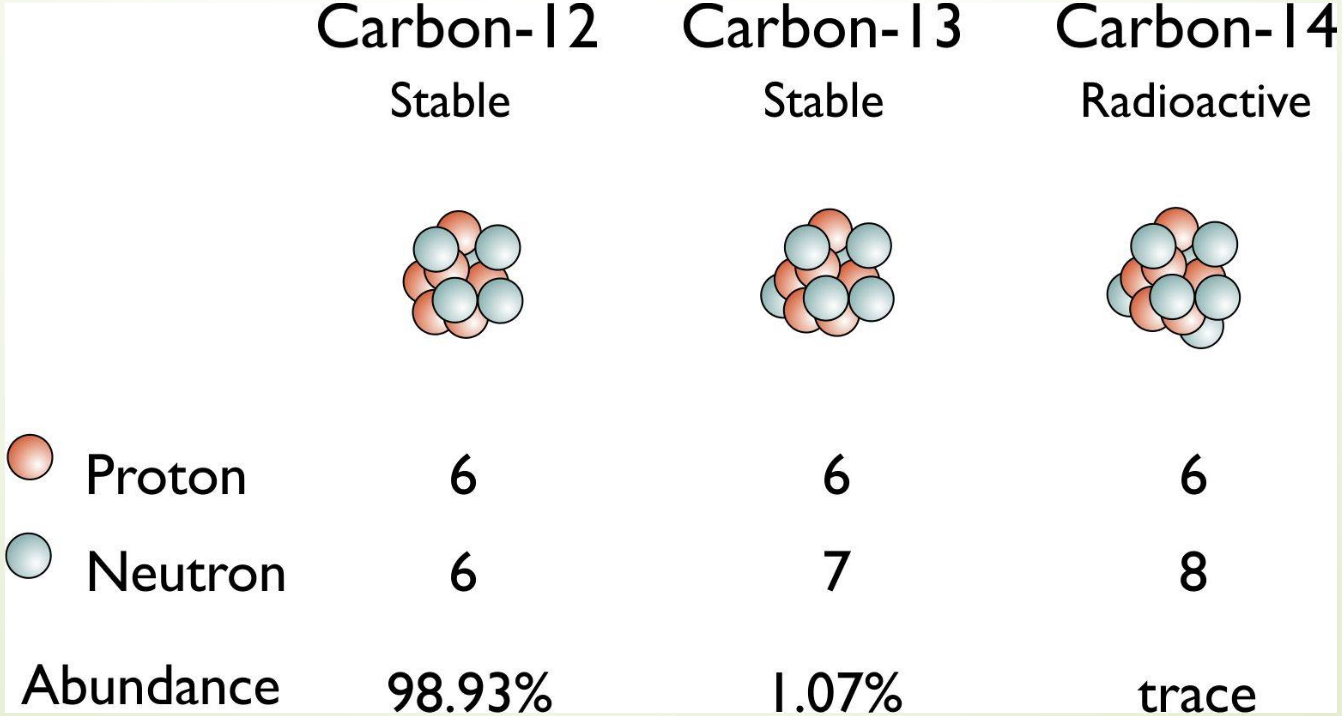
Stable Isotope Analysis

Archeological Chemistry Seminar

2023 AAS/ARAS Training Program

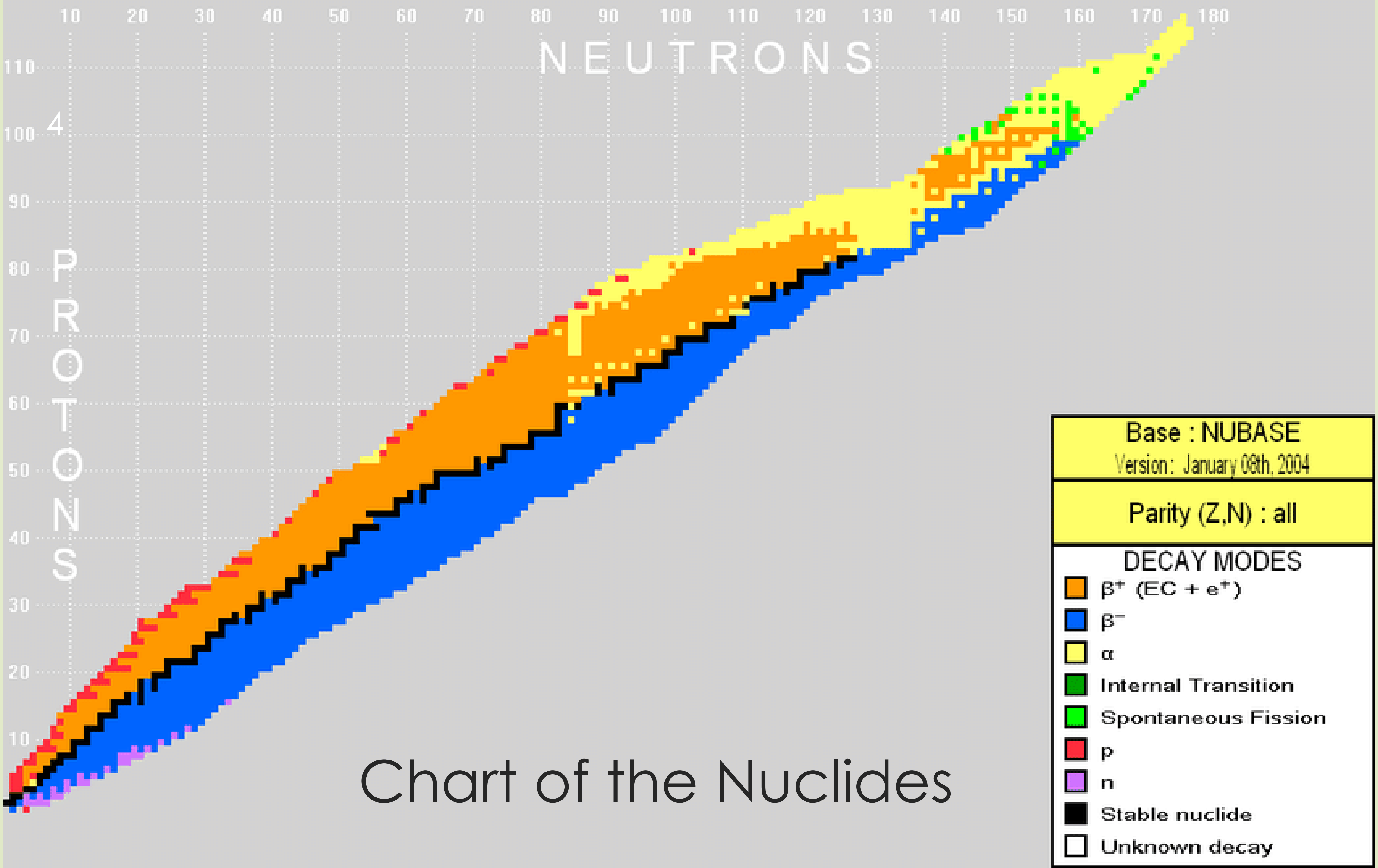
Stable Isotopes - I

- Isotopes are different distinct nuclear species of a given element
- All isotopes of an element have the same number of protons, but will have different numbers of neutrons in the nucleus.
  - Example: C-12, C-13, and C-14



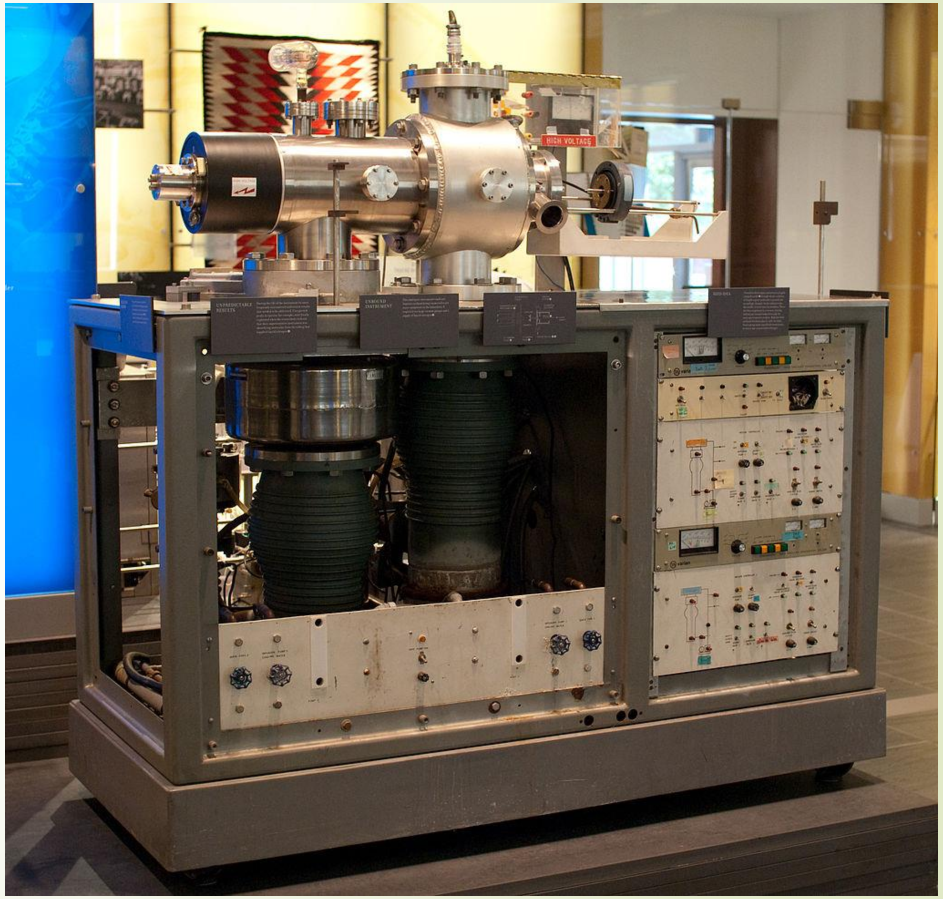
Stable Isotopes - II

- Nearly all elements have both stable and radioactive isotopes
- All isotopes of an element have similar chemical properties
  - Chemical reactions: Involve only electrons in the electron "cloud"
  - Nuclear reactions: Changes occur in nucleus (i.e. proton or neutron number may change)
- Most common stable isotopes used in archeology:
  - C-13, N-15, O-17&18, Sr-87, and Pb

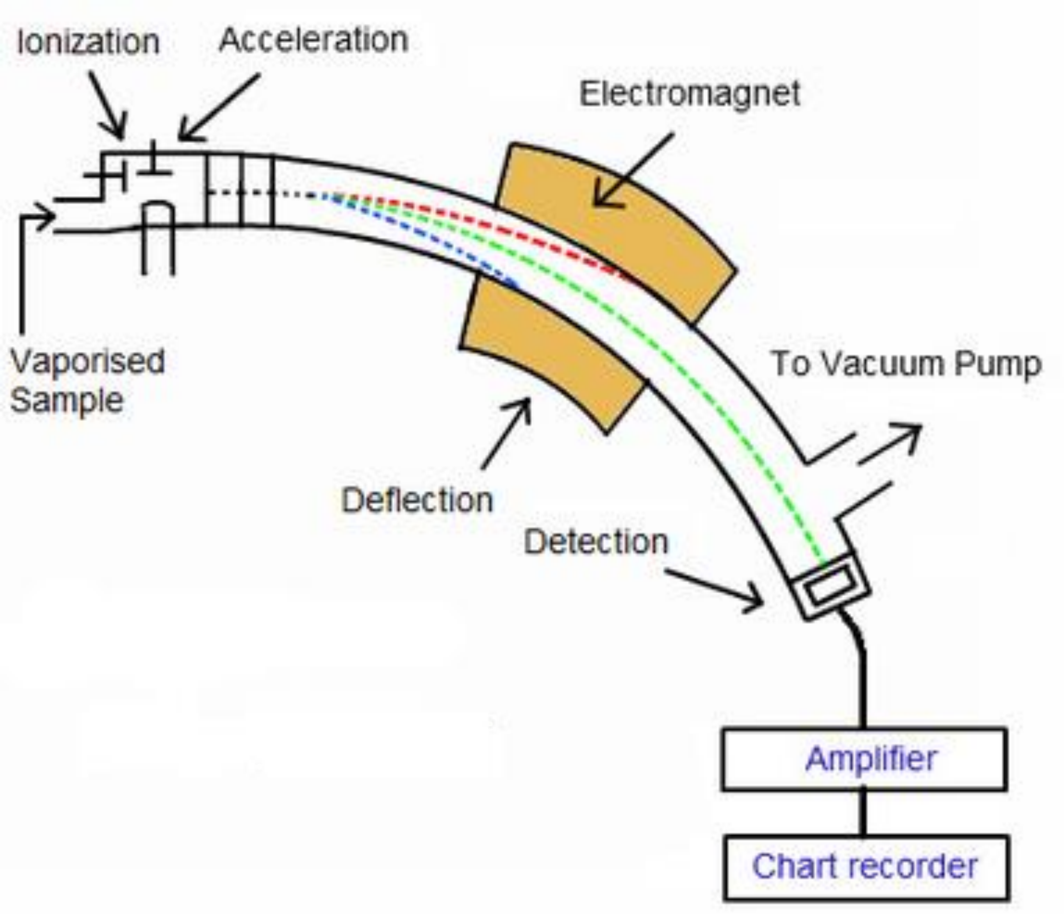

NEUTRONS
PROTONS
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
10 20 30 40 50 60 70 80 90 100 110
Base : NUBASE
Version : January 08th, 2004
Parity (Z,N) : all
DECAY MODES
β⁺ (EC + e⁺)
β⁻
α
Internal Transition
Spontaneous Fission
p
n
Stable nuclide
Unknown decay
Chart of the Nuclides

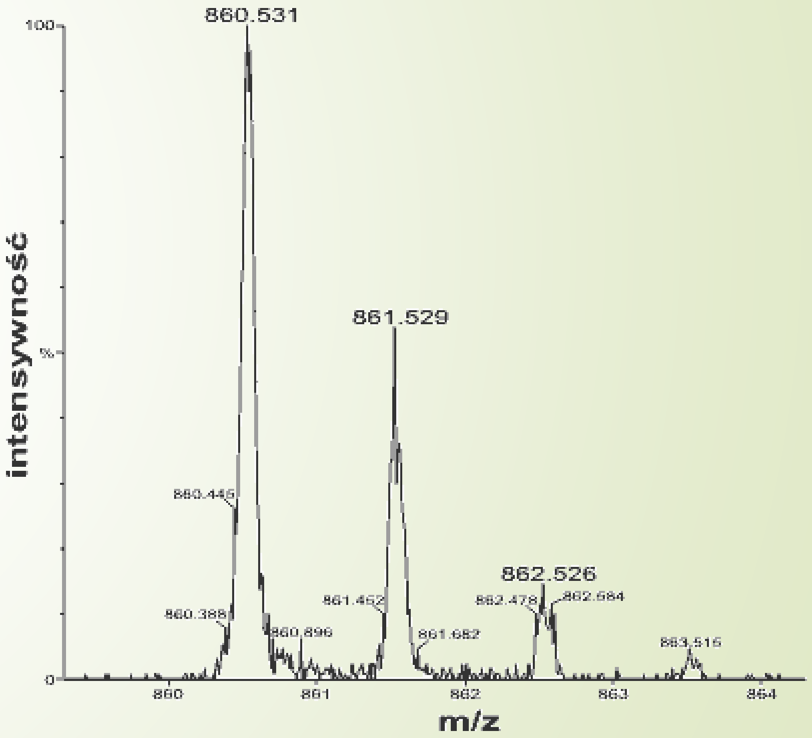
Mass Spectrometry

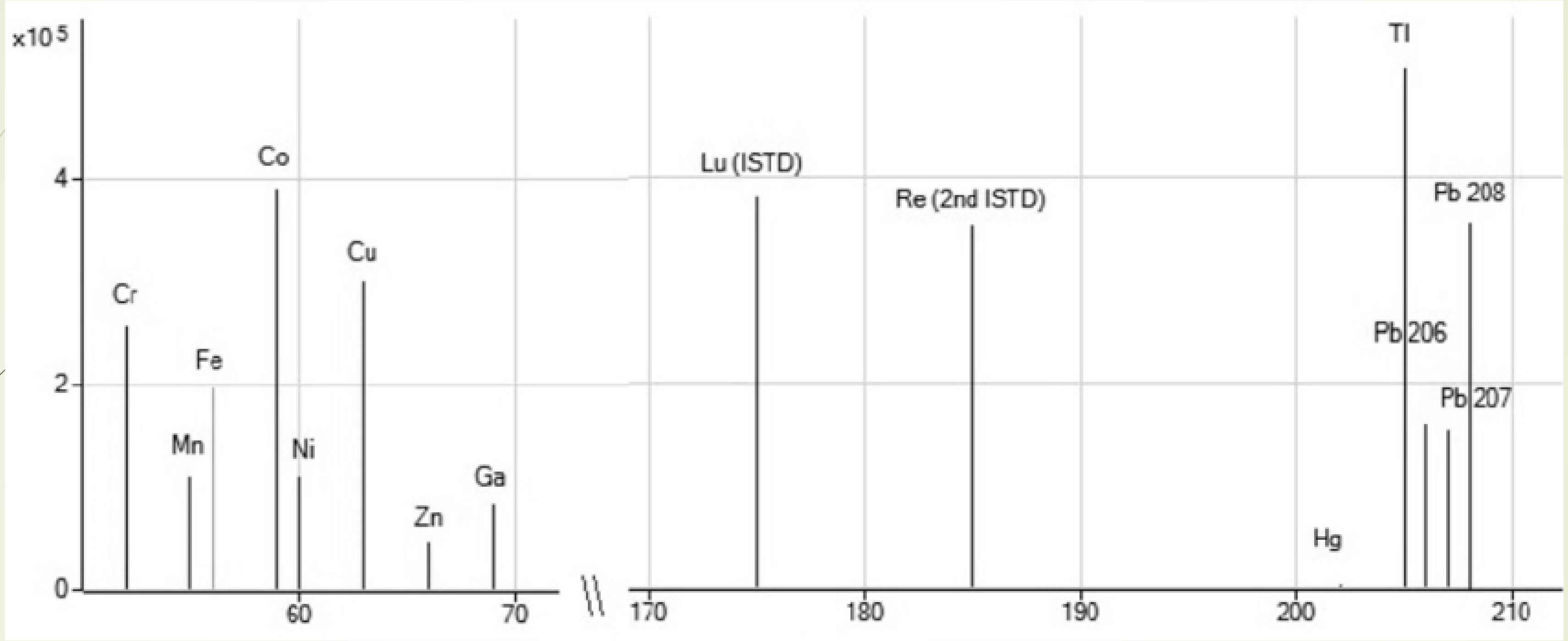
- Determining isotope abundance requires highly sensitive equipment to measure mass/charge (m/z) ratios
- Can be used to measure masses of atoms or molecules
  - Separates components based on differing atomic or molecular masses
- Typically, a sample (solid, liquid, or gas) is ionized by a beam of electrons
  - Lasers can also be used for ionization, often called “laser ablation”
- Ions are then directed down a long curved tube using magnetic fields
  - Ions with different m/z ratios will strike a detector in different places
  - Or, the time-of-flight is measured. Ions with large m/z ratios travel slower and are separated from other ions with differing m/z ratios.
- Often paired with other instrumental techniques: ICP-MS, GC-MS



Ion deflection and typical output





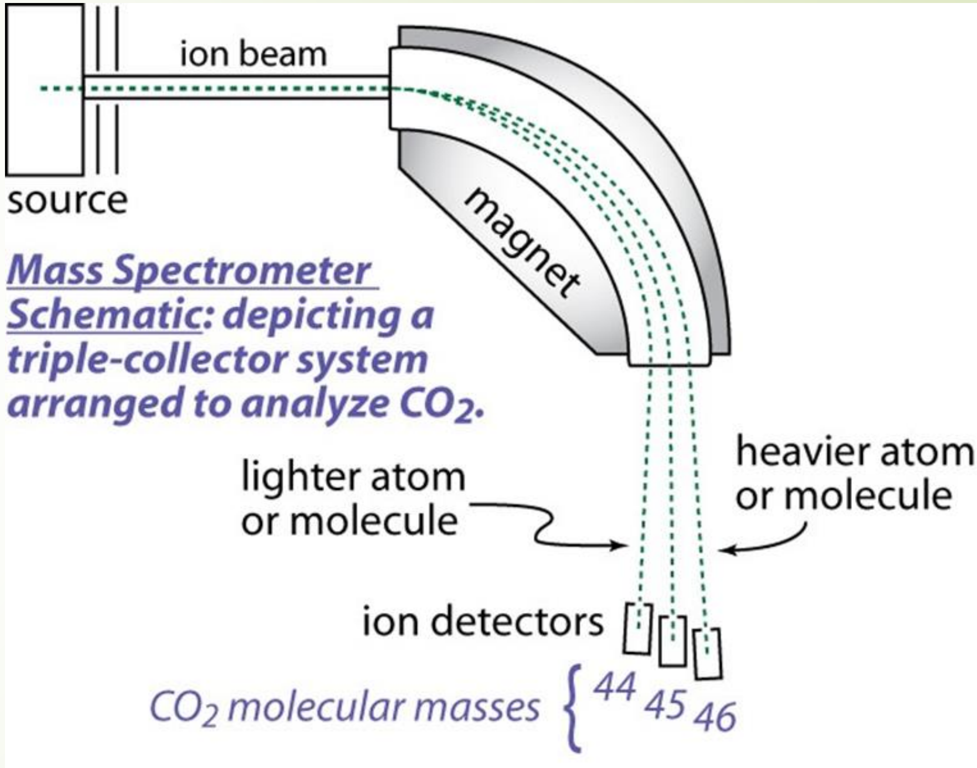


ICP-MS Spectrum of Wood showing multiple lead isotopes

Mass Spec details

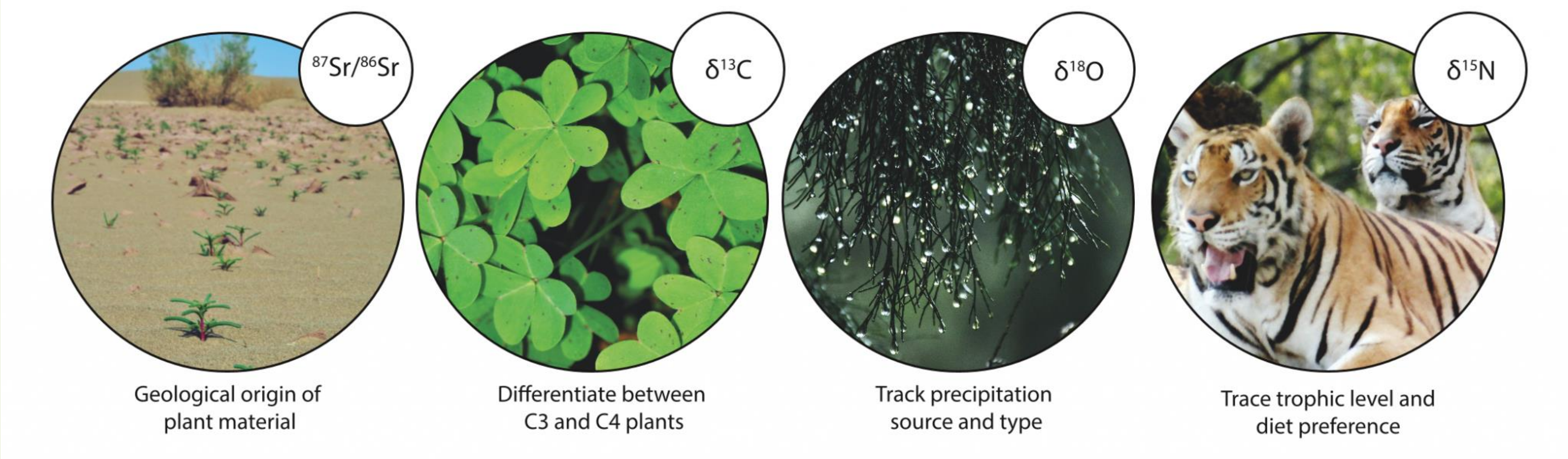
- Typically, electron beam ionizes samples in the gas phase
  - Called electron impact (EI) ionization
- All ions leaving the electron beam have the same kinetic energy: $E = eV = 1/2mv^2$
- But ions travel at different velocities due to differing mass: $v = (2eV/m)^{0.5}$
- Radius of ion curvature: $r = 1.414(V*m/e)^{0.5}/B$
- For time-of-flight (TOF) mass analyzers:

$$t = \frac{d}{\sqrt{2V}}\sqrt{\frac{m}{e}}$$ determines time ion spends in drift tube



What do stable isotopes tell us?

- Stable isotope studies fall into two groups:
  - Dietary isotopes: C-13, N-15
  - Mobility isotopes: Sr-87, O-18, Pb-204



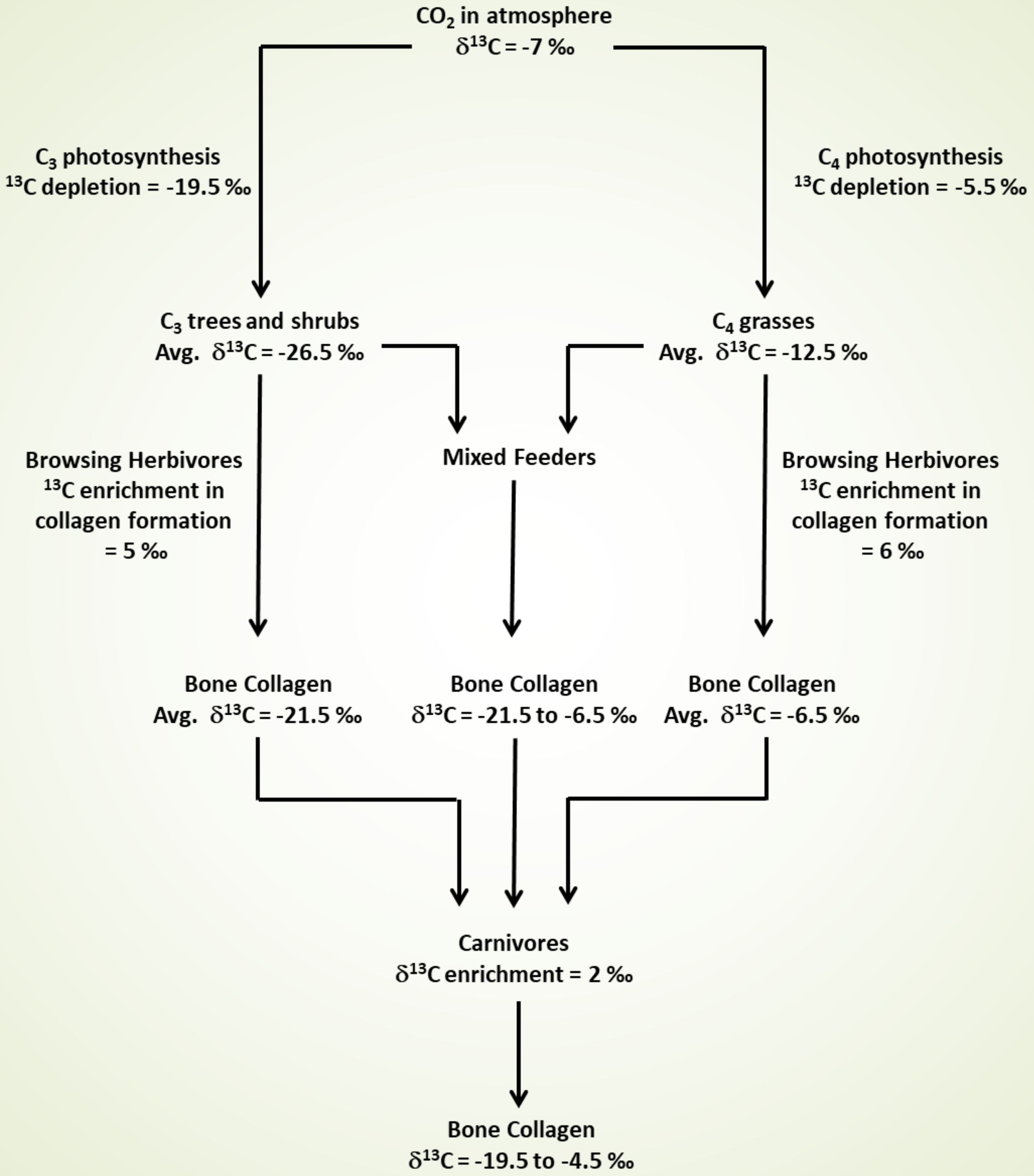
Dietary Isotope: C-13

- Carbon has three isotopes:
  - C-12 (98.90%) stable
  - C-13 (1.10%) stable
  - C-14 (trace) radioactive
- Because of the mass differences, carbon isotopes fractionate as they move through biological systems
  - Thus, an organism's leaves, stems, bones, blood, tissue, etc… will have a different isotopic composition than the local environment
- Because fractionation of isotopes is small, differences are usually reported as a delta per mil (‰) notation.

$$\delta^{13}C = \left[\frac{\frac{^{13}C_{sample}}{^{12}C_{sample}}}{\frac{^{13}C_{standard}}{^{12}C_{standard}}} - 1 \right] \times 1000\ ‰$$

Carbon biological pathways

- Majority of Earth's surface carbon is dissolved as carbon dioxide in the oceans
- Carbon dioxide released to atmosphere is isotopically lighter by 7 ‰
- Carbon dioxide enters plants through photosynthesis pathways
  - C_3 plants (most edible plants)
  - C_4 plants (includes corn)
  - CAM plants (usually found in arid environments, such as succulents)
- Fractionation of isotopes continue inside browsing herbivores
- Bone collagen δC is indicative of the trophic level and type of plant/herbivore consumption

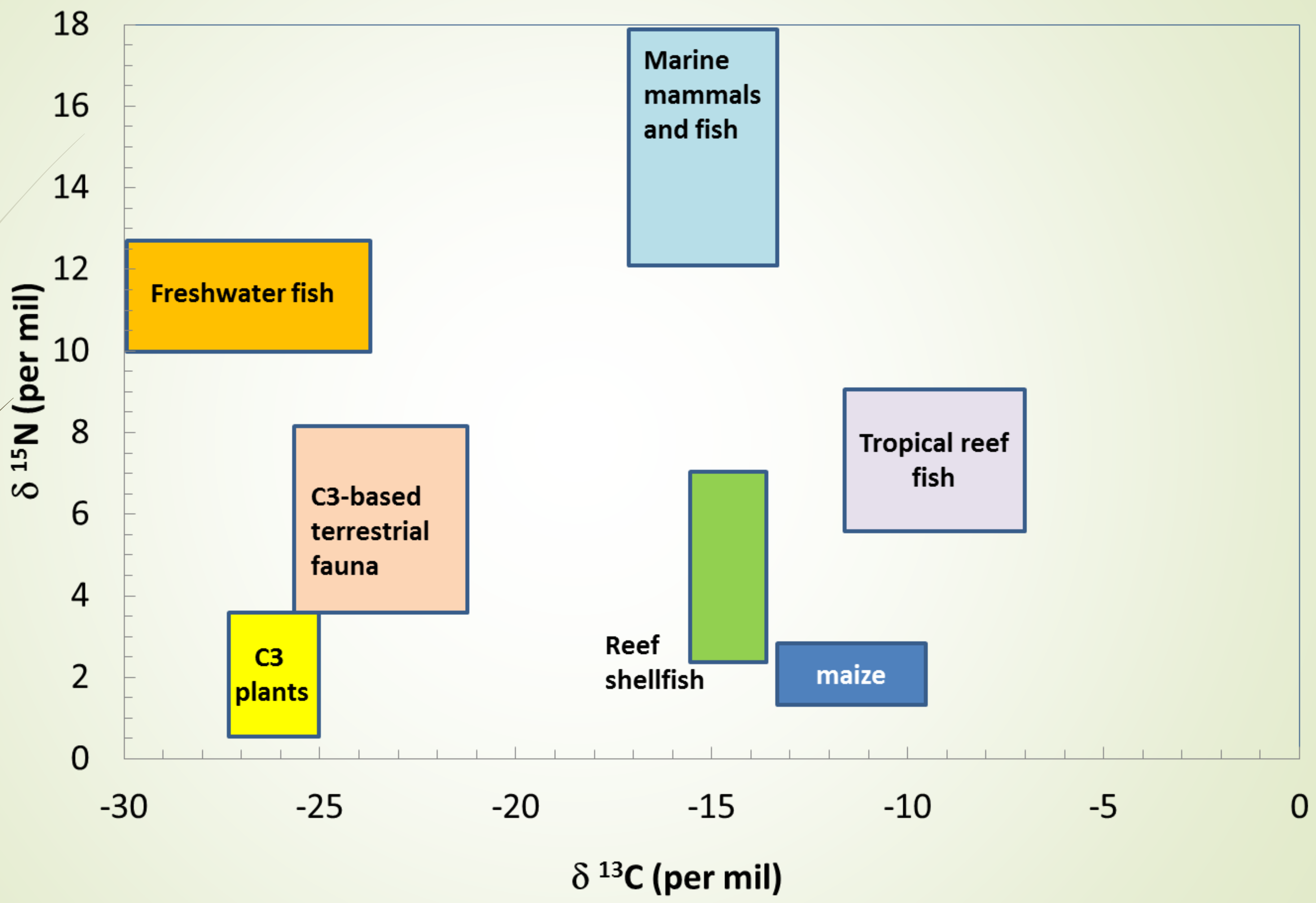


CO_2 in atmosphere
$\delta^{13}C$ = -7 ‰
C_3 photosynthesis
^{13}C depletion = -19.5 ‰
C_4 photosynthesis
^{13}C depletion = -5.5 ‰
C_3 trees and shrubs
Avg. $\delta^{13}C$ = -26.5 ‰
C_4 grasses
Avg. $\delta^{13}C$ = -12.5 ‰
Browsing Herbivores
^{13}C enrichment in collagen formation = 5 ‰
Mixed Feeders
Browsing Herbivores
^{13}C enrichment in collagen formation = 6 ‰
Bone Collagen
Avg. $\delta^{13}C$ = -21.5 ‰
Bone Collagen
$\delta^{13}C$ = -21.5 to -6.5 ‰
Bone Collagen
Avg. $\delta^{13}C$ = -6.5 ‰
Carnivores
$\delta^{13}C$ enrichment = 2 ‰
Bone Collagen
$\delta^{13}C$ = -19.5 to -4.5 ‰

Dietary Isotope: N-15

- Nitrogen has two isotopes:
  - N-14 (99.63%) stable
  - N-15 (0.37%) stable
- Because of the mass differences, nitrogen isotopes also fractionate as they move through biological systems and trophic levels
- Fractionation in plants occurs via bacterial fixation or through soil nitrates
  - Plant fractionation is <4 ‰ relative to atmospheric nitrogen
- Each trophic level enriches $\delta^{15}N$ by 3 ‰
- Because fractionation of isotopes is small, differences are usually reported as a delta per mil (‰) notation.

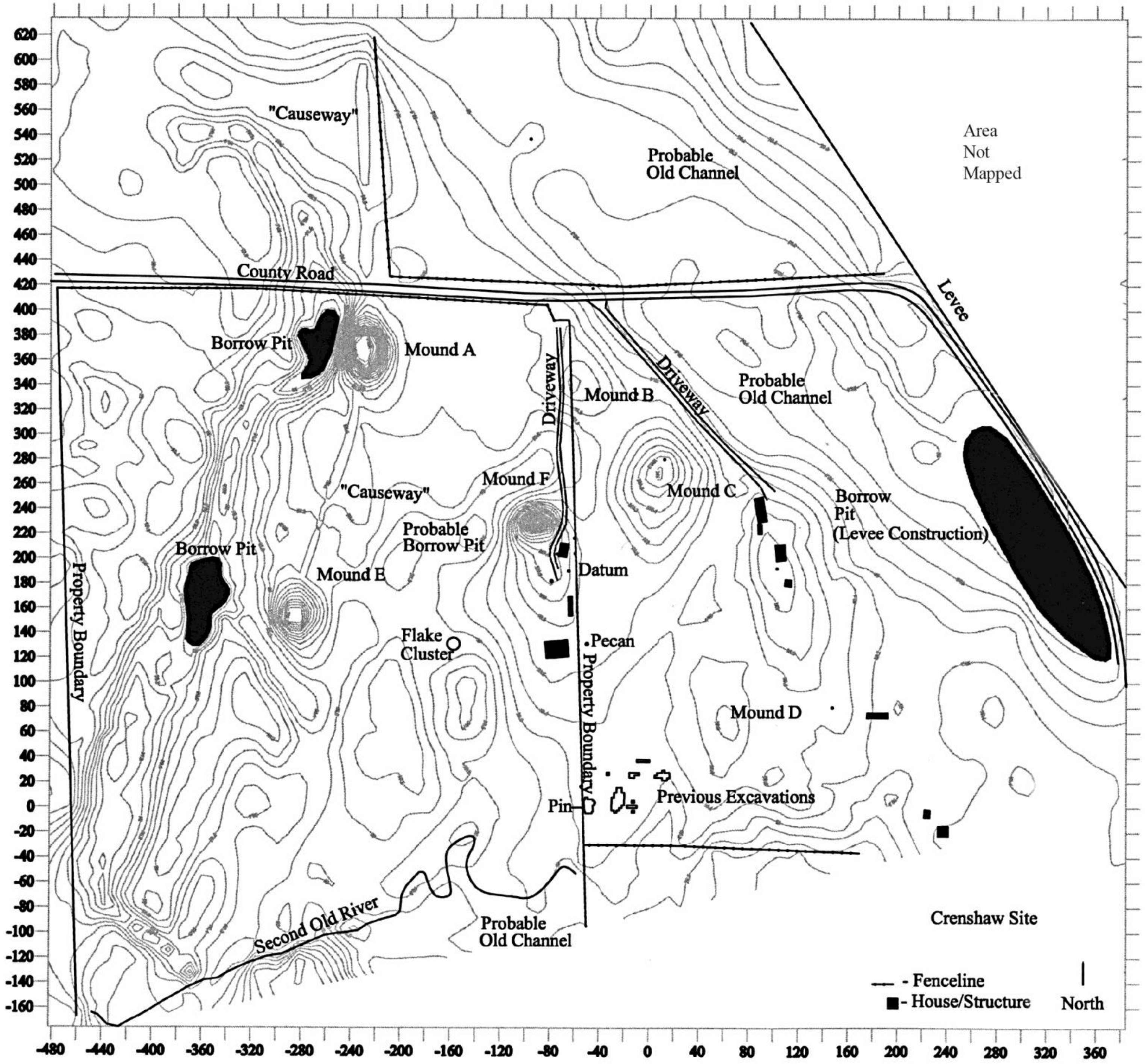
$$\delta^{15}N = \left[\frac{\frac{^{15}N_{sample}}{^{14}N_{sample}}}{\frac{^{15}N_{standard}}{^{14}N_{standard}}} - 1\right] \times 1000\ ‰$$

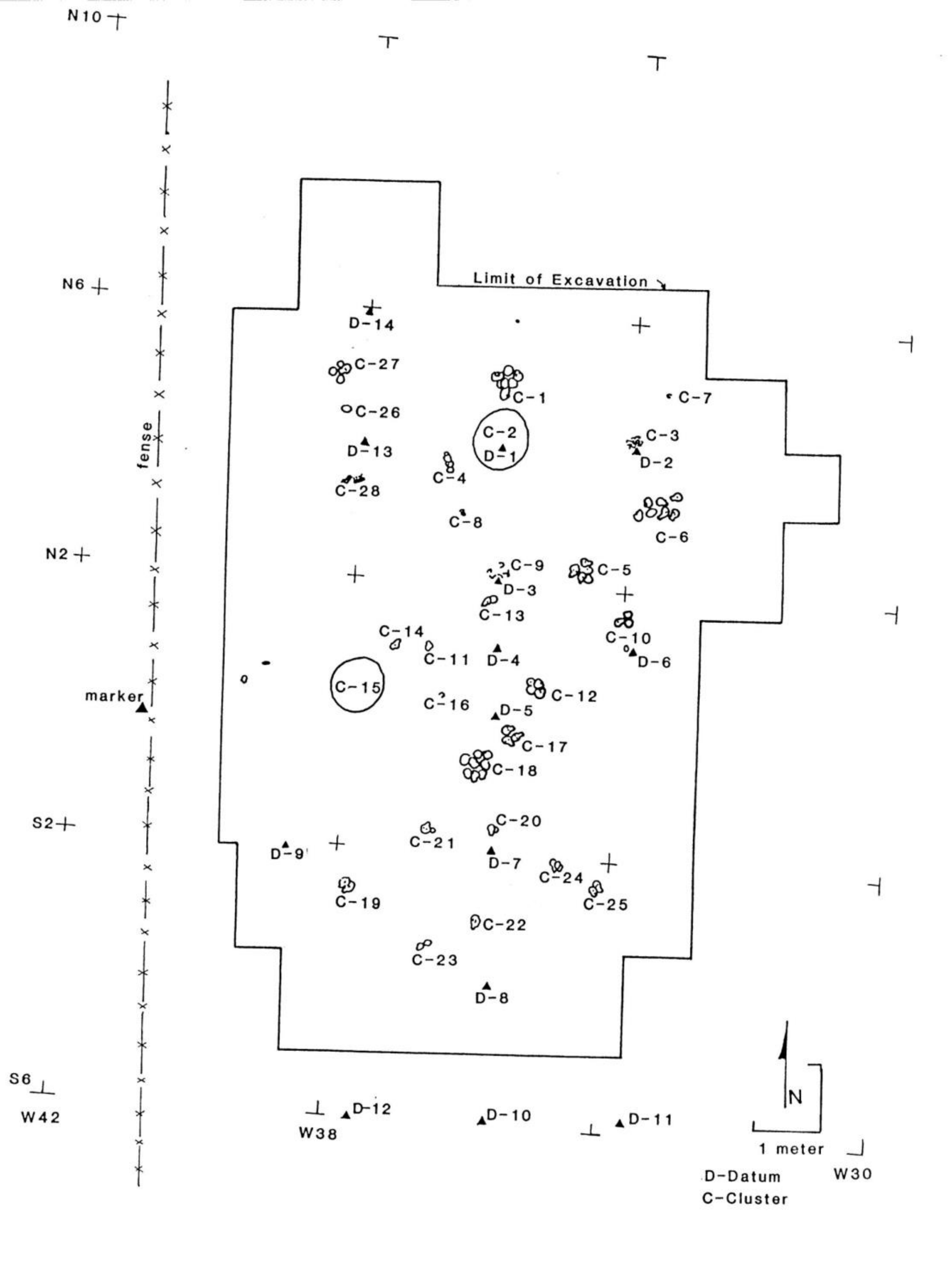


Marine mammals and fish
Freshwater fish
C3-based terrestrial fauna
Tropical reef fish
C3 plants
Reef shellfish
maize
δ 15N (per mil)
δ 13C (per mil)
18
16
14
12
10
8
6
4
2
0
-30
-25
-20
-15
-10
-5
0

Crenshaw Site (3MI6)

- Fourche Maline through Middle Caddo period (A.D. 700-1400)
- Excavated by Frank Schambach in 1960s and 1980s
- Southern portion of site contains "skull and mandible cemetery"
  - 33 buried clusters containing piles of skulls or mandibles
  - In total, 127 human skulls and 235 detached mandibles
  - Cemetery dates to A.D. 1250-1350
  - No grave goods
- Two possible explanations:
  - Regional deceased residents brought to the ceremonial Crenshaw site at certain times of the year
  - Skulls and mandibles represent "trophies" collected during raids on enemies

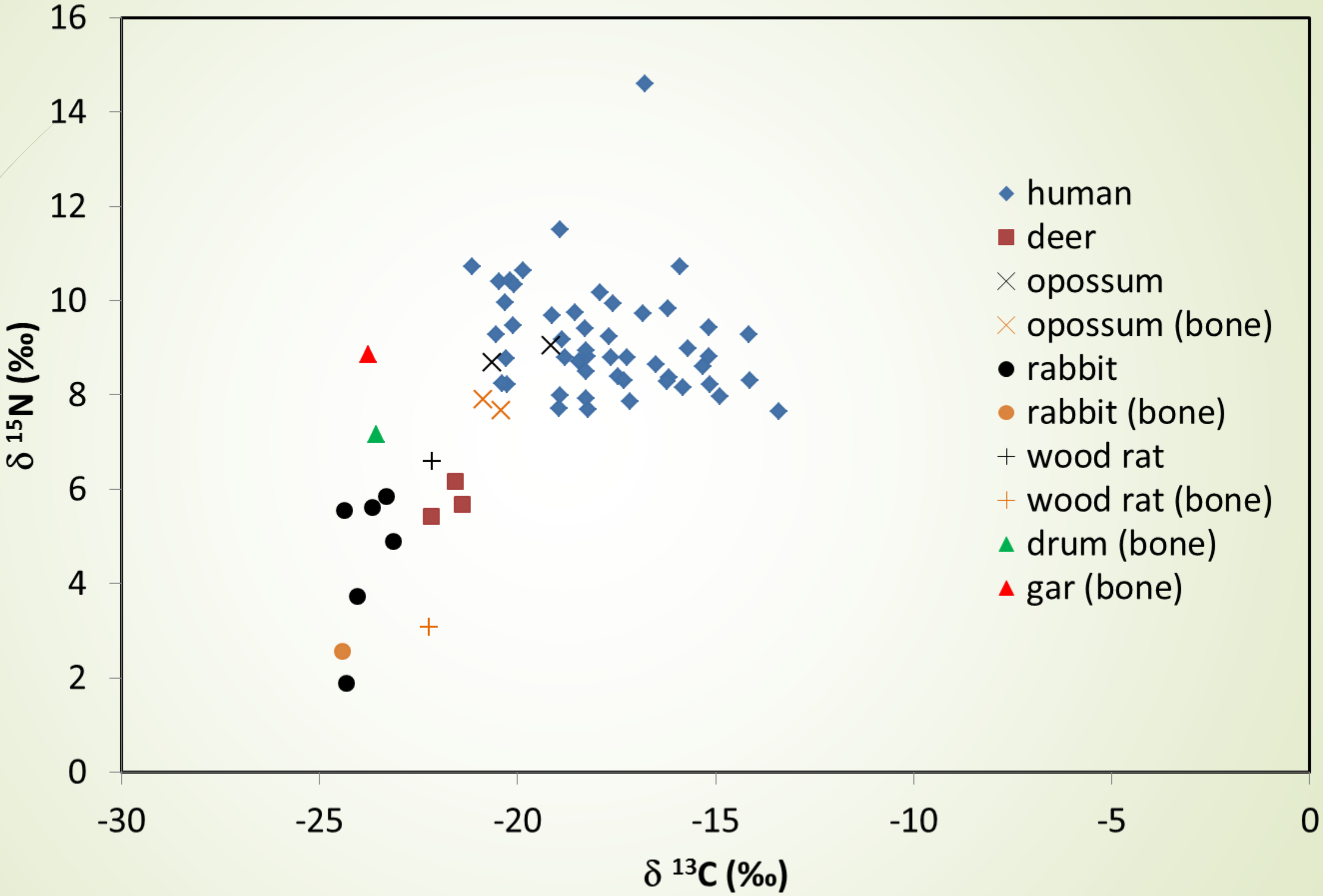

"Causeway"
Probable
Old Channel
Area
Not
Mapped
County Road
Levee
Borrow Pit
Mound A
Driveway
Mound B
Driveway
Probable
Old Channel
Mound F
"Causeway"
Mound C
Borrow
Pit
(Levee Construction)
Probable
Borrow Pit
Borrow Pit
Datum
Mound E
Property Boundary
Flake
Cluster
Pecan
Property Boundary
Mound D
Previous Excavations
Pin
Second Old River
Probable
Old Channel
Crenshaw Site
- Fenceline
- House/Structure
North



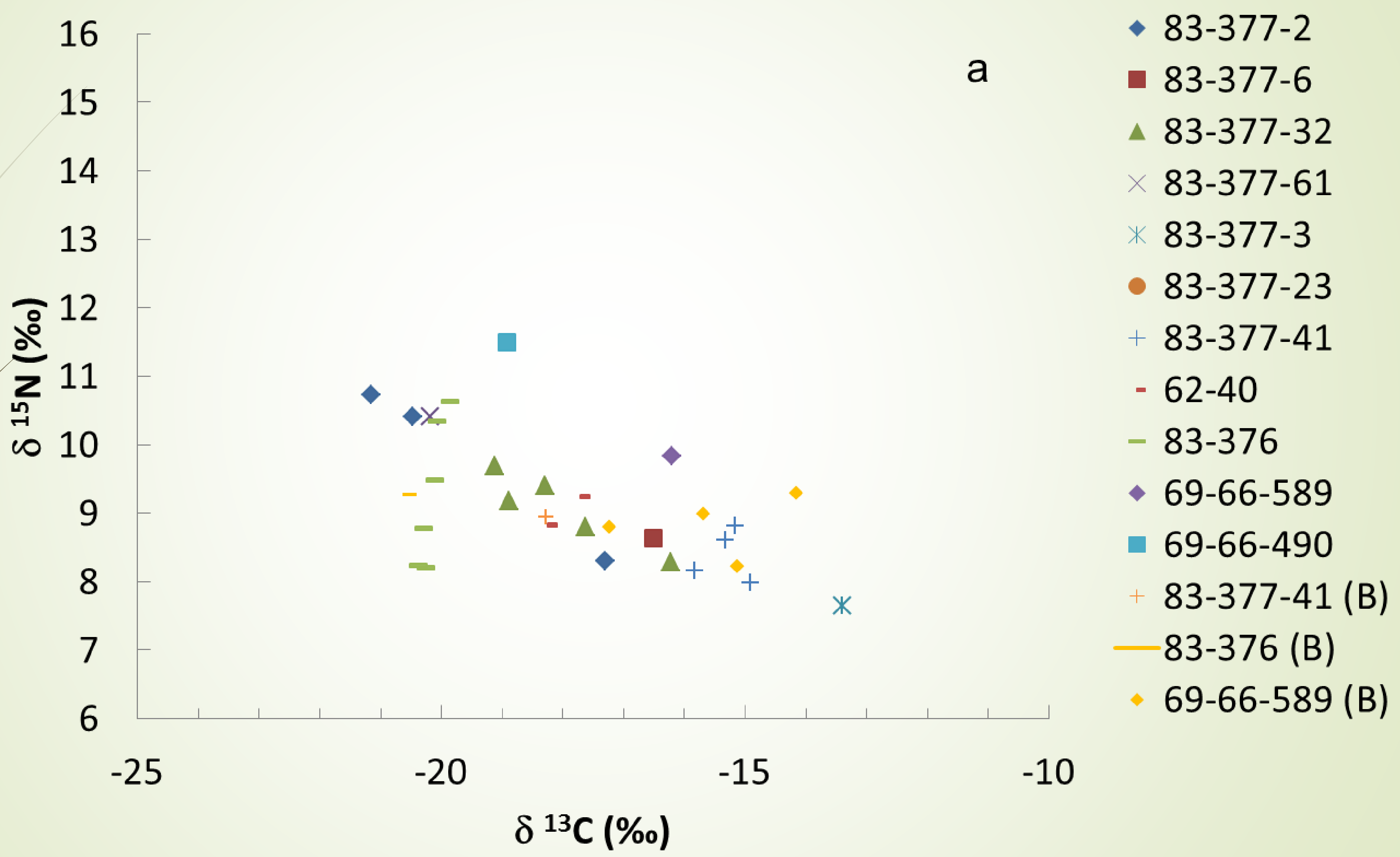
Skull and mandible clusters in the West Skull Area

Summary of location areas for human teeth chosen for isotope analysis.

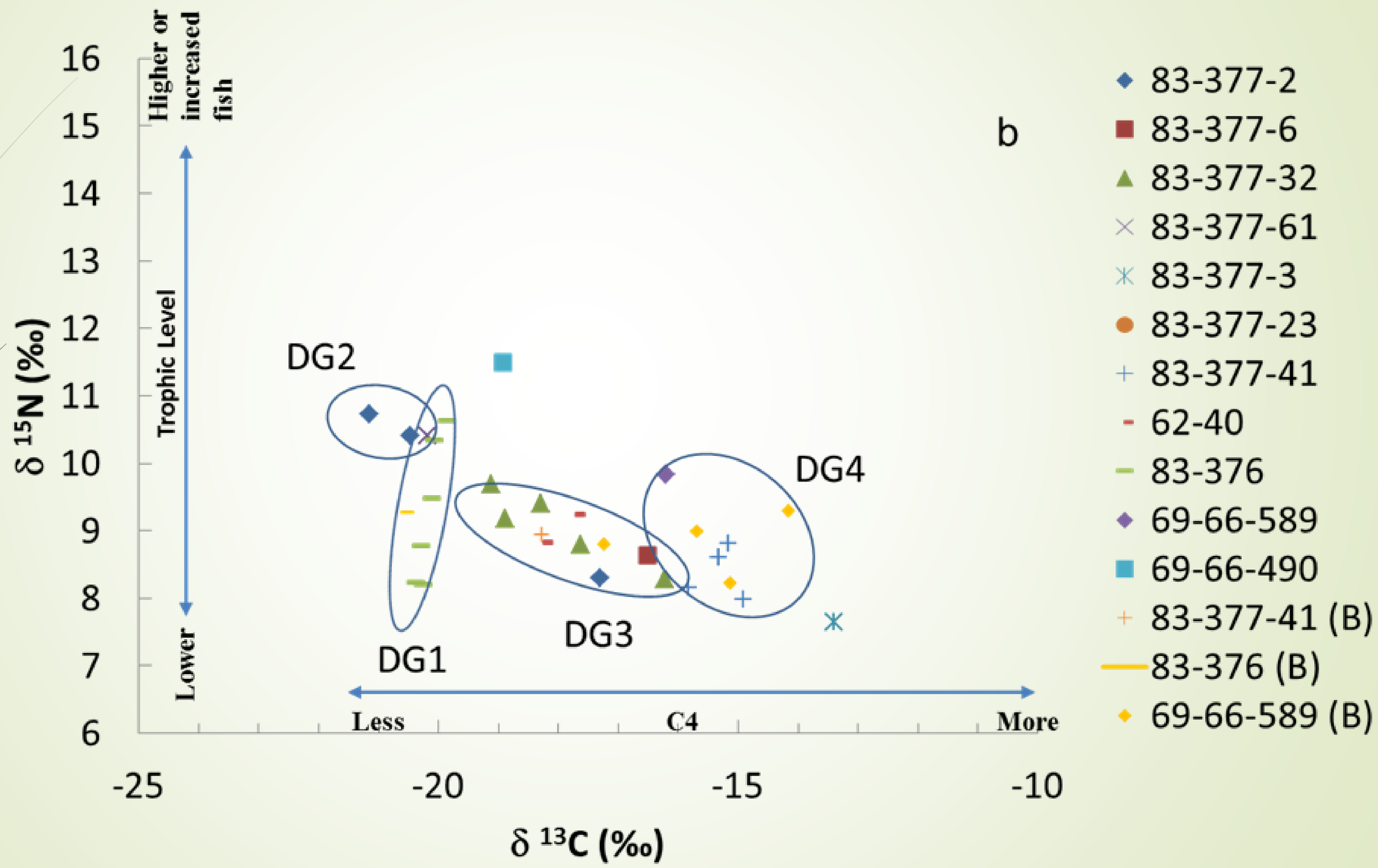
Catalog #	Location	Location Description	No. of samples submitted for isotope analysis
83-377-2	WSA Cluster 1	7 skulls, 1 mandible	5
83-377-6	WSA Cluster 5	5 skulls	5
83-377-32	WSA Cluster 18	10 skulls	9
83-377-61	WSA Cluster 25	3 skulls	3
83-377-3	WSA Cluster 2	108 mandibles	20
83-377-23	WSA Cluster 15	36-37 mandibles	8
83-377-41	NSA Cluster 8	10 skulls	9
62-40	Mound C	Raymond Wood excavated. burials	7
83-376	Mound F	Harrison excavated burials	7
69-66-589	Southwest of Md. D	8 skulls, Rayburn cluster	6
69-66-490	Feature 8a, Antler temple	1 mandible in pit with animal bone	1


16
14
12
10
8
6
4
2
0
δ 15N (‰)
-30
-25
-20
-15
-10
-5
0
δ 13C (‰)
human
deer
opossum
opossum (bone)
rabbit
rabbit (bone)
wood rat
wood rat (bone)
drum (bone)
gar (bone)

Human Teeth


a
δ 15N (‰)
16
15
14
13
12
11
10
9
8
7
6
-25
-20
-15
-10
δ 13C (‰)
83-377-2
83-377-6
83-377-32
83-377-61
83-377-3
83-377-23
83-377-41
62-40
83-376
69-66-589
69-66-490
83-377-41 (B)
83-376 (B)
69-66-589 (B)

Human Teeth Data Interpreted
DG = Diet Groups



Akridge Diet Interpretations

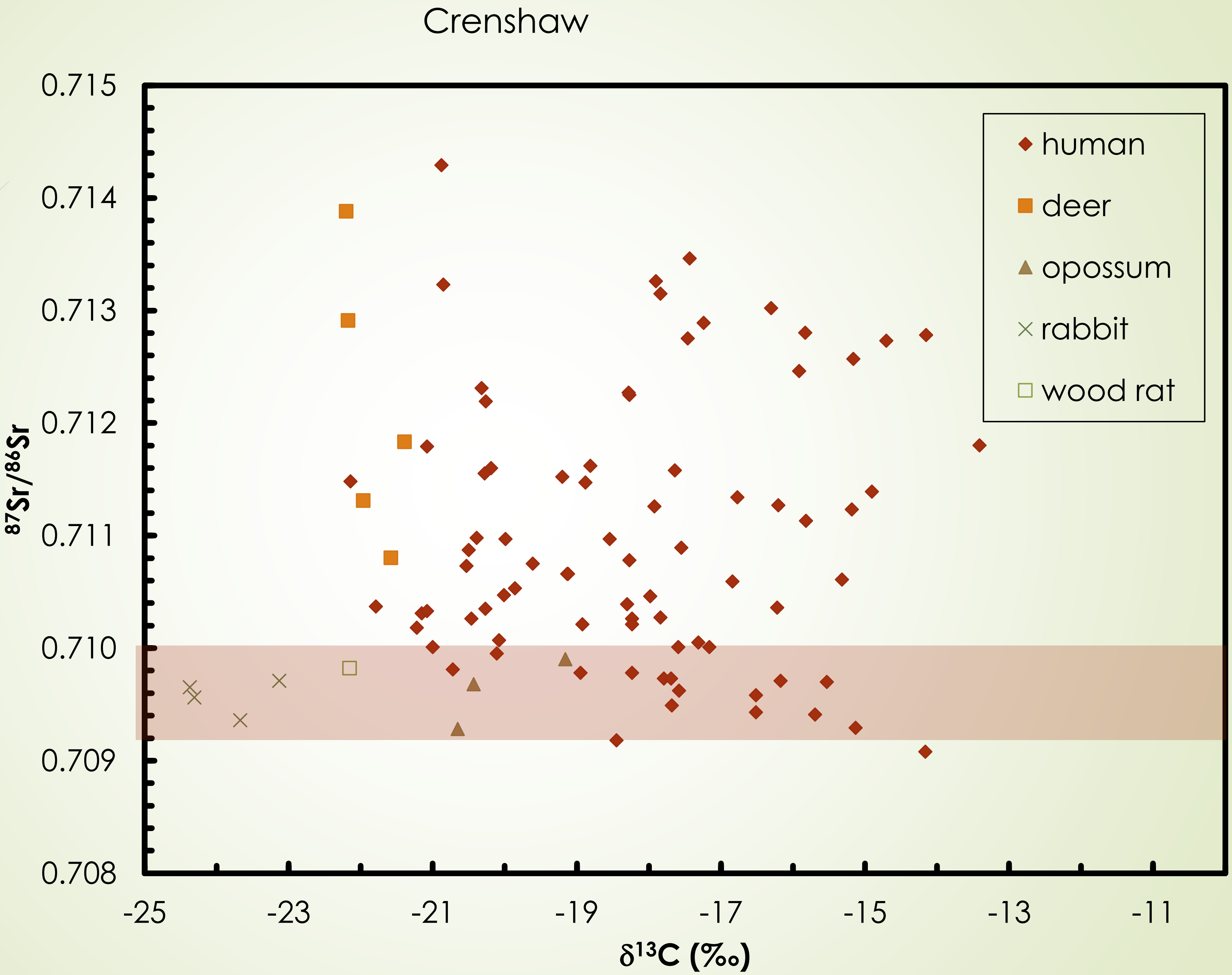
Diet Group	Samples Represented	Location(s) Represented	Diet Description	Interpretation
1	87, 88, 89, 90, 91*, 92, 93	Mound F	No C_4 with varying meat consumption	No C4 or bison
2	21, 25, 41	WSA Cluster 1; WSA Cluster 25	No C_4 with similar meat consumption	No C4 or bison
3	24, 28, 31, 34, 35, 37, 38, 71*, 82, 86, 96*	WSA Cluster 1; WSA Cluster 5; WSA Cluster 18; NSA Cluster 8; Rayburn Skulls; Mound C	Minor to moderate C_4 consumption	C4 consumption; no bison
4	73, 77, 78, 79, 94, 97*, 98*, 99*	NSA Cluster 8; Rayburn Skulls	Moderate C_4 consumption	C4 and bison consumption
--	54	WSA Cluster 2	Moderate C_4 consumption	C4 consumption
--	100	Feature 8a, Antler Temple	Minor C_4 consumption with increased meat/fish consumption	C4 with high meat consumption

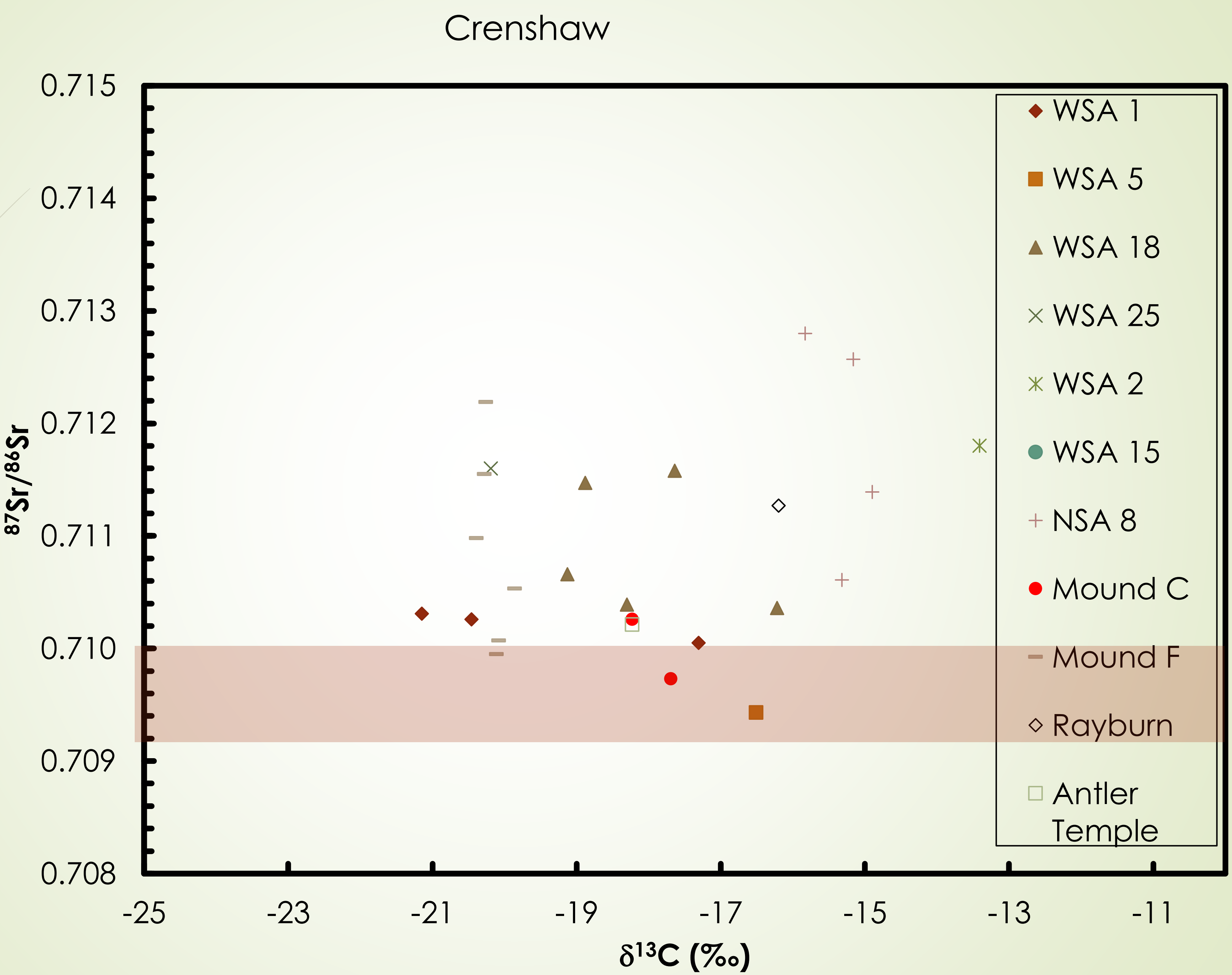
Mobility Isotope: Sr-87

- Strontium isotopes are not fractionated in biological systems
- Thus, all trophic levels reflect local soil Sr composition
- Only one Sr stable isotope is derived from radiogenic source:

  $^{87}Rb \rightarrow {}^{87}Sr + B$ Half-life = 48.8 billion years

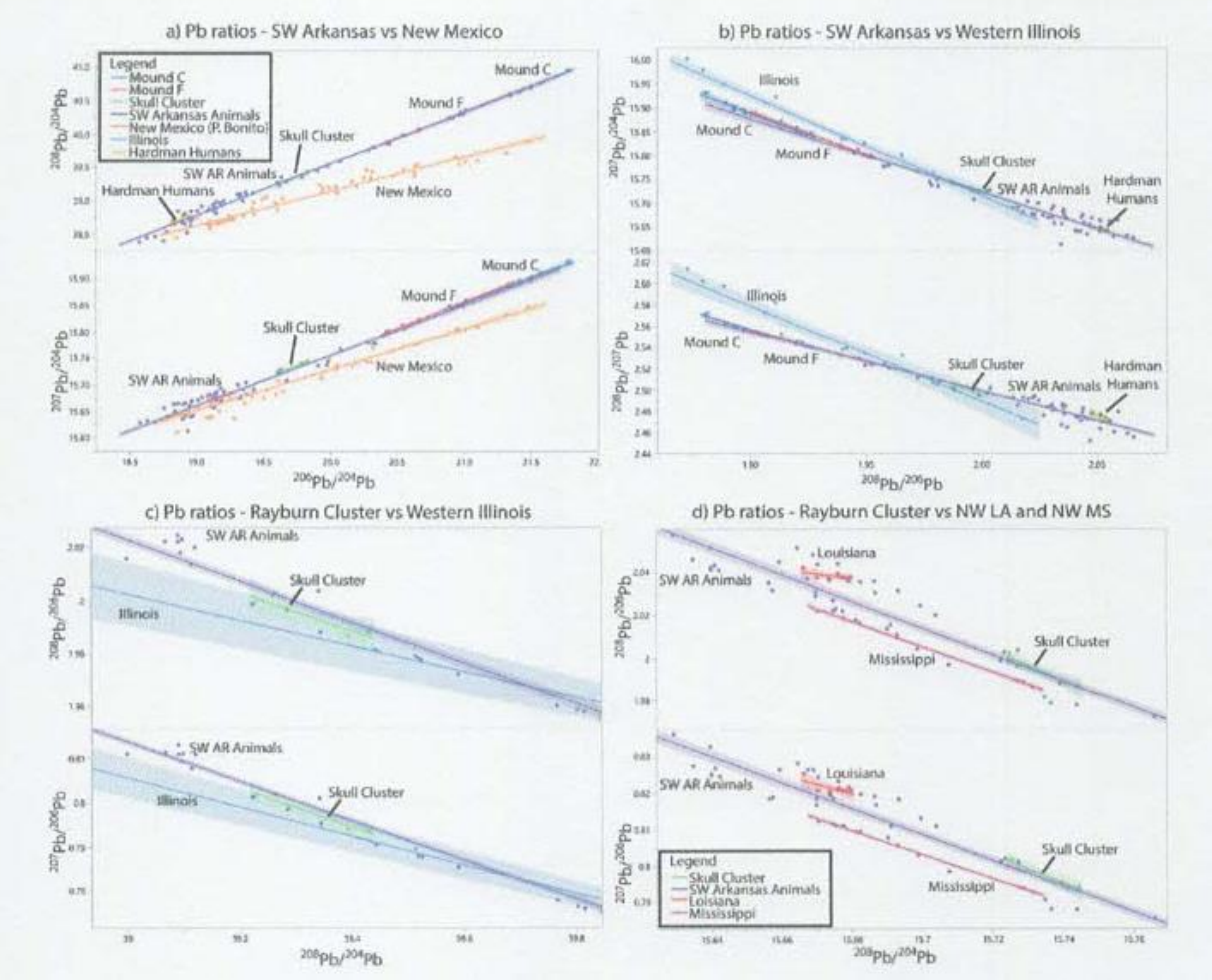
- Leads to a very slow build-up of ^{87}Sr in rocks and soils
- Usually, measured as $\frac{^{87}Sr}{^{86}Sr}$
- Older rocks/soil generally have higher $\frac{^{87}Sr}{^{86}Sr}$ ratios
- Mobility of people can be indicated by Sr ratios different from local environment


Crenshaw
0.715
0.714
0.713
0.712
0.711
0.710
0.709
0.708
$^{87}Sr/^{86}Sr$
-25
-23
-21
-19
-17
-15
-13
-11
$\delta^{13}C$ (‰)
human
deer
opossum
rabbit
wood rat


Crenshaw
0.715
0.714
0.713
0.712
0.711
0.710
0.709
0.708
87Sr/86Sr
-25
-23
-21
-19
-17
-15
-13
-11
δ13C (‰)
WSA 1
WSA 5
WSA 18
WSA 25
WSA 2
WSA 15
NSA 8
Mound C
Mound F
Rayburn
Antler Temple

Mobility Isotopes: Lead (Pb)

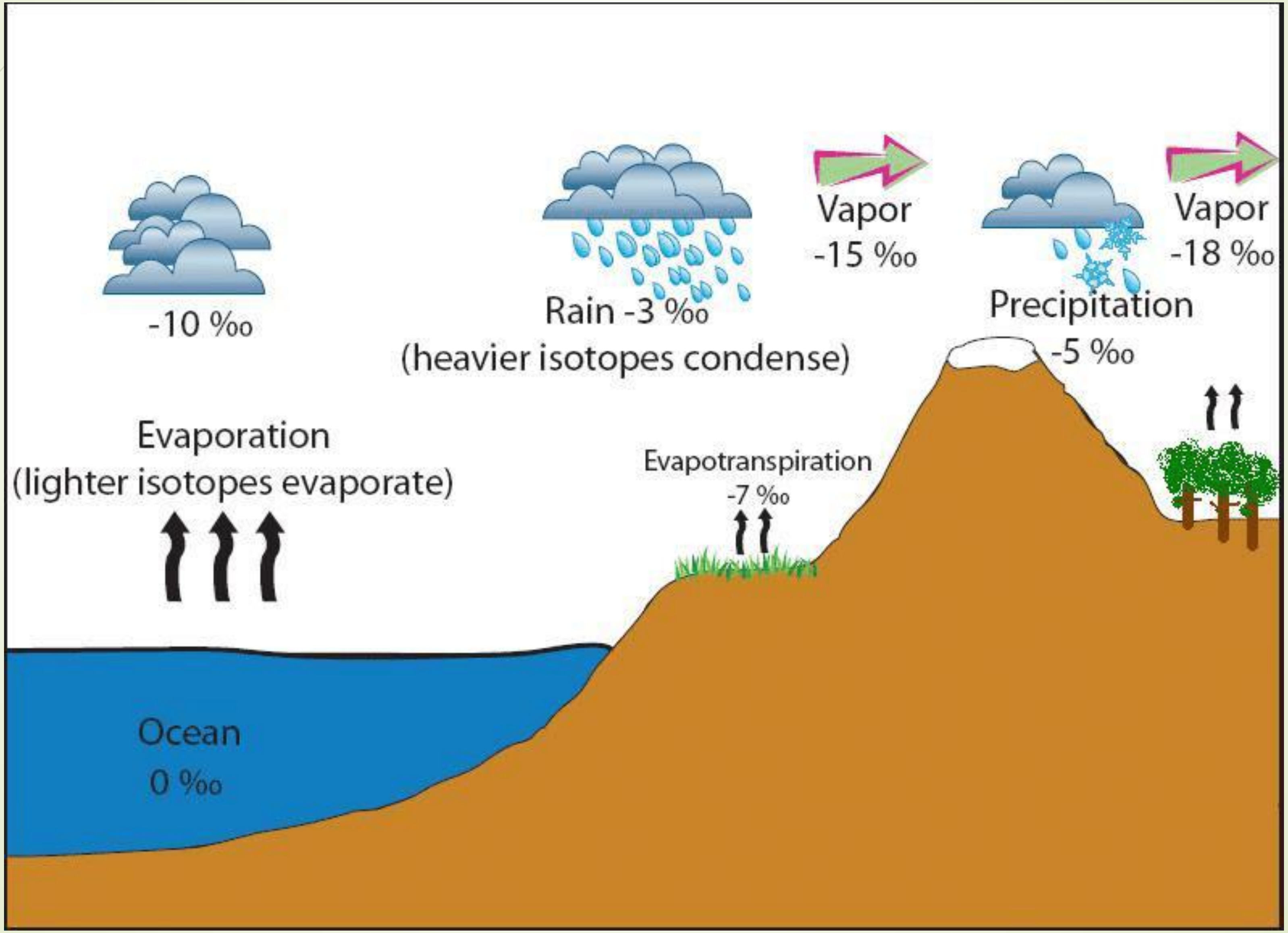
- Pb isotopes are not fractionated in biological systems
- Concept is similar to Sr isotopes
- Pb has four stable isotopes, so more ways to analyze data
  - Pb-204 non-radiogenic
  - Pb-206 radiogenic
  - Pb-207 radiogenic
  - Pb-208 radiogenic
- Thus, only Pb-204 does not increase over time

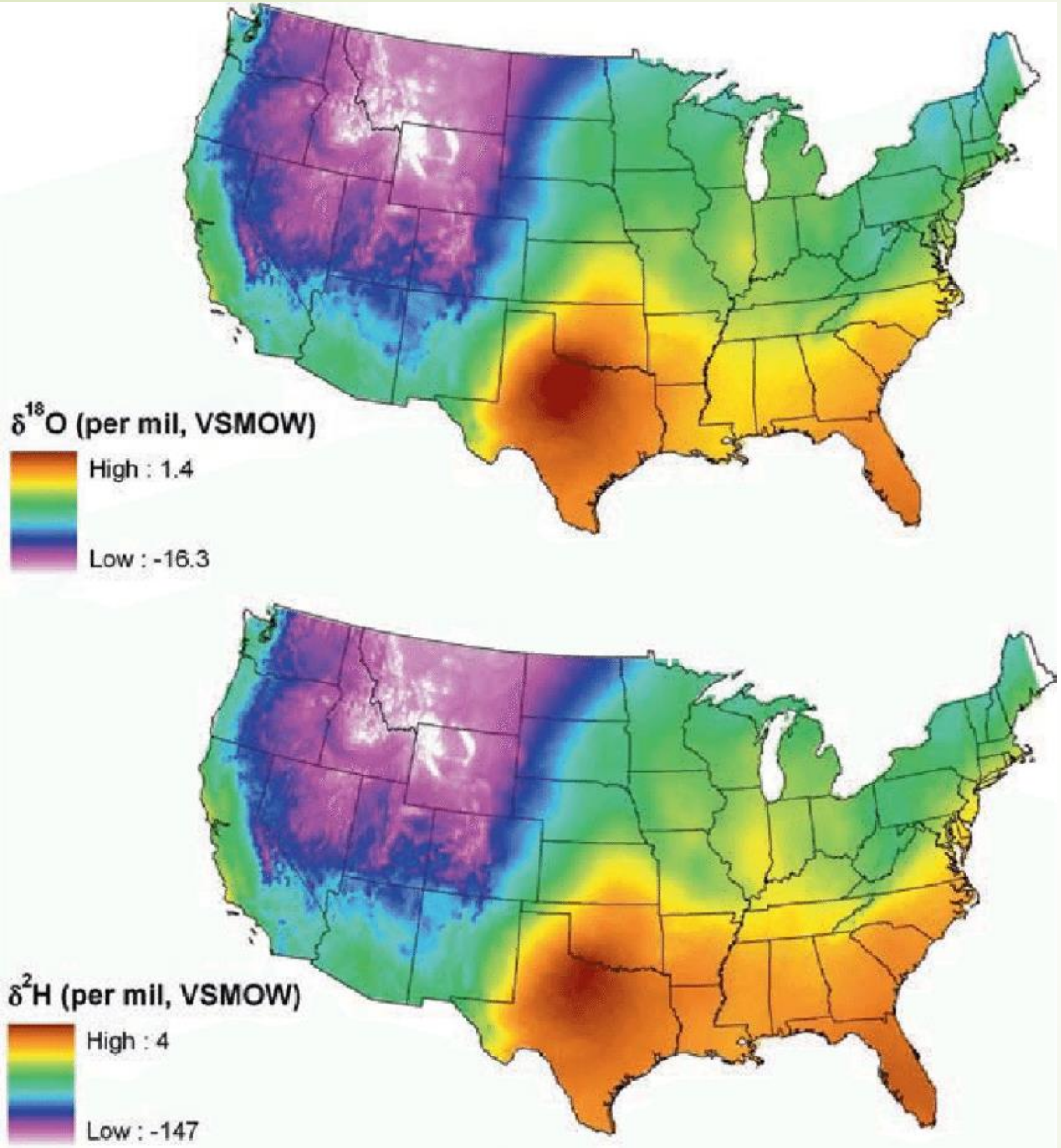

a) Pb ratios - SW Arkansas vs New Mexico
Legend
Mound C
Mound F
Skull Cluster
SW Arkansas Animals
New Mexico (P. Bonito)
Illinois
Hardman Humans
Mound C
Mound F
Skull Cluster
SW AR Animals
Hardman Humans
New Mexico
^{208}Pb/^{204}Pb
^{207}Pb/^{204}Pb
^{206}Pb/^{204}Pb
b) Pb ratios - SW Arkansas vs Western Illinois
Illinois
Mound C
Mound F
Skull Cluster
SW AR Animals
Hardman Humans
^{207}Pb/^{204}Pb
^{208}Pb/^{207}Pb
^{208}Pb/^{206}Pb
c) Pb ratios - Rayburn Cluster vs Western Illinois
SW AR Animals
Skull Cluster
Illinois
^{208}Pb/^{206}Pb
^{207}Pb/^{206}Pb
^{208}Pb/^{204}Pb
d) Pb ratios - Rayburn Cluster vs NW LA and NW MS
Louisiana
SW AR Animals
Skull Cluster
Mississippi
Legend
Skull Cluster
SW Arkansas Animals
Loisiana
Mississippi
^{208}Pb/^{206}Pb
^{207}Pb/^{206}Pb
^{208}Pb/^{204}Pb

Mobility Isotopes: Oxygen (O)

- Concept is similar to Sr isotopes
- O has three stable isotopes
  - O-16 99.755% natural abundance
  - O-17 0.039% natural abundance
  - O-18 0.206% natural abundance
- Measured as: $\delta^{18}O = \left[\frac{\frac{^{18}O_{sample}}{^{16}O_{sample}}}{\frac{^{18}O_{standard}}{^{16}O_{standard}}} - 1\right]$
- Skeletal tissue ratio determined by
  - Local fresh water ratio
  - Oxygen ratios in food

Oxygen-18 fractionations




δ18O (per mil, VSMOW)
High : 1.4
Low : -16.3
δ2H (per mil, VSMOW)
High : 4
Low : -147

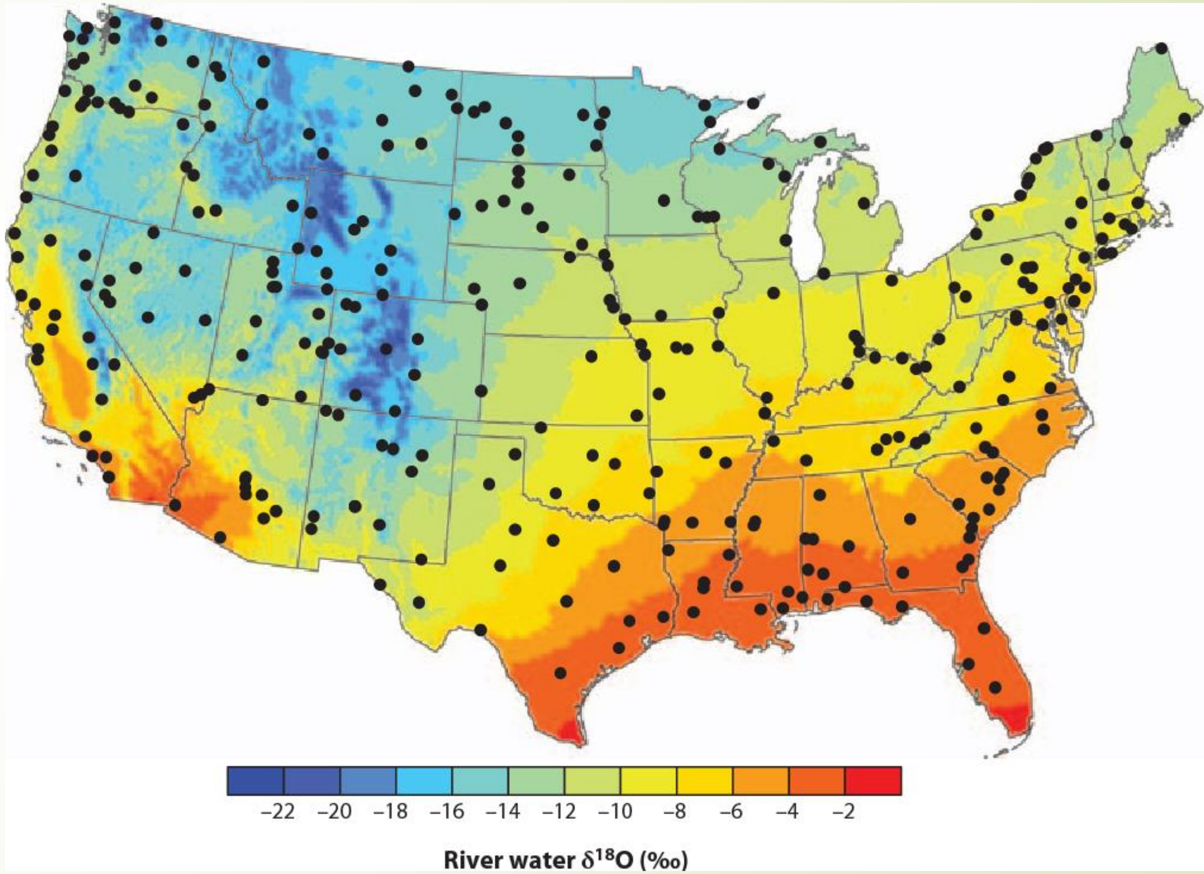

−22 −20 −18 −16 −14 −12 −10 −8 −6 −4 −2
River water δ18O (‰)

Image References

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2	https://www.pinterest.co.uk/pin/405886985142270151/	
3		
4	Investigation of the performances of an ECR charge breeder at ISOLDE: a study of the 1+ n+ scenario for the next generation ISOL facilities - Scientific Figure on ResearchGate. Available from: https://www.rese	
5	By Jeff Dahl - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=7870670	
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7	https://www.researchgate.net/figure/Spectrum-of-elements-measured-by-ICP-MS-axis-counts-per-second-against-mass_fig5_283816314	https://serc.carleton.edu/msu_nar
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9	https://isobarscience.com/tracing-diets-sr-isotopes/	
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29	https://serc.carleton.edu/microbelife/research_methods/environ_sampling/stableisotopes.html	
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