Lecture 17. Paleoceanography and Paleoclimatology

One of the assumptions geologists use to interpret the geologic historical record is that "*The Present is the Key to the Past*". As the studies of Paleoceanography and Paleoclimatology become increasingly focused on the more recent past, the hope and justification for this work is that "*The Past is the Key to the Future*". By studying the mechanisms of past climate and oceanographic changes, we will be able to better manage earth's climate in the future. The classic example is the dramatic change in pCO_2 through recent Earth history and the unprecedented rise in the pCO_2 of the atmosphere due to fossil fuel burning.

Paleoceanography and paleoclimatology are taught extensively in other classes – here we will cover only the basic state of our knowledge of paleoceanographic and paleoatmospheric changes. It makes sense to end a course on Chemical Oceanography with the study of paleoceanography, because many of the chemical tracers we discussed during the course are brought out again to unravel the secrets of the past.

We will discuss the following topics:
1. Chronology – methods used to determine the age of the historical record
2. Tracers of Past Oceanographic Changes: $\delta^{13}C$ and metal/Ca ratios of carbonate shells
3. Tracers of Past Atmospheric pCO_2 Changes: and comparison between Ice Core and Sediment Core results

Chronology

Tracers of past environmental change are preserved in systems that accumulate with time; different archives are used for different time scales starting with instrumental records, through historical and archeological records to tree rings; corals; ice cores; lake and marine Sediments.

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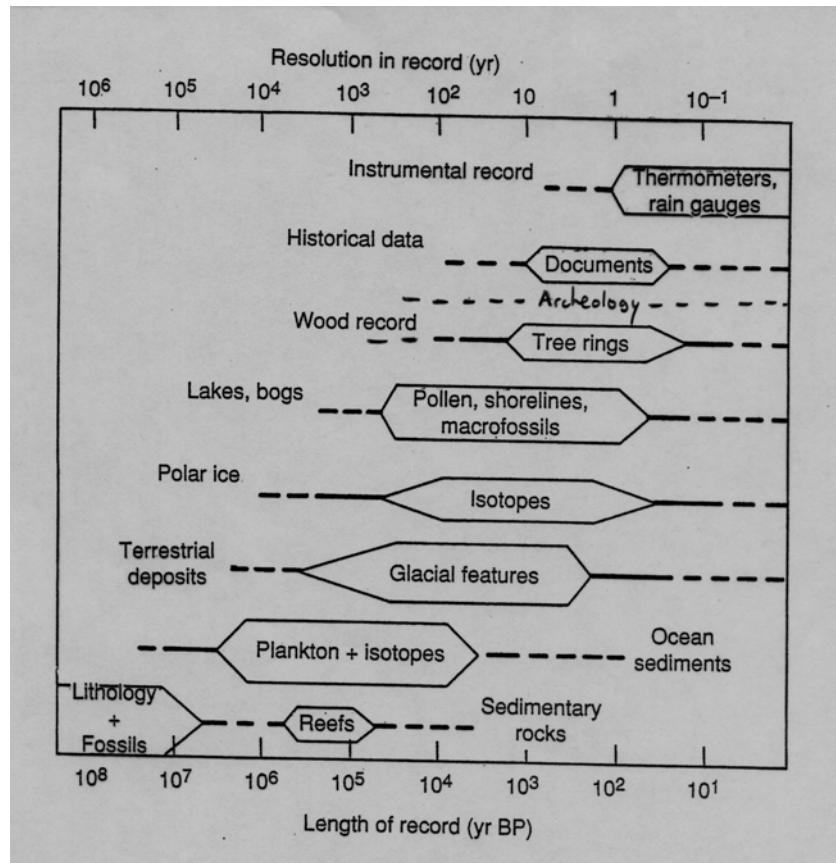
In order to determine the timing of past change, one must be able to date the records. Corals, trees, some ice cores and some anoxic sediments have annual bands that can be counted and thus used for dating. For older deposits, we must use radioactive isotopes for absolute age determination. There are two radioactive isotopes with half-lives relevant for the past few 10s to 100s of thousands of years. Carbon-14 (^{14}C; $t_{1/2}$ = 5700 yrs.) and Thorium-230 (^{230}Th; $t_{1/2}$ = 75,200 yrs)

Tree Rings and ^{14}C (Dendrochronology)

The production rate of ^{14}C in the atmosphere has changed in the past because of changes in the intensity of the sun. During periods of high sun activity, i.e. high sun spot activity, ^{14}C production is *low* because the "solar wind" repels high-energy cosmic rays away from the Earth's atmosphere. In order to use ^{14}C to derive accurate dates one must know the production rate. Since trees have built in chronology one can "correct" ^{14}C dating of the wood to derive a record of ^{14}C production. With a known production rate, the decay over time of ^{14}C could be used for radioactive age determination.
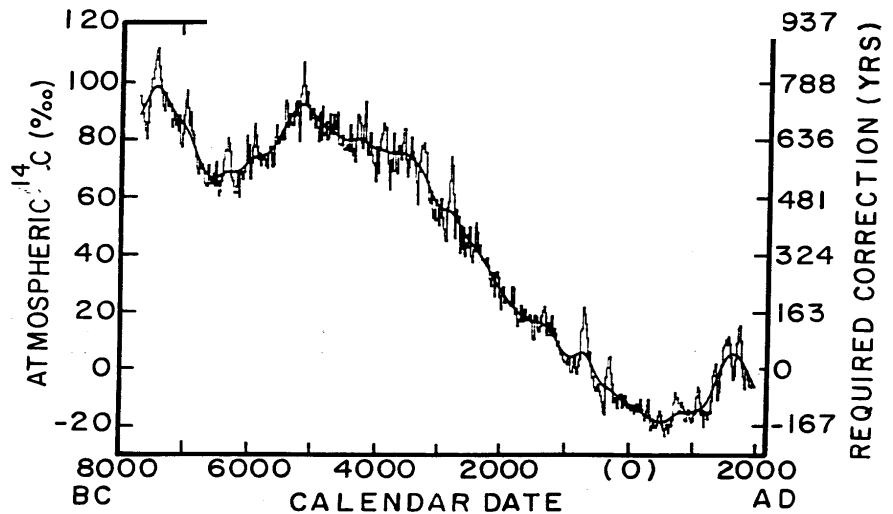

Figure 3. Atmospheric Δ ^{14}C values in per mil reconstructed from Becker's master oak chronology for the past 9600 yr. The time scale (in year A.D. or B.C.) was derived from dendrochronologically dated wood, with each data point covering 20 yr. Data from Stuiver and Pearson, 1986; Stuiver and Becker, 1986; Pearson et al., 1986; Linick et al., 1985; Stuiver et al., 1986a; Kromer et al., 1986; and Linick et al., 1986. The scale on the right shows the correction required to convert radiocarbon ages to calendar ages. For example objects with ages in the range 6000 to 7000 thousand calendar years yield radiocarbon ages averaging about 600 years too young.

Corals: Comparing ^{14}C and ^{230}Th Dating Methods
Recent discoveries have enabled geochemists to calibrate the ^{14}C record back much further than the age of the oldest trees. New methods of measuring ^{230}Th by mass spectrometry have allowed it to be used to determine relatively young ages with much greater accuracy than counting radioactive decay. Corals live for a maximum of several hundred years, but recently scientists have drilled deep-sea sediments to find ancient corals, just as archaeologists "dig" to unearth ancient dwellings. Coraline aragonite ($CaCO_3$) incorporates a lot of uranium but no thorium, so in-growth of ^{230}Th can be followed by measuring low levels of ^{230}Th.

Using the ^{230}Th determinations as the "true calendar age" the differences between the calendar age and ^{14}C age can be determined from the coral ages. The astounding result is that the differences in older records are quite large.

Marine Sediments: ^{230}Th Excess:
^{230}Th has a half-life of 75,200 years and is heavily concentrated in the sediments. The decay of ^{230}Th with depth is a measure of sedimentation rate, assuming constant accumulation of Th per unit time.

Oxygen Isotope Stratigraphy
Oxygen-18 is not a radioisotope so it holds no intrinsic dating information.

However, the δ^{18}O of seawater is determined by the earth's mass balance of water and ice. The δ^{18}O in the $CaCO_3$ tests of foraminifera depends on both the seawater isotope ratio (δ^{18}O- H_2O) and the temperature of the water in which the foraminifera grew. Benthic foraminifera record mostly the ice volume effect, because glacial/interglacial changes in temperature of the deep sea are small. If the sea level curve, as revealed by the changes in δ^{18}O of foraminifera can be accurately dated in some cores then δ^{18}O stratigraphy can be used as a dating tool ('wiggle matching').
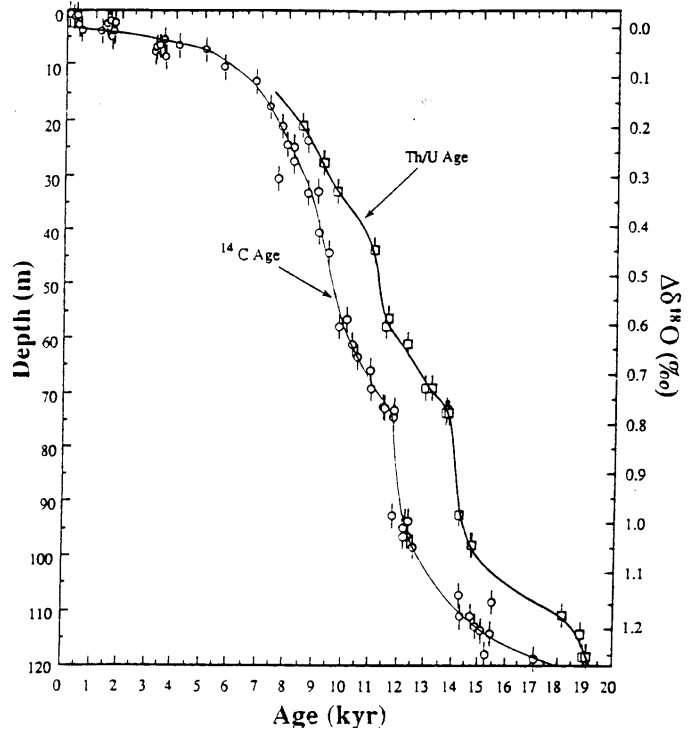
Dating the δ^{18}O Record.

Dating the first δ^{18}O cycle was possible using ^{14}C for the first "Termination" and ^{230}Th for "Termination II". The range in the δ^{18}O signal is 1 - 2 per mil from peak glacial to peak interglacial. Comparison of the "wiggles" Milankovitch frequencies can also be used to date older sediments using oxygen isotopes (see below).

Magneto stratigraphy has also been applied to date marine sediments. The time of each of the magnetic reversals is dated in volcanic rocks on land using K-Ar dating. Magnetic polarity is preserved in remnant magnetism of iron rich minerals in the sediments, so the polarity of the earth at the time of sediment deposition can be determined and the age of the reversal identified.

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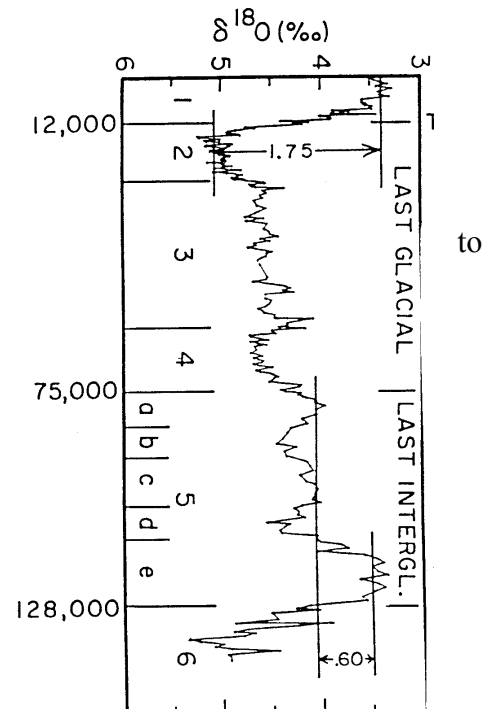
Tuning the $\delta^{18}O$ changes in foraminifera tests to changes in solar insulation is potentially a more accurate method of dating the isotope curve. Because changes in solar insulation are precisely known, we assume that the effect of solar insulation had direct and instantaneous effect on the ocean $\delta^{18}O$ (via ice formation) and the isotope fluctuations can be dated. This assumes only that the ice volume record (and hence, glacial / interglacial cycles) is synchronous with solar insulation changes.

Changes in Solar Insulation reaching the Earth's surface (Milankovitch Cycles) are caused by astronomical effects. There are four main periodic processes that alter the amount of solar heat arriving at the earth's surface.
1) The spin axis of the Earth precesses with a 24,000-year period
2) The Earth's orbit around the sun is elliptical and the ellipse revolves with a 105,000-yr cycle
3) The tilt of the spin axis of the Earth varies from 22° to 24° with a period of 41,000 yrs
4) The eccentricity of the Earth's orbit varies from round to 0.05 with a period of 100,000 yrs

(1) and (2) combine to determine the *seasonality* of the amount of solar radiation reaching the earth. Precession is caused by the gravitational pull of the sun and moon on the equatorial bulge of the Earth. It determines the area of the Earth receiving sun – thus the inter-hemisphere differences in season. The elliptical orbit affects the total amount of heat reaching the Earth's surface during the year. The most important effect is that of precession and the two combine to create a 23,000-year cycle of solar insulation (Broecker, 1995).

(3) The inclination of the plane of the Earth's orbit with respect to the gravitational plane of the solar system (*obliquity*) varies from 22° to 24° because of gravitational effects of the other planets.
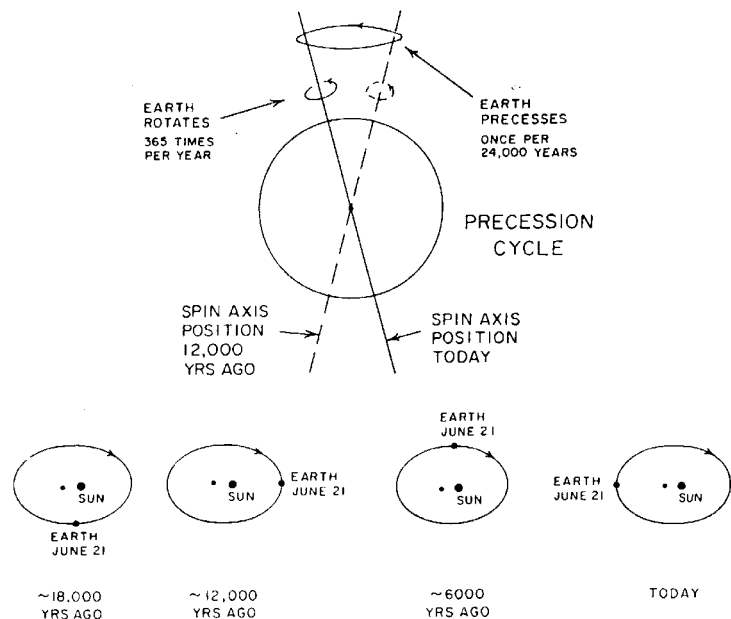
Figure 9. Like that of a top, the Earth's spin axis precesses: It takes about 24,000 years for one complete precession cycle (see text for details). The effect of this motion is to change the point on the Earth's orbit where maximum northern-hemisphere illumination (i.e., June 21) occurs. Today it occurs at the "long" end of the ellipse, reducing full simmer illumination in the northern hemisphere a bit. One-half precession cycle ago (i.e., ~12,000 years ago) it occurred at the "short" end of the ellipse, increasing full summer illumination a bit. The precession of the Earth's axis is related to the Sun's pull on the equatorial bulge produced by the Earth's rotation. Just as the Earth's gravity seeks to tip over a spinning top, the Sun's and Moon's gravity seeks to remove the tilt of the Earth's axis. As does a top, the Earth compensates for this pull by precessing.

(4) The *eccentricity* of the Earth's orbit (the difference between the long and short axes) varies from nearly perfectly round to 0.05 with a periodicity of 100,000 yrs, also in response to the gravitational pull of the other planets.

The changes in *seasonality*, *obliquity*, and *eccentricity* all effect the amount of heat that reaches the earth as a function of time and the periodicity of these effects is known precisely (Broecker, 1995).

Imbrie (1984) combined a number of $\delta^{18}O$ records from different ocean areas and adjusted the peaks and valleys to derive an average record of ice volume. He then compared the "stacked $\delta^{18}O$ record" with the solar insulation record.

The 100,000-year cycle in the isotope curve is clear even to the unaided eye. Glacial cycles over the last 700,000 years have a cycle of about 100,000 years. It is not as easy to pick out the Eccentricity cycle from the combined solar insulation curve, but we know it is there.
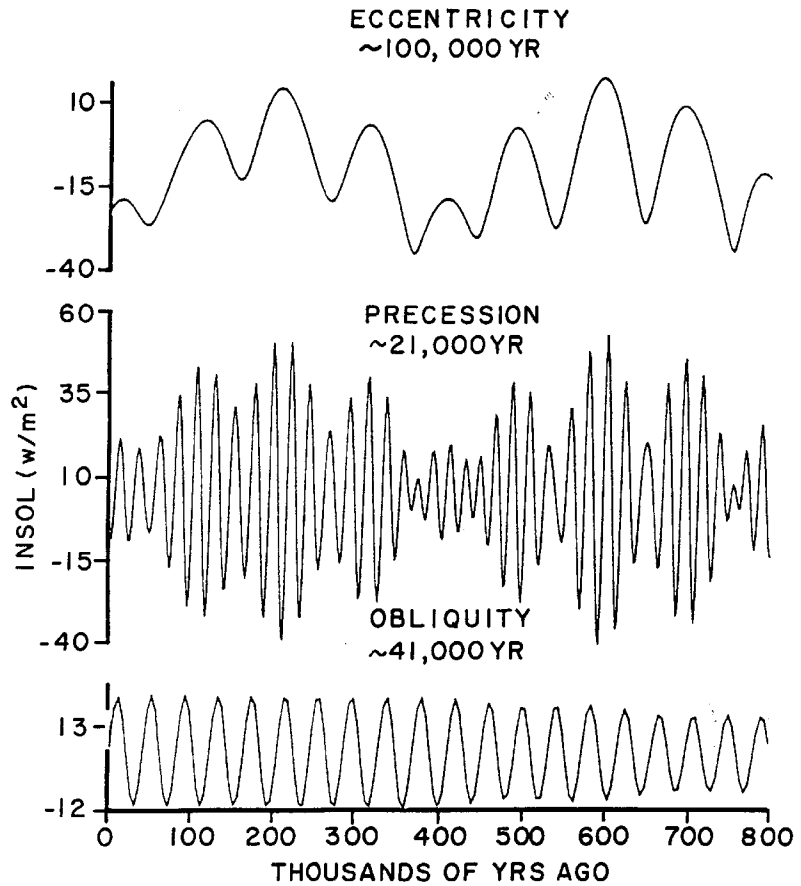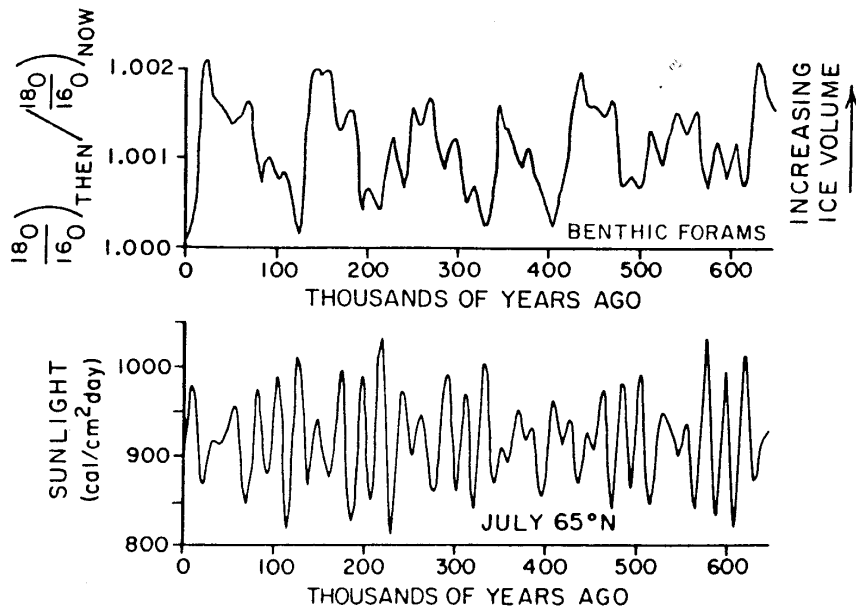

Figure 13. June insolation changes at 65°N caused by changes in the eccentricity of the Earth's orbit (100,000 and 450,000 year cycles), by changes in the phasing between the Earth's distance and tilt seasonality (19,000 and 23,000 year cycles) and by changes in the tilt of the Earth's axis (41,000 year cycle).

Using spectral analysis (determining what set of periodic sine waves can be combined to create the curve) the additional predominant cycles (41,000, and 23,000) become evident.

Tracers of Past Change in Ocean Chemistry, Circulation, and Biological Processes.

- How has the Chemistry of the Ocean Changed in the past?
- Are our assumptions about a "steady state" ocean correct?
- What was the role of the ocean in past climate change?
- How does ocean circulation and biology control/react to global changes?

To answer these questions, paleoceanographers, turn to ocean sediments to study the record of past ocean chemistry. The oldest marine sediments in the ocean are about 200 million years old, so reconstruction of past climates and environments using Ocean Drilling Cores can reveal information with respect to the past 200 million years. Older marine deposits (records of billions of years old) are exposed on land and may also be used. We will concentrate here on examples for the last past glacial and the Cenozoic.

Sedimentary Records of Glacial Interglacial Change
A short list of sediment proxies of marine chemical processes include (but there are many more):
   a. $CaCO_3$, SiO_2 content – Production / Preservation of these minerals
   b. Organic C content – Production / Preservation of organic matter
   c. Abundance / Absence of foraminiferal species – indicators of habitat change
   d. Authigenic metal abundance – REDOX state of the sediments
   e. Isotope and metal tracers in $CaCO_3$ shells of foraminifera

Isotopes that have been applied include: O, C, B, Sr, N, Si, Fe, Ca, Os, Nd, Pb, and more.
The most important metals used include: Cd, Li, Ba, Sr, Mg, U, V, Zn, Mn, and many others.

We will discuss only 4 of the most widely applied tracers:
1. $\delta^{13}C$ in $CaCO_3$ of foraminifera shells as a tracer for ocean carbon distribution between organic and inorganic reservoirs.
2. Cd/Ca in $CaCO_3$ of foraminifera shells as a tracer of ocean phosphate and ocean circulation.
3. $\delta^{15}N$ of organic matter as an indicator of sea surface NO_3 utilization.
4. $^{87}Sr/^{86}Sr$ as a tracer for changes in tectonic activities (hydrothermal, uplift, weathering)

Stable Carbon Isotopes

In today's ocean, the $\delta^{13}C$ of DIC is high in the surface water and decreases with depth with the deep Pacific having lower values than deep Atlantic. This results from the preferential uptake of ^{12}C into organic matter during photosynthesis and regeneration of this organic matter are depth and along the conveyer belt.
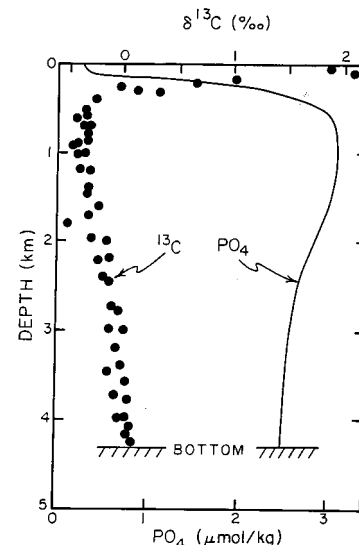
If the $\delta^{13}C$ of $CaCO_3$ in the test of foraminifera is correlated to the $\delta^{13}C$ of the DIC in which it grew, then changes in the carbon isotope ratio of foraminifera would reflect changes in the isotopic composition of DIC, thus productivity and circulation.

$\delta^{13}C$ Cibicidoides spp.

The $\delta^{13}C$ of tests of both planktonic and benthic foraminifera shells have been shown to correlate with the $\delta^{13}C$ of the DIC of the water in which they grow (Curry et al., 1988). With this observation, one can measure the $\delta^{13}C$ of the isotope ratio as a function of sediment age and determine how the $\delta^{13}C$ of DIC in past oceans has changed.
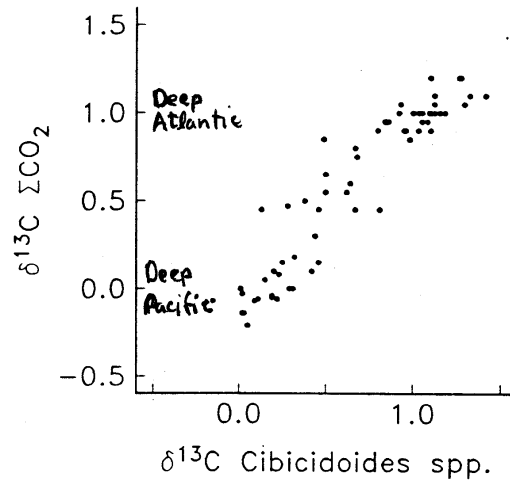
There have been two main applications:

  a. The $\delta^{13}C$ difference between planktonic and benthic species has been interpreted as an indicator of the strength of the biological pump.
  b. The global distribution of the $\delta^{13}C$ of benthics has been measured to determine the past global circulation and deep PO_4 distribution.

It was found (Curry et al., 1988) that in the last glacial period, the carbon isotope ratio of benthic foraminifera tests from all the oceans was lighter by about 0.5 ‰. This result requires a very large transformation of carbon from organic matter to inorganic matter. The only major reservoir of "light carbon" is organic matter (not taking methane into account here). How much carbon of organic-matter $\delta^{13}C$ must be added to seawater DIC to cause this change? Using a simple mass balance this can be calculated:
        present ocean + organic matter = glacial ocean

1. $DIC_{P.O.} + DIC_{O.M.} = DIC_{G.O.}$
2. $(DIC)_{P.O.} \, \delta^{13}C_{P.O.} + (DIC)_{O.M.} \, \delta^{13}C_{O.M.} = (DIC)_{G.O.} \, \delta^{13}C_{G.O.}$
3. $\delta^{13}C)_{P.O.} = 0.0,$ $\delta^{13}C)_{O.M.} = -23.0,$ $\delta^{13}C)_{G.O.} = -0.45$
4. $DIC_{G.O.} / DIC_{P.O.} = (1-0.977) / (0.99955 - 0.977) = 1.020$
5.
A 2% change in the ocean's DIC! (2% X 2000 µmol/kg = 40 µmol/ kg more DIC).
There are only two organic matter reservoirs large enough to supply this carbon to the deep ocean these are soils and trees on land and dissolved organic matter in the oceans.

Inorganic Carbon Reservoirs:	Gt	Gigatons = 10^{15} g
Atmospheric CO_2	594	
Ocean DIC	37,400	
Organic Carbon Reservoirs		
Forests	560	
Soils	1500	
Seawater DOC	1000	

A 2 % change in DIC (750 Gt,) would require almost all the DOC to be oxidized or about one third of the forest and soil reservoirs to be moved into the ocean. Shackleton (1977) suggested that during glacial periods tropical areas were arid, rain forests were small, and temperate forests were covered with ice. Thus much of the soil and forest reservoir was oxidized.

CAVEAT!
Recently, (Spero et al., 1997) showed that planktonic foraminifera grown in seawater with different carbonate ion concentration but the same DIC (and thus different pH) secrete tests with different $\delta^{18}O$ and $\delta^{13}C$. The isotope ratios are pH dependent and this has not been taken into account in the above calculation. The shell isotope ratio gets lighter as the $[CO_3]$ (μmol/kg) increases. During the last glacial maximum surface waters had a lower pCO_2 and thus higher $[CO_3]$. The difference is believed to be about 40 μmol/kg more CO_3 in glacial surface waters. This translates to a change of 0.3‰ in $\delta^{13}C$ and 0.1‰ in $\delta^{18}O$. This effect is not greatly important for the oxygen isotope glacial / interglacial change, which is between 1 and 2 ‰, but it completely wipes out the utility of $\delta^{13}C$ changes in planktonic foraminifera as an indicator of the biological pump. It is also believed that the pH of deep water may have been higher in the last glacial maximum.

The Cd Content of Foraminifera Shells as a Proxy for the PO$_4$ Content of Deep Waters

Cadmium is a "nutrient like" metal in seawater. Its concentration in deep water is correlated with phosphate (Boyle, 1986).

Like the carbon isotopes, the Cd content of the calcite shells of modern benthic foraminifera is directly proportional to the concentration in the bottom water bathing the shell. (Hester and Boyle, 1982). The case for the Cd/Ca ratio is somewhat simpler than that for $\delta^{13}C$ because there is no evidence that the ocean inventory changed with time. The Cd/Ca ratios in benthic foraminifera from two cores, one in the deep Pacific and one in the deep Atlantic, indicate that the Cd (and hence PO$_4$) concentrations were more similar in the two oceans during the last glacial maximum.
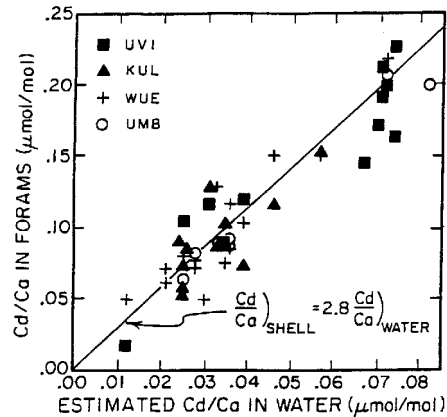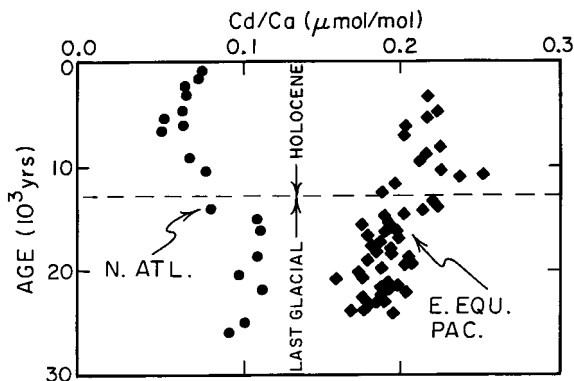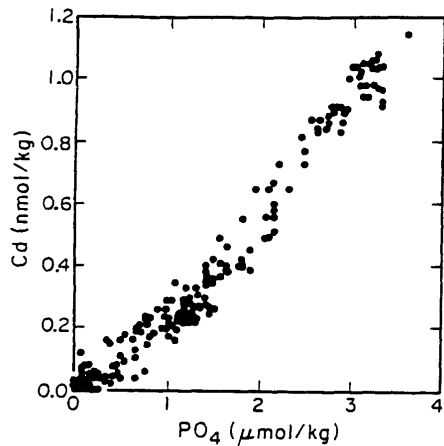
The deep waters of the Atlantic Ocean are a mixture of waters from the north (North Atlantic Deep Water) and waters from the south, (Antarctic Intermediate Water and Antarctic Bottom Waters). AAIW and AABW are nutrient rich and Cd rich (Broecker, 1997). NADW is nutrient poor and Cd poor. Today, these two sources to the deep Atlantic are about the same. If in the past this changed, it would alter the nutrient content of the deep waters. Since the Atlantic had higher Cd during the last glacial period, it has been suggested that the AABW contribution was relatively greater than NADW. The original interpretation of the Cd/Ca result was that the contribution of the NADW to the deep Atlantic mixture was less (maybe by a factor of two) than today. Since models indicate that NADW formation is very sensitive to salt content, it was attributed to a slow-down of the formation rate of NADW.

Detailed Surveys of cores from different water depths in the North Atlantic reveal that during glacial times the vertical structure of the [Cd] depth distribution was indeed different (Boyle and Keigwin, 1987). The inferred Glacial / Interglacial $[PO_4]$- depth trends indicate that the nutrient poor NADW may have become a less dense water mass that ventilated the intermediate waters while the deep waters became more nutrient rich (and probably more influenced by AABW). So Cd/Ca ratios provide information about past water mass structure and circulation.

$\delta^{15}N$ in organic matter from diatoms of sediments in the Southern Ocean

The $\delta^{15}N$ of organic matter becomes heavier as the nitrate concentration of the waters in which the plants grow becomes more scarce relative to the demand by the phytoplankton. This is because the heavy isotope is discriminated against during photosynthesis. Generally the $\delta^{15}N$ of organic matter in deep-sea sediments is correlated with the nitrate content in surface waters. Francois et al. (1997) measured the $\delta^{15}N$ in organic matter of two cores in the southern ocean south of the Polar Front ($\cong 50°$ S) where the nitrate concentration today is high. They found that the $\delta^{15}N$ of the organic matter increased during the last glacial period indicating that the NO_3 utilization in the surface ocean was higher at that time. They used this result along with other paleoceanographic indicators to suggest that upwelling of deep waters in the southern ocean was less efficient at that time, and that this was the reason for much of the pCO_2 lowering in the atmosphere during the last glacial period.

Correlating Atmospheric CO$_2$ and Ice Volume

Chemical studies of ice and trapped gases in ice cores have resulted in the first long-term, pre-industrial record of the composition of the atmosphere. The atmospheric pCO_2 record tells us about how the ocean has behaved in the past because of the overwhelming influence of the ocean on this atmospheric constituent. Correlating atmospheric pCO_2 changes determined in ice cores

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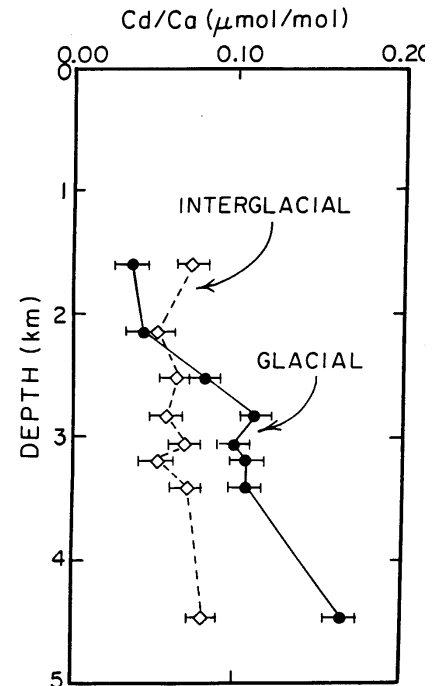
and ice volume records from deep-sea sediments provide the first glimpse of whether changes in ice volume lead or follow CO_2 changes.

Ice Core Results

Isotope Stratigraphy
Dating of the ice cores is accomplished by counting seasonal ice layers (which result from changes in ice deposition rate and dust input), and also by correlating to seasonal $\delta^{18}O$ changes (corresponding to temperature). The oxygen and deuterium isotope record of the ice itself have been used to reconstruct temperature changes in Antarctica and Greenland. Results indicates about 6 degrees cooling in the last glacial.

Gases
Air bubbles are trapped in the ice as snow re-crystallizes to firn, which on lithification looses the passages to the atmosphere.

The result is that the age determined for the ice is older than the gas trapped in bubbles. The time lag between bubble gas age and ice age is about 2-5 years (based on ice flow models) and it depends on the ice accumulation.

Trapped air from bubbles can be extracted from the ice and the concentrations of different gases determined. Significant glacial-interglacial changes have been observed in both CO_2 and methane.

Comparing results from ice cores in Greenland and Antarctica established that the nature of these changes is global (Neftel et al., 1982).

These results also indicate a synchronicity between the gas concentrations and temperature for the last full glacial cycle.
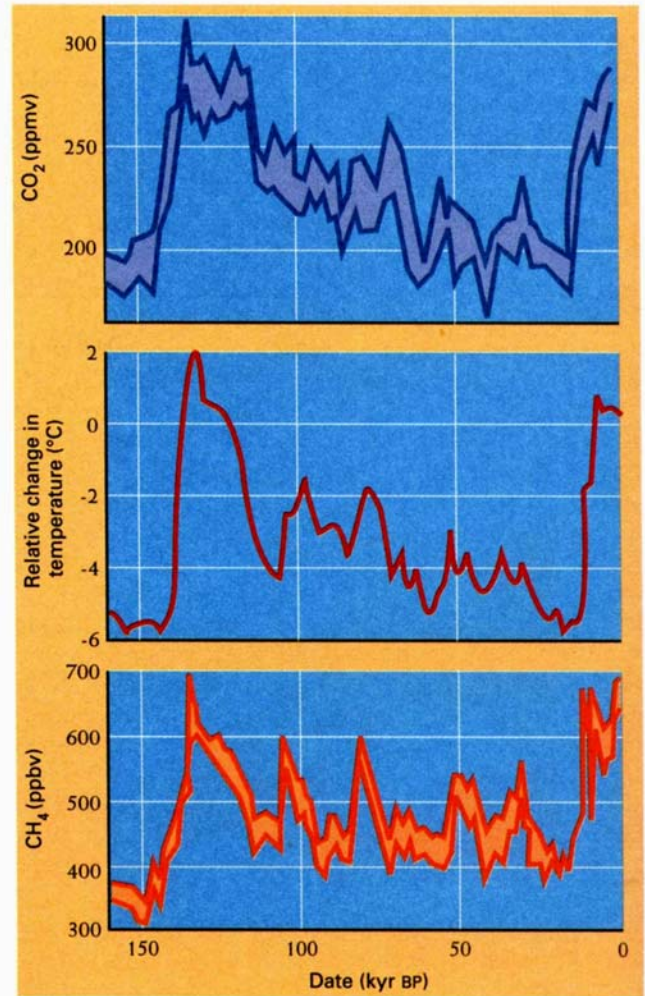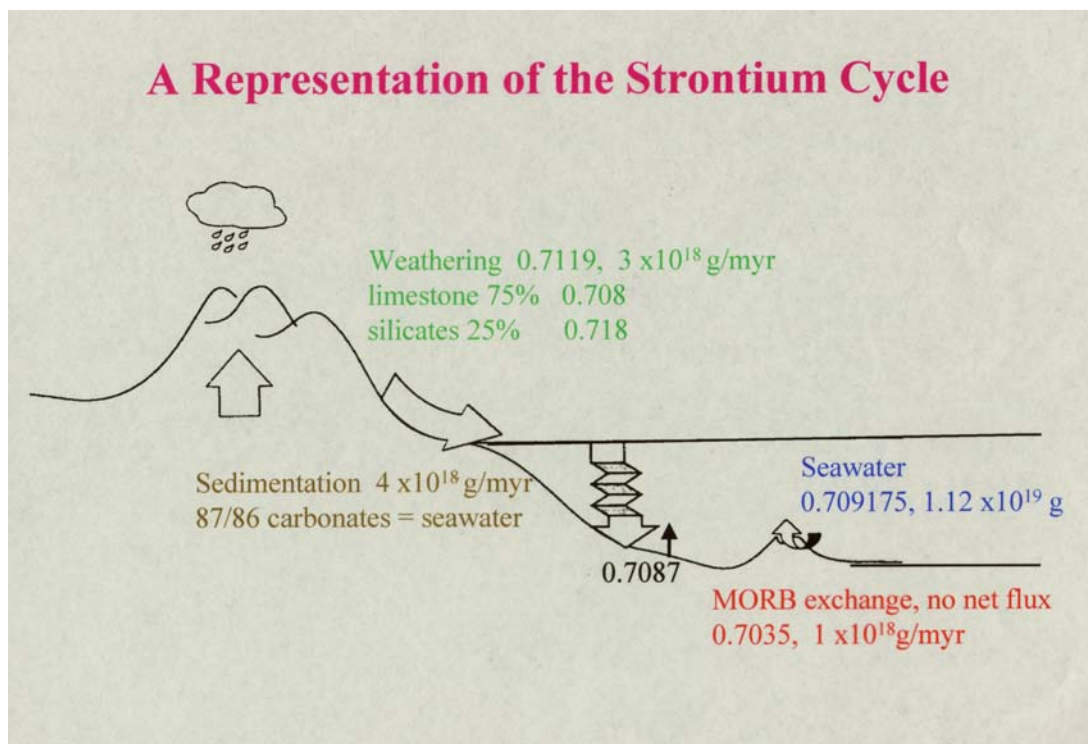

Carbon dioxide, oxygen-isotope temperature, and methane historical records from the Vostok ice core in Antarctica.

The Sr Isotope Record of Seawater: Implications to Climate Weathering and Tectonics
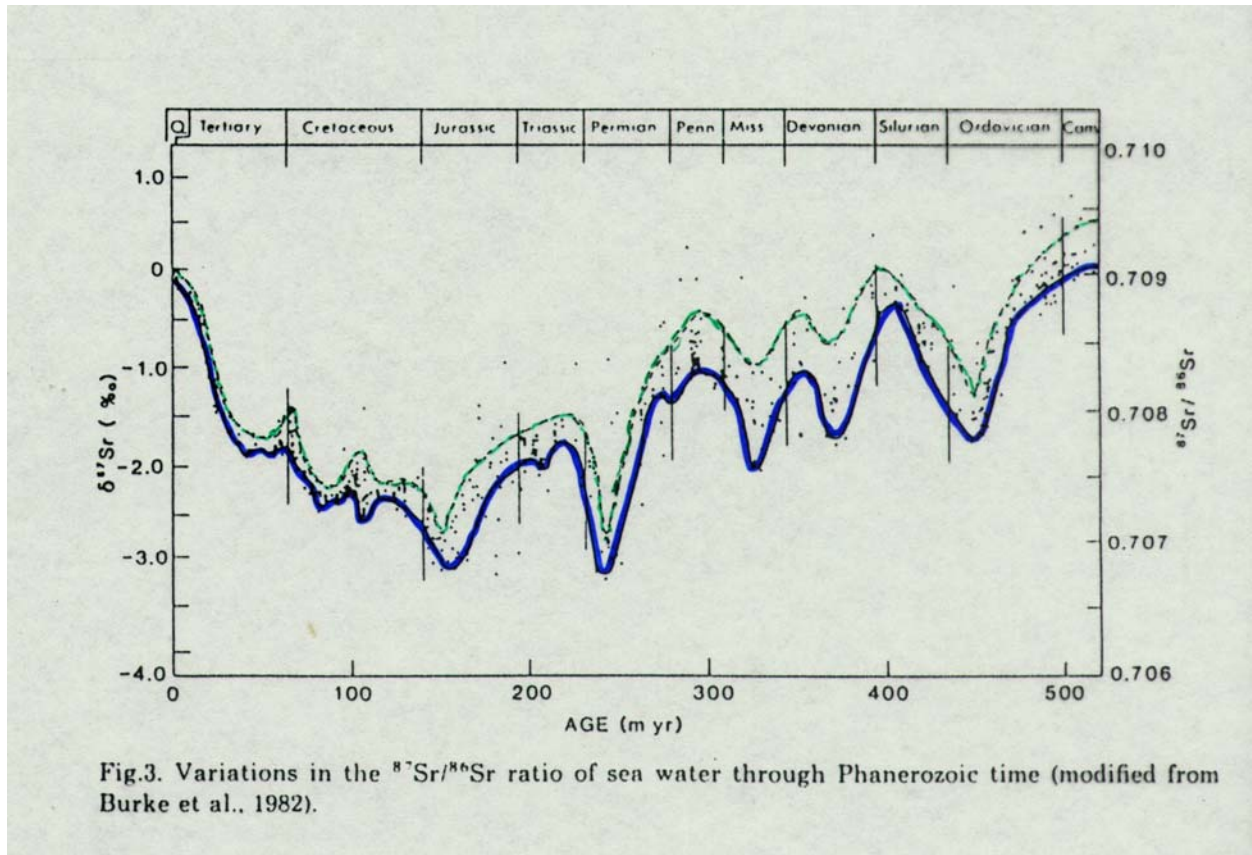
The Sr isotopic composition of seawater can reflect the balance between hydrothermal activity and weathering rates.

How does it work? ^{87}Sr is a radioactive decay product of ^{87}Rb, so rocks that have a lot of Rb will also have a lot of ^{87}Sr, thus high 87/86 Sr ratio. Billions of years ago, when continental rocks formed, Rb was partitioned preferentially into the material forming the crust – so it is depleted from the residual mantle. This results in old continental silicates having high 87/86 while young basalt rocks that form from the depleted mantle have low 87/86 ratios. Because the half-life of Rb is so long, this ratio does not change even on time scales of hundreds of millions of years allowing it to be used to track the contribution of Sr to the oceans from these different reservoirs. Another important factor is the long residence time of Sr in the ocean (2Ma) results in a well mixed reservoir with constant isotopic ratio throughout the ocean at any given time, so a global picture could be derived despite potential local diagenetic alteration.

Below is a figure of the Sr cycle in the oceans today. The seawater ^{87}Sr/^{86}Sr ratio recorded in marine carbonates reflect the balance between input of radiogenic material (87/86 of ~0.7119), weathered from continents and non-radiogenic material of (87/86 of 0.7035) introduced by hydrothermal activity through exchange with basalts. The river input isotopic composition depends on the rocks eroded. Typically, carbonate weathering brings lots of Sr with values similar to seawater and silicate weathering brings less Sr with radiogenic values. Marine carbonate dissolution also adds Sr to the ocean but this source will not have a major effect, it acts like a buffer. The seawater Sr isotope value at any given time is recorded in carbonates or barite precipitated in the ocean and a seawater curve through time could be reconstructed.

A Representation of the Strontium Cycle

Weathering 0.7119, 3 x10^{18} g/myr
limestone 75%   0.708
silicates 25%   0.718

Sedimentation 4 x10^{18} g/myr
87/86 carbonates = seawater

0.7087

Seawater
0.709175, 1.12 x10^{19} g

MORB exchange, no net flux
0.7035, 1 x10^{18}g/myr

Below is the reconstructed seawater Sr isotope record. Low values during the Cretaceous and Permian are consistent with high spreading rates and high hydrothermal activity during these periods. The pronounced change (increase in 87/86) since the Eocene (40Ma) could be due to an increased delivery of radiogenic Sr to the ocean or a decrease in hydrothermal activity. It seems like sea-floor spreading rates have been relatively constant over the past 30-40 Ma. So this change must be explained by increased delivery of radiogenic Sr from land. This could be from increased river flux of Sr, change in the river's 87/86 ratios to higher values or a combination of these factors.

Fig.3. Variations in the $^{87}Sr/^{86}Sr$ ratio of sea water through Phanerozoic time (modified from Burke et al., 1982).

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