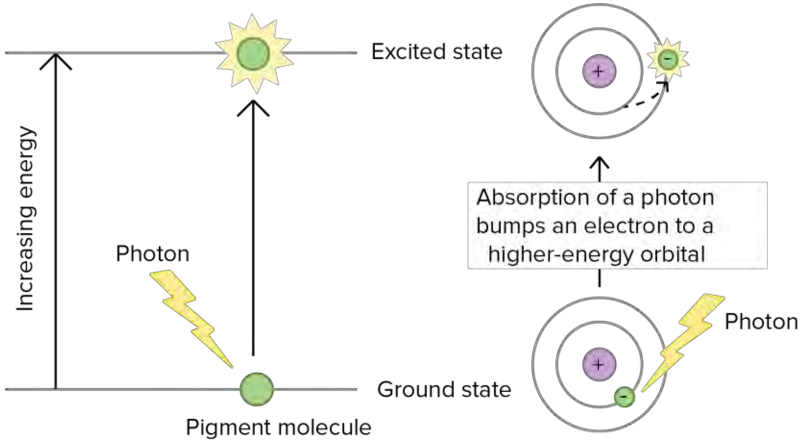
Greenhouse Gasses

- Molecules absorb photons (light) depending upon the wavelength of the light and the available energy states of the molecule.
- The available energy states depend on the number and flexibility of chemical bonds in the molecule (e.g., double vs single bonds)



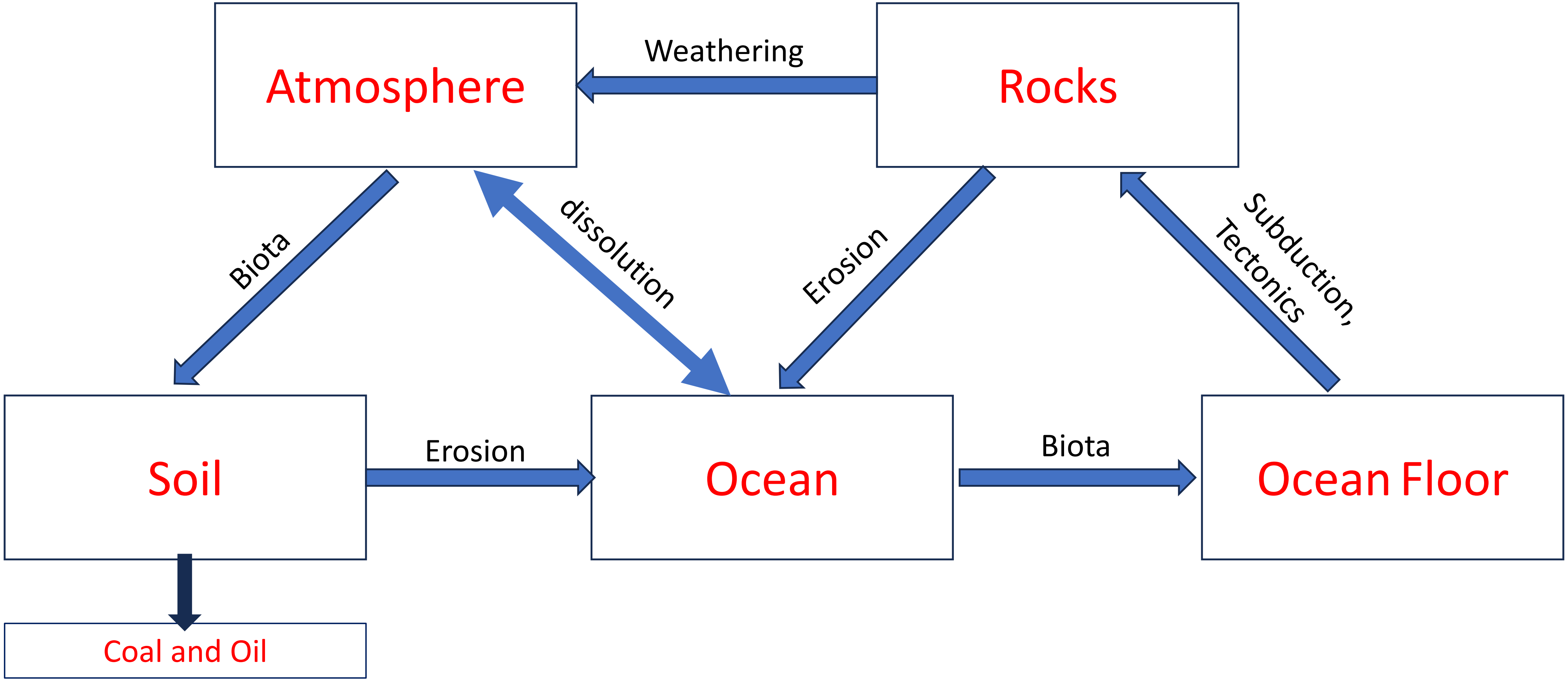
[light absorption animation]

Carbon Cycles

In Water: $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^{--} + H^+$

Shells: $Ca^{++} + 2HCO_3^- \rightleftharpoons CaCO_3 + CO_2 + H_2O$

Silicate Rocks: $2CO_2 + H_2O + CaSiO_3 \rightleftharpoons 2HCO_3 + SiO_2$



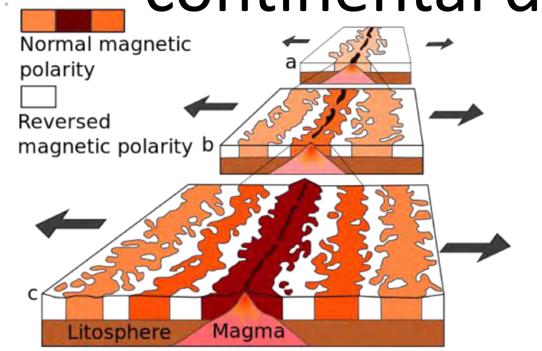
What influences the amount of CO_2 in the atmosphere?

- Inputs:
  - Volcanoes
  - Ocean warming
  - Fossil Fuels
- Removal:
  - Photosynthesis
  - Dissolution in oceans
  - Formation of calcium carbonate by marine organisms (corals, diatoms*, etc.)

*think white cliffs of Dover

How we know what we know: Relative Dates

- Stratigraphy: based on superposition. More recent strata overlay older ones.
- Dendrochronology: Tree rings
- Archeomagnetism: The earth's magnetic field reverses roughly every 10 - 70,000 years*, and in between that the poles drift, altering compass direction and declination. Magnetic particles in igneous rocks retain the orientation to the earth's magnetic field at the time they solidified. (Archeomagnetism is also used in making maps of continental drift.)



*"These reversals are random with no apparent periodicity to their occurrence. They can happen as often as every 10 thousand years or so and as infrequently as every 50 million years or more. The last reversal was about 780,000 years ago." [USGS]

How we know what we know: Absolute Dates

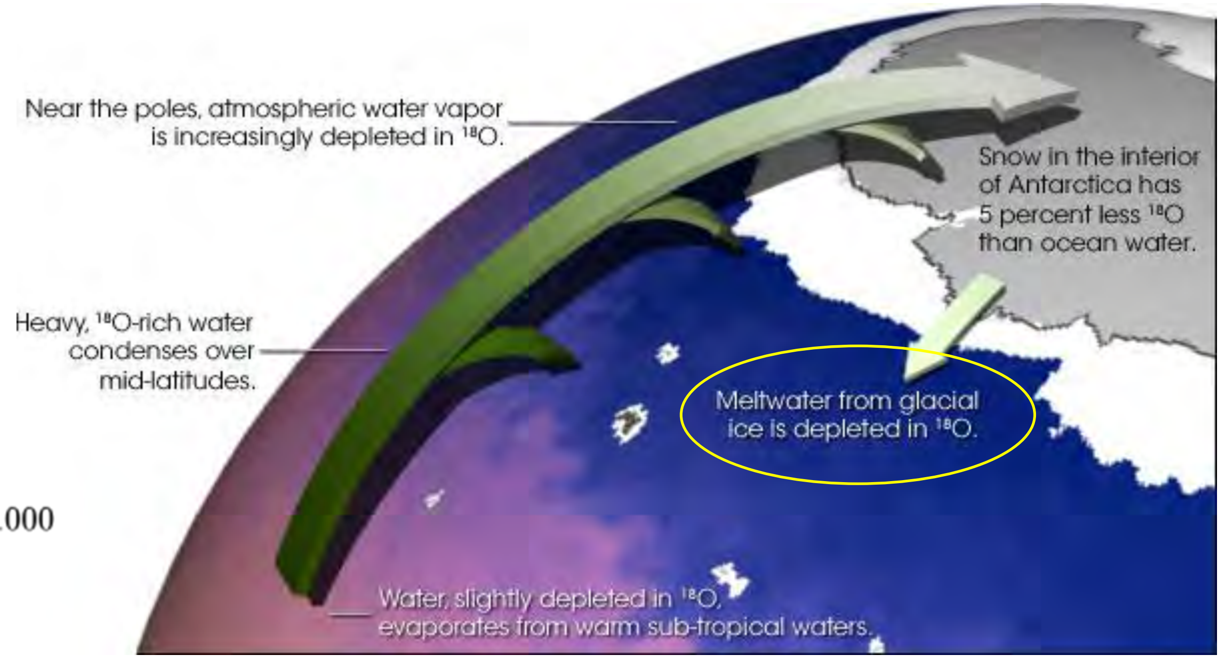
- Radioactivity: decay of isotopes (different numbers of protons in nucleus). Tells when igneous (volcanic) rocks solidified.
  - Potassium (K) has three isotopes: ^{39}K, ^{40}K, ^{41}K. ^{39}K and ^{41}K are stable, but ^{40}K gains an electron to become ^{40}Ar, with a half-life of 1.3 billion years. Using the ratio of ^{40}K to ^{40}Ar, one can determine the age of rocks. For even older rocks, ^{87}Rb decays to ^{87}Sr with a half-life of 49 billion years.
  - For more recent dating, ^{14}C is the radioactive isotope of carbon, produced by cosmic rays in the atmosphere. Plants and then animals introduce ^{14}C into their tissues when alive. That stops when they die, and gradually the 14C decays to ^{12}C (half-life 5,730 years). Comparing the ratio of ^{14}C to ^{12}C in organic tissue to that of the atmosphere can tell you how long ago the organic tissue was part of a living organism.

Fossil Organisms, Oxygen Isotopes, and Dates

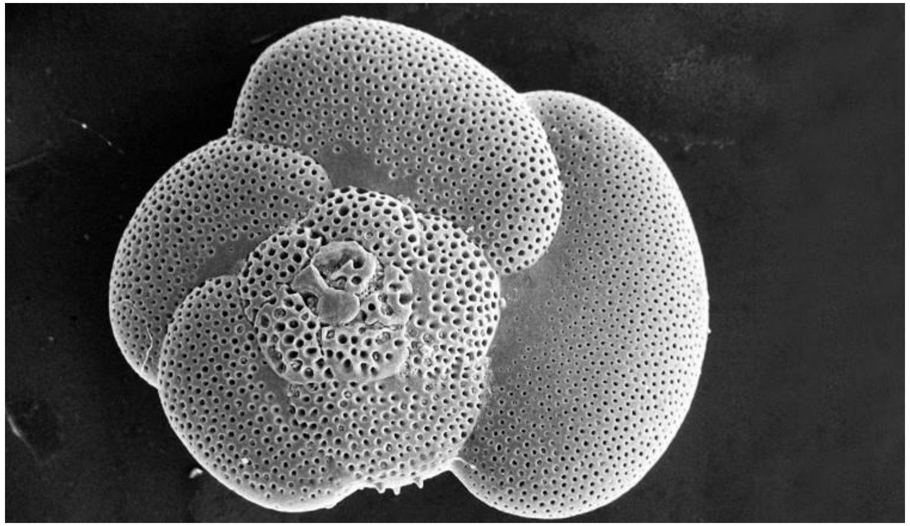
- Organisms prefer to incorporate the lighter isotope of oxygen, ^{16}O.
- Lighter ^{16}O evaporates more readily than heavier ^{18}O
- ^{18}O also condenses out as rain more readily than ^{16}O.
- During cold periods, the evaporated ^{16}O gets transported to the poles where it becomes trapped in ice, so the oceans are richer in ^{18}O

During colder times, then, organisms typically show higher ^{18}O concentrations because the heavier isotope is more readily available in the environment. The opposite is also true. During warmer periods, there is less ice on Earth and therefore more ^{16}O available to organisms for their use.

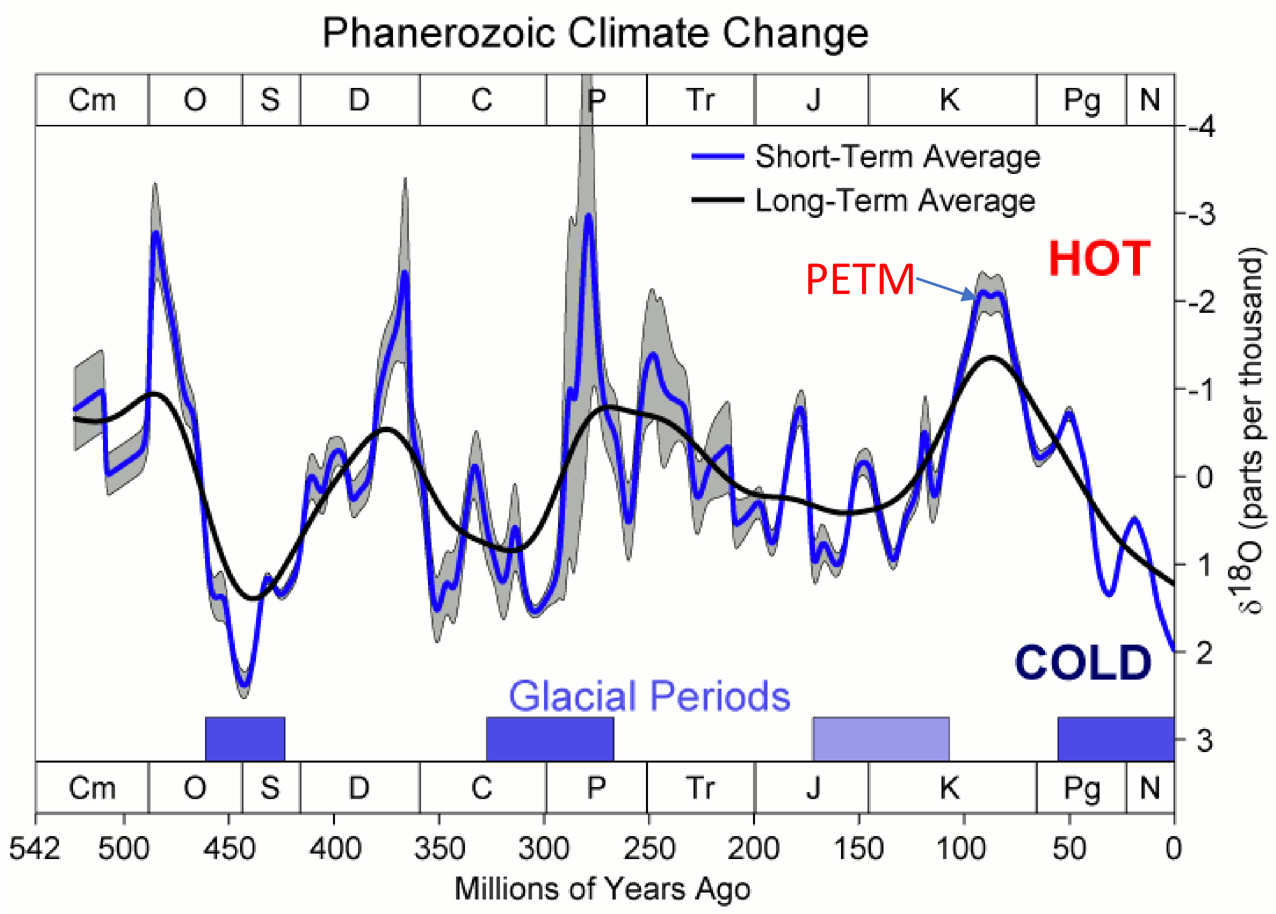
$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{\text{sample}}}{\left(\frac{^{18}O}{^{16}O}\right)_{\text{standard}}} - 1 \right) \times 1000$$



Foraminifera and Coccolithophores



δ^{18}O-derived global temperature



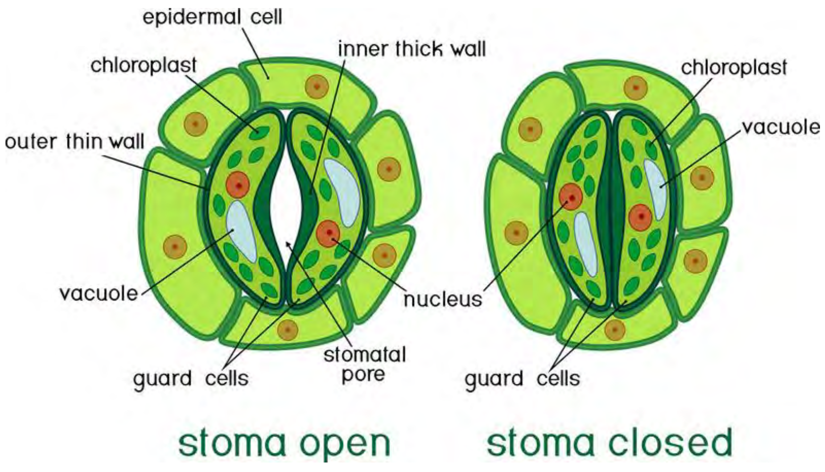
Analysis of oxygen isotopes, along with studies of fossils of temperature-sensitive biota (e.g. corals) show marked fluctuations in global temperature. It was relatively warm between 540-340Ma (Cambrian explosion, 530Ma) and again between 260-40Ma.
It was cold enough for glaciation between 340-260Ma (mid-Carboniferous-Permian). It was warm again between 260Ma and 40Ma (Age of the Dinosaurs, 245-66Ma). It has been cold ever since 40Ma.

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{standard}} - 1 \right) \times 1000$$

How We Know What We Know: ancient CO_2 levels: CCD

- The Carbonate Compensation Depth (CCD) is the boundary in the ocean floor between the sediment rich in carbonate skeletons of foraminifera and the deeper, non-fossiliferous red clay.
- It is the point at which the rate of dissolution of calcite exceeds the rate of deposition.
- The level of CO_2 in the atmosphere determines the level of CO_2 in the ocean. $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
- The H^+ is acid and increases the rate of dissolution of calcite.
- Thus, the more CO_2 in the atmosphere the shallower the CCD.

How we know what we know: Ancient CO_2 levels: stomata



Stomata in plants control the flow of CO_2 into the leaf for photosynthesis. They also regulate the loss of water due to evaporation by closing in dry conditions. When CO_2 is more abundant the plant will produce fewer stomata, since it can more easily supply the CO_2 it needs without consequent water loss.
Thus the distribution of stomata in fossil leaves is an indicator or atmospheric CO_2 when the plant was alive.

How we know what we know: Ancient CO_2 levels: Boron

1. The element Boron (B) has two isotopes: ^{10}B and ^{11}B
2. Boron in sea water exists in two aqueous forms, with the equilibrium

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$$

3. There is a marked difference in the segregation of the isotopes between the aqueous forms of boron.
4. The relative abundance of these two compounds depends on the pH (i.e.,[H^+])of the seawater, which in turn depends on the concentration of CO_2 in the atmosphere.

(continued next slide)

Ancient CO_2 and Boron (continued)

5. Since the abundance of each aqueous species varies with pH, it becomes possible to use the isotope ratio of boron as a proxy for pH.
6. One can then use ocean pH as a measure of atmospheric CO_2
7. Marine organisms like foraminifera and coccoliths incorporate boron as $B(OH)^{4-}$ into their calcite shells.

$$CaCO_3 + B(OH)_4^- \rightleftharpoons Ca(HBO_3) + HCO_3^- + H_2O$$

$$\delta^{11}B=[(^{11}B/^{10}B_{sample})/(^{11}B/^{10}B_{standard})-1] \times 1000$$

5. Other isotope ratios give the date of the foraminifera.

All this gives us a picture of CO_2 in history