Oxygen, Hydrogen and Carbon Isotopes

Fresh water - Rain, Lakes, Groundwater, Ice

Plants – Leaves and roots (also specific compounds)

Animals – bones and tissue

Seawater –

Carbonate – CaCO₃ (other minerals)
## Isotope Abundances

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Mass</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.007825</td>
<td>99.9844%</td>
</tr>
<tr>
<td>D</td>
<td>2.0140</td>
<td>0.0156</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>12.0000</td>
<td>98.89</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>13.003355</td>
<td>1.11</td>
</tr>
<tr>
<td>$^{14}$N</td>
<td>14.003074</td>
<td>99.64</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>15.000108</td>
<td>0.36</td>
</tr>
<tr>
<td>$^{16}$O</td>
<td>15.994915</td>
<td>99.763</td>
</tr>
<tr>
<td>$^{17}$O</td>
<td>16.999131</td>
<td>0.0375</td>
</tr>
<tr>
<td>$^{18}$O</td>
<td>17.999160</td>
<td>0.1995</td>
</tr>
<tr>
<td>$^{32}$S</td>
<td>31.972070</td>
<td>95.02</td>
</tr>
<tr>
<td>$^{33}$S</td>
<td>32.971456</td>
<td>0.75</td>
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<tr>
<td>$^{34}$S</td>
<td>33.967866</td>
<td>4.21</td>
</tr>
<tr>
<td>$^{36}$S</td>
<td>35.967080</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Atomic mass units (amu) are based on the mass of $^{12}$C = 12.00000.
Physical differences between stable isotopes

Characteristic constants of H$_2$O and D$_2$O (Hoefs, 1973, 1997; Criss, 1999)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>H$_2^{16}$O</th>
<th>H$_2^{18}$O</th>
<th>D$_2^{16}$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($20^\circ$C)</td>
<td>0.997</td>
<td>1.1106</td>
<td>1.1050</td>
</tr>
<tr>
<td>T$^\circ$C @ $\rho_{max}$</td>
<td>3.98</td>
<td>4.30</td>
<td>11.6</td>
</tr>
<tr>
<td>Mole vol. ($20^\circ$C, cm$^3$/mole)</td>
<td>18.049</td>
<td>18.124</td>
<td></td>
</tr>
<tr>
<td>Melting point (760 torr, $^\circ$C)</td>
<td>0.00</td>
<td>0.28</td>
<td>3.81</td>
</tr>
<tr>
<td>Boiling point (760 torr, $^\circ$C)</td>
<td>100.00</td>
<td>100.14</td>
<td>101.42</td>
</tr>
<tr>
<td>Vapour pressure (100$^\circ$C, torr)</td>
<td>760.00</td>
<td>721.60</td>
<td></td>
</tr>
<tr>
<td>Vapour pressure (25$^\circ$C, torr)</td>
<td>23.756</td>
<td>20.544</td>
<td></td>
</tr>
<tr>
<td>Viscosity ($20.2^\circ$C, centipoise)</td>
<td>1.002</td>
<td>1.056</td>
<td>1.247</td>
</tr>
</tbody>
</table>
Hydrogen isotopes (δD)
Two stable isotopes of Hydrogen. $^1$H and $^2$H (Deuterium, “D”).
Expressed in ‰ notation as:

$$\delta D = \left[\frac{(2H/1H)\text{ sample}}{(2H/1H)\text{ standard(SMOW)}} - 1\right] \times 1000$$

- Big relative mass difference so big fractionations imposed by environmental and biological processes.

Oxygen isotopes (δ¹⁸O)
Three stable isotopes of O; we mostly care about $^{16}$O and $^{18}$O
Expressed in ‰ notation as:

$$\delta^{18}O = \left[\frac{^{18}O/^{16}O\text{ sample}}{^{18}O/^{16}O\text{ standard(SMOW)}} - 1\right] \times 1000$$

- Smaller relative mass difference so smaller fractionations imposed by environmental and biological processes.
Oxygen isotope composition of water: intimately related to fractionation processes in the hydrological cycle, and to long-term storage terms.
Rainout and Rayleigh Distillation

Warm → Cold

Low elevation
Low latitude → High elevation
High latitude

$\delta^{18}O$
Effects of latitude, aridity, altitude and continentality on the hydrogen isotope composition of precipitation can be clearly seen. [reasons for variation are Temperature and Rainout]
Global meteoric water line (GMWL)

\[ \delta D = 8 \delta^{18}O + 10 \]

Mostly Equilibrium fractionation, but effect of Kinetic fractionation drags line off the origin...

8 represents the ratio of the fractionation factors between D/H and \(^{18}O/^{16}O\).
Water Sources – groundwater mixing, storm sources and history

Evaporation in lakes and reservoirs

Changes in the hydrological cycle over time

Changes in sea level

Peruvian stalagmite calcite $\delta^{18}$O record linking northern and southern high latitude ice core records (Kammer* et al., 2012)
Lake Chichancanab and Mayan Collapse
Oxygen isotope fluctuations in seawater as recorded in marine sediments can be indicative of ice volume and thus sea level changes. Temperature effects will be included as well. Indicative of exchange among water reservoirs.
Figure 1 Sea-level reconstruction since the start of the Younger Dryas, based on the $\delta^{18}O$ record from core KL11 (18° 44.5′ N, 39° 20.6′ E) including error bars of ±12 m. Chronology is based on calibrated AMS radiocarbon datings\textsuperscript{20}. The record is zeroed to modern sea level by removing the mean KL11 record for the past 7 kyr. The point from the low-resolution record of KL11 reported in the LGM is based on intercalibrated benthic $\delta^{18}O$ data\textsuperscript{19}. Black symbols are sea-level values obtained from coral reef studies\textsuperscript{21–24}. Sibrell et al., 2000
**O isotopes in carbonate**

**Controls:**
1. Ambient water $\delta^{18}O$ (we have dealt with this)
2. Carbonate growth temperature (water $\rightarrow$ carbonate equilibrium fractionation)
3. Reasons for deviations from equilibrium processes

Carbonate species in water: $(\text{CaCO}_3, \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CO}_3^{2-})$

Carbonate formation (mostly from bicarbonate, but ... see later at other influences):

$$\text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$$

Fractionation coefficient between calcite and water (O’Neil, 1969)

$$\alpha_{c-w} = \exp\left\{ (2.78 T^{-2}) \times 10^3 - 3.39 \times 10^{-3} \right\} \text{ where } T \text{ is in Kelvin}$$
Oxygen isotope composition of calcite as a function of temperature and water composition

These plots show the oxygen isotope composition of calcite precipitated at isotopic equilibrium from water of the O isotope composition shown on the X axis and at the temperature shown on the Y axis. $\delta^{18}O$ of calcite was calculated using the equation of Friedman and O'Neil (1977) whereby $10^3 \ln \alpha = \frac{2.78 \times 10^6}{T^2} - 2.89$ with $T$ in Kelvins.
**Paleotemperature equations**

\[ T \ (°C) = a + b(δ_c - δ_w) + c(δ_c - δ_w)^2 \]

<table>
<thead>
<tr>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Basis</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>-5.1</td>
<td>0.09</td>
<td>Inorganic</td>
<td>McCrea, 1950</td>
</tr>
<tr>
<td>16.5</td>
<td>-4.3</td>
<td>0.14</td>
<td>Mollusk</td>
<td>Epstein et al., 1953</td>
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<tr>
<td>16.9</td>
<td>-4.2</td>
<td>0.13</td>
<td>Mollusk</td>
<td>Craig (1965)</td>
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<tr>
<td>16.9</td>
<td>-4.68</td>
<td>0.1</td>
<td>Inorganic</td>
<td>O’Neil et al (1969)</td>
</tr>
<tr>
<td>17.04</td>
<td>-4.34</td>
<td>0.16</td>
<td>Mollusk</td>
<td>Horibe and Oba (1972)</td>
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<tr>
<td>16.9</td>
<td>-4</td>
<td>0</td>
<td>Foram &lt;16°C</td>
<td>Shackleton (1974)</td>
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<tr>
<td>16.998</td>
<td>-4.52</td>
<td>0.028</td>
<td>Pl. Foram</td>
<td>Erez and Luz (1983)</td>
</tr>
<tr>
<td>16</td>
<td>-4.14</td>
<td>0.13</td>
<td>corals</td>
<td>Swart (pers. comm)</td>
</tr>
</tbody>
</table>
Phanerozoic Climate Change

δ¹⁸O (parts per thousand)

Short-Term Average
Low Frequency Mode

HOT
COLD

Glacial Periods

 Millions of Years Ago

0 50 100 150 200 250 300 350 400 450 500 542
Zachos et al., 2001
Multiproxy Mg/Ca-$\delta^{18}O$ Approach
Calculation of SST & $\delta^{18}O_{SW}$

$$\text{Mg/Ca} = 0.38 \exp 0.09\times[SST - 0.61\text{(water depth km)}]$$

- Atlantic *G. ruber* calibration
- Dekens et al. (2002)

$$15.0 - 4.36\times(\delta^{18}O_c - \delta^{18}O_w) + 0.35 \times(\delta^{18}O_c - \delta^{18}O_w)^2 : \text{SST}$$

- High Light *Orbulina universa* can be used for *G. ruber* (white var.)
- Bemis et al. (1998); Thunell et al. (1999); Spero et al., (ms in prep)

Advantages of the Mg/Ca-$\delta^{18}O$ approach – Both signals come from the same mineral phase
Mg/Ca content of Calcite varies with T, but not with $\delta^{18}O_w$

Core top calibration

Lab Experiment calibration


Lea et al., 1999; Russell et al 2005

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
G. ruber $\delta^{18}O$ and Mg/Ca (SST proxy)

Compute $\delta^{18}O_{sw}$ by removing $T$ from shell $\delta^{18}O$
1. Trace **past climates/precipitation /environment**

Assume plants take their O and H from the **environment** around them, as environmental changes influence the $\delta^{18}O$ and $\delta D$ of meteoric water we can examine fossil plants to reconstruct ancient climates/precipitation patterns [Compound-specific particularly].
2. **Investigate the biology of the plant.**
Determine what type of plants we are looking at (C3, C4, CAM etc…). Can’t always tell just by using $\delta^{13}C$ values…

**Different fractionations in C3, C4 and CAM plants…**

- Analyse cellulose $\delta$D and $\delta^{18}O$
- Determine biosynthetic pathway of the plant

Applications for modern and fossil plants
- Marine and terrestrial organic matter
- Petroleum sources
- Plant evolution
$\delta D$ and $\delta^{18}O$ values from plant cellulose of different plants growing in same site in Texas.

Same area, therefore same input of soil $\delta D$, therefore same baseline.

C3 = lower $\delta D$ and lower $\delta^{18}O$ values

C4 = low-med $\delta D$ and higher $\delta^{18}O$ values

CAM = high $\delta D$ and low-med $\delta^{18}O$ values

Sternberg, (1989)
3. Tracing water sources for plants

Are different plants in the same environment drinking from different pools of water in the soil?

\[ \delta P = \delta A \]

\[ \delta P = f \delta B + f \delta A \]

\[ \delta P = \delta B \]

Evapotranspiration

Farquhar et al., (1989)
\( \delta^{18} \text{O} \) in fluids (body water), tissues (hair, feather) and biological minerals (focus here on apatite, not calcium carbonate)

\( \delta^{18} \text{O} \) in body water most tissues is \(^{18}\text{O}\)-enriched relative to environmental water

- Oxygen in \( \text{PO}_4 \) and \( \text{CO}_3 \) rapidly equilibrates with body water and temperature (carbonic anhydrase, pyrophosphatase and other enzymes)
Major Oxygen Fluxes

IN
• Ingested water: drinking water and water in food (not fractionated)
• Atmosphere O$_2$ (globally constant value of +20‰, fractionated)
• Food dry matter

OUT
• Respired CO$_2$ (fractionated)
• Water in urine and feces
• Water lost in exhalation, sweat, evaporation (fractionated)
Rats with a change in drinking water $\delta D$

Ehleringer et al. 2008
Geographic patterns in human hair $\delta D$

- Tap water $\delta D$ varies
- Diet constant: $\delta D_d -115\%$

27% hair H from drinking water
85% variability explained

Ehleringer et al. 2008
Changes in hair $\delta^{18}$O, $\delta$D with "migration"

Ehleringer et al. 2008
Apatite $\delta^{18}\text{O}$

- $\delta^{18}\text{O}$ depends on the temperature and body fluid $\delta^{18}\text{O}$ value from which the biomineral precipitates.

  - For homeotherms (mammals, birds), there is a constant temperature dependent difference constant offset between $\delta^{18}\text{O}$ of body water and $\text{PO}_4$ ($\sim18\%$), between body water.

  - For heterotherms, as temp. ↓, bioapatite $\delta^{18}\text{O}$ values ↑

Changes in temperature, Habitat allocation, Migration (salmon), Seasonality.
Ectotherms maintain uniform temperature only in core areas

Ectotherms = Highly variable

Endotherms = Less variable
Carbon Isotopes

Stable Carbon Isotopes: $^{12}\text{C}: 98.89\%$ $^{13}\text{C}: 1.11\%$

Isotopic fractionation: Sorting of isotopes between substances as a consequence of differences in molecular bond energies or rates of transport for different isotopes of an element.

Isotopic Notation: Because one isotope is common and the other is rare, and because isotope fractionations are often small, naturally-occurring isotopic differences between substances are often very small, in the range of parts per thousand. They are easier to remember if we report isotopic compositions of materials using: $\delta$ values

$$\delta^{13}\text{C} = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{standard}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}}\right) \times 1000 = \left(\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}}}{(^{13}\text{C}/^{12}\text{C})_{\text{standard}}} - 1\right) \times 1000$$

$\delta$ values indicate relative enrichment or depletion in $^{13}\text{C}$ to $^{12}\text{C}$. Higher $\delta$ values, relatively more $^{13}\text{C}$, less $^{12}\text{C}$: Heavier
Lower $\delta$ values, relatively less $^{13}\text{C}$, more $^{12}\text{C}$: Lighter
The units are parts per thousand or per mil ($\permil$)
The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons (GigaTons, circa 2004). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the ~70 million GtC of carbonate rock and kerogen.
On geologic timescales, the carbon cycle model can be represented by 3 reservoirs, sedimentary carbonate, sedimentary organic carbon, and the mantle, as well as fluxes between these reservoirs and the oceans and atmosphere.

Figure 38.1. The Carbon Cycle. Green numbers show the amount of carbon (in $10^{18}$ grams) in the reservoirs. Fluxes between these reservoirs (arrows) are shown in italics in units of $10^{18}$ g/yr (in red). Masses and fluxes refer to the pre-Industrial Revolution state of the system. Uncertainties on many of the masses and fluxes are large. Also shown are estimates of the carbon isotopic composition.
When more C is removed into the reduced organic C reservoir residual C in the ocean and carbonates becomes enriched in $^{13}$C (heavy), atmospheric CO$_2$ is lower and O$_2$ is higher (less consumed for oxidation).
The long-term increases in $\delta^{13}$C_{carb} (e.g. more organic C burial) that began in the Mesozoic were accompanied by major evolutionary changes among the primary producers in the marine biosphere. Three groups of eucaryotic marine phytoplankton (calcareous nannoplankton, dinoflagellates, and diatoms) began their evolutionary trajectories to ecological prominence at ~ 200 Ma. As Pangea fragmented and the Atlantic Ocean basin widened, the total length of coastline increased and sea level rose, flooding continental shelves and low-lying continental interiors. Nutrients that were previously locked up in the large continental interior were transported to newly formed shallow seas and distributed over wider shelf areas and longer continental margins. 

Katz et al., 2005
The decline since the late Miocene in addition to changes in ocean circulation could be related to the evolution of C4 plants (less fractionation in organic C burial).

Perturbations in the global C cycle.

Figure 1. Late Cenozoic carbon isotopic record of bulk marine carbonate averaged in million year increments. Data from Shackleton and Hall [1984].
McInerney and Wing 2011
Carbon Isotopes in Plants

Cerling et al. 97
Nature

C3 grasses
δ¹³C = -26.7 ± 2.3 ‰

C4 grasses
δ¹³C = -12.5 ± 1.1 ‰

Cool season grass most trees and shrubs

Warm season grass
Arid adapted dicots

δ¹³C
Food Sources for Coastal Marine Animals

$\delta^{13}\text{C}$ values of consumers can be used to indicate food source

**Fish:**
- Offshore = primarily planktonic food source
- Seagrass = some primarily planktonic, some primarily benthic

**Invertebrates:**
- Offshore = primarily planktonic food source
- Seagrass = primarily benthic food source

[France, 1995]
Tracing organic matter sources and carbon burial in mangrove sediments over the past 160 years (Gonneea et al., 2004).
C3 - C4 balance varies with climate


Tieszen et al. Oecologia (1979)
δ^{13}C varies with environment within C3 plants
Fig. 1. Effect of mean annual precipitation (MAP) on $\Delta_{\text{leaf}}$ ($n = 506$). MAP accounts for 55% ($p < 0.0001$) of the variability in $\Delta_{\text{leaf}}$ in a linear regression model. Points are coded by biome: tropical rain forest (TRF), evergreen warm mixed forest (EWMF), tropical seasonal forest (TSF), cool-cold deciduous forest (CCDF), cool-cold evergreen forest (CCEF), cool-cold mixed forest (CCMF), tropical deciduous forest (TDF), xeric woodland scrubland (XWS). In a regression model using site-means ($\Delta_{\text{leaf}}$ averaged by geographic location), MAP accounts for 52% ($p < 0.0001$) of the variability in $\Delta_{\text{leaf}}$ (SI Appendix).
Quantum Yield (moles C fixed per photon absorbed)

With equal water higher CO$_2$ is better for C3 plants but the temperature sensitivity changes.

C3 decreases in efficiency because of Photorespiration

C3 plants

C4 plants

Today (360 ppm)

LGM (180 ppm)

Ehleringer et al. 1997 Oecologia

Temperature (°C)

At the LGM, was there less C4 biomass (because of lower temperatures) or more C4 biomass (because of lower pCO$_2$)?
Great Plains ecosystems

Use isotopes in animals and soils to track $\text{C}_3$-to-$\text{C}_4$ balance
Bison isotope values track $C_3$-to-$C_4$ balance of grasslands

For C you are what you eat
\%C_4 Grass Should Increase in the LGM Based on Temperature Model
Proboscideans

Holocene - Late Glacial

Last Glacial Maximum

Pre-LGM

Horses - Bison

Holocene bison

Ingelside horses

δ¹³C (%o, VPDB)

Number of Individuals

C₃

C₄
Summary on Quaternary Prairies

1) Despite climate change, %C₄ biomass is remarkably constant through time.

2) Always lots of C₄ biomass on plains and plateaus and no C₄ consumed by mastodons.

3) Only climate-vegetation models that account for changes in pCO₂ as well as temperature provide reasonable %C₄ estimates in parts of the Quaternary with different atmospheric compositions.

Koch et al. (2004) P3
Signature of Plants (C3/C4) is reflected in soil carbon isotopes
Quade et al. (1989)

δ¹³C of paleosol carbonates from Pakistan
Diet shifts in Mio-Pliocene Mammals

Cerling et al. (1997) Nature
CO₂ reconstructions from δ¹³C in aquatic plants

Why are there variations in δ¹³C of aquatic plants?

Water Temperature

$pCO₂$ and $[CO₂]_{aq}$ ➔ Greater fractionation at higher $[CO₂(aq)]$

Growth Rate

Cell Size and Geometry

Type of Organism

Active vs. Diffusive Inorganic C uptake

CCM (CO₂ concentrating mechanisms)

Dependence of phytoplankton carbon isotopic composition on growth rate and $[CO₂]_{aq}$:
Theoretical considerations and experimental results

Edward A. Laws,¹ Brian N. Popp,¹,² Robert R. Bidigare,¹ Mahlon C. Kennicutt,³ and Stephen A. Macko⁴
The carbon isotope fractionation by haptophyte algae. Photosynthesis is related to [CO2], growth rate (food), temperature and species.

\[
\varepsilon_p = \varepsilon_f - \frac{b}{[CO_{2aq}]}
\]

\[b = 118.52 \times [PO_4^{3-}] + 84.07 \quad (r^2 = 0.78)\]

Pagani et al., 2005
\( \delta^{13}C_{\text{DIC}} \) of Surface Waters Reflects a Combination Of Physical and Biological Controls

Pacific Meridional Transect along 120\(^\circ\)W (pre 1980)
Biological Pump Controls the Vertical Carbon Isotope Gradient in the Ocean

- $\delta^{13}C$ is used to track carbon isotopes in the ocean.
- $\text{CO}_2(g)$ with $\delta^{13}C = -7\%$.
- $\epsilon = -1\%$.
- $\epsilon = +8\%$.
- $\text{HCO}_3^-$ is produced from $\text{CO}_2(\text{aq})$.
- $\text{CO}_2(\text{aq})$ is consumed by Phytoplankton.
- Photosynthesis:
  - $\delta^{13}C_{\text{org}} = -20\%$.
- Remineralization:
  - $\text{Consumer/Bacterial Respiration}$
  - $\text{CO}_2$ is released.
- Pycnocline separates different water layers.
- Mixed Layer:
  - $\text{CO}_2$ exchange with atmosphere.
$\text{PO}_4$ and $\delta^{13}C_{\text{DIC}}$ covary linearly in the Ocean; $\delta^{13}C$ can be used as a Proxy for Dissolved Nutrients

$$m = 1.1\%o \ \mu\text{mol}^{-1} \ \text{kg}^{-1}$$

Effect is due to rather constant C:N:P relationship in marine organisms - Redfield Ratio

106:16:1

(Kroopnick, 1985)
What Causes Inter-ocean Differences in nutrients such as $[PO_4]$ and other non-conservative tracers?
The $\delta^{13}C$ of DIC traces deep water currents and flowpaths because deep waters accumulate $^{13}C$-depleted respired $CO_2$ during their transit around Earth....

Greenland
Iceland/Faeroe Ridge

Western Atlantic GEOSECS $\delta^{13}C$ (PDB)

Curry and Oppo 2005
Factors Affecting Calcite/Aragonite Carbon Isotopes

• $\delta^{13}C_{DIC}$ ($\Sigma CO_2$):
  a) Ocean Temperature (air-sea exchange)
  b) Community Productivity/Respiration
  c) Ocean Circulation – Sources/Sinks

• Physiology/Biology/Vital Effects
  a) Irradiance – Symbiont photosynthesis
  b) Temperature – Respiration

• Ocean Chemistry:
  a) pH or $[CO_3^{2-}]$ – Carbonate Ion Effect
Other Applications

Oxidation of methane (C and H)

Source of methane in gas hydrates and seeps (C and H)

Forensics (C, O, H) sources of ivory, fake maple,

Archeology (C, O) migration, food source, trading

Tracking anthropogenic C in the atmosphere and ocean

Stratigraphy and correlation (O, C, H)

Radiocarbon dating ($^{14}$C)

Fluid crystallization temperatures (O, geology)

Diagenesis (of carbonates)

Strength of the biological pump (C benthic platonic difference)