Carbon Isotopes

The Basics

A Short Course VU March, 2009

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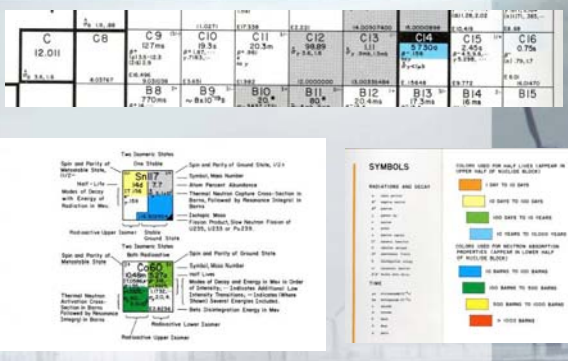
$^{14}N(n,p)^{14}C$



Nomenclature

$$\delta = \left[\frac{^{13}C/^{12}C_{Sample}}{^{13}C/^{12}C_{Standard}} \right] - 1 \quad \times 1000$$

δ ,del, or delta values are reported in ^{o} /oo or parts per thousand or per mille

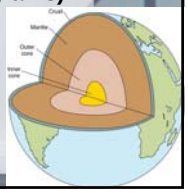
Less ^{13}C, δ values are negative or said to be light

Less ^{13}C, δ values are positive or said to be heavy

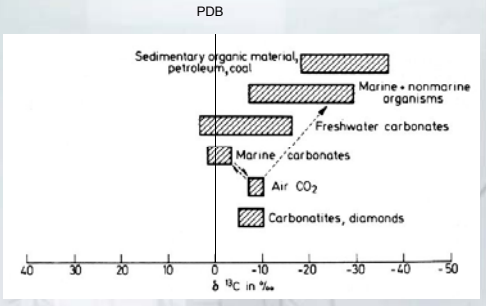
Standard is PDB (Pee Dee Belemnite)
V-PDB (Vienna Pee Dee Belemnite)

Forms of Carbon

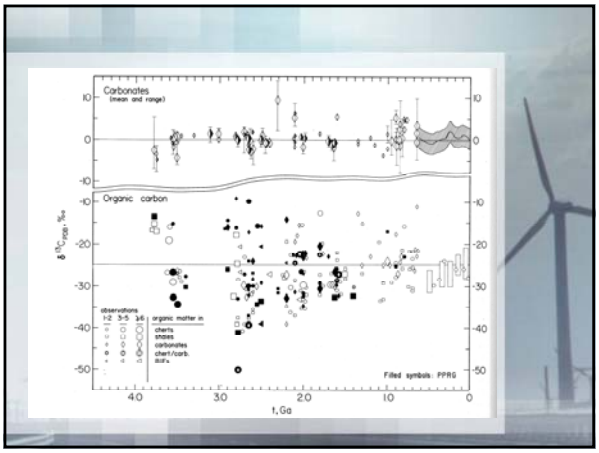
- **Primordial Carbon (324,000,000 10^{15} grams)**
  - **Methane**
  - **Graphite**
  - **Diamond**
  - **Other ??**
- **Carbonates (60,000,000 10^{15} grams)**
- **Reduced Carbon (15,000,000 10^{15} grams)**
  - **Gas**
    - **Thermogenic**
    - **Biogenic**
  - **Solid**
    - **Bitumen**
    - **Coal**

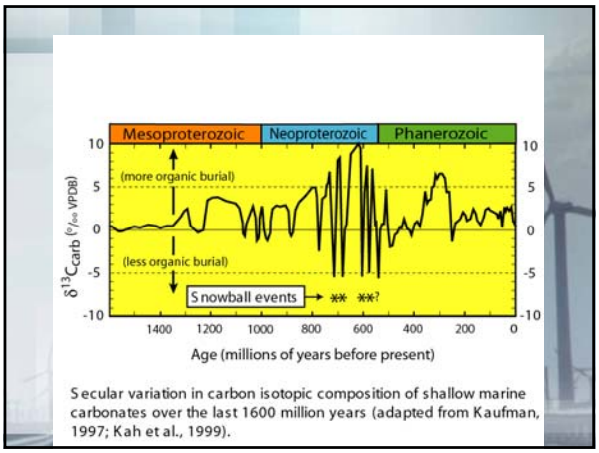


Range of Carbon Isotopes



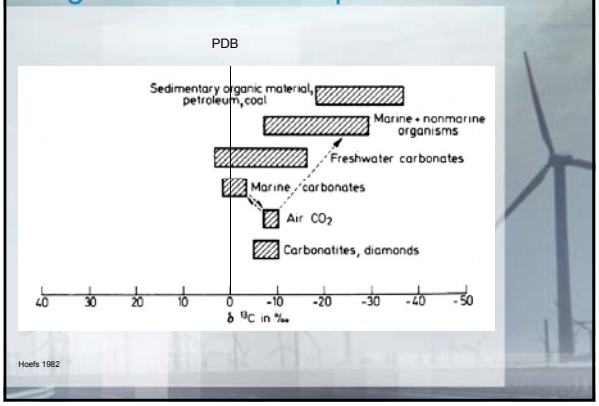
Hoefs 1982

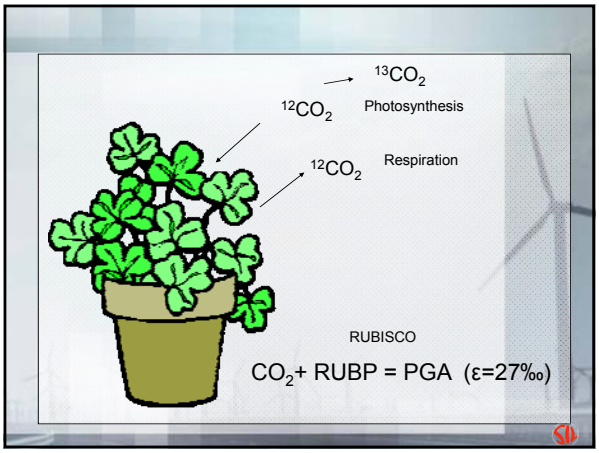




Secular variation in carbon isotopic composition of shallow marine carbonates over the last 1600 million years (adapted from Kaufman, 1997; Kah et al., 1999).

Range of Carbon Isotopes



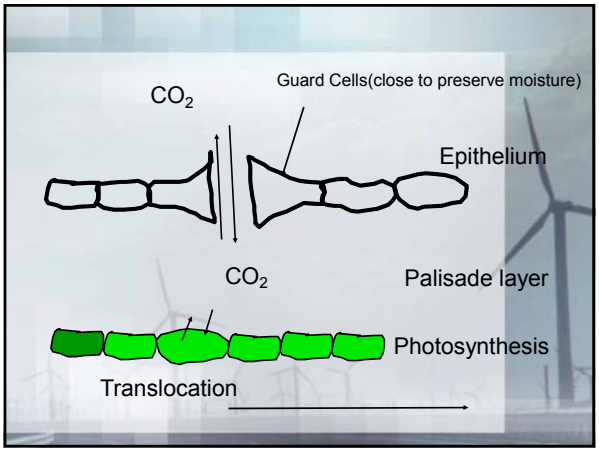


Photosynthesis

- Major fractionation step involves the utilization of CO_2 by plants in the process of photosynthesis

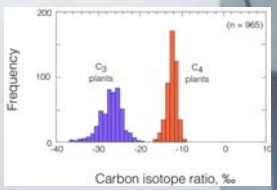
CO_2 + RuBP = PGA (α= 1.027)
RUBISCO

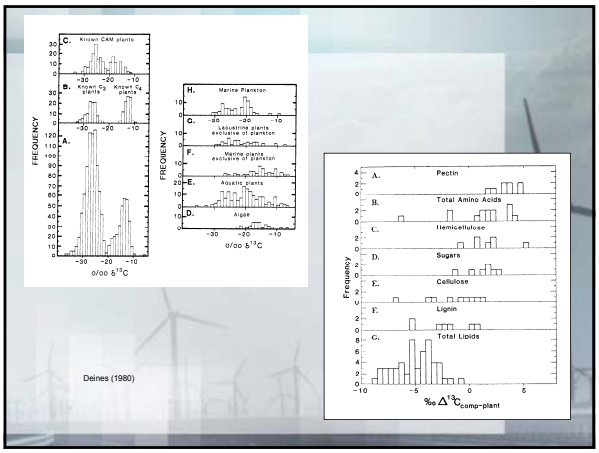
RuBP= Ribulose bis-phosphate
RUBISCO= Ribulose bis-phosphate carboxylase
PGA=Phosphoglyceraldehye



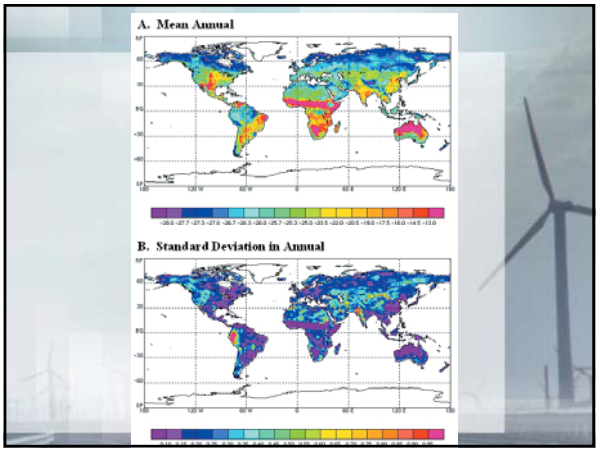
Carbon in plants

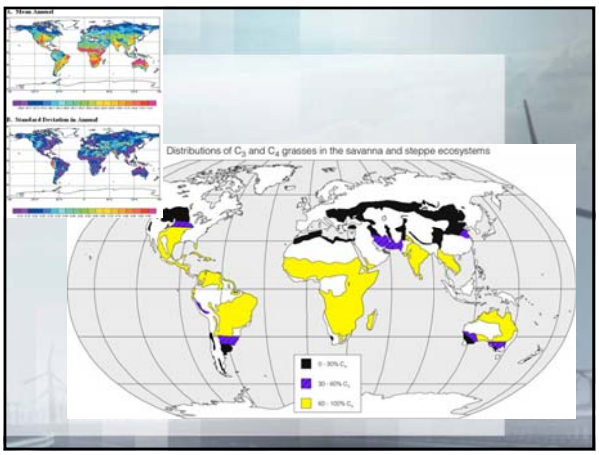
- C-3 plants have been around for over 600 myrs. Comprise most plants other than grasses.
- C-4 plants only evolved in the last 10 myrs
- Algae and marine plants are heavier than C-3 plants and therefore differences in the geological record are mainly terrestrial (-20 to -30 per mille) and marine (-10 to -20 per mille)

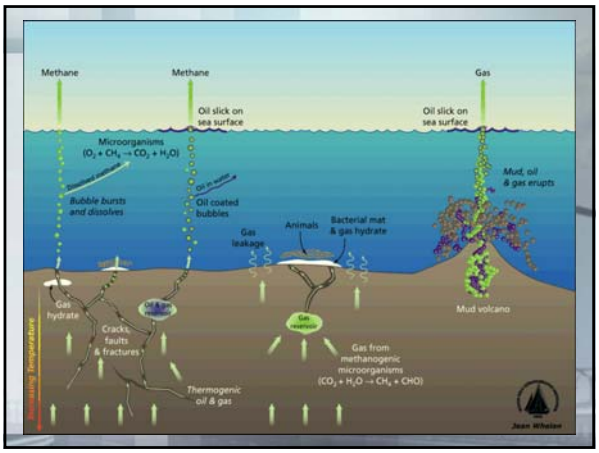



C. Known CAM plants
B. Known C4 plants
Known C3 plants
A.
FREQUENCY
o/oo δ13C
H. Marine Plankton
G. Estuarine plants exclusive of plankton
F. Marine plants exclusive of plankton
E. Aquatic plants
D. Algae
FREQUENCY
o/oo δ13C
A. Pectin
B. Total Amino Acids
C. Hemicellulose
D. Sugars
E. Cellulose
F. Lignin
G. Total Lipids
Frequency
‰ Δ13C comp-plant

Deines (1980)


A. Mean Annual
B. Standard Deviation in Annual


Distributions of C3 and C4 grasses in the savanna and steppe ecosystems



Diagenesis

- **Remineralization**

Oxidation

$CH_2O + O_2 = CO_2 + H_2O$ -20

Sulfate reduction

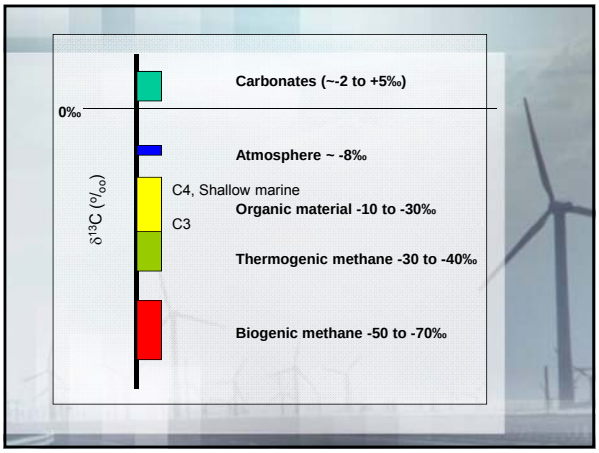
$CH_2O + SO_4^{2-} = HS^- + HCO_3^-$ -20

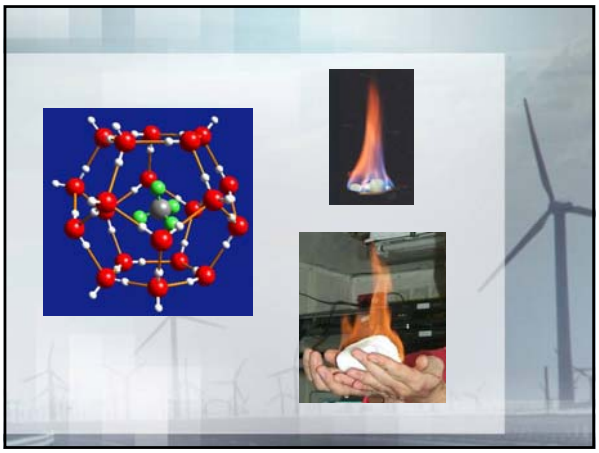
Methanogenesis

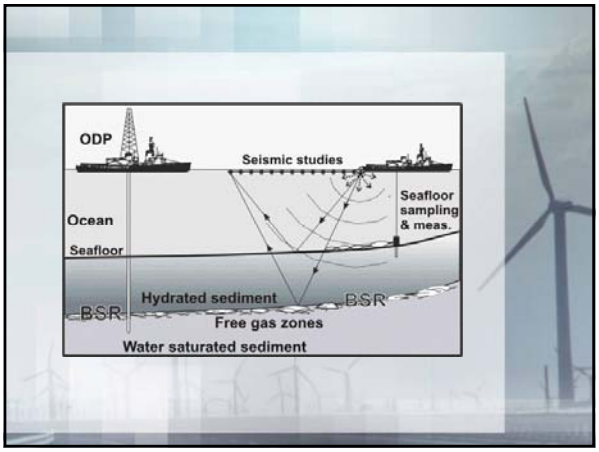
$CH_2O + CO_2 = CH_4 + CO_2$ -60 and +10

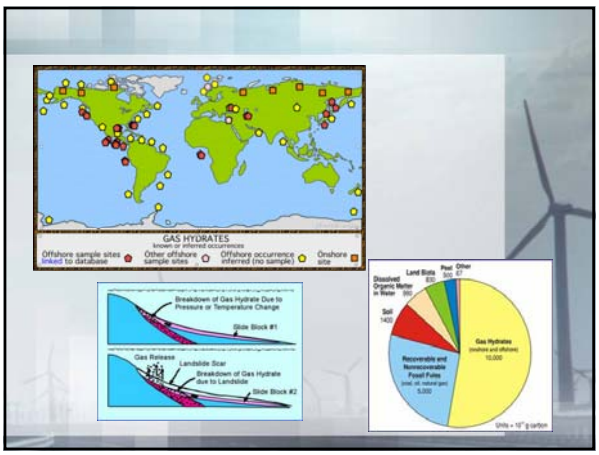
Thermogenic Production

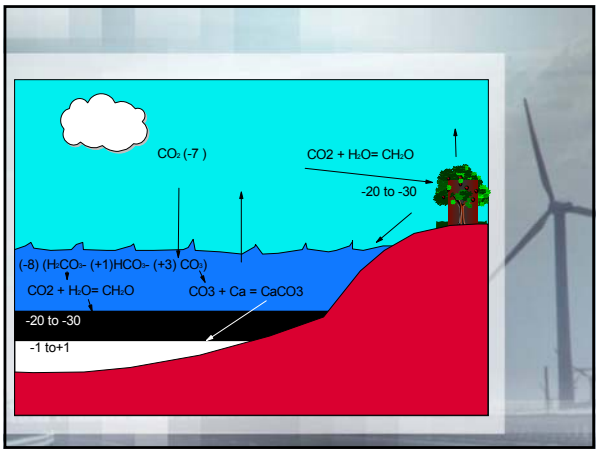
$2CH_2O = CH_4 + CO_2$ -30

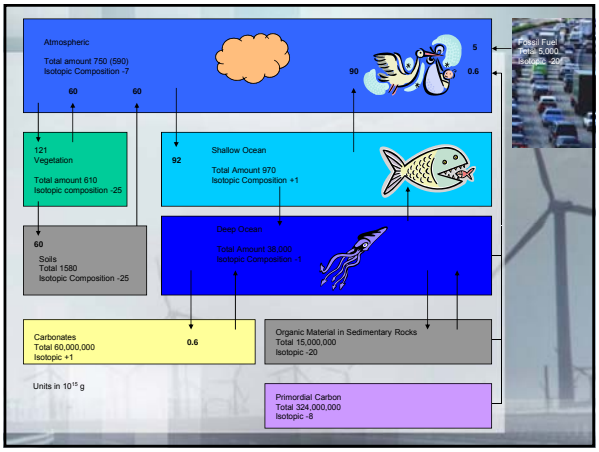





ODP
Seismic studies
Seafloor sampling & meas.
Ocean
Seafloor
Hydrated sediment
BSR
BSR
Free gas zones
Water saturated sediment


GAS HYDRATES
Offshore sample sites linked to database
Other offshore sample sites
Offshore occurrence inferred (no sample)
Onshore site
Breakdown of Gas Hydrate Due to Pressure or Temperature Change
Slide Block #1
Gas Release
Landslide Scar
Breakdown of Gas Hydrate due to Landslide
Slide Block #2
Dissolved Organic Matter in Water
Land Biota
Peat
Other
Soil
Recoverable and Nonrecoverable Fossil Fules
Gas Hydrates





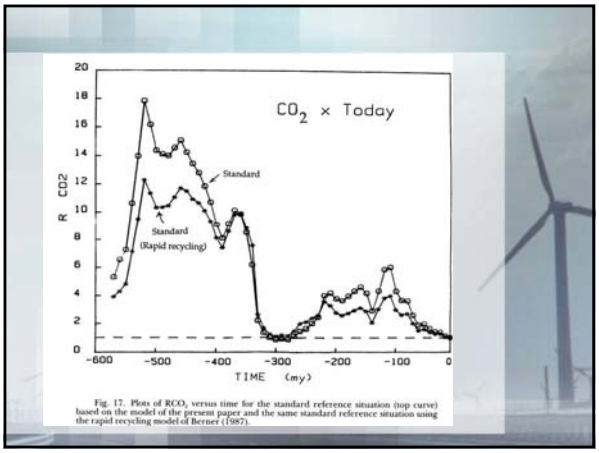


Fig. 17. Plots of RCO_2 versus time for the standard reference situation (top curve) based on the model of the present paper and the same standard reference situation using the rapid recycling model of Berner (1987).

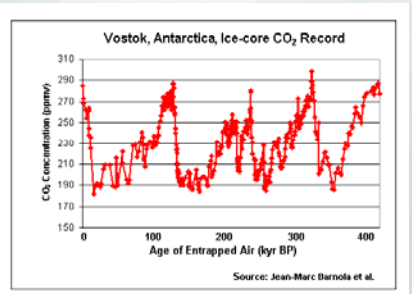
Chemical Reactions

- $CO_2 + CaSiO_3 = CaCO_3 + SiO_2$
- $CO_2 + MgSiO_3 = MgCO_3 + SiO_2$
- $CH_2O + O_2 = CO_2 + H_2O$

➢The more CO_2 in the atmosphere, the faster weathering occurs and the faster there is a draw down of CO_2
➢There is extremely little CO_2 in the atmosphere compared to that in the rocks
➢Weathering of carbonate rocks has little effect as carbon is quickly returned to the reservoir

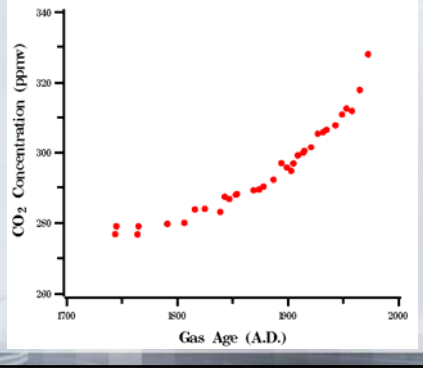
Carbon Isotope Forcing

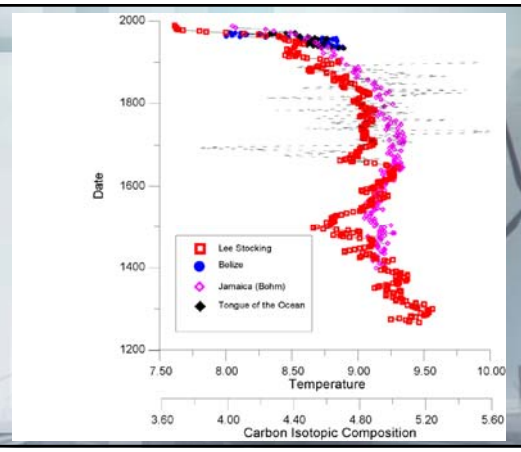
- **Sea-Level**
  - **High sea-level enhanced burial of organic material**
  - **Low sea-level enhanced oxidation of organic material**
- **Anoxic Basins**
  - **Enhanced preservation of organic material**
- **High Rates of Organic Material Formation**
  - **High concentrations of oxygen leading to enhanced oxidation of sulfur**
  - **High rates of organic carbon oxidation**



Barnola, J.-M., D. Raynaud, C. Lorius, and N.I. Barkov. 2003. Historical CO2 record from the Vostok ice core. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.A.

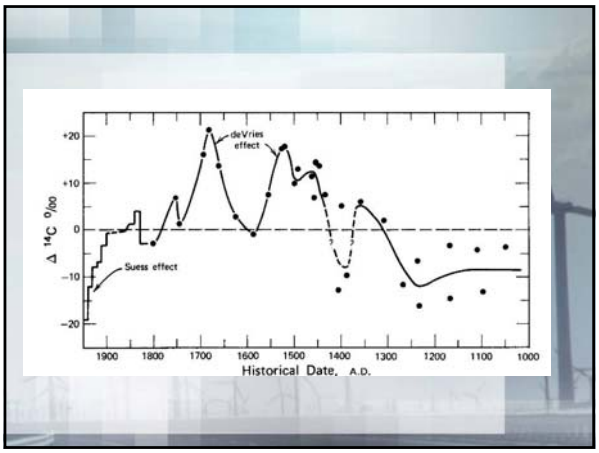
Neftel, A., H. Friedli, E. Moor, H. Lötscher, H. Oeschger, U. Siegenthaler, and B. Stauffer. 1994. Historical CO2 record from the Siple Station ice core. In Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn., U.S.





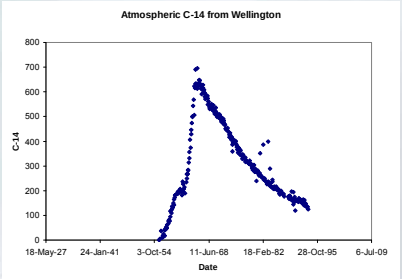
Suess Effect

- The decrease in the ^{14}C of atmospheric CO_2 as a result of the burning of fossil CO_2
- The Suess effect is superimposed upon the addition of ^{14}C as a result of the bomb test.
- Carbon 14 is produced in the atmosphere as a result of the interaction with the solar wind
- $^{14}N(n,p)^{14}C$



Suess Effect

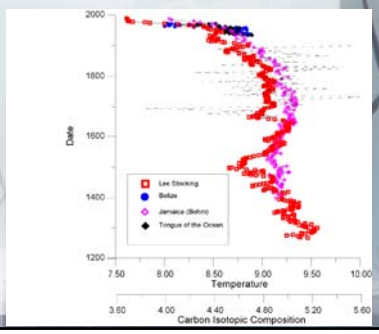
- **Rate of production of C-14 is not constant because of**
  - **Variation in the strength of solar wind**
  - **Variation in the Earth's magnetic field**
  - **Anthropogenic**
    - **Bomb blasts**

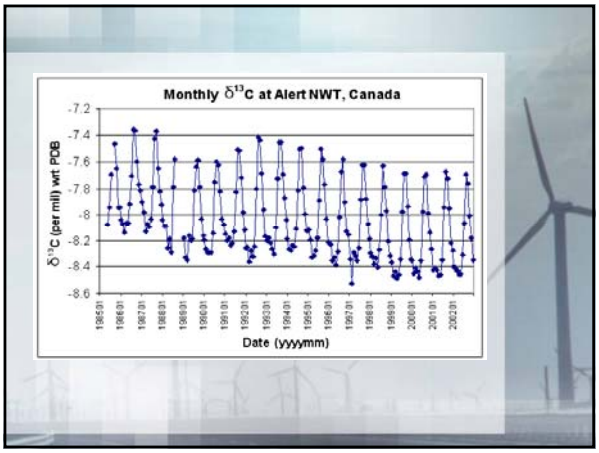


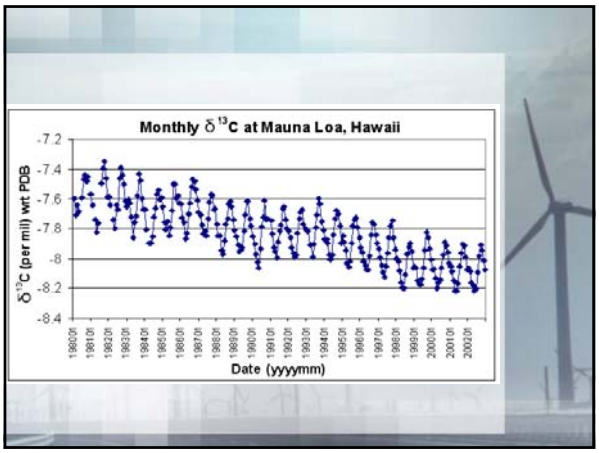
Manning, M.R., D.C. Lowe, W.H. Melhuish, R.J. Sparks, G. Wallace, C.A.M. Brennninkmeijer, and R.C. McGill. 1990. The use of radiocarbon measurements in atmospheric studies. *Radiocarbon* 32:37-58.

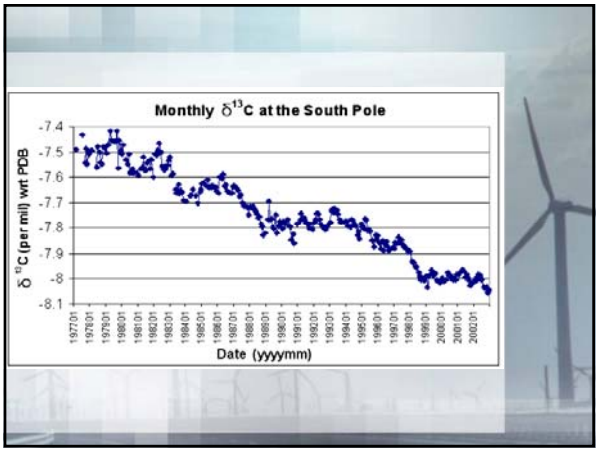
C-13 Suess Effect

- **Change in the ^{13}C of the atmospheric CO_2 as a result of the addition of fossil CO_2**

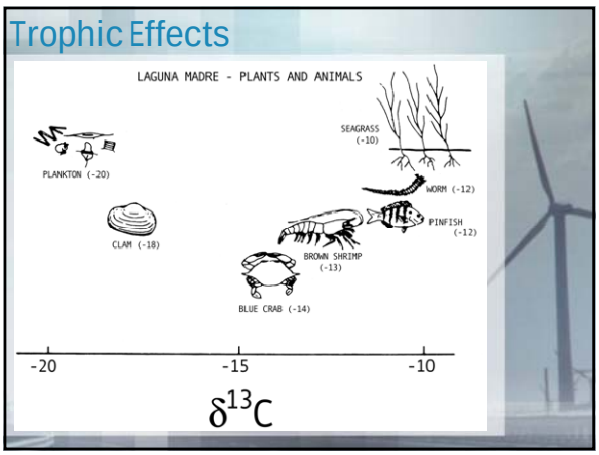








Trophic Effects



Isotopes and Carbonate Equilibrium

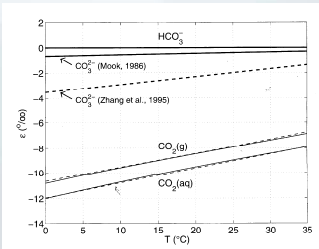


Figure 3.2.12: Carbon isotope fractionation between the species of the carbonate system as a function of temperature with respect to HCO_3^-. Values according to Mook (1986) and Zhang et al. (1995) are indicated by solid and dashed lines, respectively.

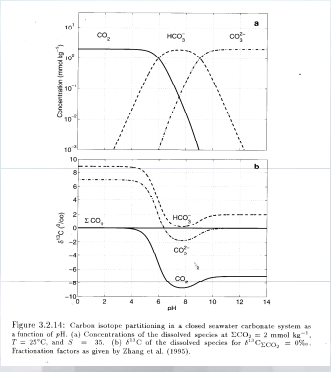


Figure 3.2.14: Carbon isotope partitioning in a closed seawater carbonate system as a function of pH. (a) Concentrations of the dissolved species at $\Sigma CO_2 = 2$ mmol kg^{-1}, $T = 25$°C, and $S = 35$. (b) $\delta^{13}C$ of the dissolved species for $\delta^{13}C_{\Sigma CO_2} = 0$‰. Fractionation factors as given by Zhang et al. (1995).

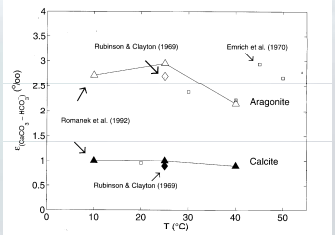
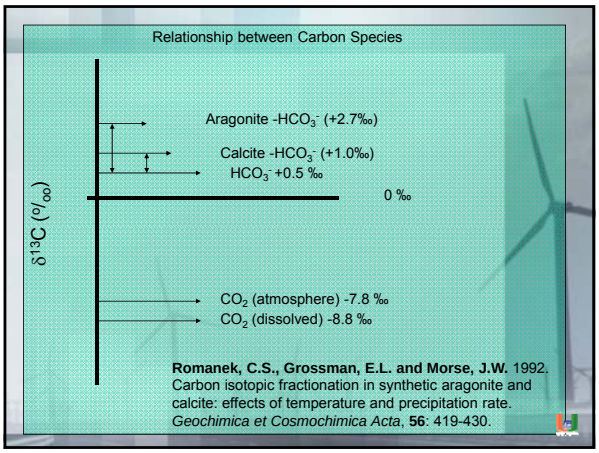
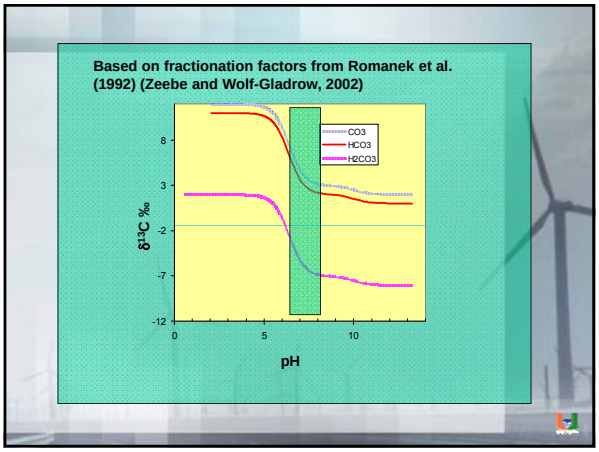
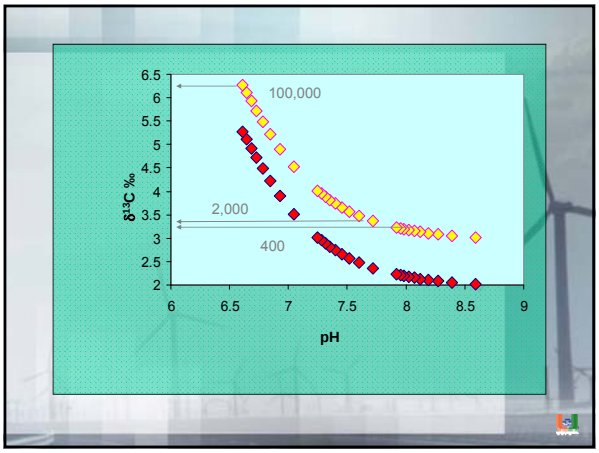


Figure 3.2.13: Carbon isotope fractionation between calcium carbonate and HCO_3^- as a function of temperature (solid symbols refer to calcite whereas open symbols refer to aragonite). The mineralogy of the samples of Emrich et al. (1970) (squares) is inconclusive since mineralogy was not controlled.


Relationship between Carbon Species
Aragonite -HCO3- (+2.7‰)
Calcite -HCO3- (+1.0‰)
HCO3- +0.5 ‰
0 ‰
δ13C (o/oo)
CO2 (atmosphere) -7.8 ‰
CO2 (dissolved) -8.8 ‰
Romanek, C.S., Grossman, E.L. and Morse, J.W. 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. Geochimica et Cosmochimica Acta, 56: 419-430.


Based on fractionation factors from Romanek et al. (1992) (Zeebe and Wolf-Gladrow, 2002)
CO3
HCO3
H2CO3
δ13C ‰
8
3
-2
-7
-12
0
5
10
pH


100,000
2,000
400
δ13C ‰
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
6
6.5
7
7.5
8
8.5
9
pH


Clumped Isotopes