Methodology

Stable Isotopes et al

A Short Course VU March, 2009

Peter Swart University of Miami

Nomenclature

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

δ ,del, or delta values are reported in^{0}/oo or parts per thousand or per mille

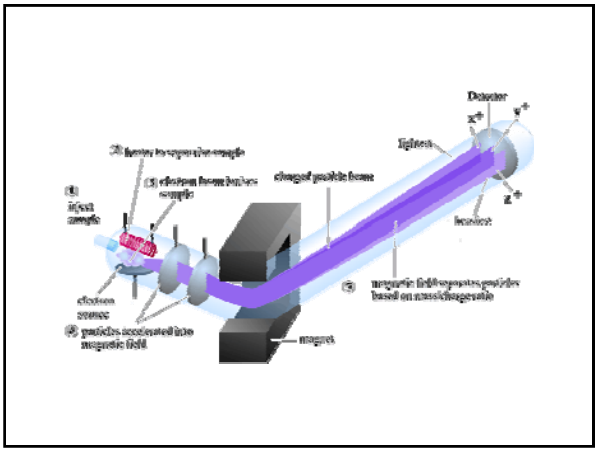
Less ^{13}C, δ values are negative or said to be light

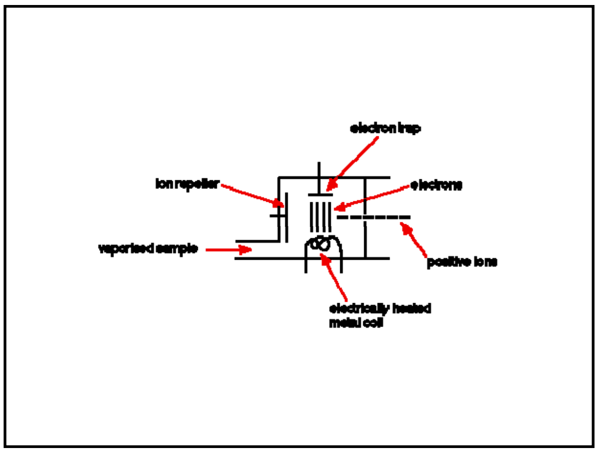
Less ^{13}C, δ values are positive or said to be heavy

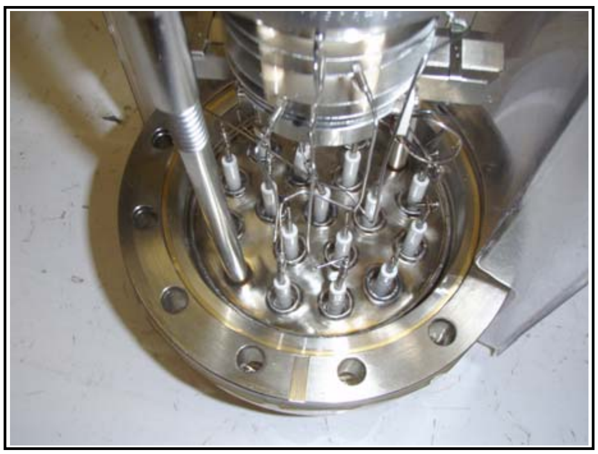
Standard is PDB (Pee Dee Belemnite)
V-PDB (Vienna Pee Dee Belemnite)

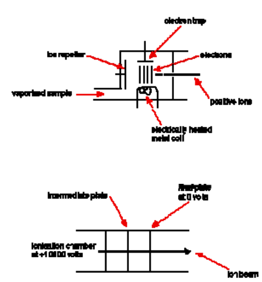
Mass Spectrometer Types

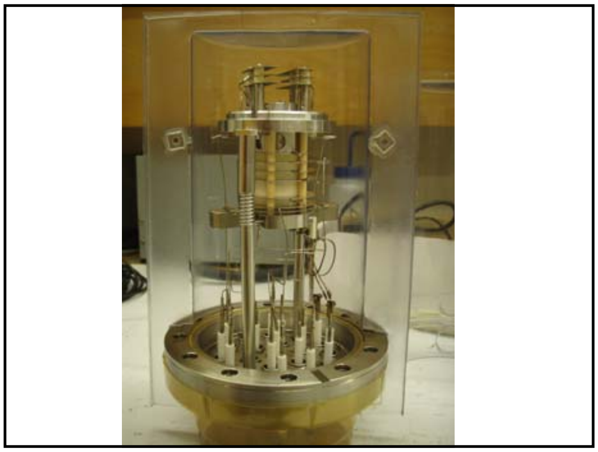
- **Gas**
  - Dynamic
  - Static
  - Continuous Flow
- Solid Source
- ICP Source
  - Magnetic
  - Quadropole
- Ion Probe

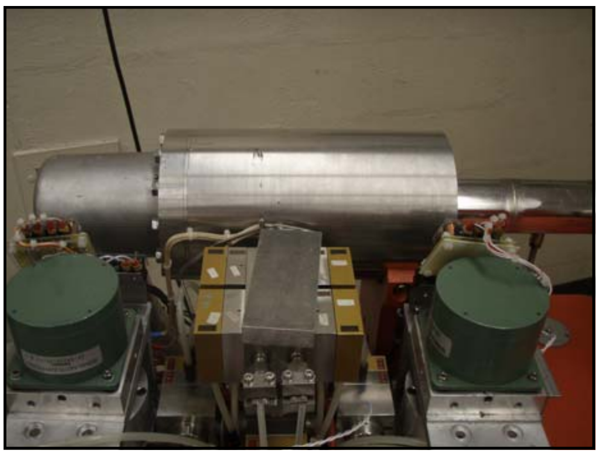

Detector
magnet


electron trap
ion repeller
electrons
vaporized sample
positive ions
electrically heated
metal coil




electron trap
ion repeller
electrons
vaporised sample
positive ions
electrically heated
metal coil
intermediate plate
ion beam






ACHTUNG
ATTENTION

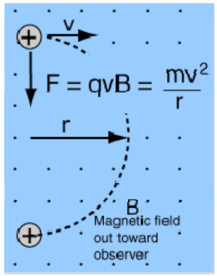
$$r = \frac{mv^2}{qvB} = \frac{mv}{qB}$$ Radius of path produced by magnetic field

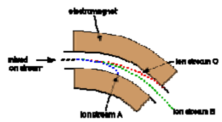
If the velocity v is produced by an accelerating voltage V:

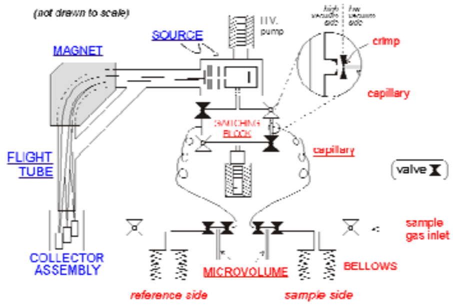
$$\frac{1}{2}mv^2 = qV\ ;\quad v = \sqrt{\frac{2qV}{m}}$$

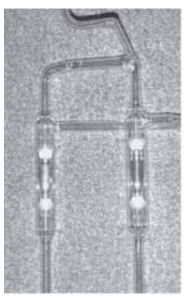
Substitution gives:

$$r = \frac{1}{B}\sqrt{\frac{2mV}{q}}$$

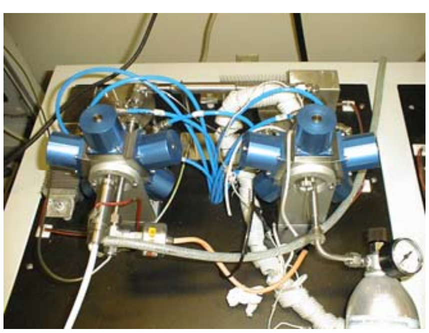








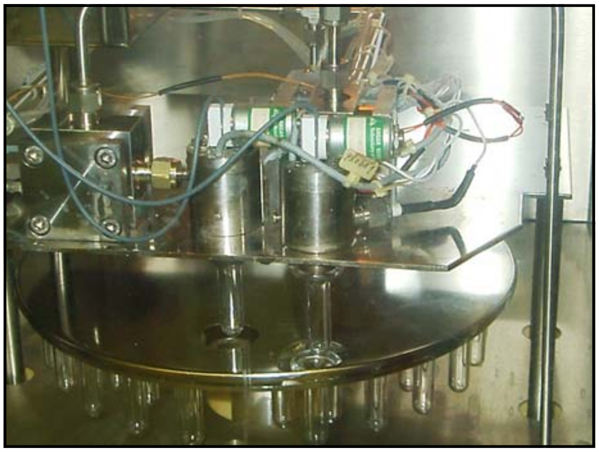
From Sharp (2002)

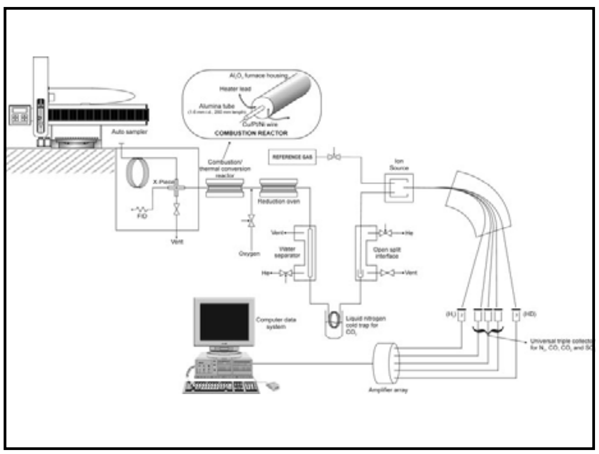


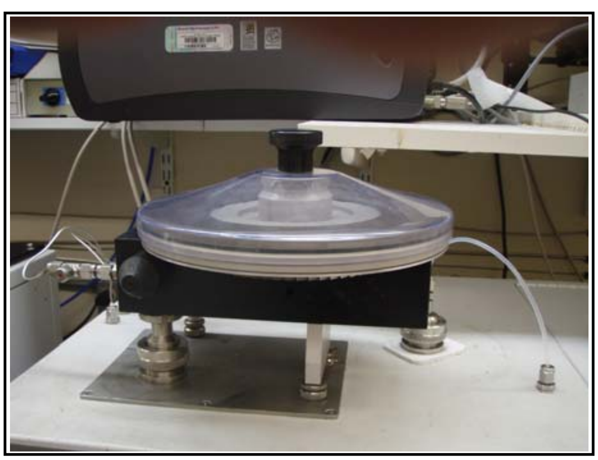
Methodology

- Carbonates
  - Reaction with acid which produces CO_2
  - Masses 45/44 give the 13/12
  - Masses 46/44 give the 18/16
- Organic material
  - Burn material in the presence of oxygen

Mass 45 = $^{13}C^{16}O^{16}O$




Al2O3 furnace housing
Heater lead
Alumina tube
Cu/Pt/Ni wire
COMBUSTION REACTOR
Auto sampler
REFERENCE GAS
Ion Source
Combustion/ thermal conversion reactor
X-Piece
FID
Vent
Reduction oven
Oxygen
Vent
Water separator
He
He
Open split interface
Vent
Computer data system
Liquid nitrogen cold trap for CO2
(H2)
(HD)
Universal triple collector
Amplifier array



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- **ICP Source**
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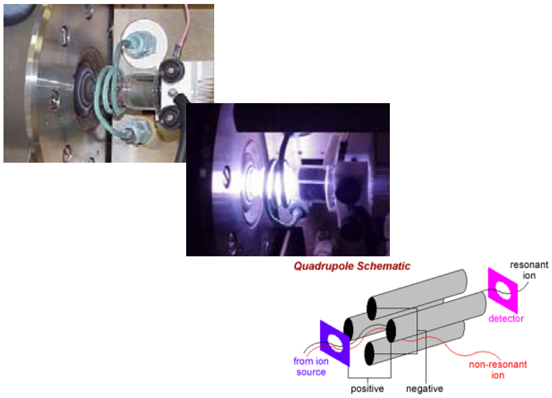
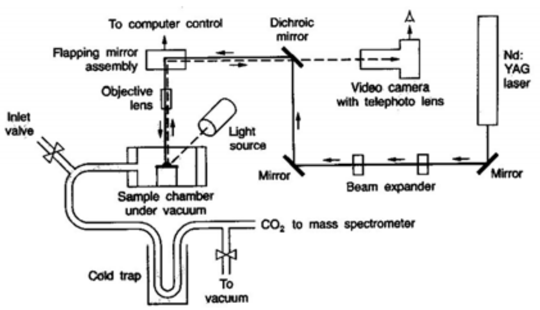
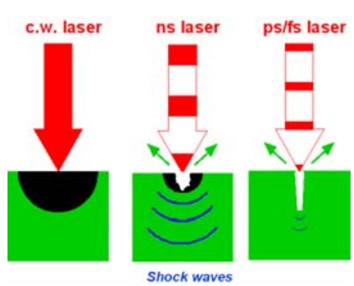
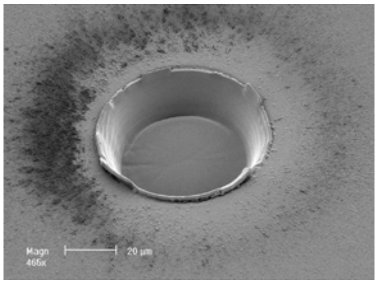

Quadrupole Schematic
resonant ion
detector
from ion source
non-resonant ion
positive
negative


To computer control
Dichroic mirror
Flapping mirror assembly
Objective lens
Inlet valve
Light source
Video camera with telephoto lens
Nd: YAG laser
Mirror
Beam expander
Mirror
Sample chamber under vacuum
CO₂ to mass spectrometer
Cold trap
To vacuum


c.w. laser
ns laser
ps/fs laser
Shock waves



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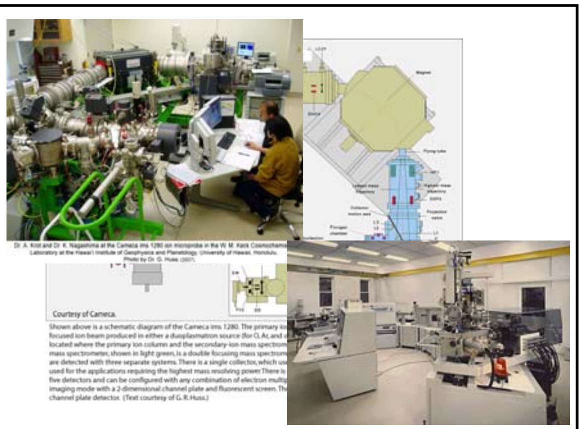

Fractionation

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Fractionation

- Equilibrium
- Kinetic

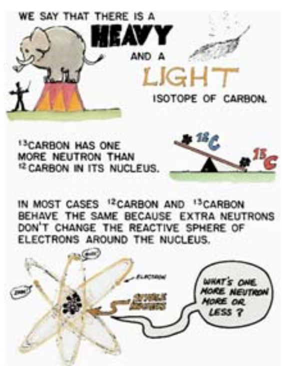


Figure from Fry (2006)

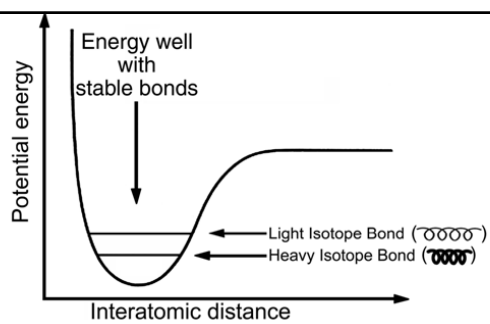


Fig. 7.1. A chemical diagram showing why fractionation occurs when bonds are broken in kinetic reactions. Bonds are often compared to springs, with light isotope bonds depicted as the less massive, easier-to-break springs. Light isotope bonds are slightly wider and have more potential energy than heavy isotope bonds. Adding equal energy to both kinds of bonds results in more rapid bond breaking for the light isotope bonds that need less energy climb out of the energy well as they elongate and break. When bonds are broken, atoms move apart to the right in this diagram, and interatomic distance increases. Bonds are only stable within the energy well. See text for further explanation. Reprinted with permission from Bigeleisen, J. 1965. Chemistry of isotopes. Science 147:463-471. Copyright 1965, AAAS.

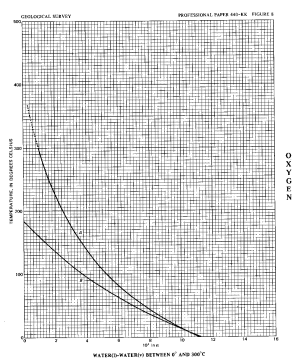
Equilibrium

$H_2O_{(v)} = H_2O_{(l)}$

$\alpha = K = H_20_{(l)}/H_2O_{(v)}$

FIGURE 8

A, This expression is based on the experimental data from 134° to 300°C (Bottinga, 1968b; Bottinga and Craig, 1968) and the data presented in figure 5 (Y. Bottinga, written commun., 1973):
$10^3\ln\alpha = +0.7.664(10^6T^{-2})+1.2051(10^3T^{-1})-3.493$.
B, Uvarov, Sokolov, and Zavoronkov (1962): (0° to 209°C).
$10^3\ln\alpha = 7.599(10^3T^{-1})-16.62$.



- Kinetic

Rule of Thumb is that for any reaction the initial material which has reacted has isotopically more negative material than the later reacted material because the bonds of the lighter isotopes break more easily.

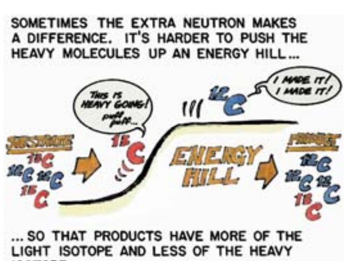


Figure from Fry (2006)

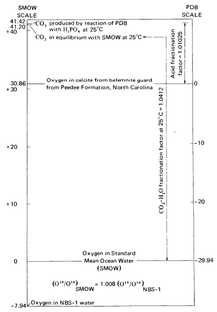


FIGURE 1.—Relationship between PDB, SMOW, and other oxygen standards.

$\delta_{SMOW} = 1.03086\,\delta_{PDB} + 30.86$

$\delta_{PDB} = 0.97006\,\delta_{SMOW} - 29.94$