STABLE ISOTOPES IN PALEOCLIMATOLOGY II

CARBON ISOTOPES, OCEAN CIRCULATION, AND CLIMATE

In the previous lecture, we noted the need for feedback mechanisms to amply the Milankovitch signal, which is the primary driving force of Quaternary climate oscillations. We observed that the Milankovitch variations only change the distribution of solar energy received by the Earth, not the total amount. If this were the only factor in climate change, we would expect that the glaciation in the southern and northern hemispheres would be exactly out of phase. This, however, is not the case. Thus there must be feedback mechanisms at work capable of producing globally synchronous climate variation. Broeker (Broeker,1984 and subsequent papers) argued that one of these was the deep circulation of the ocean.

The role of surface ocean in climate is well understood: for example, the south-flowing Califonia Current keeps the West Coast of the U.S. relatively dry and the coastal regions cooler than they would otherwise be. The role of the deep, or thermohaline, circulation of the oceans is less odvious, but perhaps no less important. Whereas the surface ocean ciruclation is wind-driven, the deep circulation is driven by density, which is in turn controlled by temperature and salinity.

In the present ocean, most deep ocean water masses "form" in high latitudes. Once these deep water masses form, they do not return to the surface for nearly a thousand years. The principal site of deep water formation is the Southern Ocean where the Anaractic Intermediate Water (AAIW) is formed in the Antarctic Convergence and Antarctic Bottom Water (AABW), the densest of ocean water masses, is formed in the Weddell Sea. A lesser amount of deep water is also formed in the North Atlantic during winter south of Iceland; this water mass is called North Atlantic Deep Water (NADW). The only "deep water" formed at intermediate latitudes is Mediterranean Intermediate Water (MIW), which sinks as a result of evaporation in the Mediterranean increasing salinity and hence density. MIW, however, is a smaller water masses than the others, and furthermore has only intermediate density. Formation of deep water thus usually involves loss of thermal energy by the ocean to the atmosphere. Therefore, the present thermohaline circulation of the oceans keeps high latitude climates milder than they would otherwise be. In particular, energy extracted from the Atlantic Ocean water in the formation of NADW keeps the European climate relatively mild.

We saw in Lecture 27 that $\delta^{13}C$ is lower in deep water than in surface water (Figure 27.5). This results from biological cycling: photosynthesis in the surface waters discriminates against ^{13}C, leaving the dissolved inorganic carbon of surface waters with high $\delta^{13}C$, while oxidation of falling organic particles rich in ^{12}C lowers $\delta^{13}C$ in deep water: in effect, ^{12}C is pumped from surface to deep water more efficiently than ^{13}C. $\delta^{13}C$ values in the deep water are not uniform, varying with the "age" of the deep water: the longer the time since the water was at the surface, the more enriched it becomes in ^{12}C and the lower the $\delta^{13}C$. Since this is also true of total inorganic carbon and nutrients such as PO_4 and NO_3, $\delta^{13}C$ correlates negatively with nutrient and ΣCO_2 concentrations. NADW has high $\delta^{13}C$ because it contains a large of amount water that was recently at the surface (and hence depleted in ^{12}C by photosynthesis). No deep water is formed in either the Pacific or the Indian Oceans; all deep waters in those oceans flow in from the Southern Ocean. Hence deep water in the Pacific, being rather "old" has low $\delta^{13}C$. AABW is a mixture of young NADW, which therefore has comparably high $\delta^{13}C$, and recirculated Pacific deep water and hence has lower $\delta^{13}C$ than NADW. Thus these water masses can be distinguished on the basis of $\delta^{13}C$.

Examining $\delta^{13}C$ in benthic foraminifera in cores from a variety of locations, Oppo and Fairbanks (1987) concluded that production of NADW was lower during the last glacial maximum and increased to present levels in the interval between 15000 and 5000 years ago. Figure 35.1 shows an example of data from core RC13-229, located in the South Atlantic. $\delta^{13}C$ values increase as $\delta^{18}O$ increases. As we saw in the previous lecture, $\delta^{18}O$ in marine carbonates is a measure of glacial ice volume and, indirectly, climate. As the climate warmed at the end of the last glacial interval, $\delta^{13}C$ values in bottom water in the South Atlantic increased, reflecting a increase in the proportion of NADW relative to

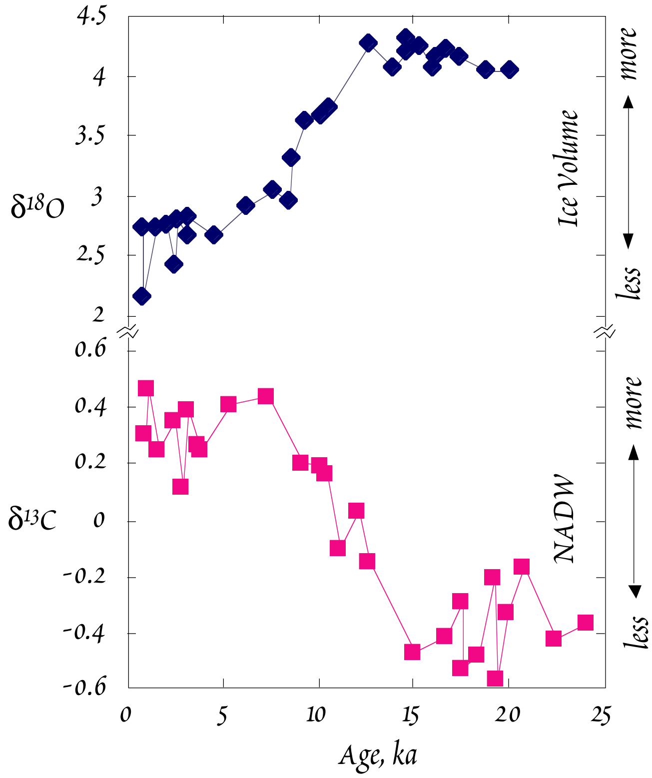

Figure 35.1. Variation in $\delta^{18}O$ and $\delta^{13}C$ in benthic foraminfera from core RC13-229 from the eastern South Atlantic. $\delta^{13}C$ data suggest the proportion of NADW in this region increased as the climate warmed. Data from Oppo and Fairbanks (1987).

AABW in this region. From $\delta^{13}C$ variations in Mediterranean and Central Atlantic cores, Oppo and Fairbanks (1987) also concluded that the production of MIW was greater during the last glacial maximum. Thus the mode of ocean circulation apparently changes between glacial and interglacial times; this change may well amplify the Milankovitch signal.

Further evidence for the role of North Atlantic Deep Water was provided by a 1992 study by Charles and Fairbanks. Working with a high resolution core (i.e., high sedimentation rate) from the Southern Ocean, they found $\delta^{13}C$ increased dramatically just over 12,000 years ago (Figure 35.2), indicating a greatly increased flux of NADW to the region. The increase in NADW occurred just as ice volume was beginning to decrease rapidly (as judged from increasing sealevel in Barbados). The rather suddden melting of the continental ice caps is hard to explain by the slowly increasing Northern Hemisphere insolation at that time. If production of NADW suddenly started, it would have warmed the North Atlantic climate, accerating melting of glaciers. Thus NADW production may represent a positive feedback amplifying the primary "Milankovitch" signal. However, why NADW production should suddenly increase dramatically remains a mystery.

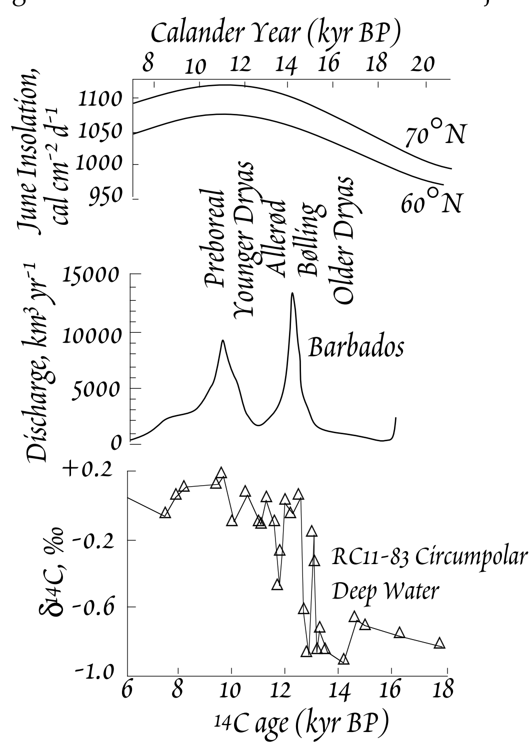

Figure 35.2. Calculated northern hemisphere insolation changes (due to orbital changes), glacial melt water discharge (calculated from sealevel rise rates determined from ^{14}C dating of fossil coral reefs off Barbados), and $\delta^{13}C$ in bethic foraminfera in core RC11-83 (41°36′ S, 94° 48′ E) from the Southern Ocean. The $\delta^{13}C$ data are a measure of the proportion of NADW in Circumpolar Deep Water. European pollen assemblages are also shown. From Charles and Fairbanks (1992).

The Tertiary $\delta^{18}O$ Record

Imbrie's (1985) analysis suggests that the climate system's response to Milankovitch forcing has changed significantly even over the last 800,000 years. The present glacial-interglacial cycles began only 2 million years ago, yet the Milankovitch forcing must have been present before that. This suggests the climate system's response has changed even more drastically over the past few million years. In addition to ocean circulation and atmospheric CO_2, the positions of land masses relative to the poles and elevation of land masses may play an important role in global climate. All these factors have varied during the Tertiary, so it is perhaps not surprising that there have been significant climatic changes through the Tertiary. These changes have been recorded by $\delta^{18}O$ in deep sea sediments.

Figure 35.3 shows the Tertiary $\delta^{18}O$ variations in benthic and planktonic foraminifera recorded in three DSDP cores from the South Pacific. The data show an increase in $\delta^{18}O$ through this time. Because extensive northern hemisphere glaciation only began in the Pleistocene or late Pliocene, variations in $\delta^{18}O$ through most of the Tertiary are thought to primarily reflect temperature changes rather than changes in ice volume, though the latter, mainly in Antarctica, were also important. The $\delta^{18}O$ record therefore testifies to gradual cooling through the Tertiary.

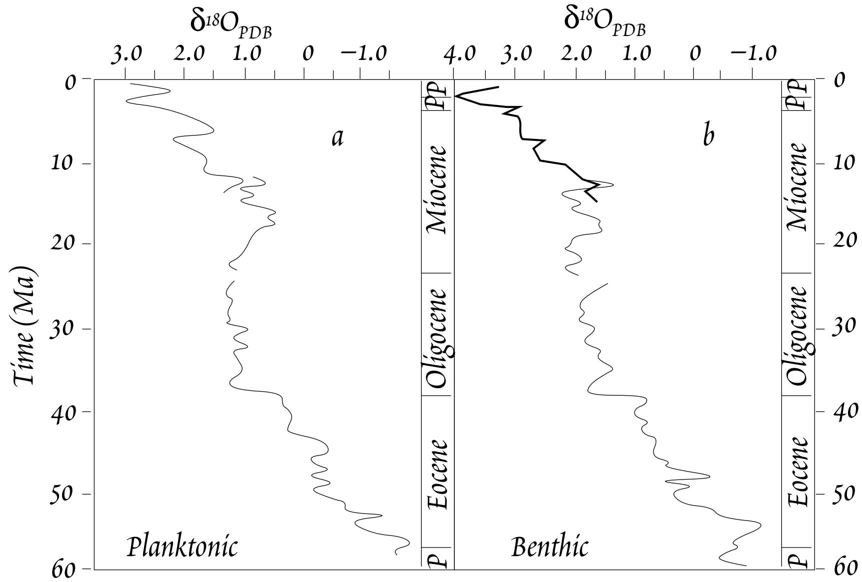

Figure 35.3. Variation in $\delta^{18}O$ in planktonic (a) and benthic (b) foraminifera over the past 60 million years in 3 DSDP cores from the South Pacific. Note that $\delta^{18}O$ is relative to PDB, rather than SMOW. This is conventional for carbonates. After Shackleton and Kennett (1975).

Superimposed on the general increase in $\delta^{18}O$ are some important "events" in which $\delta^{18}O$ changes more rapidly. Going backward through time, these include the shifts that mark the onset of Pleistocene glaciation, the rapid increase in $\delta^{18}O$ from mid-Miocene through Pliocene, and the nearly 1‰ increase at or near the Eocene-Oligocene boundary, and a more steady decrease, amounting to nearly 2‰ during the Eocene. Comparison of cores from different parts of the ocean shows that the changes are globally synchronous.

Studies of spatially distributed cores suggest that global temperatures were some 2° C warmer during the Eocene that at present. Perhaps more significantly, the latitudinal gradient in temperature may have been only half the present one. This suggests oceanic and atmospheric circulation was different from the present, and on the whole much more efficient at transporting heat from equator to poles. Why this was so remains unclear.

The Eocene-Oligocene shift is thought to represent the beginning of present system where temperature variations dominate thermohaline circulation in the oceans, and initiation of extensive East Antarctic glaciation. As we found in the previous section, deep ocean water masses are formed at high latitudes and are dense mainly because they are cold. Typically deep water today has a temperature between 2° and –2° C. Before the Eocene, deep water appears to have been much warmer, and thermohaline circulation may have been dominated by salinity differences. (The formation of Mediterranean Intermediate Water, which forms as a result of evaporative increase in salinity, can be viewed as a remenant of this salinity-dominated circulation.) It was probably not until late Miocene that the present thermohaline circulation was completely established. Even subsequent to that time, important variations may have occurred, as we have seen.

The mid-Miocene increase in $\delta^{18}O$ probably represents the expansion of the Antarctic ice sheets to cover West Antarctica. This interpretation is supported by δD analyses of sediment porewater. Even though pore water exchanges with sediment, water dominates the deuterium budget so that δD values are approximately conservative (diffusion also affects δD, but this effect can be corrected for). An increase of about 10‰ δD occurs between mid and late Miocene, which is though to reflect the accumulation of deuterium-depleted water in Antarctic ice sheets.

CONTINENTAL ISOTOPIC RECORDS

Climate change has left an isotopic record on the continents as well as in the deep sea. As with the deep sea records, it is the isotopic composition of H_2O that is the paleoclimatic indicator. The record may be left directly in ice, in carbonate precipitated from water, or in clays equilibrated with water. We will consider examples of all of these in this lecture.

As we noted with the deep sea carbonate record, the preserved isotopic signal can be a function of several variables. Continental records tend to be even more difficult to interpret than marine ones. All the isotopic records we will consider record in some fashion the isotopic composition of precipitation in a given region. The isotopic composition of precipitation depends on a host of factors:

(1) The isotopic composition of the oceans (the ice volume effect).

(2) The isotopic composition of water in the source area (the $\delta^{18}O$ of surface water in the ocean varies by a per mil or more because of evaporation, precipitation and freezing and is correlated with salinity).

(3) Temperature and isotopic fractionation in the source area (when water evaporates a temperature dependence isotopic fraction occurs; kinetic affects will also occur, and will depend on the vigor of mixing of water at the sea surface; higher wind speeds and more turbulent mixing will reduce the kinetic fractionation).

(4) Atmospheric and oceanic circulation patterns (as we saw in earlier lectures, the isotopic composition of water vapor is a function of the fraction of vapor remaining, which is not necessarily simple function of temperature; changes in atmospheric and oceanic circulation may also result in changes in the source of precipitation in a given region).

(5) Temperature in the area where the precipitation falls, as this determines the fractionation between vapor and water.

(6) Seasonal temperature and precipitation patterns. The isotopic record might reflect water falling during only part of the year, and the temperature recorded may therefore be that of only a single season rather than an annual average. For example, even in a wet area such as Ithaca, recharge of ground water occurs almost entirely in winter; during summer, evaporation usually exceeds precipitation.

(7) Evaporation of water or sublimation of ice. The isotopic record might be that of water remaining after some has evaporated. Since evaporation involves isotopic fractionation, the preserved isotopic record will not necessarily be that of the precipitation that falls.

All of these are climatic factors and are subject to change between glacial and interglacial periods. Changes in these factors do not mean that stable isotope record in a given region are not recording climatic changes, but they do mean that the climatic changes recorded might not be global ones.

Vostok Ice Core

Climatologists recognized early on that continental ice preserves a stratigraphic record of climate change. Some of the first ice cores recovered for the purpose of examining the climatic record and analyzed for stable isotopes were taken from Greenland in the 1960's (e.g., Camp Century Ice Core). Subsequent cores have been taken from Greenland, Antarctica, and various alpine glaciers. The alpine glaciers generally give isotopic records of only a few thousand years, but are nevertheless useful, recording events such as the Little Ice Age. The Greenland and Antarctic cores provide a much longer record. The most remarkable and useful of these cores is the 2000 m core recovered by the Russians from the Vostok station in Antarctica (Jouzel, et al., 1987), and is compared with the marine $\delta^{18}O$ record in Figure 35.4. The marine record shown is the SPECMAP record, which is a composite record based on that of Imbrie et al. (1984), but with further modification of the chronology. The core provides a 160,000 year record of δD and $\delta^{18}O_{ice}$, as well as CO_2, and $\delta^{18}O_{O_2}$ in bubbles (the latter, which was subsequently published and not shown in Figure 35.4, provides a measure of $\delta^{18}O$ in the atmosphere and, indirectly, the ocean), which corresponds to a full glacial cycle.

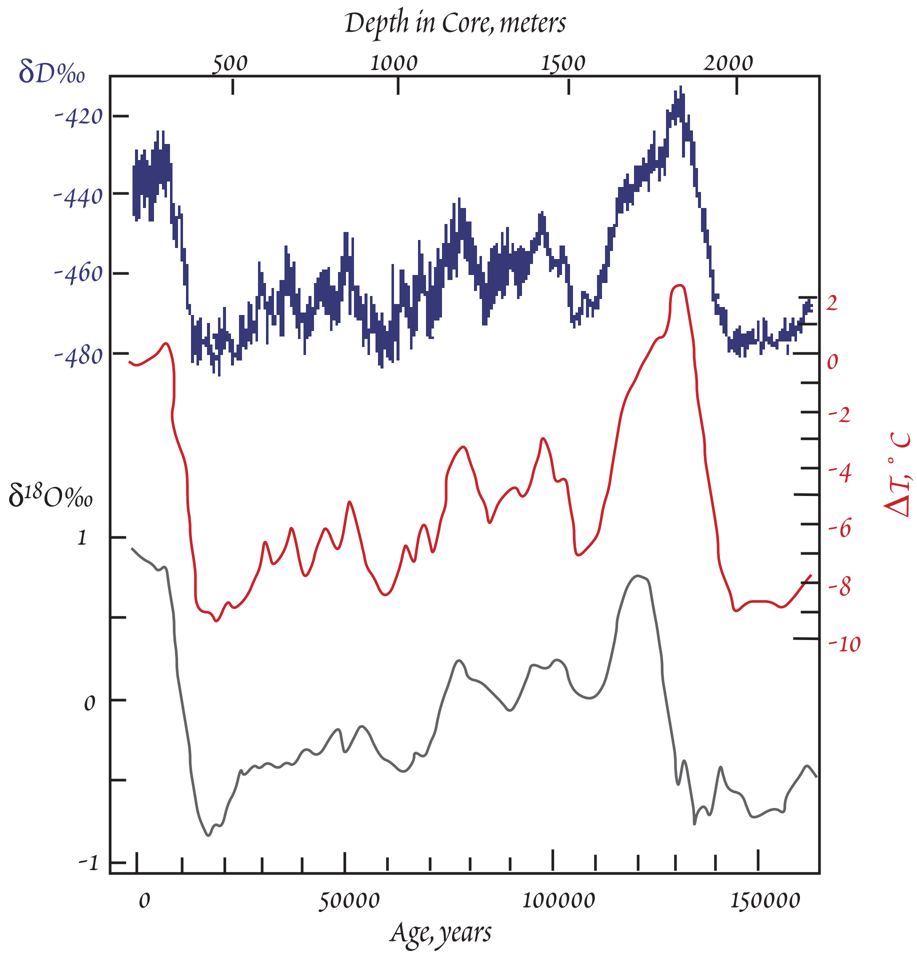

Figure 35.4. Climate record of the Vostok Ice core compared with the marine $\delta^{18}O$ record. The upper curve shows δD in the Vostok ice core. The second curve shows the calculated temperature difference relative to the present mean annual temperature, and the lower curve shows the marine carbonate SPECMAP $\delta^{18}O$ curve. (From Jouzel, et al., 1987).

Jouzel et al. (1987) converted δD to temperature variations after subtracting the effect of changing ice volume on δD of the oceans. The conversion is based on the a 6‰/°C relationship between δD and temperature in Antarctic snow (they found a similar relationship using circulation models). The hydrogen isotopic fractionation of water is a more sensitive function of temperature than is oxygen fractionation. Since this relationship might have changed between glacial periods and the present, there is some uncertainty in these temperature estimates, but they point out that the are consistent with a relationship between crystal size and temperature. Their results, taken at face value, show dramatic 10° C temperature variations between glacial and interglacial times.

Dating of the Vostok ice core was based only on an ice-flow model. Nevertheless, the overall pattern observed is in remarkable agreement with the marine $\delta^{18}O$ record, particular from 110,000 years to the present. The record of the last deglaciation is particularly similar to that of the marine $\delta^{18}O$ record, and even shows evidence of a slight return trend toward glacial conditions from 12 kyr to 11 kyr BP, which corresponds well to the well documented Younger Dryas event of the North Atlantic (though the amplitude of this event in the Vostok core is much smaller than in North Atlantic records). It is also very significant that spectral analysis of the Vostok isotope record shows strong peaks in variance at 41 kyr (the obliquity frequency) and at 25 kyr, which agrees with the 23 kyr precessional frequency when the age errors are taken into consideration. Thus the Vostok ice core data appear to confirm the importance of Milankovitch climatic forcing. It is interesting and significant that even in this core, taken at 78° S, it is primarily insolation at 65° N that is the controlling influence. There are, however, some differences between the Vostok record and the marine record, and we will consider these further in a subsequent section.

Ice Records from Summit, Greenland: GRIP and GISP2

To compliment the remarkable record of the Vostok core, drilling was begun in the late 1980's on two deep ice cores at the summit of the Greenland ice cap. A core drilled by a European consortium project, called GRIP (Greenland Ice Core Project), was located exactly on the ice divide; a core by a U. S. consortium, called GISP2 (Greenland Ice Sheet Project), was drilled 28 km to the west of the GRIP site. Drilling on these 3000 m cores was completed in 1992 and 1993 respectively. These cores provide very detailed climate records of the Holocene and the most recent glacial maximum. The also provide a record of climate in the northern hemisphere, and in the North Atlantic in particular, the region which undoubtedly holds the key to Quaternary glacial cycles.

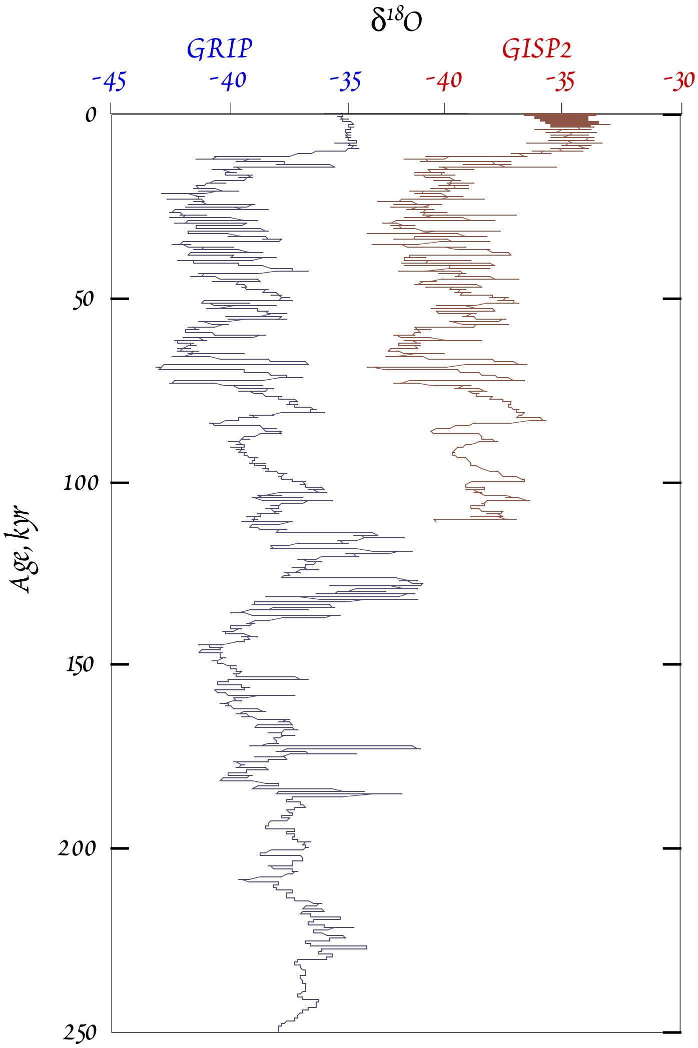

Figure 35.5. $\delta^{18}O$ records as a function of age from the GRIP and GISP2 ice cores from Summit, Greenland. The GRIP data is a 200 year average and thus appears somewhat smoother than the GISP2 data. Data from Grootes et al. (1993) and Stuiver et al. (1995) (GISP2 $\delta^{18}O$), Meese et al. (1994) and Sowers et al., (1993) (GISP2 time scale), and Dansgaard et al. (1993) and Taylor et al. (1993) (GRIP data).

$\delta^{18}O$ records for both cores are shown in Figure 35.5. Down to depths of approximately 2700 m, which corresponds to roughly to the past 110,000 years, there is an excellent correlation in $\delta^{18}O$ between the two cores. Both also agree well with the marine $\delta^{18}O$ records and the Vostok record. Below this depth, $\delta^{18}O$ and other parameters are not correlated between the cores, and the $\delta^{18}O$ variations are not consistent with those in the marine or Vostok records. This is most likely due to ice flow and folding in the Greenland cores.

Perhaps the most important result from these cores so far is the highly variable nature of climate during the most recent glacial period, though this had been already observed in some of the marine records. The last glacial interval, spanning the period from roughly 110,000 years ago to 14,000 years ago. was a time during which climate alternated from periods nearly as warm as the present to much colder ones. The highly detailed record provided by the Greenland cores demonstrated that the transition between the two climate "states" was very rapid, occurring on time periods of a century and less

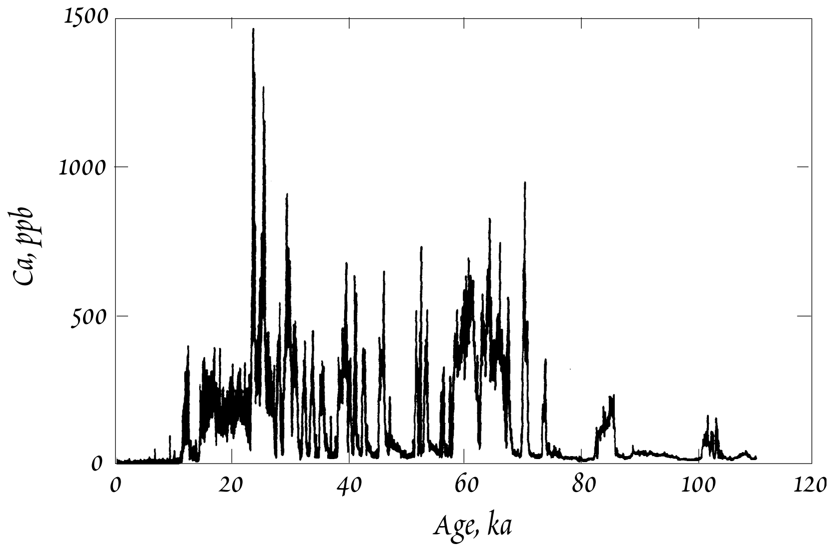

Figure 35.6. Ca^{2+} variation in ice from the GISP2 core. High and variable Ca^{2+} ion concentrations are found during cold periods, lower concentrations during warm periods. Ca ion, derived mainly from calcite in arid region soils, serves a measure of the atmospheric dust concentration. From Mayewski and Bender (1995).

in may cases. These rapid climate variations have been subsequently correlated to $\delta^{18}O$ variations in high resolution (i.e., high sedimentation rate) sediment cores from the North Atlantic.

The $\delta^{18}O$ record from the GRIP core suggests that the last interglacial period, which ended about 115,0000 years ago was also characterized by highly unstable climate. While marine cores do confirm the climatic unstability of the last glacial period, they do not do so for the last interglacial. Nor is this instability seen in the Vostok core. Whether the rapidly varying $\delta^{18}O$ and δD observed in the GRIP core at depths corresponding to the last glacial period actual reflect climatic variations or instead result from folding and interlayering of ice during flow remains a matter of debate, though the weight of the evidence may now support the latter interpretation.

A number of other chemical and physical parameters are being or have been measured in these cores. Perhaps the most important finding to date is that cold periods were also dusty periods (again, this had previously been suspected from marine records). Ice formed in glacial intervals has high concentrations of Ca^{2+} (Figure 35.6), derived from soils in arid regions, as well as dust, indicating higher atmospheric dust transport during glacial periods, reflecting perhaps both dustier and windier conditions. Windier conditions could well result if thermohaline circulation was reduced, as the pole to equator temperature gradient would increase. Atmospheric dust may be an important feedback in the climate cycle: dust can act as nuclei for water condensation, increasing cloud cover and cooling the climate (Walker, 1995). It may also serve as a feedback in another way. There is now firm evidence that the abundance of dissolved Fe in surface waters may limit biological productivity, at least in some regions. In parts of the ocean far from continents wind blown dust is a significant source of Fe. Increased winds during the last glacial period may have fertilized the ocean with Fe, effectively turning up the biological pump and drawning down atmospheric CO_2. This idea however, remains speculative.

Devil's Hole Vein Calcite Record

Another remarkable isotopic record is that of vein calcite in Devil's Hole in Nevada. Devil's Hole is an open fault zone near a major groundwater discharge area in the southern basin and range in southwest Nevada (Devil's Hole is located in the next basin east from Death Valley). The fissure is lined with calcite that has precipitated from supersaturated ground water over the past 500,000 years. A 36 cm long core was recovered by SCUBA divers and analyzed by Winograd, et al. (1992). The results are compared with the Vostok and SPECMAP records in Figure 35.7. Ages of the Devil's Hole core are based 22 U-Th ages determined by mass spectrometry.

Though the Devil's Hole record is strongly similar to the SPECMAP record, there are some significant differences. In particular, Winograd et al. (1992) noted that Termination II, the end of the second to the last glacial epoch, in the Devil's Hole and Vostok records precedes that seen in the

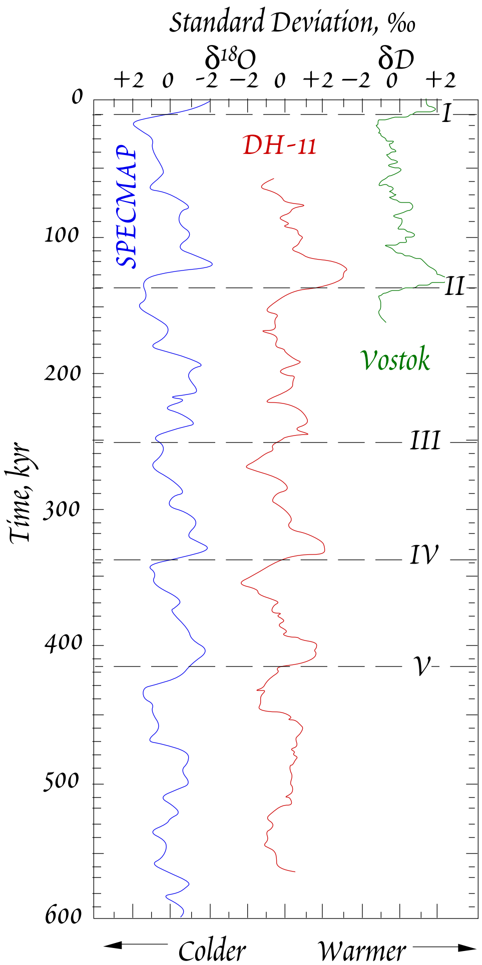

Figure 35.7. Comparison of Devil's Hole (DH-11) $\delta^{18}O$, marine carbonate (SPECMAP) $\delta^{18}O$, and Vostok ice core δD climate records. Dashed lines show the times of Terminations I-V. After Winograd, et al. (1992).

SPECMAP record by about 13 kyr (140 kyr vs. 127 kyr). This is an important point because Termination* II in the SPECMAP record corresponds with a peak in northern hemisphere summer insolation. Since Termination II in the Devil's Hole record, which is much better dated than the other two, appears to precede the peak in summer insolation, Winograd et al. argued that the Milankovitch theory must be wrong, i.e., that insolation variations due to orbital changes cannot be driving glacial cycles.

The subtle differences between the Vostok, Devil's Hole, and SPECMAP records have been carefully considered by Grootes (1993). He noted that the age control on the SPECMAP record is weak. Ages on this record have been adjusted to correlate with sea level changes as determined by dating of coral reefs and terraces and "tuned" to Milankovitch cycles. Recent high precision mass spectrometric U-Th dates on coral terraces from Barbados and New Guinea are in fact about 7 thousand years older than earlier alpha counting dates, which were used to adjust the SPECMAP time scale. Thus the age of Termination II in the marine carbonate record needs to be revised upward from 127 kyr to 135 kyr. Once this revision is made, Grootes notes that the completion of the glacial-interglacial change coincides in the 3 records (at about 130-132 kyr), but the beginnings differ.

Grootes (1993) argues that all 3 records may be correct but may be recording different aspects of climate change. These differences may provide some insight into the exact manner in which glacial epochs end. The onset of the $\delta^{18}O$ increase in the Vostok record, which occurs at 145 kyr, significantly precedes the northern hemisphere increase in insolation, but it does coincide well with an increase in southern hemisphere summer insolation. The Vostok temperature increase may well reflect this increased southern hemisphere insolation. This is consistent with an earlier inference that melting of what were probably quite substantial ice shelves around Antarctica preceded melting of the northern hemisphere ice cap and caused the initial increase in $\delta^{18}O$ in the ocean. Southern hemisphere insolation waned at about 138 kyr, and subsequent warming and sea level drive would have been driven by northern hemisphere warming and interhemispheric coupling by ocean currents and CO_2.

Grootes (1993) was also able to explain much of the remaining discrepancy between the Devil's Hole and SPECMAP records. The isotopic variations in Devil's Hole are due local temperature changes, changes in ocean isotopic composition, and all the other factors we discussed above. Grootes (1993) first corrected the Devil's Hole record for changing oceanic $\delta^{18}O$. The effect of this is to make the residual $\delta^{18}O$ variations greater than the uncorrected ones. He suggested that differences in tem-

* The ends of glacial epochs are called Terminations. They are quantitatively defined as the mid-point in the $\delta^{18}O$ rise and are numbered successively backward in time.

perature at the site of evaporation and increased wind velocity† during the glacial maxima just before Termination II would reduce the fractionation recorded in the Devil's Hole area. The increase in Devil's Hole $\delta^{18}O$ may reflect this reduced fractionation. A change in ocean-atmosphere circulation patterns may have effectively blocked cold Arctic air from reaching the Devil's Hole area and moderated temperatures there. The controversy surrounding the Devil's Hole record emphasizes the complexity of factors influencing continental isotopic records and the difficulty in their interpretation.

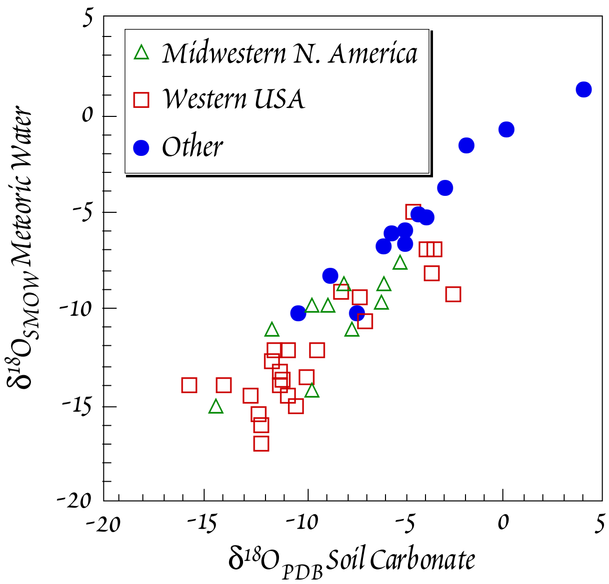

Figure 35.8. Relationship between $\delta^{18}O$ in local average meteoric water and soil carbonate. From Cerling and Quade (1993).

Soils and Paleosols

The concentration of CO_2 dissolved in soil solutions is very much higher than in the atmosphere, reaching 1% by volume. As a result, soil water can become supersaturated with respect to carbonates. In soils where evaporation exceeds precipitation, soil carbonates form. The carbonates form in equilibrium with soil water, but the isotopic composition of soil water tends to be heavier than that of mean annual precipitation. There are 2 reasons for this. First, soil water enriched in ^{18}O relative to meteoric water due to preferential evaporation of isotopically light water molecules. Second, rain (or snow) falling in wetter, cooler seasons in more likely to run off than during warm seasons. Thus there is a strong correlation between $\delta^{18}O$ in soil carbonate and meteoric water, though soil carbonates tend to be about 5‰ more enriched than expected from the calcite-water fractionation (Figure 35.8). Because of this correlation, the isotopic composition of soil carbonate may be used as a paleoclimatic indicator.

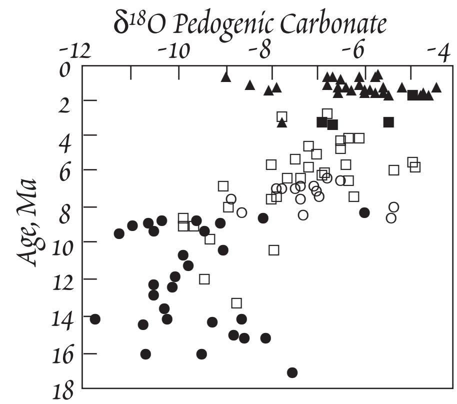

Figure 35.9. $\delta^{18}O$ in paleosol carbonate nodules from the Potwar Plateau in northern Pakistan. Different symbols correspond to different, overlapping sections that were sampled. After Quade et al. (1989).

Figure 35.9 shows one example of $\delta^{18}O$ in paleosol carbonates used in this way. The same Pakistani paleosol samples analyzed by Quade et al. (1989) for $\delta^{13}C$ (Figure 33.7) were also analyzed for $\delta^{18}O$. The $\delta^{13}C$ values recorded a shift toward more positive values at 7 Ma that apparently reflect the appearance of C_4 grasslands. The $\delta^{18}O$ shows a shift to more positive values at around 8 Ma, or a million years before the $\delta^{13}C$ shift. Quade et al. interpreted this as due to an intensification of the Monsoon system at that time, and interpretation consistent with marine paleontological evidence.

Clays, such as kaolinites, are another important constituent of soil. Savin and Epstein (1970) showed that during soil formation, kaolinite and montmorillonite form in approximate equilibrium with meteoric water so that their $\delta^{18}O$ values are systematically shifted by +27 ‰ relative the local meteoric water, while δD are shifted by about 30‰. Thus kaolinites and montmorillonites define a line parallel to the meteoric water line (Figure 35.10), the so-called kaolinite line. From this obser-

† Both the increased equator-to-pole temperature gradient and increased concentration of dust in ice cores indicate higher wind speeds at glacial maxima.

vation, Lawrence and Taylor (1972) and Taylor (1974) reasoned that one should be able to deduce the isotopic composition of rain at the time ancient kaolinites formed from their δD values. Since the isotopic composition of precipitation is climate dependent, as we have seen, ancient kaolinites provide another continental paleoclimatic record.

Lawrence and Meaux (1993) conclude, however, that most ancient kaolinites have exchanged hydrogen subsequent to their formation, and therefore a not a good paleoclimatic indicator (this conclusion is, however, controversial). On the other hand, they conclude that oxygen in kaolinite does preserve the original $\delta^{18}O$, and that can, with some caution, be used as a paleoclimatic indicator. Figure 35.11 compares the $\delta^{18}O$ of ancient Cretaceous North American kaolinites with the isotopic composition of modern precipitation. If the Cretaceous climate were the same as the present one, the kaolinites should be systematically 27‰ heavier than modern precipitation. For the southeastern US, this is approximately true, but the difference is generally less than 27‰ for other kaolinites, and the difference decreases northward. This indicates these kaolinites formed in a warmer environment than the present one. Overall, the picture provided by Cretaceous kaolinites confirm what has otherwise be deduced about Cretaceous climate: the Cretaceous climate was generally warmer, and the equator to pole temperature gradient was lower.

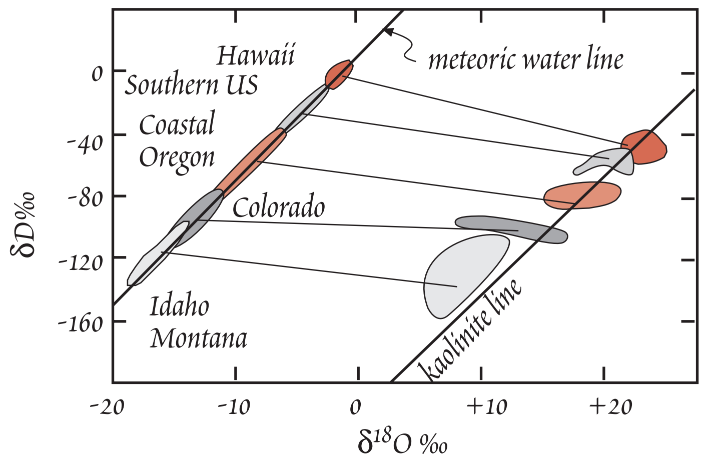

Figure 35.10. Relationship between δD and $\delta^{18}O$ in modern meteoric water and kaolinites. Kaolinites are enriched in ^{18}O by about 27‰ and ^{2}H by about 30‰. After Lawrence and Taylor (1971).

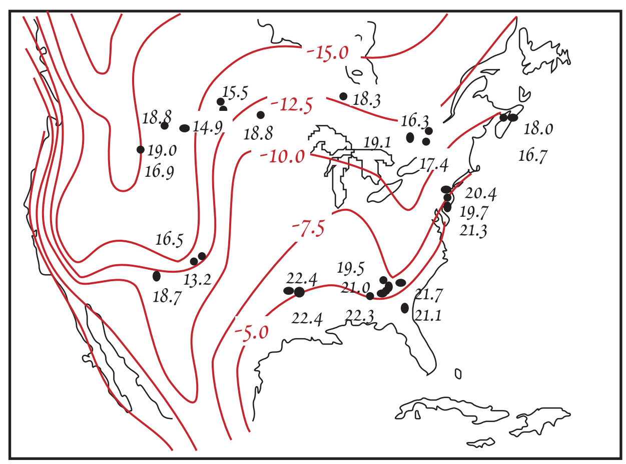

Figure 35.11. $\delta^{18}O$ in Cretaceous kaolinites from North American compared with contours of $\delta^{18}O$ (value shown in outline font) of present-day meteoric water. After Lawrence and Meaux (1993).

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