STABLE ISOTOPES IN PALEOCLIMATOLOGY I

INTRODUCTION

At least since the classic work of Louis Agassiz in 1840, geologists have contemplated the question of how the Earth's climate might have varied in the past. But until 1947, they had no means of quantifying paleotemperature changes. In that year, Harold Urey initiated the field of stable isotope geochemistry. In his classic paper "The thermodynamic properties of isotopic substances", Urey calculated the temperature dependence of oxygen isotope fractionation between calcium carbonate and water and proposed that the isotopic composition of carbonates could be used as a paleothermometer (Urey, 1947). Urey's postdoctoral associate Samuel Epstein and several students tested Urey's idea by growing molluscs in water of various temperatures (Epstein et al., 1953). They found the following empirical relationship:

$$\Delta = \delta^{18}O_{cal} - \delta^{18}O_{water} = 15.36 - 2.673\,(16.52 + T)^{0.5} \qquad 34.1$$

This equation was in good, though not exact, agreement with the theoretical prediction of Urey (Figure 34.1). Thus was born the modern field of paleoclimatology.

THE RECORD OF CLIMATE CHANGE IN DEEP SEA SEDIMENTS

It is perhaps ironic that while glaciers are a continental phenomenon, our best record of them is from the oceans. In part, this is because each period of continental glaciation destroys the record of the previous one. In contrast, deep sea sediments are generally not disturbed by glaciation. Thus while much was learned by studying the effects of Pleistocene glaciation in North America and Europe, much was left unresolved: questions such as the precise chronology, cause, temperatures and ice volumes (ice area could of course be determined, but this is only part of the problem). The question of chronology has been completely resolved through isotopic studies of deep sea biogenic sediments, and great progress has been made toward resolution of the remaining questions.

The principles involved in paleoclimatology are fairly simple. As Urey formulated it, the isotopic composition of calcite secreted by organisms should provide a record of paleo-ocean temperatures because the fractionation of oxygen isotopes between carbonate and water is temperature dependent. In actual practice, the problem is somewhat more complex because the isotopic composition of the test of an organism will depend not only on temperature, but also on the isotopic composition of water in which the organism grew, vital effects (i.e., different species may fractionate oxygen isotopes somewhat differently), and post-burial isotopic exchange with sediment pore water. As it turns out, the latter two are not very important for carbonates (at least for late Tertiary/Quaternary sediments), but the former is.

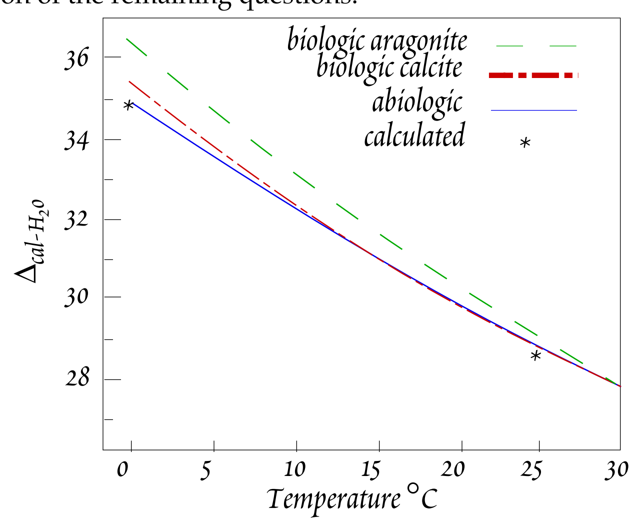

Figure 34.1. Fractionation of oxygen isotopes between calcium carbonate and water as a function of temperature for biologically precipitated calcite (molluscs; Epstein et al., Craig, 1965), biologically precipitated aragonite, and abiologically precipitated calcite. Also shown are the calculated fractionation factors of Urey (1947) for 0° C and 25°C.

The Quaternary δ^{18}O Record

The first isotopic work on deep sea sediment cores with the goal of reconstructing the temperature history of Pleistocene glaciations was by Emiliani (1955), who was then a student of Urey at the University of Chicago. Emiliani analyzed $\delta^{18}O$ in foraminifera from piston cores from the world ocean. Remarkably, many of Emiliani's findings are still valid today. He concluded that the last glacial cycled had ended about 16,000 years ago, and found that temperature increased steadily between that time and about 6000 years ago. He also recognized 14 other glacial–interglacial cycles over the last 600,000 years, and found that these were global events, with notable cooling even in low latitudes. He concluded that bottom water in the Atlantic was 2° C cooler, but that bottom water in the Pacific was only 0.8° C cooler during glacial periods. He also concluded that the fundamental driving force for Quaternary climate cycles was variations in the Earth's orbital parameters.

Emiliani had the field of oxygen isotope paleoclimatology virtually to himself until about 1970. In retrospect, it is remarkable how much Emiliani got right. By that time, others saw the value of this approach and got into the act. Their work resulted in significant modifications to some of Emiliani's conclusions. One of the main improvements was simply refining the time scale using paleomagnetic stratigraphy as well as some of the geochronological tools we discussed earlier in the course (^{10}Be, Th isotopes, etc.). In his initial work, Emiliani had only ^{14}C dating available to him, and he dated older sections simply by extrapolating sedimentation rates based on ^{14}C dating.

Another important modification to Emiliani's work was a revision of the temperature scale. Emiliani had realized that the isotopic composition of the ocean would vary between glacial and interglacial times as isotopically light water was stored in glaciers, thus enriching the oceans in ^{18}O. Assuming a $\delta^{18}O$ value of about –15‰ for glacial ice, Emiliani estimated that this factor accounted for about 20% of the observed variations. The remainder he attributed to the effect of temperature on isotope fractionation. However, Shackleton and Opdyke (1973) argued that storage of isotopically light water in glacial ice was actually the main effect causing oxygen isotopic variations in biogenic carbonates, and that the temperature effect was only secondary. Their argument was based on the observation that nearly the same isotopic variations occurred in both planktonic (surface-dwelling) and benthic (bottom dwelling) foraminifera. Because of the way in which the deep water of the ocean is formed, Shackleton and Opdyke argued that deep water temperature should not vary between glacial and interglacial cycles.

The question of just how much of the variation is deep sea carbonate sediments is due to ice build-up and how much is due to the effect of temperature on fractionation is a still debated question, upon which there is little consensus. After Shackleton and Opdyke's work, climate modeling suggested deep water temperatures may indeed vary, though probably not as much as Emiliani had calculated. It is fairly clear that the average $\delta^{18}O$ of glacial ice is probably less than –15‰, as Emiliani had assumed. Typical values for Greenland ice are –30 to -40‰ (relative to SMOW) and as much as -50‰ for Antarctic ice. If the exact isotopic composition of ice and the ice volume were known, it would be a straightforward exercise to calculate the effect of

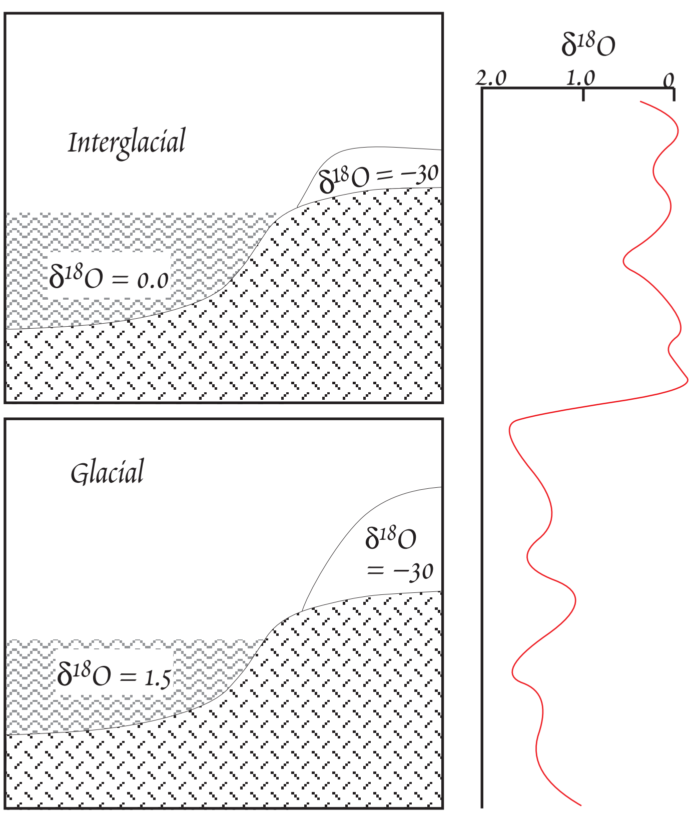

Figure 34.2. Cartoon illustrating how $\delta^{18}O$ of the ocean changes between glacial and interglacial periods.

continental ice build up on ocean isotopic composition. For example, the present volume of continental ice is 27.5×10^6 km^3, while the volume of the oceans is 1350×10^6 km^3. Assuming glacial ice has a mean $\delta^{18}O$ of –30‰ relative to SMOW, we can calculate the $\delta^{18}O$ of the hydrosphere as –0.6‰ (neglecting freshwater reservoirs, which are small). At the height of the Wisconsin Glaciation, the volume of glacial ice is thought to have increased by 42×10^6 km^3, corresponding to a lowering of sea level by 125 m. If the $\delta^{18}O$ of ice was the same then as now (–30‰), we can readily calculate that the $\delta^{18}O$ of the ocean would have increased by 1.59‰. This is illustrated in Figure 34.2.

To see how much this affects estimated temperature changes, we can use Craig's* (1965) revision of the Epstein calcite-water geothermometer:

$$T°C = 16.9 - 4.2\ \Delta_{cal\text{-}water} + 0.13\Delta^2_{cal\text{-}water} \qquad 34.2$$

According to this equation, at 20° C, the fractionation should be 33‰. At 14°C the fractionation is 31.5‰. Thus is a glacial foram shell were 2 ‰ lighter, Emiliani would have made a correction of 0.5‰ for the change in oxygen isotopic composition of seawater and attributed the remainder of the difference, 1.5‰, to temperature. Thus he would have concluded that part of the ocean was 6‰ cooler. However, if the change in the isotopic composition of seawater is actually 1.5‰, the calculated temperature difference is only about 2° C. Thus the question of the volume of glacial ice, and its isotopic composition must be resolved before $\delta^{18}O$ in deep sea carbonates can be used to calculate paleotemperatures. It is now generally assumed that the $\delta^{18}O$ of the ocean changed by 1.5‰ between glacial and interglacial periods, but the exact value is still debated. Comparison of sealevel curves derived from dating of terraces and coral reefs indicate that each 0.011‰ variation in $\delta^{18}O$ represents a 1 m change in sealevel.

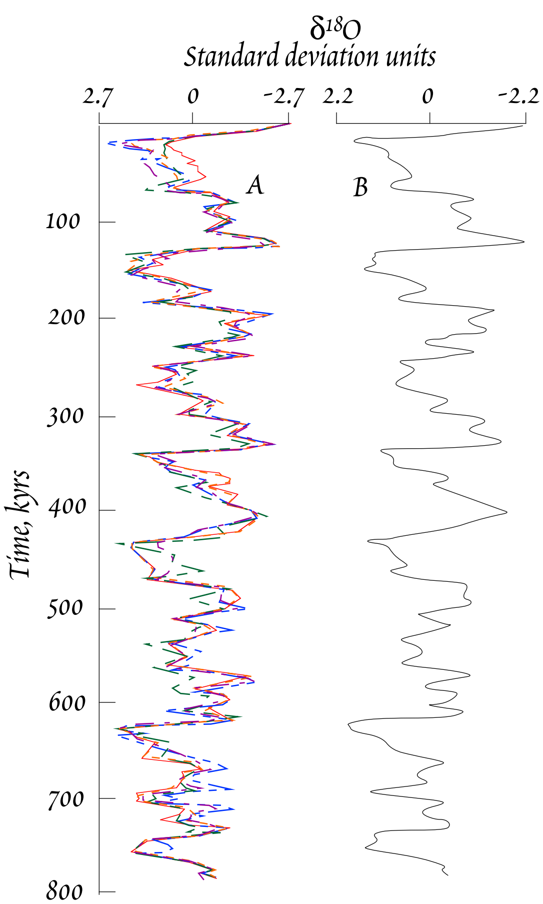

Figure 34.3. A. "Stacking of five cores" selected by Imbrie et al. (1984). Because the absolute value of $\delta^{18}O$ varies in from core to core, the variation is shown in standard deviation units. B. Smoothed average of the five cores in A. After Imbrie et al. (1984).

By now, hundreds, if not thousands of deep sea cores have been analyzed for oxygen isotope ratios. Though most reveal the same general picture, the $\delta^{18}O$ curve varies from core to core. In addition to the changing isotopic composition of the ocean, the $\delta^{18}O$ in a given core will depend on several other factors: (1) The temperature in which the organisms grew. (2) The faunal assemblage, as the exact fractionation will vary from organism to organism. For this reason, $\delta^{18}O$ analyses are often performed on a single species. However, these "vital effects" are usually small, at least for planktonic foraminifera. (3) Local variations in water isotopic composition. This is important in the Gulf of Mexico, for example. Meltwater released at the end (termination) of glacial stages flooded the surface of the Gulf of Mexico with enough isotopically light meltwater to significantly change its isotopic composition relative to the ocean as a whole. (4) Sedimentation rate varies from core to core, so that $\delta^{18}O$ as a function of depth in the core will differ between cores. Changes in sedimentation rate at a give locality will distort the appearance of

* Harmon Craig was also a student of Harold Urey.

the $\delta^{18}O$ curve. (5) Bioturbation, i.e., burrowing activity of seafloor animals, which may smear the record.

The Cause of Quaternary Glaciations

For these reasons, correlating from core to core and can sometimes be difficult and constructing a "standard" $\delta^{18}O$ record is a non-trivial task. Nevertheless, it is the first step in understanding the global climate change signal. Figure 34.3 shows the global $\delta^{18}O$ record constructed by averaging 5 cores (Imbrie, et al., 1984). A careful examination of the global curve shows a periodicity of approximately 100,000 years. The same periodicity was apparent in Emiliani's initial work and led him to conclude that the glacial-interglacial cycles were due to variations in the Earth's orbital parameters. These are often referred to as the Milankovitch cycles, after M. Milankovitch, a Serbian astronomer who argued they caused the ice ages in the early part of the twentieth century†.

Three parameters describe these variations: e: eccentricity, ε: obliquity (tilt), and precession: $e \sin \omega$, where ω is the longitude of perihelion (perihelion is the Earth's closest approach to the Sun). The *eccentricity* (i.e., the degree to which the orbit differs from circular) of the Earth's orbit about the Sun, and the degree of tilt, or *obliquity*, of the Earth's rotational axis vary slightly. Precession refers to the change in the direction in which the Earth's rotational axis tilts when it is closest to the Sun (perihelion). These variations, which are illustrated in Figure 34.4, affect the pattern of solar radiation , called insolation, that the Earth receives. Changes in these parameters have negligible effect on the total insolation, but they do affect the pattern of incoming radiation (insolation). For example, tilt of the rotational axis determines seasonality, and the latitudinal gradient of insolation. It is this gradient that drives atmospheric and oceanic circulation. If the tilt is small, seasonality will be reduced (cooler summers, warmer winters), and the average annual insolation gradient will be high. Precision relative to the eccentricity of the Earth's orbit also affects seasonality. For example, the Earth presently is closest to the Sun in January. As a result, northern hemisphere winters (and southern hemisphere summers) are somewhat milder than they would be otherwise. For a given latitude and season, precession will result in a ±5% difference in insolation. While the Earth's orbit is only slightly elliptical, and variations in eccentricity are small, these variations are magnified because insolation varies with the inverse square of the Earth-Sun distance.

Variation in tilt approximate a simple sinusoidal function with a period of 41,000 yrs. Variations in eccentricity can be approximately described with characteristic period of 100,000 years. In actuality variation in eccentricity is more complex, and is more accurately described with periods of 123,000 yrs, 85,000 yrs, and 58,000 yrs. Similarly, variation in precession has characteristic periods of 23,000 and 18,000 yrs.

While Emiliani suspected $\delta^{18}O$ variations were related to variations these

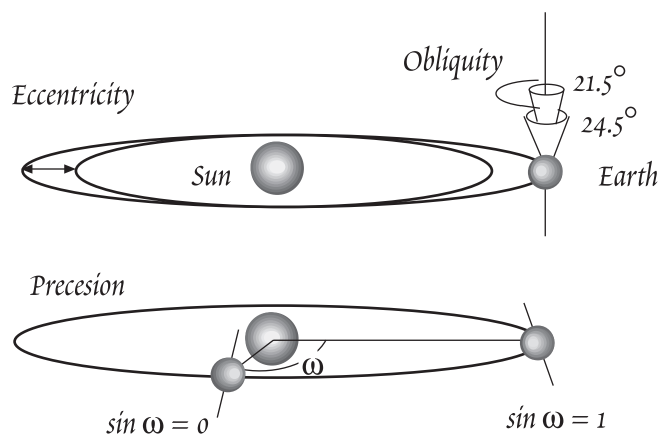

Figure 34.4. Cartoon illustrating the "Milankovitch parameters". The eccentricity is the degree the Earth's orbit departs from circular. Obliquity is the tilt of the Earth's rotation axis with respect to the plane of the ecliptic. Obliquity varies between 21.5° and 24.5°. Precision is the variation in the direction of tilt at the Earth's closest approach to the Sun (perihelion). The parameter ω is the angle between the Earth's position on June 21 (summer solstice), and perihelion.

† While Milankovitch was a strong and early proponent of the idea that variations in the Earth's orbit caused ice ages, he was not the first to suggest it. J. Croll of Britian first suggested it in 1864, and published severl subsequent papers on the subject.

"Milankovitch" parameters, the first quantitative approach to the problem was that of Hayes et al. (1976). They applied Fourier analysis to the $\delta^{18}O$ curve, a mathematical tool that transforms a complex variation such as that in Figure 34.3 to the sum of a series of simple sine functions. Hayes et al. then used spectral analysis to show that much of the spectral power of the $\delta^{18}O$ curve occurred at frequencies similar to those of the Milankovitch parameters. By far the most elegant and convincing treatment, however, is that of Imbrie (1985). Imbrie's treatment involved several refinements and extension of the earlier work of Hayes et al. (1976). First, he used improved values for Milankovitch frequencies. Second, he noted these Milankovitch parameters might vary with time, as might the climate system's response to them. The Earth's orbit and tilt are affected by the gravitational field of the Moon and other planets. In addition, other astronomical events, such as bolide impacts, can affect them. Thus Imbrie treated the first and second 400,000 years of Figure 34.3 separately. The power spectrum for these two parts of the $\delta^{18}O$ curve is shown in Figure 34.5.

Imbrie observed that climate does not respond instantaneously to forcing. For example, maximum temperatures are not reached in Ithaca until mid or late July, 3 to 4 weeks after the maximum insolation, which occurs on June 21. Thus there is a *phase* difference between the forcing function (insolation) and climatic response (temperature). Imbrie also pointed out that the climate might respond differently to different forcing functions. As an example, he used temperature variations in the Indian Ocean, which respond both to annual changes in insolation and to semiannual changes in ocean upwelling. The response to these two forcing functions differs in different localities. The extent to which climate responds to a particular forcing function is the *gain*. The phase lag may also differ from locality to locality. Mathematically, the climatic response can be expressed as:

$$y = g_1(x_1 - \phi_1) + g_2(x_2 - \phi_2) \qquad 34.3$$

where y is the climatic response (temperature) x_1 and x_2 are the two forcing functions (insolation and upwelling), g_1 and g_2 are the gains associated with them and ϕ_1 and ϕ_2 are the phase lags).

Imbrie (1985) constructed a model for response of global climate (as measured by the $\delta^{18}O$ curve) in which each of the 6 Milankovitch forcing functions was associated with a different gain and phase. The values of gain and phase for each parameter were found statistically by minimizing the residuals of the power spectrum (Figure 34.5). Table 34.1 gives the essential parameters of the model. σ_x is the strength of each forcing function, and σ_y is the strength of the response (given in meters of sealevel reduction), k is the coefficient of coherency, g is the gain (σ_y/σ_x), and ϕ is the phase difference between input function and the climatic response. The resulting model is shown in comparison with the data for the past 400,000 years and the next 25,000 years in Figure 34.6. The model has a correlation coefficient, r, of 0.88 with the data. Thus about r^2, or 77%, of the variation in $\delta^{18}O$, and therefore presumably in ice volume, can be explained Imbrie's Milankovitch model. The correlation for the period 400,000–782,000 yrs is somewhat poorer, around 0.80, but nevertheless impressive.

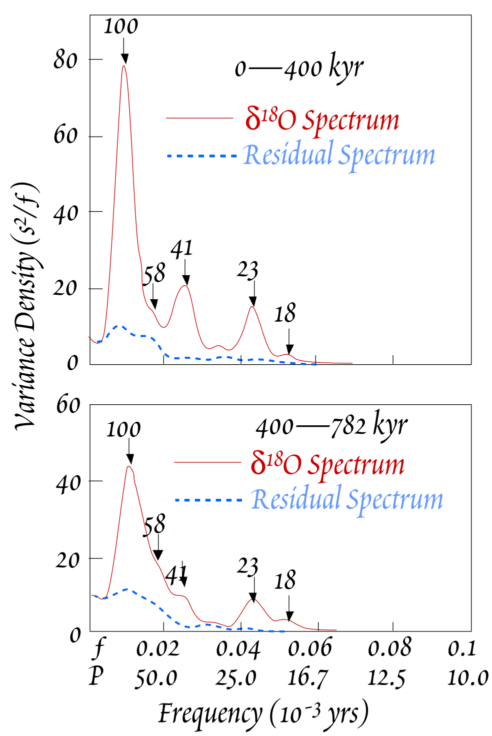

Figure 34.5. Power spectrum of the composite $\delta^{18}O$ curve shown in Figure 36.3 as a function of frequency. Peaks in the spectrum correspond with the frequencies of the variations of the Milankovitch parameters. The residual spectrum shows the variance remaining after subtracting a phase and gain model based on the Milankovitch parameters. The upper figure shows the power spectrum for 0-400 kyr BP, the lower figure for the period 400-782 kyr. After Imbrie (1985).

TABLE 34.1 GAIN AND PHASE MODEL OF IMBRIE (1985)

Frequency band	σ_y (m)	σ_x (u)	k	g (m/u)	ϕ ka
e_{123}	19.5	0.167	0.58	68	–5
e_{95} 19.3	0.250	0.83	64	-3	
e_{59} 12.2	0.033	0.79	292	-12	
ε	15.0	0.394	0.92	35	-9
p_{23} 13.0	0.297	0.95	42	-6	
p_{18} 5.3	0.154	0.81	28	-3	

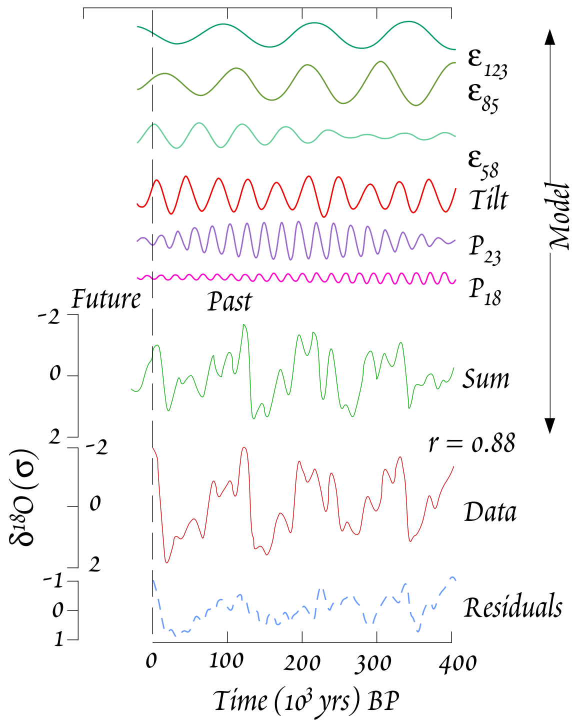

Figure 34.6. Gain and phase model of Imbrie relating variations in eccentricity, tilt, and precession to the oxygen isotope curve. Top shows the variation in these parameters over the past 400,000 and next 25,000 years. Bottom shows the sum of these functions with appropriated gains and phases applied and compares them with the observed data. After Imbrie (1985).

Since variations in the Earth's orbital parameters do not affect the average annual insolation the Earth receives, but only its pattern in space and time, one might ask how this could cause glaciation. The key factor seems to be the insolation received during summer by high northern latitudes. This is, of course, the area where large continental ice sheets develop. The southern hemisphere, except for Antarctica, is largely ocean, and therefore not subject to glaciation. Glaciers apparently develop when summers are not warm enough to melt the winter's accumulation of snow.

Nevertheless, the total variation in insolation is small, and not enough by itself to cause the climatic variations observed. Apparently, there are feedback mechanisms at work that serve to amplify the fundamental Milankovitch forcing function. One of these feedback mechanisms was identified by Agassiz, and that is ice albedo, or reflectance. Snow and ice reflect much of the incoming sunlight back into space. Thus as glaciers advance, they will cause further cooling. Any additional accumulation of ice in Antarctica, however, does not result in increased albedo, because the continent is fully ice covered even in non-glacial time, hence the dominant role of northern hemisphere insolation in driving climate cycles. What other feedback mechanisms might be at work is still a matter of much speculation. Isotope geochemistry provides some interesting insights into 2 of these possible feedback mechanisms, carbon dioxide and ocean circulation, and we will discuss them in the next few lectures.

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