions of miles. The intrinsic Earth controls operate over similar, if not longer, timescales up to hundreds of million of years, with exceptionally small atmospheric and oceanic gas concentrations measured in parts per million (eg. CO_2) and parts per billion (eg. CH_4). In this context, it cannot be surprising that there are time lags of hundreds of thousands of years.

Despite advances in our current state of knowledge, there are still many uncertainties and controversies about the relative importance of sources and sinks of carbon within the carbon cycle (Figure 20). The cycle is complex with contributions from chemical, physical and biological processes. Review of the processes in a geological perspective provides some basis for demonstrating the contribution that an ‘Earth System’ approach can make to developing our understanding of the relationships between climate change and the carbon cycle in both a short and long-term perspective.

The terrestrial carbon cycle is relatively well known. Processes, particularly forest sinks, are well-established as they are generally the most accessible to study and monitor, although recent studies in the Amazon suggest that they are not as well known as we would like to believe. They have received most attention from researchers in the field of carbon dynamics. The advantage of terrestrial sinks is that they are politically convenient under the Kyoto Protocol in the context of reducing anthropogenic CO_2 emissions and the processes of short term CO_2 sequestration as understood. Most important are the relationships between weathering and atmospheric CO_2, and the impact of fossil fuel burning and land-use changes, still not fully understood. Longer term flux between soils and the atmosphere requires further study.

The atmosphere-deep ocean exchange of CO_2 is also well researched. However, the transport of CO_2 within the ocean through thermohaline circulation, a major driver of climate change, operating over short timescales, is not well understood. THC may not only be direct control on global CO_2 levels it may also indirectly influence the catastrophic release of CH_4 into the atmosphere. Carbon controls by the THC are also intimately associated with biomass production by phytoplankton that in turn are nutrient limited through provision of iron in aeolian dust, production and transport of which is itself dependent upon local climate conditions. Additionally, THC is dependent upon ocean basin morphology that is determined by internal Earth, plume dependent, heat fluxes (if plumes exist). Recent research suggests that plume fluxes controlling the ocean basin morphology operate over shorter timescales than previously thought.

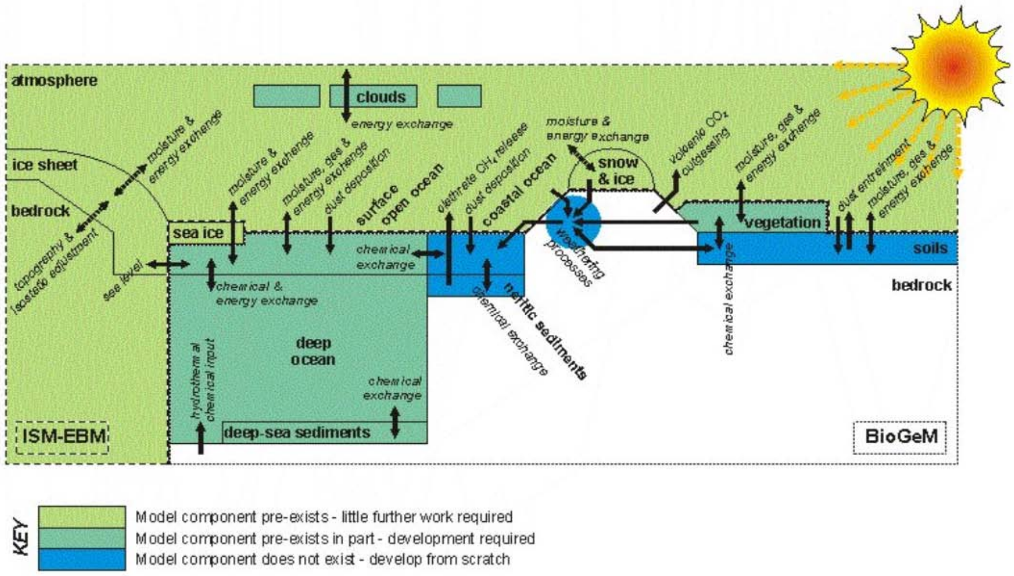


Figure 20. Land/Ocean/Atmosphere model GENIE illustrating the levels of understanding of fluxes (Courtesy of A. Ridgwell, from John Shepherd, QUEST Meeting).

The reef carbonate flux is well known, but although reefs form a major sink for carbon they do not form a major sink of CO_2. Sealevel, and hence climate, control carbonate deposition. At times of low sealevel carbon is mainly stored as reef carbonate, when sea level is high carbonate is deposited in the deep ocean basins. The evidence that coral reefs worldwide are in imminent danger of destruction will have a major, and unknown impact on global carbon flux. Geological evidence, supported by our understanding of climate processes, shows that periods of high sealevel correlate with high temperatures. In the light of the foregoing, are we witnessing a precursor to major sea level change?

The carbon flux across continental shelves requires further study. The shelves represent a major link between the land and the deep ocean. On present evidence some shelves are carbon sinks whereas others are carbon sources. The complex interrelationship between riverine supply (increasingly modified by irrigation and flood protection schemes) of organic carbon to the ocean, the absorption of this in various volumes in the ocean and over varying timescales in continental shelf waters and in sediments, requires further elucidation.

The role of gas hydrate in global carbon flux and abrupt climate change is controversial, as is whether it is a major catalyst of global climate change. Carbon budget studies suggest that it may not be the major climate driver that some authors believe, although it probably has a contributory effect. Further study is required to identify its impact.

The steep rise in levels of atmospheric CO_2 taking place over the past 200 years, since the Industrial Revolution, is proven. The rise is attributable to anthropogenic causes, mainly due to the burning of fossil fuels with a subsidiary component from land use changes, that can be traced back over thousands of years. The latter effects may have been taking place since the rise of early agriculture 5000 years ago. The effects on global warming due to the increase in the atmosphere of greenhouse gases including CO_2 is established to all but the most hardened opponents of the idea. The natural carbon cycle is a closed system and the anthropogenic impacts in the long-term context of continually rising levels of atmospheric CO_2 are not yet understood.

The simple answer is to cut anthropogenic CO_2 emissions, with the Kyoto Protocol formulated to this end. However, cuts have to be made immediately to be effective otherwise warming will accelerate beyond man's control. . Over the timescale of hundreds of years, geological evidence proves that there are abrupt if not non-linear changes in climate that cannot yet be predicted. These may be addressed and better understood through study of longer-term climate processes based on our geological knowledge.

10 RECOMMENDATIONS FOR FUTURE STUDY

Resulting from this review, which is by no means exhaustive, there is an obvious role for geology in the investigation of the carbon cycle and in addressing issues related to the longer-term aspects of the global carbon flux. With the continued rise of CO_2 levels and the unknown impact of these, the previous history of carbon fluxes will provide some insight into what we can anticipate, although there will still be surprises in store. In the context of a closed natural system, now increasingly stressed by anthropogenic CO_2 emissions, there is the likelihood that the high rate of increase of anthropogenic CO_2 will affect how natural carbon sinks respond and probably change. These changes may well be rapid and/or non-linear. The Earth System approach is obviously the most appropriate way forward and BGS as an integrated, well equipped, geological organisation, addressing most aspects of geological research, it is an appropriate mechanism through which the research could be undertaken. Notwithstanding, contributions to carbon/climate change science should initially be identified on the basis of our present programme as well as our expertise and experience that potentially could be applied.

It should be noted that study of CO_2 sequestration is the responsibility of the Sustainable Energy and Geophysical Surveys Programme, thus artificial sequestration of CO_2 is not addressed here.

10.1 LAND – OCEAN FLUXES; THE CONTINANTAL SHELF CARBON BUDGET

Recent studies show that continental margins are complicated systems with highly active physical and biogeochemical processes that affect the global carbon cycle. Carbon fluxes between the land and the deep ocean across the margins are poorly understood (Figure 19). They are vulnerable to perturbations from human activities, as projects such as LOICZ show. By comparison with the deep ocean, continental margin carbon fluxes are so heterogeneous that they are not adequately represented by the coarsely-gridded maps of global ocean carbon fluxes that have been compiled. Currently available data and information from as many different margins as possible require synthesizing to obtain a global estimate of the contribution of continental margins and seas to CO_2 sequestration, and horizontal fluxes of carbon, nitrogen and phosphorus across the ocean-continental margin boundary.

Using the North Sea as an example, a conceptual framework is required to integrate continental margin carbon, nitrogen and phosphorus fluxes and to assess anthropogenic influence on the fluxes. Carbon, nitrogen and phosphorus fluxes across the margin are required. The observational and laboratory data needs to be utilized in modeling studies. Is there a short-term role for enhanced carbon storage on shelves? Estimates of fluvial input to the ocean via the shelf are based on pre-industrial levels. This input has changed over the past 200 years as land and river management systems have changed the riverine flux to the sea, and thereby decreased the organic content carried. By contrast, in tropical areas, deforestation has led to increased rates of erosion and an increase in sediment input to the sea. Carbon flux to the sea will have changed due to this.

Regional studies demonstrate that in temperate regions continental shelves in areas of coastal upwelling may remain weak net CO_2 sources. But overall continental margins as a whole are a weak CO_2 sink with approximately three quarters of the carbon buried in marine sediments being buried on continental shelves. However, this situation may be different in tropical regions where shelves may be net atmospheric sources of carbon.

An additional part of the study could be the investigation of coastal wetland evolution. Methane release from wetlands during the Holocene may well have been a major driver of climate warming after the last glaciation. Recent research from Sweden shows that as a result of global warming the subarctic permafrost layer is thawing and methane is being released (Christensen et al., 2004). Between 1970 and 2000 methane emissions have increased between 20 and 60%. The annual mean temperature at the site of the study is –0.7°C, but recently this has increased to above 0°C.

In parts of Britain, peat bogs were once a common occurrence, expanding in the mid-Holocene as the climate ameliorated and with large areas present until the late Medieval times. Their loss, mainly due to artificial drainage and reclamation of land for agriculture, and past burning of peat for fuel, has removed a significant natural store of carbon from the landscape. The accumulation of organic matter in acidic bog conditions effectively prevents microbial degradation of the carbon-rich material. The latest climate change predictions anticipate sea level to rise by up to 85 cm around the coast of Britain by 2080, which could lead to the decision to abandon some agricultural land to marine flooding and allow natural wetland regeneration. The Fens of eastern England would be an ideal area to study how wetland regeneration would impact on the local carbon cycle, particularly as the Wash will be the first case example in the Estuary Report Series produced by BGS. Evidence from the study of peat horizons in Holocene cores (thickness, TOC values, and lateral extent of peat beds) could be used to estimate how much carbon could accumulate and be stored under reducing lake waters if organic matter was allowed to accumulate on newly flooded agricultural land. Estimates of the rate of carbon accumulation in peat beds could be compared to estimates for the amount of carbon fixed in an equivalent area of woodland over comparable time scales to assess the relative effectiveness of these terrestrial sinks. The results would have relevance to wetland regeneration in temperate environments worldwide.

10.2 LIGNINS AS PALAEOCLIMATE INDICATORS

BGS, in collaboration with the Fuel and Energy Centre at the Nottingham University, has been developing a method to determine palaeotemperatures based on oxygen isotopic analysis of lignins. The oxygen isotopes are effectively recording the state of evapotranspiration at the time of tree growth, which can be used as a proxy for palaeotemperature. The method used is called catalytic hydropyrolysis. The study is currently using the techniques developed for analysis of oak fragments to other wood types. Due to its nearly random but repetitive structure that offers some protection to bacterial attack, lignin is commonly preserved within sediments. The method is a novel approach in that it generates data on climate change from terrestrial sites and provides an alternative method to the analysis of ice cores for determining past climates.

The present research will be developed and applied to climate changes that are already well documented, such as the 8200 B.P. cooling event, or the Little Ice Age, to establish how well these are recorded by terrestrial vegetation. The study of oak tree stumps from peat bogs in Ireland and at other European sites would provide the bulk of the material for analysis. Calibration of the method and corroboration of existing knowledge of climate change events would allow the technique to be applied with confidence to other periods within the Holocene and possibly the Quaternary, although preservation of the organic material could be the limiting factor with the method. Funding for the research will be sought from the NERC QUEST programme.

Data from terrestrial climate records will be site-specific, but could also contribute towards a picture of regional climate evolution providing sufficient organic material of differing ages could be analysed from a variety of sites. Site-specific terrestrial palaeoclimate data could reveal much about the speed of climate change. There is the tantalising prospect of finding a tree trunk that was growing during a period of rapid climate change and which could be analysed by the lignin isotopic method.

10.3 HYDRATE INSTABILITY AND RAPID CLIMATE CHANGE

There are two main aspects to this research topic.

10.3.1 Laboratory based studies

A laboratory study to model the pressure-temperature stability field of hydrates within representative host substrates could help to predict their natural stability. Although hydrate occurrences in the marine environment are likely to remain stable under a rising sea level, global warming will be a threat to their stability in arctic/periglacial environments. The permafrost in Arctic regions, which hosts substantial amounts of hydrates, is very susceptible to even slight global warming.

10.3.2 Continental margin instability due to climate change

On the northwest European shelf from north Norway to southern Britain there are numerous submarine failures at all scales from the giant Storegga Slide off Norway to the tiny Afen slide off of the Shetlands. Except for the two examples noted the dating of these events is poorly constrained: Afen is 2 Myr BP and Storegga is 8 Myr BP. The most recent failure of the Storegga slide resulted in a tsunami wave with run-ups of 10-15m along the east coast of Scotland. Thus failure of other slides may present a similar tsunami hazard.

In the context of the ‘Clathrate gun hypothesis’ investigation of the ages of the submarine slides would provide evidence on whether there was a major series of failures coinciding with a massive release of hydrate as proposed by Kennet *et al*. (2002).

10.6 THE DEEP OCEAN BASIN

Controls on carbon in the deep ocean are poorly understood. They depend not only on the physical controls through THC, but also are dependent on biological productivity from phytoplankton photosynthesis. Biomass production is iron limited and thus sources, mainly terrestrial, of iron are a further control. THC is climate dependent, but also deep-water cold current flows are controlled by the morphology of ocean basins. Ocean basin morphology is the product of interior Earth temperature flux as well as plate tectonics. THC is proved to be unstable and thereby a potential cause of abrupt climate change.

Studies on the carbon fluxes and dependent climate changes in ocean basins may be conducted by investigation of sediments deposited in the deep ocean. The results can then be used as controls for models. The BGS expertise off the NW coast of Europe and in the North Atlantic could be utilised to investigate changes over the past hundreds of thousands of years. There is scope for sedimentological study associated with studies on sediment geochemistry including isotope proxies.

10.7 TECTONICS AND CLIMATE CHANGE

The BGS has great international and national expertise. This could be utilised now and in the future, in the organisation of its programme, focussed on invetsigating the impact of tectonics on climate through multidisciplinary programmes.

10.8 CONTROLS ON MODELLING

Carbon research is intrinsically important, but it does provide controls on modelling studies. The data and results from research projects can be utilised in improving carbon and climate models.

10.9 METHODOLOGIES

Thematic studies are identified above, but there are numerous methodologies that can be applied to carbon flux study that BGS has expertise in.

10.8.1 Isotopes in climate change

The NERC Isotope Geosciences Laboratory has expertise in isotopes that are applicable to carbon and climate research.

10.8.2 Ocean Drilling

The Ocean Drilling Programme and its predecessors have acquired much of the deep ocean sediment data upon which much of our understanding of carbon fluxes and climate change is based. BGS has never been seriously involved with this. The new IODP programme will continue to address climate change.

10.8.3 Collaboration with other NERC institutes and UK Universities

BAS, CEH and SOC have carbon and climate change projects. Mark Williams just left BGS to join BAS to work on a climate change project. There are numerous University Departments studying climate Change. There is also climate Centres of Excellence, such as the Tyndall Centre, leading to numerous opportunities for collaboration.

Appendix 1

KYOTO PROTOCOL

(From Royal Society Report: The role of land carbon sinks in mitigating global climate change, Policy Document 10/01. July 2001)

Overview of the Framework Convention on Climate Change and the Kyoto Protocol

The *United Nations Framework Convention on Climate Change* (UNFCCC) was opened for signatures in 1992. The UNFCCC aims to stabilise GHGs at a level that avoids dangerous anthropogenic interference with the climate system. With respect to land carbon sinks, signatories (Parties to the Convention) are called upon to promote programmes that mitigate climate change by addressing sources of anthropogenic emissions greenhouse gases and sinks of GHGs. To date 186 countries have signed the UNFCCC. The *Kyoto Protocol* was adopted in 1997 at the third Conference of the Parties (COP3) to the UNFCCC. The Protocol aims to reduce emissions from developed countries (listed in Annex 1 of the Protocol and therefore referred to as Annex 1 countries) by at least 5% below 1990 levels in the commitment period of 2008-2012

(Article 3.1 of the Protocol). To this end individual countries or groups of countries (such as the European Union) have been assigned emissions targets. The EU's target is a reduction of 8% below 1990 levels. Some countries have been permitted to increase their emissions to allow economic growth.

Articles 3.3 and 3.4 of the Kyoto Protocol make provision for net changes in GHG emissions by sources and removal by land carbon sinks resulting from direct human-induced land use change and forestry activities to be considered in relation to a country's reduction target. Under Article 3.3 this is limited to afforestation, reforestation and deforestation since 1990. Article 3.4 provides the potential for additional human-induced activities (agricultural, land use change and forestry) undertaken since 1990 to be considered but allows subsequent COPs to decide exactly how these should be incorporated into a country's emissions targets. Under both Articles, these direct human-induced activities must be reported in a transparent and verifiable manner.

Countries may also meet their emissions targets through other flexibility mechanisms such as Joint Implementation (JI) and the Clean Development Mechanism (CDM).

Under JI (Article 6), emissions reduction units can be exchanged between Annex 1 (developed countries). These units can be gained from projects, including those aimed at enhancing land carbon sinks, providing it can be demonstrated that the mitigation is additional to any that would otherwise occur. Similarly, the CDM (Article 12) allows Annex 1 countries to gain credit for emission reduction projects in developing countries (know as non- Annex 1 countries). Such projects must demonstrate real, measurable and long-term benefits related to the mitigation of climate change and as with the JI they must show that the mitigation is additional to any that would otherwise occur. Projects that aim to enhance the land carbon sink are not specifically mentioned under Article 12.

Finally, the Kyoto Protocol also commits Annex 1 countries to promote sustainable development in meeting their emissions targets (Article 2). Specifically they are directed to take measures to protect and enhance sinks of GHGs through sustainable agriculture and forestry practices. The links to the full text of both the UNFCCC and the Kyoto Protocol and lists of signatories can be found at http://www.unfccc.int/resource/index.html. 1.2 Issues raised by the inclusion of land carbon sinks in the Kyoto Protocol This section outlines the requirements that are implicit in the inclusion of land carbon sinks in the Kyoto Protocol.

The scientific methods that must be used to meet these requirements, and their associated uncertainties are evaluated in Section 5.

Quantification: In order to become binding commitments, which can be used to offset fossil fuel emission reductions, land carbon sinks need to be quantified with an acceptable degree of accuracy. Methods are needed to quantify (i) areas of land where changes in land use have been implemented, and (ii) the change in amount of carbon stored per unit area (carbon density) over specified periods of time.

Verification: In order to obtain numeric credits for any carbon storage scheme, it is fundamental that a third party is able to verify the claim. In order to verify land areas, the geographic location of land areas needs to be specified, which can be achieved using remote sensing techniques. Carbon density verification requires ground sampling. There can be problems of verifying the historical status; for instance, of soil carbon before afforestation, or the carbon stock before deforestation (i.e. the baseline). In some countries, existing forest inventory procedures could be extended to include repeat soil sampling for soil organic carbon with established quality control and assurance procedures (QCQA). Procedures for sampling carbon within other land uses can be also defined47. Certifying that the methods include QCQA within specified standards may be sufficient in some cases. However, difficult decisions need to be made by the Conference of Parties on what types of certification and verification is required, when it is done and by whom.

Annex 1 Land carbon sinks and the international climate change process

Additionality: It was agreed at Kyoto that offsets could be claimed only for land carbon sinks that are directly human induced after 1990 and would not occur anyway, such as new afforestation and changes in tillage practices, and not for sinks created by changes in the atmosphere and historic land use. Negotiators wish to know that the action taken will add to any carbon sequestration that would occur anyway. Thus, it is necessary to predict the changes in carbon density that would occur ‘for free’, as a result of historic land use or changes in the atmosphere.

Leakage: Leakage occurs when activities to increase carbon storage in some places inadvertently promote activities elsewhere which either decrease carbon storage (negative leakage) or increase carbon storage (positive leakage). Thus, tree planting or regeneration for carbon storage may provide timber which undermines incentives for forestry elsewhere (negative), or lessens the need to destroy or log native forests (positive), or provides an example which others follow (positive). Basically, leakage is caused by a shift in demand for, or supply of, a commodity that then displaces an activity on to other land. The three most important commodities are agricultural products, fuelwood and timber – all of which require land. Locally, leakage is greatest where the demand for the product is inelastic, for example where carbon storage takes land required for staple food crops in populous areas49. The leakage problem is complex and can greatly magnify uncertainties in calculating credits or debits. There are two approaches to the leakage problem. First, more extensive carbon accounting lessens the problem by capturing carbon losses and gains within a region or nation. Any enlargement of a forestry project to include agricultural and fuelwood provision within a region will lessen ('internalise') the problem. Second, where leakage is anticipated, the options are (i) to reduce the credits claimed for a carbon storage activity, or take additional carbon storage measures to compensate, or (ii) to take action outside the boundary of the project to lessen any anticipated shift in level of demand and supply of agricultural products, fuelwood or timber.

Permanence: It is never possible to guarantee the permanence of carbon stored in forests and soils. Losses can occur from fire, insect outbreaks, changes in socio-economic and political circumstances and as a result of climate change. Methods need to be agreed to assess the value of land carbon sinks which evaluate these risks. It would be unwise to store an amount of carbon on land which would pose an unacceptable risk if it were released to the atmosphere at a later date. As outlined in Section 6, climate change will potentially have an impact on the entire land carbon sink. Any release of greenhouse gases from new land carbon sinks created as a result of the Kyoto Protocol e.g. from so called 'Kyoto Forests' will be insignificant in comparison.

Trace greenhouse gases: Land-use change and management practices designed to increase carbon sequestration may either positively or negatively impact on emissions of CH4 and N2O. As outlined in Section 5, the calculation of the full trace gas inventories of even the most simple land-use transition is complex and the science in this area is still poorly understood.

References can be found in Section 8.

Appendix 2

CARBON PROCESSES

1 TERRESTRIAL PROCESSES

Higher plants acquire CO_2 by diffusion through their leaves and, through photosynthesis, use the CO_2 and water to build carbohydrate, a process known as gross primary production (GPP). Half of GPP is used in plant growth and incorporated into new plant tissue such as leaves, roots and wood, and half converted back to atmospheric CO_2 by autotrophic respiration. Annual plant growth is the difference between photosynthesis and respiration, termed net primary production (NPP) estimated globally at 60GtC/yr.

Eventually, virtually all carbon fixed in NPP is returned to the atmospheric CO_2 pool through two processes: heterotrophic respiration (Rh) by decomposers, such as bacteria and fungi, and herbivores and by combustion in natural or human fires. The dead biomass enters the detritus and soil organic matter pools where it is respired at a rate dependent upon its composition and the local environment. There are several soil carbon pools with different residence/turnover times: detrital and microbial biomass have a short residence time of <10 years, modified soil organic carbon has a residence time of between 10 and 100 years and inert soil organic carbon is mainly resistant to further decomposition. The difference between NPP and Rh determines how much carbon is lost or gained by the ecosystem in the absence of other disturbances such as harvesting or fire; it is termed the net ecosystem production. With other carbon losses from harvesting/removals, fires, erosion and transport of dissolved or suspended carbon (DOC) by rivers to the ocean, what remains is the net biome production (NBP), this is the carbon accumulated by the terrestrial biosphere. In a steady-state ecosystem Rh and other carbon losses would equal NPP and NBP would be zero. However, in reality, human activities, natural disturbances and climate variability alter NPP and Rh, thereby causing transient changes in the terrestrial carbon pool. Thus practically NBP is never zero. When the rate of carbon input (NPP) changes Rh also changes in proportion: this results in a time lag between changes in NPP and changes in the corresponding carbon pools (which may be slow in responding). Step increases in NPP results in an initial increase in NBP followed by a decrease to zero over years to decades (averaged globally at 10-30 years) as the respiring pool catches up. A continuous increase in NPP results in a sustained increase in NBP as long as NPP increases and there are no compensating increases in mortality or disturbance.

At present the terrestrial system is acting as global sink for carbon, with likely sink mechanisms known but with relative contributions uncertain. Natural climate variability and disturbance regimes affect the NBP. Human impacts occur through changes in land use, and land management, as well as through indirect effects on climate, and fertilisation due to elevated CO_2 and deposition of nutrients. Primary mechanisms are as follows:

1.1 Land use and land management

This affects the amount of carbon in plant biomass and soils. Date for 1850 to 1990 as follows. Estimated land use emissions - 121GtC. Estimated net terrestrial flux to the atmosphere – 39GtC inferred from atmospheric increase of 144GtC with a release of 212Gtc from fossil fuel burning and a modelled ocean-atmosphere flux of –107GtC. The residual land-atmosphere flux (terrestrial sink) is –82GtC.

Forests: deforestation (with a 20% decrease in global forest area) accounts for 90% of emissions from land use change since 1850.

Savannas and grassland – fire and grazing: vulnerable to environment and management change. Increase in plant density has resulted in a carbon sink.

Peatlands/wetlands: a large reserve of carbon because of anaerobic soil conditions and (in northern areas) low temperatures that reduce decomposition and promote accumulation of organic matter. Total carbon stored in northern peatlands estimated at 455 GtC with current uptake of 0.07GtC/yr. Anaerobic decomposition releases methane with a global warming potential 23 times that of CO_2. The balance between CH_4 and CO_2 is poorly understood. Draining peatlands releases carbon.

Agricultural land: converting natural vegetation to farmland is a major source of CO_2. Conversely, use of high-yielding plants, fertilisers, irrigation, residue management and reduced tillage can increase carbon uptake.

Scenarios: For the period 2008-2012 there is an estimated deforestation flux of –0.2 to –0.58GtC/yr with a net release of 1.59 to 1.2 GgtC/yr. Net carbon storage potential from improved land use management amounts to a global land-atmosphere flux of approximately –1.3 GtC/yr in 2010 and –2.5GtC/yr in 2040 (not including wood products and bioenergy.

1.2 Effects of climate

Solar radiation, temperature and available water affect photosynthesis, plant respiration and decomposition, thus climate change can lead to changes in NEP. Results of global warming will be varied and depend on latitudinal and local climatic controls.

1.3 Effects of increasing atmospheric CO_2

Again the effects of increasing CO_2 are varied, involving direct effects of carbon assimilation and indirect effects such as those via water saving and interactions between carbon and nitrogen cycles.

2 OCEAN CARBON PROCESSES

There is an input of carbon to the ocean from both the atmosphere and the land. The total amount of carbon in the ocean is about 50 times that in the atmosphere. The total amount of carbon in the ocean is 38000 Gt.

2.1 Ocean-atmosphere exchange

Exchanged of CO_2 between the ocean and the atmosphere operates on a time-scale of several hundred years. Atmosphere-Land flux of CO_2 is 90GtC/yr. CO_2 dissolved in seawater takes three forms, the sum of which constitutes the total dissolved inorganic carbon (DIC): dissolved CO_2 (1%), bicarbonate ion HCO_3 (91%) and the carbonate ion CO_3 (8%). With an increase in atmospheric CO_2 there is an increase in dissolved CO_2 with most of the added CO_2 converting to HCO3. However, because CO2 reacts with ionic CO_3 to form ionic HCO_3, the reduction of CO_3 available to react with atmospheric CO_2 results in a reduced uptake of CO_2. Thus as levels of atmospheric CO_2 rise there is a decrease in ocean CO_2 uptake. Other factors affecting CO_2 uptake include seawater temperature, salinity and alkalinity. The latter is primarily controlled by $CaCO_3$ formation in shells and corals and dissolution.

Regional net natural transfers (as opposed superimposed anthropogenic uptake) of CO_2 are governed by ocean heating and cooling and biological production and respiration. Carbon is transferred within the ocean from sink to source regions via ocean circulation mechanisms and the sinking of carbon rich particles. CO_2 solubility is temperature dependent: with the greatest uptake in cooler waters, and with warming driving outgassing. Biological processes also drive fluxes.

2.2 Land-Ocean exchange

Organic and inorganic carbon also enters the ocean from rivers. The input comprises CO_2 from both natural and anthropogenic sources. The global natural input is about 0.8GtC/yr, with equal organic and inorganic inputs. Anthropogenic production (mainly organic carbon) is estimated at 0.1GtC/yr. Much of the organic carbon does not pass out beyond the coast and remains mainly in estuaries. The natural DIC transport via rivers is part of large-sale cycling between the open ocean and the land associated with the dissolution and precipitation of carbonate minerals.

2.3 Uptake of anthropogenic CO2

Dissolution in the ocean provides a large sink for anthropogenic CO_2. Unlike the land the processes of uptake are mainly physically and chemically controlled. Uptake of anthropogenic CO_2 is strongest in regions of ‘old’ ocean waters, exposed after long periods in the ocean interior. Re-equilibration of the older waters with the present atmosphere takes about a year, during which time CO_2 levels increase. Uptake of CO_2 is limited by the rate at which the older waters mix with the present atmosphere. Thus the rate of exposure of the older waters is critical in the process. In principle there is sufficient capacity to take 70-80% of anthropogenic CO_2. With the rate of mixing though this will take several hundred years. Chemical neutralisation of CO_2 through reaction with $CaCO_3$ in deep-ocean sediments has the potential to uptake another 9-15% of CO_2, reducing the airborne fraction of cumulative emissions by about a factor of 2. However, the response time of the deep ocean sediments is in the order of 5000 years.

2.4 Future changes in ocean CO_2 uptake

Physical and chemical processes
Buffering changes: as atmospheric CO_2 levels increase surface water uptake decreases. This is a significant impact.
Emissions rate: as the emission rate of CO_2 increases the ocean uptake rate decreases. This is because of the finite rate of exposure of 'older' ocean water at the ocean surface.
Warming: warming of the ocean surface would tend to drive CO_2 into the atmosphere.
Vertical mixing and stratification: models show that global warming would result in an increase in vertical stratification of the ocean. This would reduce the rate of mixing and therefore the rate of deep ocean uptake of CO_2 on the longer timescales. This may also cause a change(s) in the driving of the natural ocean cycle that are difficult to predict.

Biologically-linked processes
These are more speculative and more likely to take place over longer times, eg. glacial-interglacial periods. They have been listed as:

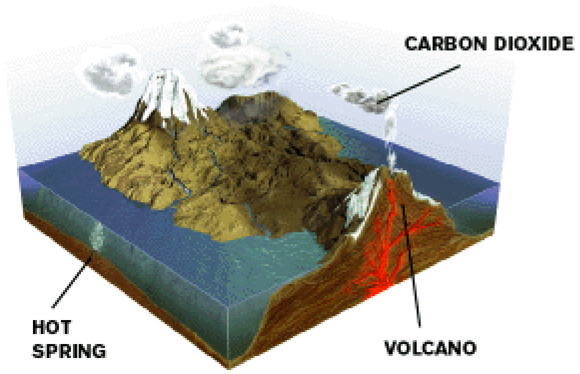
1) changes in surface nutrient utilisation: change carbon export and storage in the ocean interior,
2) changes in total ocean major nutrient content, such as N, P Fe and Si or changes in removal rates, and
3) changes in the elemental composition of biogenic material: such as changes in the distribution of calcareous versus siliceous planktonic organisms could affect CO_2 uptake. Precipitation of $CaCO_3$ removes CO_3 ion, decreasing surface water alkalinity and a reduction in the dissolution of atmospheric CO_2. As a direct result of increasing atmospheric and surface water pCO_2 levels, oceanic calcification will decrease over the next 100 years: a decrease in coral reef calcification rates of 17-35% relative to pre-industrial rates are possible.

Appendix 3

EVOLUTION OF SNOWBALL EARTH

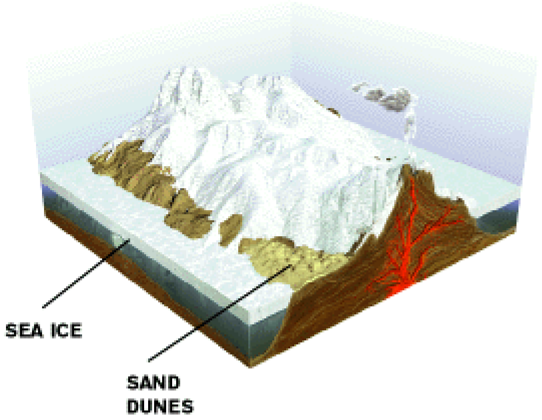
(From Scientific American, January 17th 2000)

Stage 1: Snowball Earth Prologue



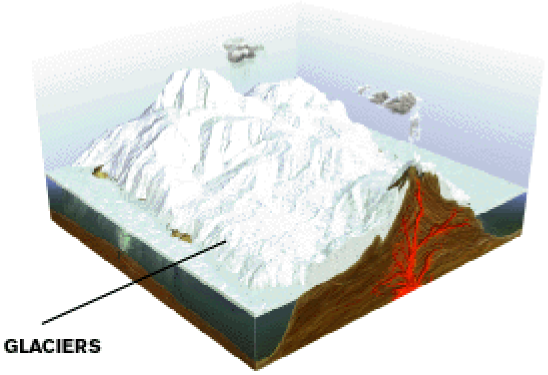
Breakup of a single landmass 770 million years ago leaves small continents scattered near the equator. Formerly landlocked areas are now closer to oceanic sources of moisture. Increased rainfall scrubs more heat-trapping carbon dioxide out of the air and erodes continental rocks more quickly. Consequently, global temperatures fall, and large ice packs form in the polar oceans. The white ice reflects more solar energy than does darker seawater, driving temperatures even lower. This feedback cycle triggers an unstoppable cooling effect that will engulf the planet in ice within a millennium

Stage 2: Snowball Earth at Its Coldest



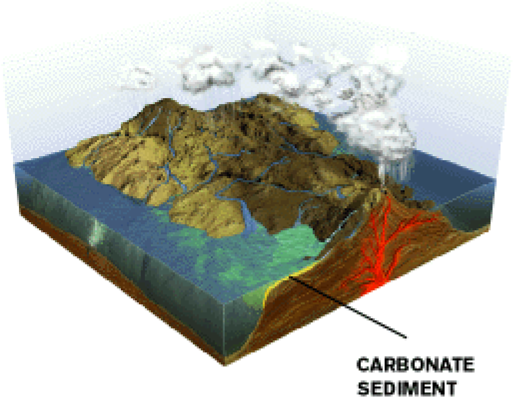
Average global temperatures plummet to -50 degrees Celsius shortly after the runaway freeze begins. The oceans ice over to an average depth of more than a kilometer, limited only by heat emanating slowly from the earth's interior. Most microscopic marine organisms die, but a few cling to life around volcanic hot springs. The cold, dry air arrests the growth of land glaciers, creating vast deserts of windblown sand. With no rainfall, carbon dioxide emitted from volcanoes is not removed from the atmosphere. As carbon dioxide accumulates, the planet warms and sea ice slowly thins.

Stage 3: Snowball as It Thaws



Concentrations of carbon dioxide in the atmosphere increase 1,000-fold as a result of some 10 million years of normal volcanic activity. The ongoing greenhouse warming effect pushes temperatures to the melting point at the equator. As the planet heats up, moisture from sea ice sublimating near the equator refreezes at higher elevations and feeds the growth of land glaciers. The open water that eventually forms in the tropics absorbs more solar energy and initiates a faster rise in global temperatures. In a matter of centuries, a brutally hot, wet world will supplant the deep freeze.

Stage 4: Hothouse Aftermath



As tropical oceans thaw, seawater evaporates and works along with carbon dioxide to produce even more intense greenhouse conditions. Surface temperatures soar to more than 50 degrees Celsius, driving an intense cycle of evaporation and rainfall. Torrents of carbonic acid rain erode the rock debris left in the wake of the retreating glaciers. Swollen rivers wash bicarbonate and other ions into the oceans, where they form carbonate sediment. New life-forms--engendered by prolonged genetic isolation and selective pressure--populate the world as global climate returns to normal.

Appendix 4

STATUS OF THE WORLD'S CARBONATE REEFS

1.1 STATUS OF CORAL REEFS IN REGIONS OF THE WORLD

Of approximately 600 000 Km^2 of coral reefs world-wide (0.17% of the Ocean surface), an estimated ^{c}10% have already degraded beyond recovery & 30% are thought to likely to decline significantly within the next 20 years.

Table 1: The State of the Worlds Coral Reefs

Regions of the World	**% reef destroyed pre 1998**	**% reef destroyed in 1998**	**% reef in critical stage, loss 2-10 years**	**% reef threatened loss 10-30 years**
Arabian region	2	33	6	6
Wider Indian Ocean	13	46	12	11
Australia & Papua New Guinea	1	3	3	6
Southeast & East Asia	16	18	24	30
Wider Pacific Ocean	4	5	9	14
Caribbean Atlantic	21	1	11	22
Status 2000 Global*	**11**	**16**	**14**	**18**

**Mean values adjusted for the proportional area in each region of the global total of coral reefs (Wilkinson C, 2000).*

Assessments to late 2000 are that 27% of the world's reefs have been effectively lost, with the largest single cause being the massive climate-related coral bleaching event of 1998. This destroyed about 16% of the coral reefs of the world in only 9 months during the largest El Niño and La Niña climate changes ever recorded. While there is a good chance that many of the 16% of damaged reefs will recover slowly, it is also estimated that half of these reefs will never adequately recover. These will add to the 11% of the world's reefs already lost due to human impacts such as sediment and nutrient pollution, over-exploitation and mining of sand and rock and development on, and 'reclamation' of, coral reefs (Wilkinson C, 2000). Those at greatest risk are South & South East Asia, East Africa & Caribbean reef ecosystems (Jameson *et al.* 1995). (See Table 1)

1.2 ARABIAN REGION:

Overall the reefs of the Middle East are generally in good shape. At present there is a lack of human impact directly from coastal towns, and a lack of river & rain input lowers the influences of natural sedimentation. Development of oil-related industrial centres and tourist ports might pose a future threat. Only a few natural disturbances affect the reefs, mainly cold weather fronts and extremely low tides (Jameson *et al.* 1995). The reefs in the Red Sea continue to be healthy, with the major threats coming from tourism, oil industry developments and shipping (Wilkinson, 2000).

However, the reefs in the Arabian/Persian Gulf were virtually obliterated by severe coral bleaching in 1996 and 1998. In the Arabian Gulf coral reefs occur mainly as patch reefs with fringing reefs found around the offshore islands. Oil, domestic and urban pollution, sedimentation and dredging form the main anthropogenic threats. Fishing is intensive in some areas and anchor damage is a problem in several locations (Jameson *et al.* 1995).

The *Gulf of Aqaba* represents the northern most limits for coral reefs in the Indian Ocean region and there are serious threats to water quality around this area due to pollution from port facilities. Fine sand is imported for the beaches and sedimentation now poses a large threat to the coral reef ecosystem along with other anthropogenic influences such as sewage pollution (eutrification) fishing and diving (kicking, trampling and holding of reef components) (Jameson *et al.* 1995). Reefs near *Yemen* and *Oman* are under constant threat from oil pollution, although human stresses in these areas are minimal because coastal populations are relatively small.

1.3 SOUTH ASIA:

In the wider Indian Ocean, 59% of the reefs are lost, however for the remote reefs that are not affected by human pressures there is a reasonable chance of recovery. Most reefs were severely damaged during the extreme climate events of 1998 and some were totally devastated. Reefs on the *Maldives, Sri Lanka* and parts of western *India* lost much of their coral cover, and these losses have added to major anthropogenic damage from coral mining, over-fishing and pollution (Wilkinson C, 2000).

Coral reefs of the *Maldive-Chagos* region ridge are one of the areas with the lowest human influences in the Western Indian Ocean, therefore any changes are more likely to be global rather than local influences. Comparison of the 1958, 1964, 1992 and 1999 Maldivian benthic surveys suggest that hard coral cover is at the lowest recorded having decreased from ~60% to 8%, with the branching corals being the most affected (McClanahan, 2000).

Countries such as *Thailand, India* and *Sri Lanka* suffer over-fishing, tourism, over-collecting and industrial growth. Coral mining is especially serious in the *Maldives* (used for road construction), *Sri Lanka* and *India* where tens of thousands of tons are removed annually. Most reefs in the Eastern Indian Ocean are found offshore. *Chagos* located in the central part of the Indian Ocean contains the best, most developed and greatest variety of reefs in the central Western Indian Ocean (Jameson *et al.* 1995).

1.4 EAST AFRICA AND SOUTHERN INDIAN OCEAN:

Sediment runoff, nutrient pollution and over-exploitation of reef resources continually damage reefs off continental *Africa* and *Madagascar*. During the El Nino climate disruption in 1998, severe bleaching hit *Comoros, Kenya, Seychelles* and *Tanzania* with overall live coral losses of 80 to 90%. Up to 70% of Kenya's corals were bleached and damaged, but there are signs of a potential for slow recovery. Reefs in the south were only slightly affected (Wilkinson, 2000).

The *Somali* Coast has few reefs due to seasonal upwelling of cold water and those that do occur are not well developed. Well-developed fringe and patch reefs occur off *Tanzania* and only are discontinuous when large rivers meet the sea. Small fringing reefs are common off the *Seychelles.* Trampling and destructive fishing practices by fishermen have degraded coral reefs in the region especially in *Tanzania, Kenya* and *Mauritius*. Over 250 tons of shells and coral were exported from *Tanzania* in 1974 and exploitive collection has now moved off the depleted areas to other more pristine islands. Over 500 000 tons of coral sand are excavated annually from *Mauritius* (Jameson *et al.* 1995).

1.5 SOUTHEAST AND EAST ASIA:

34 % of the reefs of Southeast and East Asia are damaged and although there is a reasonable chance for slow recovery on the remote reefs, there are dire predictions for the future of the remaining reefs of the area (Wilkinson, 2000).

The world's largest areas of coral reefs with the highest biodiversity are probably under the greatest threats from human activities, including an explosive growth in damaging fishing activities: blast fishing and the use of cyanide for the live reef fish trade. Coral bleaching caused major losses of corals in southern *Japan, Taiwan* and *Vietnam* and parts of the *Philippines* and *Indonesia*, with many losses of 30-60%, and some as high as 80-90% with localised extinctions of prominent corals. Co-management with local communities is emerging as the best method to implement sustainable management (Wilkinson, 2000).

Reefs off *Brunei* are rich in species, as fishing pressures are low. Generally reefs are in good shape with some of the larger reef animals (e.g. turtles) have been exploited. Reefs of *Vietnam* have been damaged extensively by sedimentation as well as blast and cyanide fishing (Wilkinson *et al*. 1993)

Indonesia (81000 Km Coastline and 17000 islands) coral reefs are extensive and represent the most significant reef resource in South East Asia but the reef conditions vary. Off *Java* and *Sumatra* over-exploitation, sedimentation and organic pollution has caused reef damage. To the Far East and North reefs are in good shape. In Central *Indonesia* the reefs are damaged from the high occurrence of blast fishing, cyanide fishing and general over fishing/ collection – but if these are controlled the reefs may recover. Fishing and tourist opportunities are also affecting the reefs of *Palau Seribu.* The reefs of Western Indonesia are under greater influence of anthropogenic stresses and coastal water circulation, such that they have been classified as critical with more degradation the probable outcome as populations continue to grow along with more extensive clearing of forests. (Wilkinson *et al*. 1993)

Malaysian coral reefs suffer from organic and sediment pollution and over exploitation but not as much as the other regions. All reefs in the Peninsula Malaysia region are expected to decline significantly in the next 20 years as a result of sedimentation and water pollution (Jameson *et al.* 1995).

Coral cover near the *Philippines* is rapidly declining. The loss of 80% of the mangrove area and more than half the total forest area since 1920 has stressed reefs with sedimentation. Between 1966 and 1986 the productivity of coral reefs in the Philippines dropped by one third as the national population doubled (McAllister, 1988). The Philippines is the major exporter of coral for displays and aquariums despite being prohibited within the country and by the states where tourists import them.

The reefs of *Singapore* are being severely degraded by construction of port and oil processing facilities and other coastal development. Coral cover is high on the outer reefs and reduced (<50%) on the nearshore reefs. Heavy sedimentation loads limit coral distribution to <10 m depth. Coral collecting for the aquarium trade are also threats (Wilkinson *et al,* 1993).

Thailand's nearshore reefs are suffering form coastal development while offshore reefs have relatively high coral cover. Domestic and industrial pollution has almost totally destroyed the reefs of the northern *Gulf of Thailand*. Reefs off the western coast are in better shape with a total coral cover exceeding 50 %.

Recent reports however show that coral cover is declining by 20 % a year due to tourist-related coastal clearing and sewage pollution. Healthy reefs with over 75% cover can be found in the *Andaman Sea* off *Smilan* and *Surin* Islands. Off *Phuket* reefs are being stressed by over fishing, tourist activities and sewage.

Hong Kong has no true reefs but 49 species of coral do grow on hard bottom along the eastern and southern coasts (Jameson *et al.* 1995).

Japan, Taiwan and *China* reef ecosystems all suffer from tourist abuse, over fishing, sedimentation and explosive fishing. Off *Japan* coral bleaching has also affected some reefs

The reefs in the vicinity of Jakarta, a city of 9.5million are dead or destroyed as a result of a combination of the effects of eutrophication from untreated sewage, sedimentation, reduced light intensity, coral mining and physical destruction. Information on the condition of reefs in this vast region is highly variable. For areas such as Taiwan, the Philippines and Thailand greater emphasis has been put on surveys nearshore rather than off shore. For other areas, including Indonesia, scientists have examined fewer than 10% of the reefs. (Wilkinson *et al*. 1993)

1.6 AUSTRALIA AND PAPUA NEW GUINEA:

Australian reefs are generally in good condition and continue to be well managed, with low levels of human impacts. However, sediment and nutrient runoff from over-grazed rangelands and increasing fishing pressures are affecting the Great Barrier Reef. Coral bleaching was intense in early 1998, but only on inshore reefs. Crown-of-thorns starfish are again attacking the offshore reefs. Similarly most PNG reefs are in good condition, except for damage from excessive logging and exploitation on some nearshore reefs. Management capacity and commitment for management needs to be enhanced (Wilkinson, 2000).

Coral reefs near the coast are being affected by eutrophication, where over 85 % of the coastal catchment area is under agricultural development. (Bell and Tomascik, 1993) Coral communities of islands off New Zealand are not under much stress naturally or anthropogenically. The only potential threat is the growing problem of over fishing.

Australia's Great Barrier Reef has experienced bleaching for the past 20 years and severe bleaching occurred there in 1998. In 1998 bleaching affected over 1000Km of inshore coral reefs forming part of the Great Barrier Reef, in some cases 80% of inshore Corals were bleached (Henderson, 1998).

1.7 THE PACIFIC – MICRONESIA, MELANESIA AND POLYNESIA:

These vast coral reef areas mostly escaped coral bleaching mortality in 1998 with the exception of major losses in Palau, and significant bleaching coral losses in Fiji and the Solomon Islands in early 2000. Most of the reefs are in good to excellent condition, with some damage from development on the high islands and over-fishing around centres of population. Few countries are conserving their coral reefs by establishing marine protected areas, but traditional management of coral reef resources is still active and effective (Wilkinson, 2000).

Melanesian coral reef ecosystems are mostly in excellent condition although many are coming under increasing threat from soil erosion and the resulting sedimentation, along with sewage discharge, industrial pollution and over fishing. In the 840 islands that make up Fiji, natural disturbances affect the reefs (e.g. Earthquakes and tropical cyclones. Over fishing and over harvesting are degrading the reefs near population centres (Jameson *et al.* 1995).

In Micronesia, much of the poor reef development around the numerous different groups of islands is due to natural factors such as volcanoes, earthquakes and tropical cyclones. Over fishing, sewage and thermal discharges, soil erosion and construction also causes degradation to various different islands reef systems. Residual damage from nuclear testing has also impacted on some reefs (Jameson *et al.* 1995).

Heavy wave action, cyclones and earthquakes also disturb the coral reef growth of Polynesia (for example the reefs of Hawaii) and land clearing, agricultural development, dredging over fishing and tourism are some of the human factors which effect the reef. The volcanic islands of Western Samoa are surrounded by fringing reefs however growth is also interrupted by lava flow. Results of recent surveys show that reefs are in generally in poor condition except for those off Olosega Island and Rose Atoll (Jameson *et al.* 1995).

Extended disruption by El Nino of Pacific currents has raised sea temperatures in the area of the Galapagos Islands by 5^{o}C in 1998 and widespread bleaching has been observed (Henderson, 1998).

Overall the condition of the reefs in the Pacific was rated to be about 70% excellent to good and about 30% fair to poor. Approximately 50% of the reef stress impacts were judged to be natural, such as El Nino events and large storms, and the other 50% related to anthropogenic factors, although it is estimated that only 10% of Pacific reefs have been visited by scientists (Jameson *et al.* 1995).

1.8 THE AMERICAN CARIBBEAN:

The US Coral Reef Task Force has catalysed action in Puerto Rico and the U.S. Virgin Islands to overcome serious over-fishing and damage to coastal mangroves and seagrasses. There is greater urgency to conserve Florida reefs from pollution from massive agriculture and growing human populations wanting to enjoy coral reefs, and exploit key target species. There is an ambitious target of having 20% of reef resources managed as no-take reserves within the next few decades (Wilkinson, 2000).

Bermuda: fairly good shape but sedimentation due to the Bermuda Air terminal construction caused massive mortality, and since 1940 13 major ship groundings have destroyed around 1% of the outer reef (Cooke *et al*. 1993).

South Florida and Florida Keys: Freshwater management practices are having serious affects on coral reef health & coral recruitment. (Porter, 1995). Coral bleaching linked to unfavourable warm conditions during long-lasting Doldrums. Also major anthropogenic stresses since 1930's.

No obvious signs of decline in the reefs of atoll like Bermuda and the few reef capped prominences of north western Gulf of Mexico. Although there uncertainties as to the aerial extent of the changes, there are well-substantiated reports of local declines in coral populations in south east Florida, based on long-term monitoring of quadrats, where the reefs are heavily used for fishing diving and tourism. The extensive reefs rimming the vast archipelago of Bahama banks are poorly known.

1.9 CARIBBEAN AND WESTERN ATLANTIC ISLANDS:

Caribbean/Atlantic Region – 22% lost due mostly to previous human stresses, hurricanes, bleaching and coral diseases (Wilkinson, 2000).

Most islands have narrow coastal shelves with over-fishing and sediment and pollution impacting directly on the reefs e.g. Eastern Antilles, Jamaica, Haiti and the Dominican Republic. Exploitation and pollution are much less over the broad shelves e.g. Cuba, Bahamas, Turks and Caicos Islands. Tourist industries on Bermuda, Bonaire, the Cayman Islands and some of the Eastern Antilles are enhancing reef conservation by demanding healthy fish populations and providing alternative livelihoods. Coral cover has decreased on most islands because of coral diseases and pollution (e.g. on northern Jamaica, coral cover dropped from 52% in the 70s, to 3% in the early 90s, with some recent recovery to 10-15%. On St. Lucia cover dropped from 50% to 25% at 3m depth and from 35% to 17% at 10m). Capacity to conserve reef resources near rising populations is variable; some countries are implementing community-based, or tourism-funded, management and monitoring, whereas others need assistance (Wilkinson, 2000).

Rapid development over last 50 years therefore anthropogenic influences mostly threaten the reef system (diving, over collection of coral, fishing, blast fishing, trampling, anchor damage etc). Deforestation has led to erosion and increased soil runoff causing significant siltation of reefs. Hurricanes and prolonged algal blooms also causing wide spread damage (Jameson *et al.* 1995).

Destruction of the reefs by hurricanes and the loss of grazing sea urchins feeding on microalgae are believed to be principal causes of the declines at several sites, over fishing is a major factor in Jamaica and elsewhere. For some areas, runoff from the islands or from dredging are also considered to be contributory causes of reef decline.

1.10 SOUTH AND CENTRAL AMERICA

Reefs were seriously degraded during the 1980s and 90s by increased sediment and nutrient pollution on nearshore reefs from deforestation, poor agriculture and diversion of rivers, as well as repeated coral bleaching, coral diseases, and major hurricanes. Offshore reefs are increasingly over-exploited for fisheries, coral rock and sand, resulting in distinct declines of coral cover and fish populations (Wilkinson, 2000).

Deforestation has led to erosion and increased soil runoff causing significant siltation of reefs

Barbados: hurricane damage & loss of Macroalgae grazing Urchins

Costa Rica: sedimentation (agricultural related)

San Blas Islands: Coral Bleaching, loss of grazing Urchins, mining Pollution sedimentation and eutrophication (Ginsburg 1994)

Belize Coral Reef Complex- largest most varied luxuriant reefs in western Atlantic

The first serious coral-bleaching event in the Caribbean, thought to be the result of global warming and the El Nino event, occurred off the city of Belize and caused virtually all the Belize coral colonies to bleach and die. The record temperature of 31.5^{0}C recorded in Belize in 1998 and the subsequent months of raised heat levels, is suspected to have caused the first mass die-off of coral in the region for 3000 years.(http://news.bbc.co.uk/1/hi/sci/tech/735941.stm)

Combination of natural and anthropogenic effects have produced significant local declines in reef populations, including hurricane damage & loss of Macroalgae grazing Urchins in Barbados, Colombia off Santa Marta City, where reefs suffer pollution an runoff, less diverse and have lower coral cover with more dead coral showing at distance. This area also includes Costa Rica where a small fringing reef is being smothered by terrestrial runoff from areas being cleared for agriculture. A comparison of the reef between the late 1970`s- early 1980`s and 1993 reveal live coral cover has decreased from 40% to 11%, whilst dead coral, algae covered carbonate substrate and coral rubble have increased from 60% to 89%. (Cortés, 1983)

1.11 NORTHERN EUROPE

In temperate waters such around Northern Europe, there are a few species of hard or scleractinian coral as well as many soft corals. One of these hard corals is *Lophelia pertusa* and is unusual because it is a hard coral composed of a colony of individual polyps, where as temperate hard corals are usual solitary. Also, unlike its tropical cousins it is found in deep dark cold waters. Most of the records for this coral are from the North East Atlantic but it has also been recorded in the Mediterranean Sea, along the coasts of eastern north America Brazil, West Africa and on the mid Atlantic Ridge

Cold water corals do not live in symbiosis with algae as tropical corals do and therefore are not dependent on sunlight. *Lophelia* is found beyond the reaches of sunlight, most frequently on the continental shelves at depths of between 200- 400m and 4-8^o, but have also been found at depths of over 2000 metres (Kj•lner T. and Knoph M.B. 1998). The largest colony is thought to be the Sula Ridge, which is found to be 14 Km in length, 700 metres wide and rise to approx. 35m above the seabed. Living *Lophelia* reefs of such size and concentrations, as those on the Norwegian continental shelf between 60 and 70^o N have not been found anywhere else in the world (Kj• lner T. and Knoph M.B. 1998).

Until recently the deep waters where *Lophelia* is found remained entirely undisturbed by human activity. However now fish trawling is moving into ever-deeper water and the coral is trawled up and thrown back over the sides. A study of the condition of the coral reefs along the Norwegian coastline in 1998 by the Norwegian Institute of Marine research (NIMR) discovered some totally crushed and complete destruction of reefs due to demersal trawling at Storegga. Subsequently the Norwegian Ministry of Fisheries informed they were developing regulations to protect the reefs from further damage due to demersal trawling (Kj•lner T. and Knoph M.B. 1998). Technological advances over the last 20 years have now made it economically viable to extract oil and gas in deep waters such as those of the Atlantic Frontier to the West of Scotland therefore increasing the possibility of damage to the deep water corals.

The reefs in the Norwegian coastal waters can also be damaged by the laying of pipelines, cables and other construction work on the ocean floor, by anchoring on the reefs and by pollution. Discharges of drill mud and drill cuttings from oil exploration companies on the continental shelf are a particularly relevant problem for this area (Kj• lner T. and Knoph M.B. 1998).

1.12 GLOBAL PERSPECTIVE

According to Jameson *et al.* (1995), the major causes of coral reef ecosystem decline appear to be:

- The over exploitation of reef resources
- Excessive domestic and agricultural pollution
- Poor land use practices that increase sedimentation.

Bleaching involves the expulsion by the corals of the single celled algae, which normally live in their tissues and on which they depend as a major food source. Increasing cases of widespread bleaching may be a consequence of global warming.

Sedimentation combines the effects of increased runoff, the dumping of mine tailings and the sedimentation form various construction projects. Sediment in low amounts reduces coral growth and resilience to stress. In large amounts, particularly during storms, sediment can bury corals or whole coral communities.

Pollution is a rising problem, particularly that from urban centres and organic pollution from coastal villages and tourist facilities. Organic pollution often enables seaweed to overgrow coral communities, and there is a need to develop more practical, low-cost methods to reduce this pollution in coastal situations

Blast fishing is widely dispersed and rapidly growing. As with other forms of destructive fishing associated with the condition known as Malthusian overfishing, such as poisoning and muro ami fishing, the problem tends to increase as human populations increase, resulting in increasingly desperate competition for reef resources. To date, more than 40 countries are known to have problems with blast fishing on coral reefs, and more than 15 have reported cyanide fishing.

1. 13 CORAL GROWTH AND CO_2 CLIMATE CHANGE

1.13.1 Temperature changes

Effects are likely to be serious, causing bleaching and death to intolerant species. But a warming trend may also extend the range of habitable seas. Bleaching events have become more widespread and severe since the early 1980’s (Henderson, 1998).

1.13.2 Sea Level Rise

The average vertical growth rate of reefs is 1-10mm /yr. The present day estimate of sea level rise is 6mm/yr, this implies that it should be within reef building capacities to keep pace with the rise. This may also lead to changes in current and wave action that can damage reefs.

1.13.3 Carbon Flux

The reefs are often thought of as carbon sinks, because CO_2 from the atmosphere is converted into calcium carbonate rock. However reefs are also a minor source of CO_2, as although reef building stores CO_2 in coral rock, the precipitation of $CaCO_3$ lowers the pH of the water. This increase in acidity alters the balance of $CO_{2,}$ HCO_3^- and CO_3^{-2}, known as the bicarbonate buffer system, and more bicarbonate is converter to CO2 that is released into the atmosphere. This is estimated as 1% of annual anthropogenic release.

First order estimates show that coral reefs contribute about 0.05% of the estimated net CO_2 fixation rate of the global oceans.

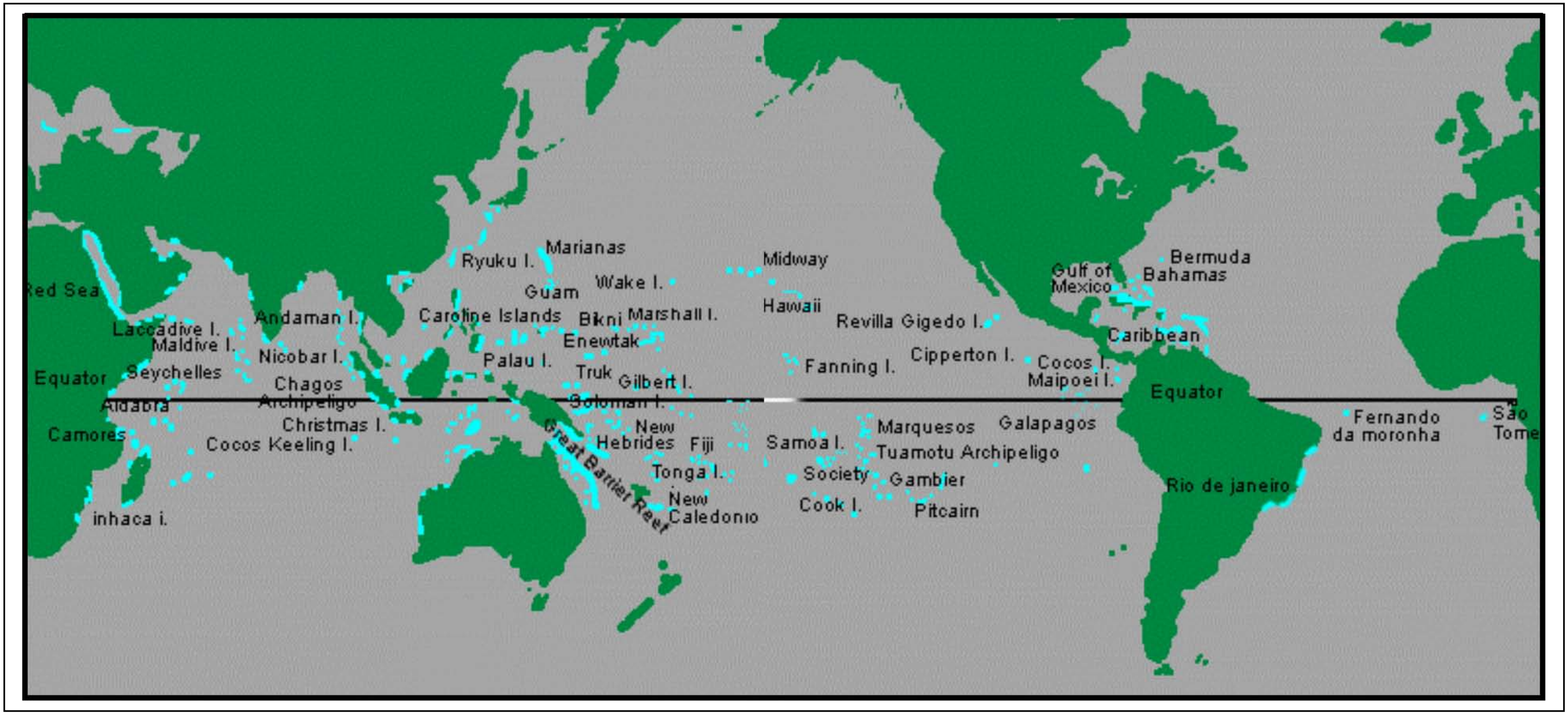
Gross CO_2 fixation		700 x 10^{12}g C year $^{-1}$	Most of this is recycled in the reefs.
Excess net production of organic material (*E*)		20 x 10^{12} g C year $^{-1}$	(Much smaller!)
Of that	buried in reef structures	3 x 10^{12} g C year $^{-1}$	15% of *E*
	Available of for sustained human harvest	2 x 10^{12} g C year $^{-1}$	10% of *E*

(Crossland *et al* 1991)

Scientists calculate that the precipitation of calcium carbonate has already fallen by an average of between 6-11 % since the industrial revolution. They also believe that if the atmospheric CO_2 levels increase to double the level pre industrial times (expected to be as early as $^{\underline{c}}$ 2065) that precipitation may fall by a further 8 to 17%. (http://news.bbc.co.uk/1/hi/sci/tech/309805.stm)

1.13.4 Experiment

The chemistry causing concern is the ability of carbon dioxide to react with water, producing bicarbonate ions. Once carbonates in the surrounding water are converted into bicarbonates, corals are unable to use them. Biosphere 2 experimental greenhouse in the Arizona desert includes an artificial ocean holding 2650 cubic metres of seawater and a fully functional coral reef. The team carried out a number of experiments in the artificial ocean, altering carbonate concentration to mimic the effects of changing carbon dioxide levels. The results were used to predict that between 1880 and 2065 there will have been a decrease in coral growth of 40%. This also supports work from Monaco and CNRS in France, which predicts a drop in calcification of 21% by 2065. **(**Ambrose, 2000**)**



Distribution of Coral reefs.

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Introduction to Global Change 1 Lecture Notes: The Coral Reef ecosystem
http://www.sprl.umich.edu/GCL/paper_to_html/coral.html

Appendix 5

ROLE OF PHYTOPLANKTON IN THE MARINE CARBON SINK

Phytoplankton are microscopic plants that live in the ocean (Figure..). Collectively, phytoplankton grow abundantly in oceans around the world and are the foundation of the marine food chain. Small fish, and some species of whales, eat them as food. Larger fish then eat the smaller fish. Humans catch and eat many of these larger fish. Since phytoplankton depend upon certain conditions for growth, they are a good indicator of change in their environment. For these reasons, and because they also exert a global-scale influence on climate, phytoplankton are of primary interest to oceanographers and Earth scientists around the world.

Figure… Landsat satellite image of a phytoplankton bloom in the English Channel off the coast of Cornwall, 24 July 1999. The bloom was sampled six days later by scientists at Plymouth Marine Laboratory and positively identified as Ehux. (Image courtesy of Andrew Wilson and Steve Groom).

THE LIFE AND DEATH OF PHYTOPLANKTON

Like their land-based relatives, phytoplankton require sunlight, water, and nutrients for growth. Because sunlight is most abundant at and near the sea surface, phytoplankton remain at or near the surface. Also like terrestrial plants, phytoplankton contain the pigment chlorophyll, which gives them their greenish colour. Chlorophyll is used by plants for photosynthesis, in which sunlight is used as an energy source to fuse water molecules and carbon dioxide into carbohydrates—plant food. Phytoplankton (and land plants) use carbohydrates as "building blocks" to grow; fish and humans consume plants to get these same carbohydrates.

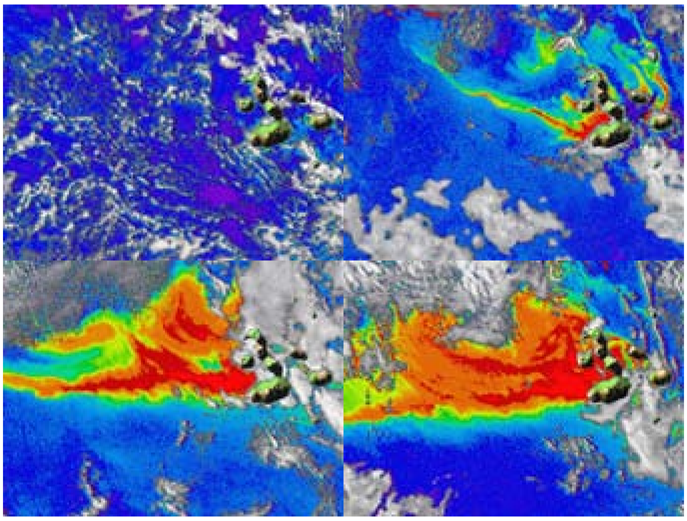
The atmosphere is a rich source of carbon dioxide, as millions of tons of this gas settle into the ocean every year. However, phytoplankton still require other nutrients, such as iron, to survive. When surface waters are cold, deeper depths are allowed to upwell, bringing these essential nutrients toward the surface where the phytoplankton may use them. However, when surface waters are warm (as during an El Niño), they do not allow the colder, deeper currents to upwell and effectively block the flow of life-sustaining nutrients. As phytoplankton starve, so too do the fish and mammals that depend upon them for food. Even in ideal conditions an individual phytoplankton only lives for about a day or two. When it dies, it sinks to the bottom. Consequently, over geological time, the ocean has become the primary storage sink for atmospheric carbon dioxide. About 90 percent of the world's total carbon content has settled to the bottom of the ocean, primarily in the form of dead biomass.

Because phytoplankton use carbon dioxide for photosynthesis, the larger the world's phytoplankton population, the more carbon dioxide gets extracted from the atmosphere, hence, the lower the average temperature due to lower volumes of this greenhouse gas. Scientists have found that a given population of phytoplankton can double its numbers on the order of once per day. Thus phytoplankton respond very rapidly to changes in their environment. Large populations of this organism, sustained over long periods of time, could significantly lower atmospheric carbon dioxide levels and, in turn, lower average temperatures.

Phytoplankton as indicators of change

Phytoplankton depend upon sunlight, water, and nutrients to survive. Physical or chemical variance in any of these ingredients over time for a given region will affect the phytoplankton concentrations there. Populations of this marine plant will grow or diminish rapidly in response to changes in its environment. Changes in the trends for a given phytoplankton population,such as its density, areal distribution, and rate of population growth or diminishment, will alert Earth scientists that environmental conditions are changing there. Then, by comparing these phytoplankton trends to other measurements, such as temperature, scientists can learn more about how phytoplankton may be contributing to, and affected by, climatic and environmental change.

Due to their pigment (chlorophyll) phytoplankton preferentially absorb the red and blue portions of the light spectrum (for photosynthesis) and reflect green light. So, the ocean over regions with high concentrations of phytoplankton will appear as certain shades, from blue-green to green, depending upon the type and density of the phytoplankton population there.



Sequence of SeaWiFS ocean color imagery showing the impact of 1997-98 El Niño on the productivity of phytoplankton around the Galapagos Islands in the Pacific Ocean. The top left image was taken during the height of the El Niño, while the bottom right image was taken during the more recent La Niña. Note the gradually flourishing bloom of phytoplankton as the surface waters cool, allowing the deeper, more nutrient-rich waters to upwell. (Courtesy of the SeaWiFS Project).

Phytoplankton affect the carbon cycle in two very significant ways:

- Living phytoplankton remove carbon dioxide from seawater by photosynthesis, releasing oxygen as a by-product.
- Dead phytoplankton sink to the ocean floor, acting as a sink for carbon**.**

If fewer phytoplankton existed, atmospheric carbon dioxide would increase. But this is a simplistic conclusion. It is estimated that ~95% of phytoplankton cells die and are decomposed in the surface waters, re-releasing their internal CO_2. ~5% of phytoplankton debris sinks to deeper in the ocean, where it remains out of contact with the atmosphere for 1000 years or so. ~0.2% sinks to the sea floor and becomes incorporated in sediments.

Coccolithophore blooms act to oppose global warming, though probably not in the most obvious manner. Coccolithophores take up bicarbonate to form their $CaCO_3$ tests by the following reaction:

$Ca + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$

The removal of two bicarbonate molecules and the addition of one carbon dioxide molecule results in the growth of coccolithophores paradoxically producing more dissolved carbon which will escape into the atmosphere. However, the importance of organic matter adhering to the coccoliths is recognised as an additional factor. Because coccolith calcite is rather dense, zooplankton faecal pellets containing coccoliths and “marine snow” sink faster than organic matter. Thus there is less time for the organic matter to be attacked by bacteria and therefore less CO_2 escaping into the surface waters (Buitenhuis *et al*., 1996).

This co-transport of organic matter with coccoliths probably offsets the atmospheric CO_2 increase that would otherwise be caused, and makes coccolithophore blooms act to oppose global warming rather than to intensify it.

Phytoplankton are highly sensitive to changing environmental conditions (Sir Alistair Hardy Foundation for Ocean Science, Ecological Importance of the CPR Survey, http://192.171.163.165/ecological_importance.htm). Are phytoplankton blooms becoming more intensive??

Notes:

Dissolved carbonate must exist chiefly as H_2CO_3 in acid solutions (pH < 6.4), as CO_3^{2-} in basic solutions (pH > 10.3), and as HCO_3 in the intermediate range.

1Gt =10^{15}g

Pt – Petatonne

The solubility of $CaCO_3$ in pure water decreases with temperature rise.

CO_2 is less soluble in hot water than cold water. $CaCO_3$ dissolves at greater depths in the ocean where the water is perennially cold, but precipitates near the surface, especially in the tropics, where the water is warm. Krauskopf p.53.

Equilibrium considerations

The breakdown of organic material and formation of early diagenetic carbonate cements is dependent upon *low sedimentation rates.* Limestones can only form in environments where the terrigenous clastic input is low or negligible. Yet with increasing loss of forest cover, increased rainfall intensity and therefore elevated runoff, nearshore sedimentation rates must be increasing.

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