GS331 Oceanography
Marine Stable Isotope Records and Paleoclimate

I. Introduction
   A. stable isotopes - isotopes of elements that do not undergo radioactive decay
   B. stable isotopes - provide basis for understanding of past climates
      1. atmospheric conditions
      2. oceanic conditions
   C. Understanding the history of past conditions provides insight into potential future conditions
      1. natural global change
      2. anthropogenic global change
   D. Oxygen Stable Isotopes (O^{16}, O^{18}) and Paleo-Reconstruction of Ocean Conditions
      1. water temperatures
      2. ice-sheet sizes
      3. salinity variations over time
   E. Carbon Stable Isotopes (C^{12}, C^{13})
      1. water circulation patterns
      2. nutrient levels
      3. atmospheric CO_2 concentrations
   F. Stratigraphic Record: Accumulation of Ocean Sediments
      1. sediments accumulate over time on the seafloor
         a. law of superposition
            (1) oldest layer on bottom
            (2) youngest layer on top
         b. sediment composition
            (1) biogenic
            (2) lithogenic
      2. biogenic sediments as records of stable isotopes
         a. marine organisms are very sensitive to changes in ocean water chemistry
         b. change is ocean isotope composition is recorded as a change in marine organism composition
      3. Stratigraphic analysis and age dating of sediments
         a. place sedimentary strata in a time frame of Earth history
         b. demonstrating synchrony of isotope changes around the earth = powerful tool for reconstruction of global change

II. Oxygen Isotope Variations in Natural Environment
   A. Oxygen Isotopes:
      1. O^{16}, = 8 p+, 8 e-, 8 n
         a. most abundant isotope
         b. 99.8% of oxygen in ocean system
      2. O^{18} = 8 p+, 8 e-, 10 n
         a. minimal component of ocean system
         b. 0.2% of oxygen in system
      3. Oxygen Isotope Ratio
         a. O^{18}/O^{16}
         b. determined by use of mass spectrometry

c. Standardized Ratio (necessary for comparison of values)

$$\delta^{18}O = \frac{O^{18}/O^{16}\text{ Sample} - O^{18}/O^{16}\text{ Standard}}{O^{18}/O^{16}\text{ Standard}} \times 1000$$

where O^{18}/O^{16} = number of atoms of O^{18} divided by number of atoms of O^{16}, and $\delta^{18}O$ is in units of parts per thousand (ppt)

Hence, as $\delta^{18}O$ increases in value, the relative ^{18}O content is increasing.

d. reference standards
  (1) carbonate samples (shell material)
    (a) PDB = belemnite fossil from PeeDee Fm of South Carolina
  (2) water samples
    (a) SMOW = standard mean ocean water

Example Problem: A mass spectrometer is used to analyze a water sample to determine the $\delta^{18}O$ value compared to a standard ocean water chemistry. In this example, the number of O18 and O16 atoms were detected by the mass spectrometer, the results are listed below.

	unknown water sample	SMOW sample
Number of ^{18}O atoms	4	4
Number of ^{16}O atoms	1994	1996

(1) From each sample, determine the total percentage of O^{18} and O^{16}, respectively.

(2) Determine the $\delta^{18}O$ value for the unknown sample.

III. Oxygen Isotope Paleothermometry

A. Approach: use of modern mollusks living in a wide range of water temperatures
  1. organism shells are composed of CaCO3 which is biogenically precipitated in the ocean water environment
    a. mollusks
    b. foraminifera
    c. coral
  2. measured $\delta^{18}O$ ratios in shells
  3. determined temperature relationships

  4. Paleotemperature Equation (Empirically determined)

$$T = 16.5 - [4.3(\delta^{18}O_{calcite} - \delta^{18}O_{water})] + [0.14(\delta^{18}O_{calcite} - \delta^{18}O_{water})^2]$$

where temperature is in degrees C

Example Problem:

A modern mollusk shell is analyzed for oxygen isotopes and has an $\delta^{18}O$ value of -4, the $\delta^{18}O$ value of the water it is found in is -2. Calculate the temperature of the water in degrees celsius. How about degrees F?

IV. Origin of Oxygen Isotope Variations

- A. O^{18}/O^{16} ratios are variable in space and time
  - 1. temperature significantly effects the evaporation of water molecules that are constructed of O^{18} and O^{16}
  - 2. Temperature and evaporation siginificantly impact the marine $\delta^{18}O$ calcite record in shells through time

- B. Water Cycle and Oxygen Isotopes
  - 1. General Circulation
    - a. evaporation of H_2O at equator and transport toward poles

  - 2. Ease of evaporation of isotopically "light" and "heavy" water molecules
    - a. H_2O^{18} = resistant to evaporation (less reactive)
    - b. H_2O^{16} = easily evaporated (more reactive)

NET RESULT = "isotopic fractionation" in ocean water

  - 3. Isotopic Fractionation
    - a. Seawater Evaporation
      - (1) $>H_2O^{16}$ in water vapor
      - (2) $<H_2O^{16}$ in remaining seawater
        - (a) relative enrichment of H_2O^{18} in seawater
    - b. Atmospheric Condensation
      - (1) condensation of rain from clouds:
        - (a) concentrates H_2O^{16} in snow
    - c. Thus temperature controls $\delta^{18}O$ values in seawater, and result calcium carbonate shells

  - 4. Latitudinal Changes in $\delta^{18}O$ in modern ocean water
    - a. Low Latitudes = warm temp = > evaporation
      - (1) tropical seawater enriched in $\delta^{18}O$
        - (a) ~ -2 parts per thousand
    - b. High Latitudes = cold temp = < evaporation
      - (1) polar seawater depleted in $\delta^{18}O$
        - (a) ~ -20 parts per thousand

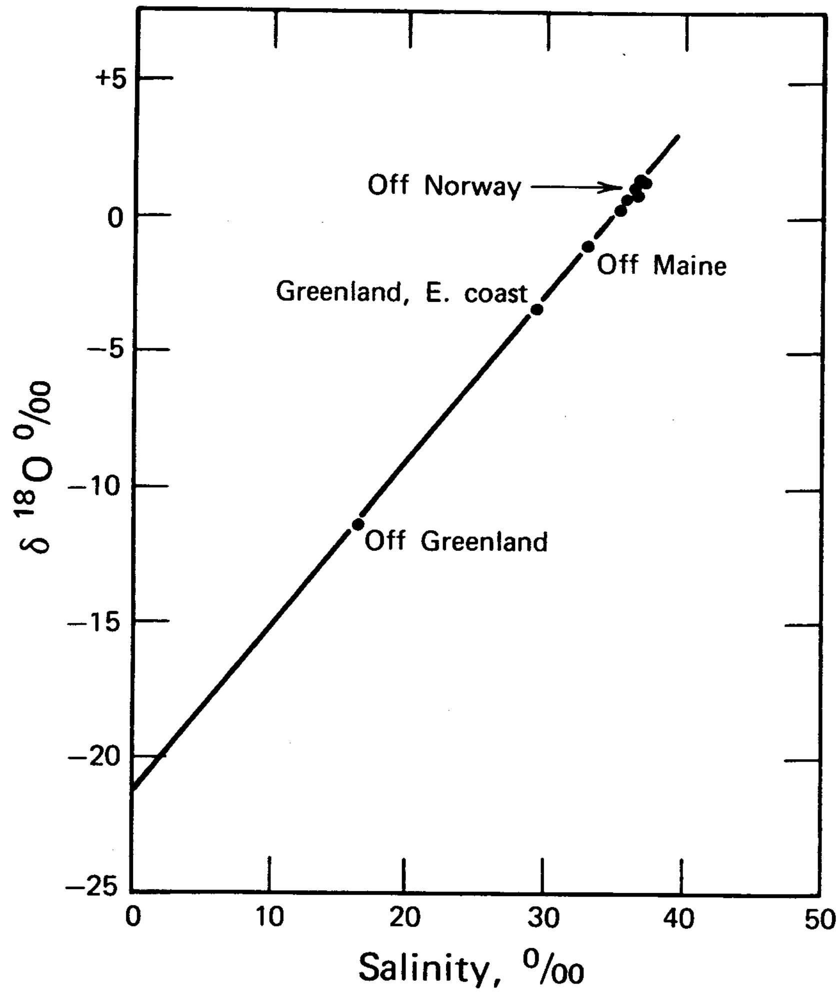

Figure 24.7 Relationship between $\delta^{18}O$ and salinity of surface water from the North Atlantic Ocean. (Data from Epstein and Mayeda, 1953, and Craig and Gordon, 1965.) The standard is SMOW.

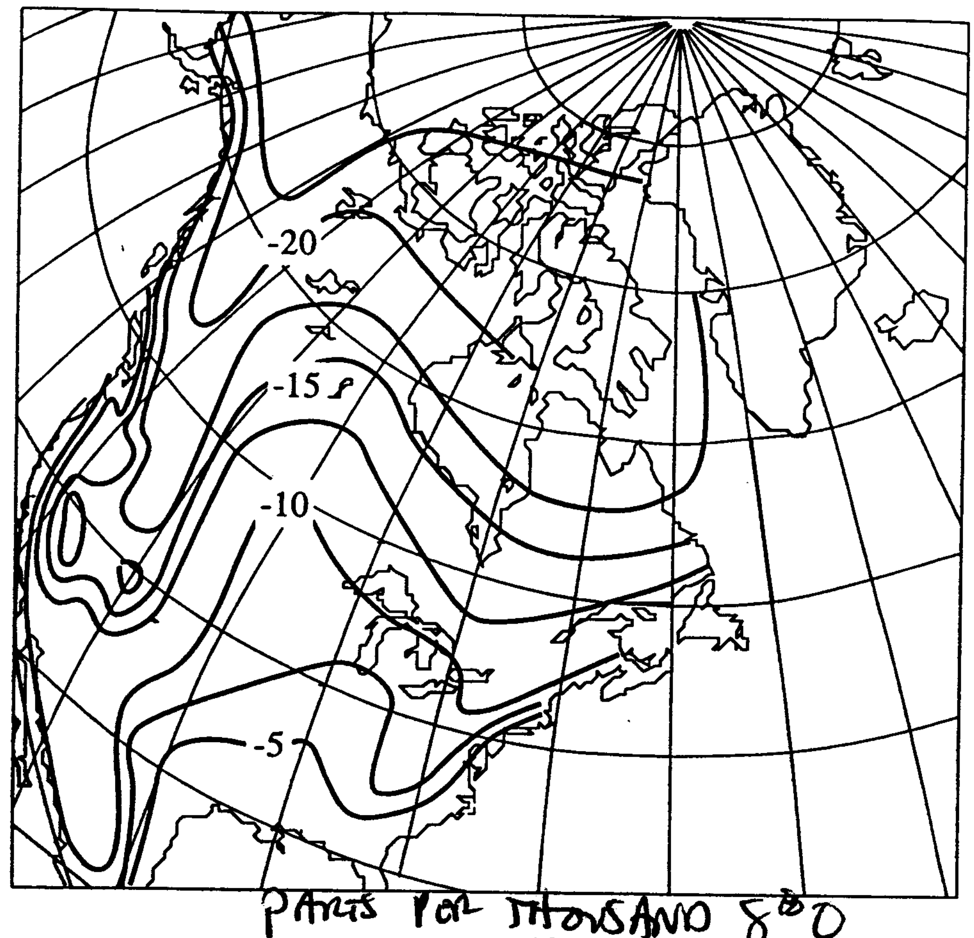

Figure 1. Generalized map of the $\delta^{18}O$ values of precipitation in North America (after Fairbanks, 1982), showing the regional variability. The pattern in $\delta^{18}O$ values reflect larger the surface air temperature gradients (i.e., changes with latitude and elevation).

5. O isotope changes according to salinity

   a. Increased evaporation not only enriches O18, but also increases salinity in remaining water
   b. direct correlation between increase in salinity and increase in O18
   c. Empirical relationships based on modern variations

$\delta^{18}O = -21.2 + 0.61(S)$

where S = salinity in parts per thousand, and $\delta^{18}O$ is in parts per thousand

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Example problem, a seawater sample from the North Atlantic has a $\delta^{18}O$ = -10 ppt, what is it's salinity? answer in parts per thousand.

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6. Glacial / Interglacial Influences on Oxygen Isotopes
   a. Glacial Climate
      (1) build-up of ice sheets, removal of water from ocean
      (2) ^{16}O is easily evaporated and stored in ice sheets
         (a) ice sheets show low amounts of ^{18}O
         (b) Ice sheets are enriched in ^{16}O, hence causing the $^{18}O/^{16}O$ ratio to decrease (in the ice sheet)
      (3) relative concentration of ^{18}O increases in ocean
      (4) The ocean change in ^{18}O is opposite of that in the related ice sheet

   b. Interglacial Climate
      (1) melting of ice sheets, release of water from storage to ocean
      (2) ^{16}O is released back to ocean
      (3) results in relative decrease in ^{18}O ratio

   c. Example Last Glacial Episode (late Wisconsinan)
      (1) maximum ice build-up at ~20,000 years ago
      (2) sea level ~120 m lower than present (< in 3% of ocean volume)
         (a) $\delta^{18}O$ content of sea water 20,000 yr ago compared to SMOW ~1.2 parts per thousand
            i) i.e. the ^{18}O content was higher in the oceans 20,000 years ago, due to increased evaporation / removal of ^{16}O.

At present, high-latitude precipitation returns to the oceans through summer melting. During glacial intervals, however, large ice sheets store the lighter isotope (^{16}O). The difference in $\delta^{18}O_{water}$ values between the ice sheet and mean ocean was large ($\delta^{18}O_{ice}$ = -35 to -40 per mil versus $\delta^{18}O_{water}$ mean ocean = ~0 per mil). As a result, variations in ice sheet sizes are reflected in the variable oceanic $\delta^{18}O_{water}$ values. The most recent glacial to interglacial transition provides the best illustration of how ice sheets affect the ocean $\delta^{18}O_{water}$ value (Fig. 2). During the last glacial maximum, the amount of water stored in ice sheets caused the global sea level to be 120 m lower than present (Fairbanks, 1989). This change in sea level represents a decrease of ~3 percent in the ocean vol-

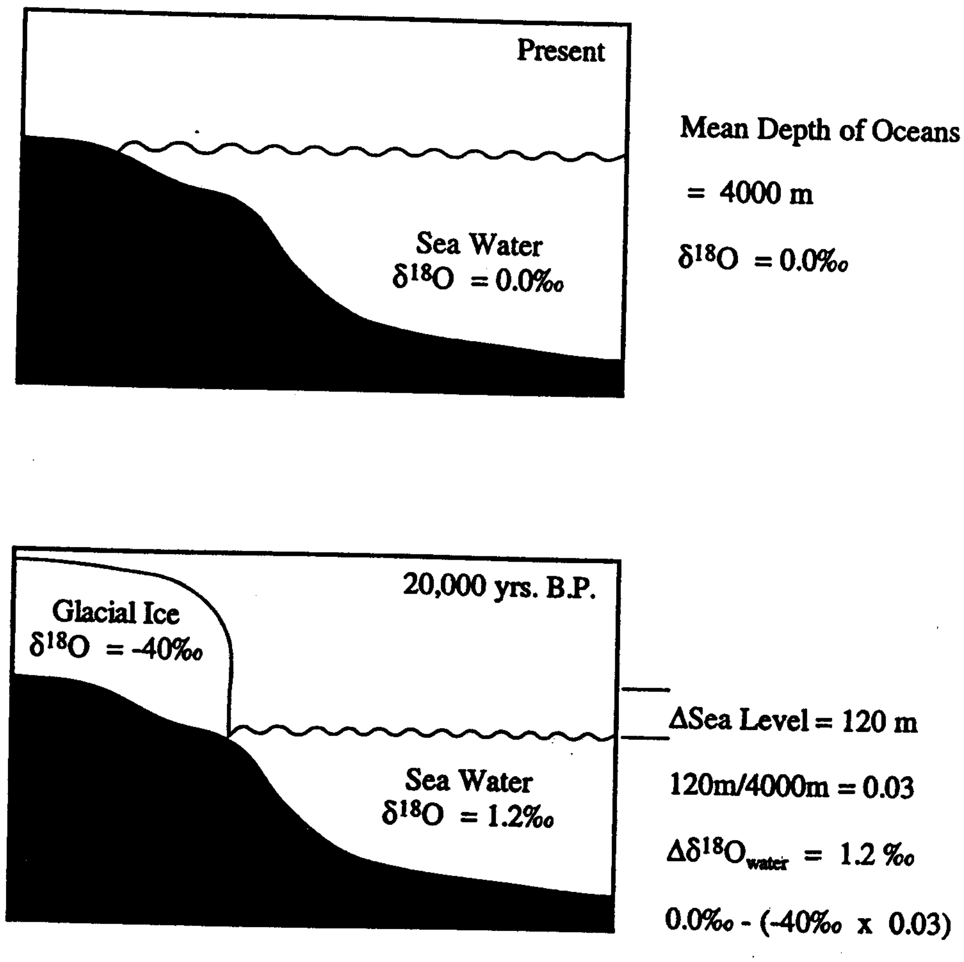


Figure 2. The effect of large ice sheets on the $\delta^{18}O$ composition of the ocean can be significant. The removal of 3 percent of the ocean's water during the last glacial maximum lowered sea level by 120 m. The $\delta^{18}O$ difference between the ocean and the ice is 40 per mil, causing a whole ocean $\delta^{18}O$ change of 1.2 per mil.

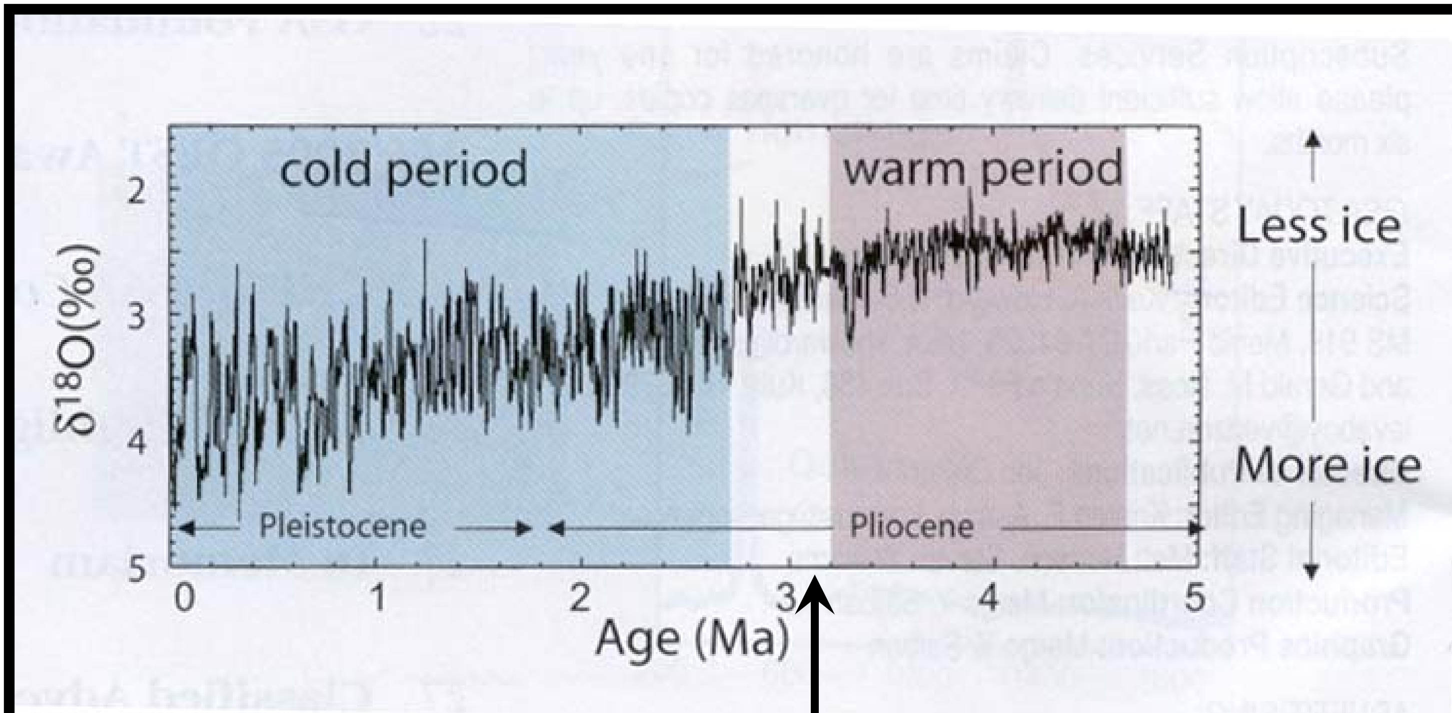
OXYGEN ISO

The first system: isotope record was from planktonic fora sils) in Caribbean dee recognized the cyclic ues and concluded tha glacial intervals. Wit seven most recent cl spanned the last 280, cate that they represe Paleotemperature Equ estimated that ice she was relatively small ($\delta^{18}O_{calcite}$ variability t vals represented temp 10°C with the glacial ed the $\delta^{18}O_{calcite}$ record ignated with odd numb and the cold stages Stage 1" would refer t "Isotope Stage 2" wou od (Fig. 3).

A numerical tim marine isotope stages which age estimates in down core $\delta^{18}O_{calcite}$ Emiliani's $\delta^{18}O_{calcite}$ re on the sediments youn existing terrestrial reco glacial high stand of Several aspects of this phy were questioned, ice sheet-induced $\delta^{18}C$ the 100,000 year date (Broecker and others, Emiliani's pioneering w ic framework for corre

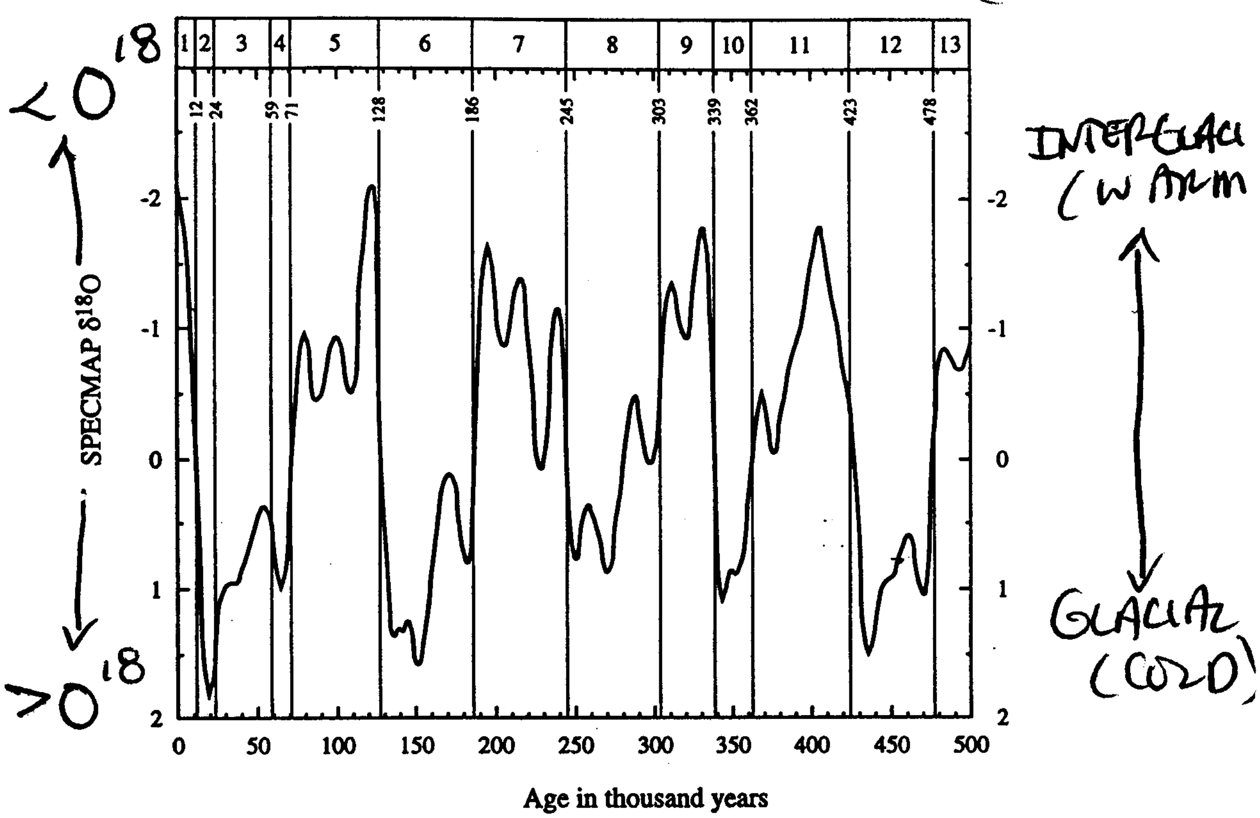
Oxygen Isotope-Climate Record (0 – 5 m.y. BP)

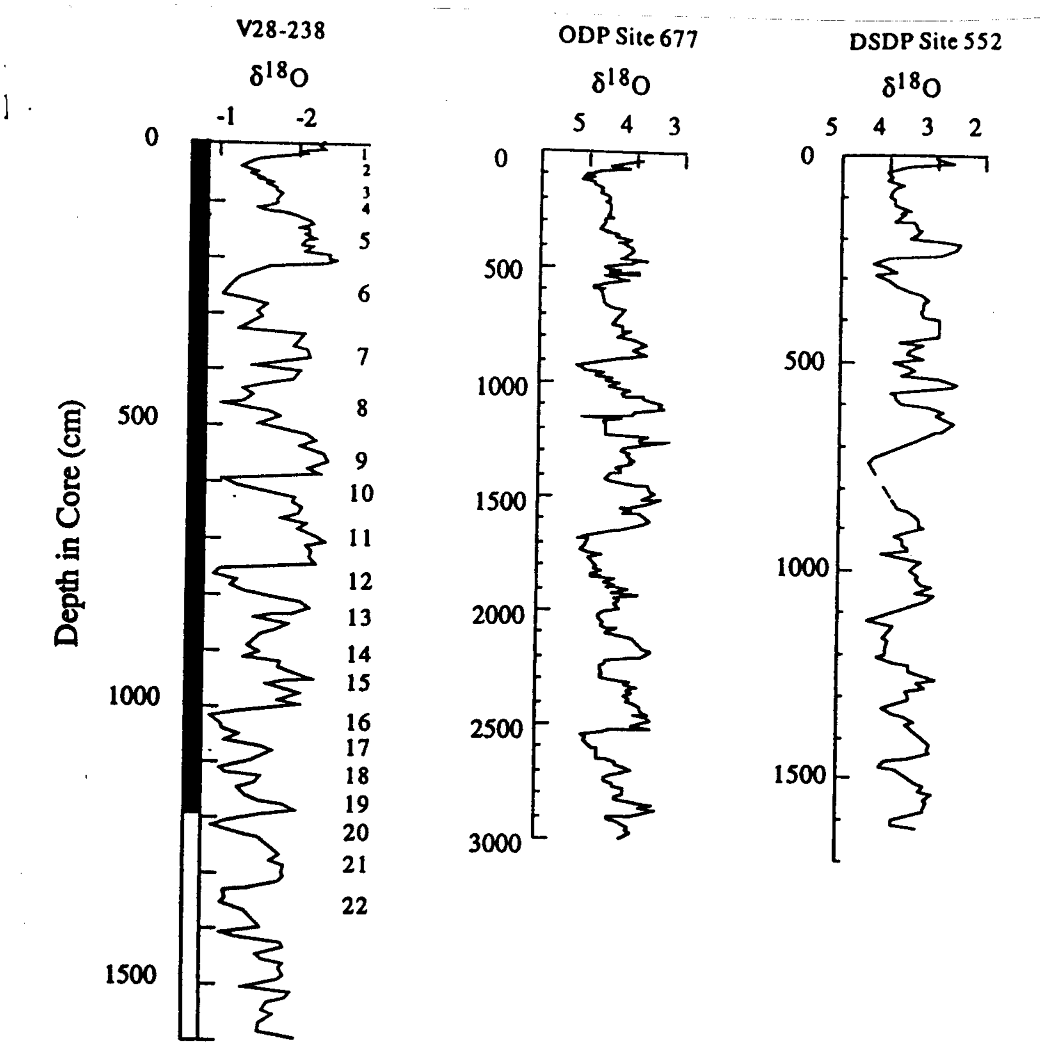
Benthic forams; ODP 1990 and 2001



Onset of Northern Hemisphere Glaciation ~ 3 Ma

GLOBAL CLIMATE RECORD (O^{18}/O^{16})





V. Oxygen Isotope Stratigraphy - Looking Back in Time

A. Seafloor sediment analysis of oxygen isotopes
   1. deep sea drilling and core samples
   2. layer-cake stratigraphy of sediment
   3. planktonic foraminifera fossils
      a. calcium carbonate microfossils

B. Oxygen isotope patterns in sediment layers
   1. cyclic patterns of low and high $\delta^{18}O$ calcite
   2. interpretation
      a. low spikes = interglacial (warm climate)
         (1) < ice volume globally (dilution of O18)
      b. high spikes = glacial (cold climate)
         (1) > ice volume globally (enrichment of O18)

   3. Oxygen isotope stages - letters and numbers applied to patterns
      a. stage 1 = present interglacial
      b. stage 2 = last glacial maximum (~20,000 yrs BP)

   4. global correlation
      a. replication of patterns from multiple drilling sites around the globe suggest that the oxygen isotope changes through time represent global, synchronous changes in climate
      b. correlating between known stratigraphy and unknown
         (1) must use similar species for analysis (different animals interact with O isotopes differently)
         (2) need to know something about chronology or time

   5. Radiometric dating
      a. carbon-14 and Uranium series dating of sedimentary strata
      b. global chronology of isotope stage

VI. Solar Activitiey and Causes of Global Climate Change in Last 2 m.y.

A. Characteristics of Glacial / Interglacial Climate on Earth

   1. Common glacial / interglacial climates in last 2 m.y., but NOT commonly observed in the record prior to 2 m.y. ago
   2. Global Temperatures fluctuate between 2°C to 6°C during glacial and interglacial climates
   3. Snowlines in alpine regions fluctuate by about 1000 m during glacial / interglacial climate cycles
   4. Glacial and interglacial climates are synchronous in both northern and southern hemispheres
   5. Desert areas experience increased rainfall ("pluvial" conditions) during glacial climate cycles

B. Short Term Climate Changes as Related to Solar Energy

1. Sun Spot Activity
   a. Sun Spots - dark spots on the surface of the sun
      (1) up to 1000's of miles in diameter
      (2) short-lived
         (a) hours to days up to months
      (3) lower temperature spots
         (a) ~1500 K less than surrounding part of photosphere
      (4) Sun Spot Cycles
         (a) the number and frequency of sun spots changes over time
            i) 11 year cycle: > in sun spot activity
               a) switching between high frequency and low

   b. Low Sun Spot Activity
      (1) polar winds / high pressure increase
      (2) shift of mid-latitude storm tracks toward equator
      (3) increased evaporation / storms
      (4) colder and wetter climates, in general

   c. High Sun Spot Activity
      (1) polar winds / high pressure decreases
      (2) mid-latitude storm tracks shift poleward
      (3) decreased evaporation / storms
      (4) warmer and drier climates

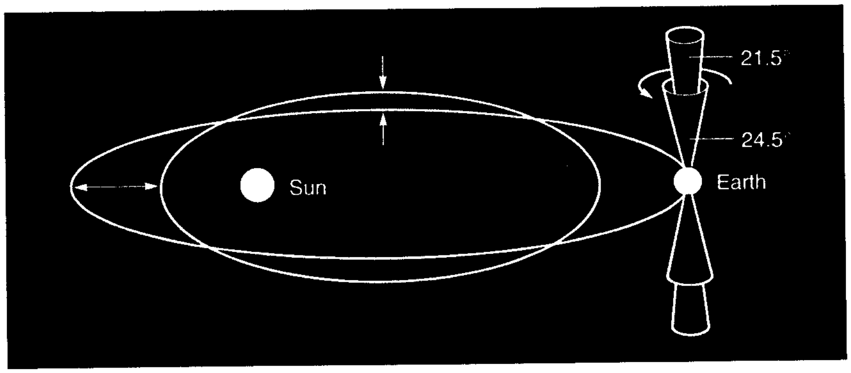
C. Long Term Climate Changes: Milankovitch Theory - Orbital Forcing of Climate Change

1. glacial climate variation the result of changes in levels of solar energy influx due to variations in Earth's orbital parameters

   a. redistribution of solar energy on Earth

2. Frequency of climate change recorded in oxygen isotope record, climate cycles (glacial-interglacial frequency) on order of:
   a. 100,000 yr (The dominant frequency predicting glacial / interglacial)
   b. 40,000-43,000 yr
   c. 19,500 - 24,000 yr

3. Astronomical Changes in Earth Orbit Parameters
   a. **Obliquity:** Axial wobble
      (1) Axis wobbles, circumscribing a circle on the celestial sphere
         (a) present: north pole points to polaris
         (b) 2000 BC north pole poined between big dipper and little dipper
         (c) 4000 BC, north pole pointed to handle of big dipper
      (2) Tilt of earth's axis changes over time
         (a) range from 21.8° to 24.4°



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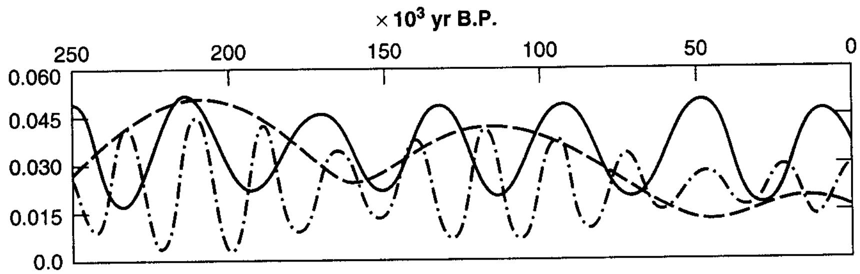

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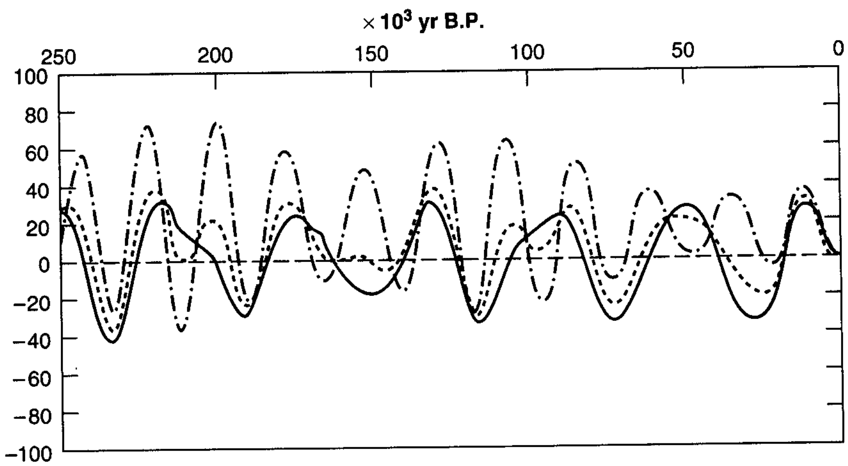

C.

FIGURE 14–23
(A) Cyclic changes in earth-sun relationships; (B) variation of eccentricity (----), precession (-·-·-·), and obliquity (— —) over the last 250,000 years; (C) Northern Hemisphere summer solar radiation at 80°N (— —), 65°N (·····), and 10°N (_._.) latitude (expressed as departures from A.D. 1950 values). The radiation signal at high latitudes is dominated by the ~41,000-year obliquity, whereas the ~23,000-year precessional cycle is dominant at lower latitudes. (B and C, from Bradley, 1985; after Berger, 1978)

(3) Periodicity of axial tilt: ~41,000 yr cycle
(4) Effects on Climate
  (a) > tilt angle, > seasonal difference in climate: hotter summers and colder winters

b. **Precession of Equinoxes**
  (1) precession: axial wobble and rotation of elliptical orbit cause equinoxes and solstices to shift slowly along orbital path

    (a) summer solstice occurs at position closest to sun vs. farthest from sun
      i) present, summer solstic occurs when earth is farthest from sun
      ii) position relative to distance from sun shift through time
    (b) Frequency of precession
      i) 21,000 yrs

    (c) Climate Effect
      i) tilt-distance seasonality relationships
      ii) when tilt towards sun is maximized at closest position in orbital path, results in increased intensity of seasons
        a) hotter summers and colder winters

c. **Eccentricity** of Earth's Orbital Path through Time

  (1) circular vs. elliptical orbital path - varies through time
    (a) the more circular, the less variation in seasonal heating / cooling
    (b) the more elliptical, the more variation in seasonal heating / cooling
      i) > distance at closest and farthest points relative to the sun

  (2) Present Configuration
    (a) Northern Hemisphere Summer Solstice = at pt. farthest from sun
    (b) Southern Hemisphere Winter Solstice = at pt. closest to sun

  (3) variations in Eccentricity will effect intensities of seasons

  (4) Frequency : eccentricity ~ 100,000 yr cycle

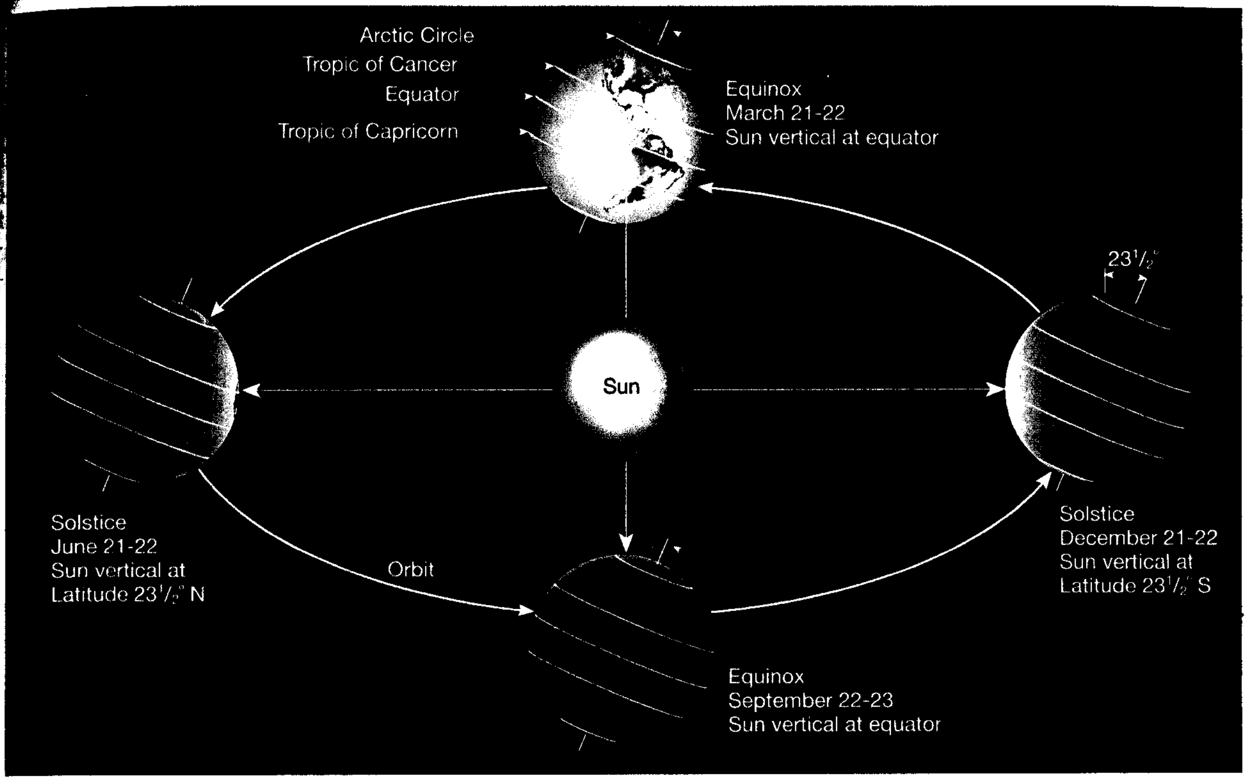

Figure 14.10 Earth–Sun relationships.

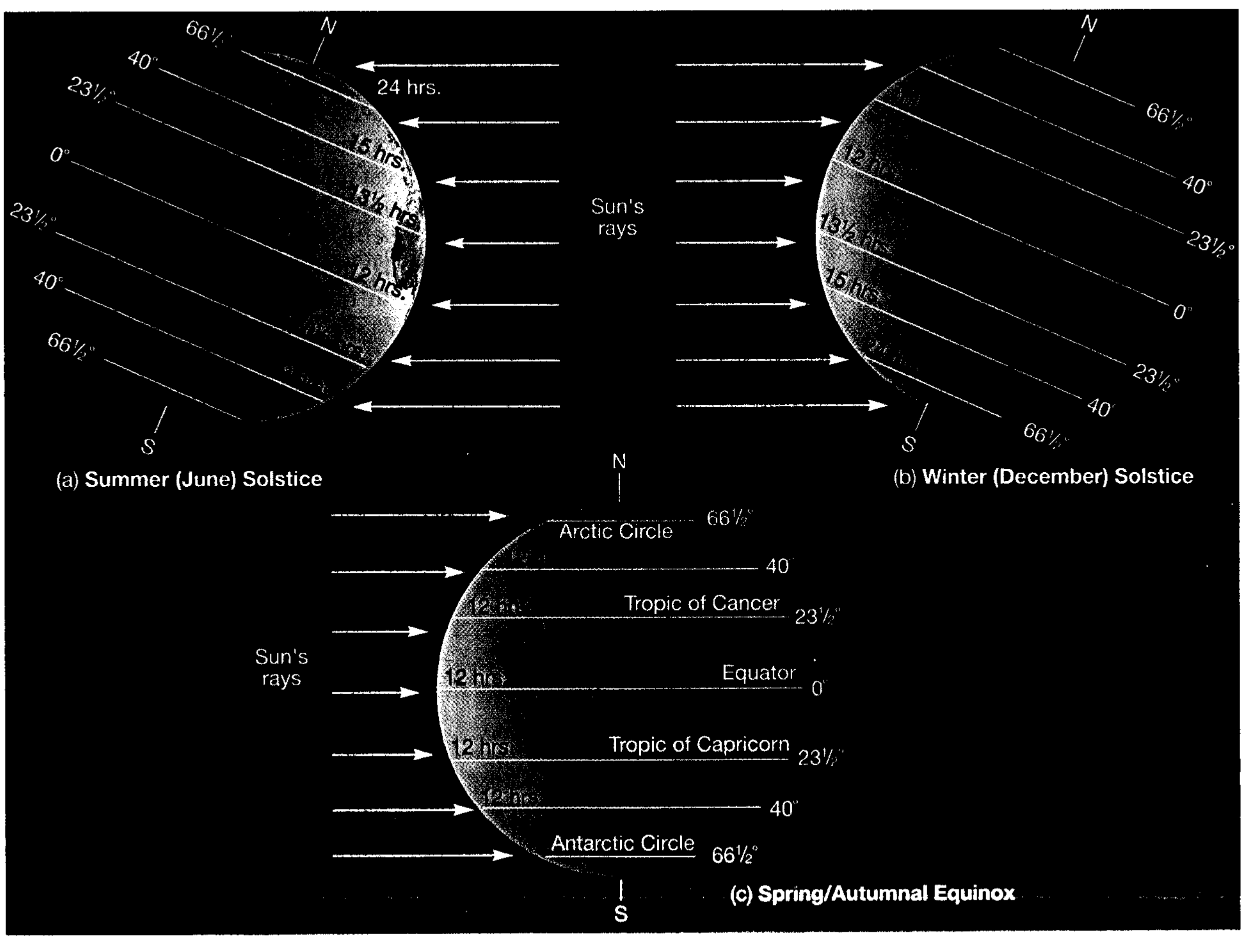

Figure 14.11 Characteristics of the solstices and equinoxes.

D. Summary of Climate Models

1. The correlation between the oxygen isotope / climate change record and the predicted Earth orbital parameters suggest that changes in the orbit of the Earth about the Sun may cause climate change from glacial to interglacial.

2. It appears that eccentricity of Earth orbit accounts for most of major glacial - interglacial climate change ~ 100,00 yr cycle

3. Maximized Glacial Conditions (Cold Climate)
   a. maximum eccentricity (elliptical) orbit
   b. maximum tilt angle of earth axis
   c. correlation of solstices with farthest points away from sun during elliptical orbit
   d. Requirement: maximized cold climate conditions at poles, maximized evaporation / atmospheric moisture at equatorial zone

4. Seasonality effects on glaciation
   a. < summer solar influx, > glacier size = accumulation
   b. >summer solar infllux, < glacier size = melting
   c. positive feedback
      (1) > ice area, > albedo, < incoming solar radiation, < temperatures, > ice accumulation
      (2) vice versa for melting of ice sheets