

Stable Isotopes as Natural Tracers

Using Established Technologies in Unconventional Ways

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Outline

- Background
 - Stable Carbon Isotopes 101
- Mud Gas Isotope Analysis
 - Sample collection (from the mud stream and cuttings) during drilling.
 - Examples
 - Compartment – Uinta Basin
 - Baxter Isotope Cross Sections – Vermillion Basin
 - Interpretive Plots
 - Isotope Reversals and Compartments – Haynesville Shale
 - Resolute Proprietary Example – Powder River Basin

There is no free lunch!

PERIODIC TABLE OF THE ELEMENTS

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H Hydrogen 1.0079	2 He Helium 4.0026	3 Li Lithium 6.941	4 Be Beryllium 9.0122	5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.179	11 Na Sodium 22.990	12 Mg Magnesium 24.305	13 Al Aluminium 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulphur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.91	56 Ba Barium 137.33	57-71 La Lanthanide	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89-103 Ac Actinide	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Uun Ununnilium (271)	111 Uuu Unununium (272)	112 Uub Ununbium (285)	113 Uut Ununtrium (284)	114 Uuq Ununquadium (289)	115 Uup Ununpentium (288)	116 Uuh Ununhexium (291)	117 Uus Ununseptium (286)	118 Uuo Ununoctium (294)

Electron Shells

	K	L	M	N	O	P	D	F
1	2	8	18	2	6	10		
2	2	8	18	2	6	10	14	
3	2	8	18	2	6	10	14	18
4	2	8	18	2	6	10	14	18
5	2	8	18	2	6	10	14	18
6	2	8	18	2	6	10	14	18
7	2	8	18	2	6	10	14	18
8	2	8	18	2	6	10	14	18

Lanthanide

57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
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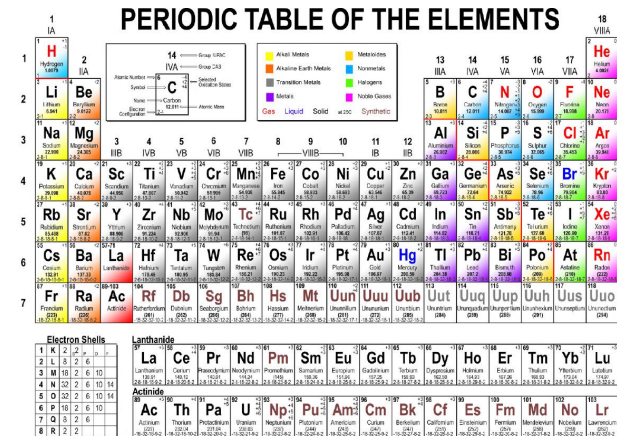
Actinide

89 Ac Actinium (227)	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)
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What is an Isotope?

- Many basic chemistry texts do not challenge the assumption that atoms of a given element are alike. **THEY ARE NOT.**
- About a century ago, chemists were shocked to learn that all elements are very nearly the same but exhibit slight differences.

PERIODIC TABLE OF THE ELEMENTS



The periodic table shows elements organized by atomic number (1 to 118). It includes a legend for physical states (Gas, Liquid, Solid) and categories (Alkali Metals, Alkaline Earth Metals, Transition Metals, Main Group, Noble Gases, Lanthanides, Actinides). Below the main table are separate sections for Electron Shells (1 to 8) and Lanthanide/Actinide series.

Isotopes of a Given Element

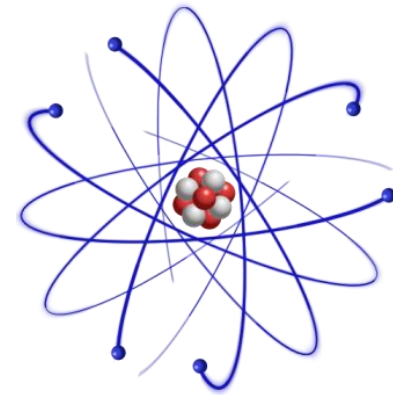
1. The atoms of any given element have the same number of electrons.
2. The atoms of any given element have the same number of protons (atomic number).
3. But the nuclei of a given atom may contain **different numbers of neutrons**.

Number of protons + Number of neutrons = atomic mass (or weight)

Let's just talk about Carbon!

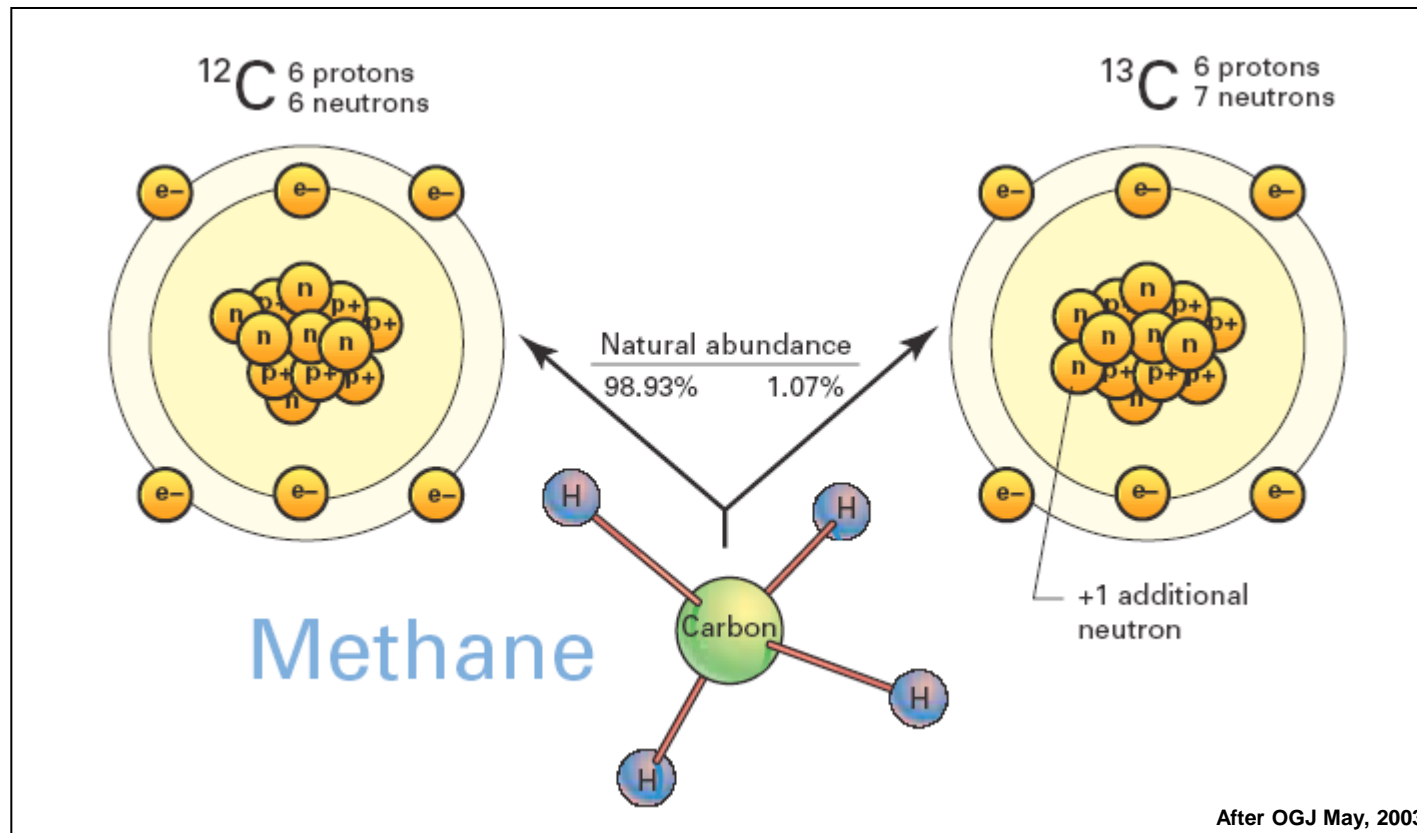
Stable vs. Radiogenic Carbon Isotopes

- ^{11}C Radiogenic Isotope of Carbon - Unstable
 - Half-Life = 20.33 minutes decays to Boron-11
- ^{12}C **Stable Carbon Isotope**
 - **Natural Abundance = 98.93%**
 - **Lighter than ^{13}C**
 - **^{12}C bonds slightly weaker than ^{13}C**
- ^{13}C **Stable Carbon Isotope**
 - **Natural Abundance = 1.07%**
 - **8.3% heavier than ^{12}C**
 - **^{13}C bonds slightly stronger than ^{12}C**
- ^{14}C Radiogenic Isotope of Carbon – Unstable
 - Half-Life = 5730 ± 40 years
 - Carbon – dating technique.



Carbon Atom

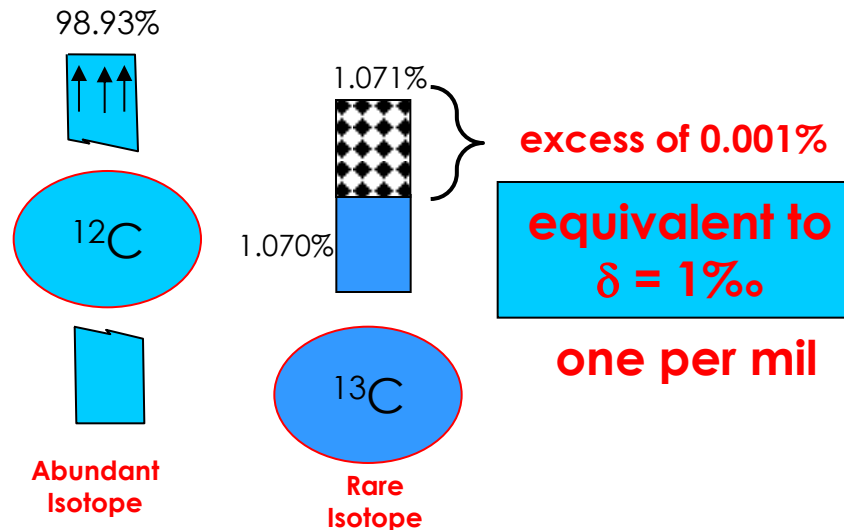
Stable Carbon Isotopes



δ (del) Notation

Natural Abundance (%)

These are
defining
nucleus-level
variations in
Carbon

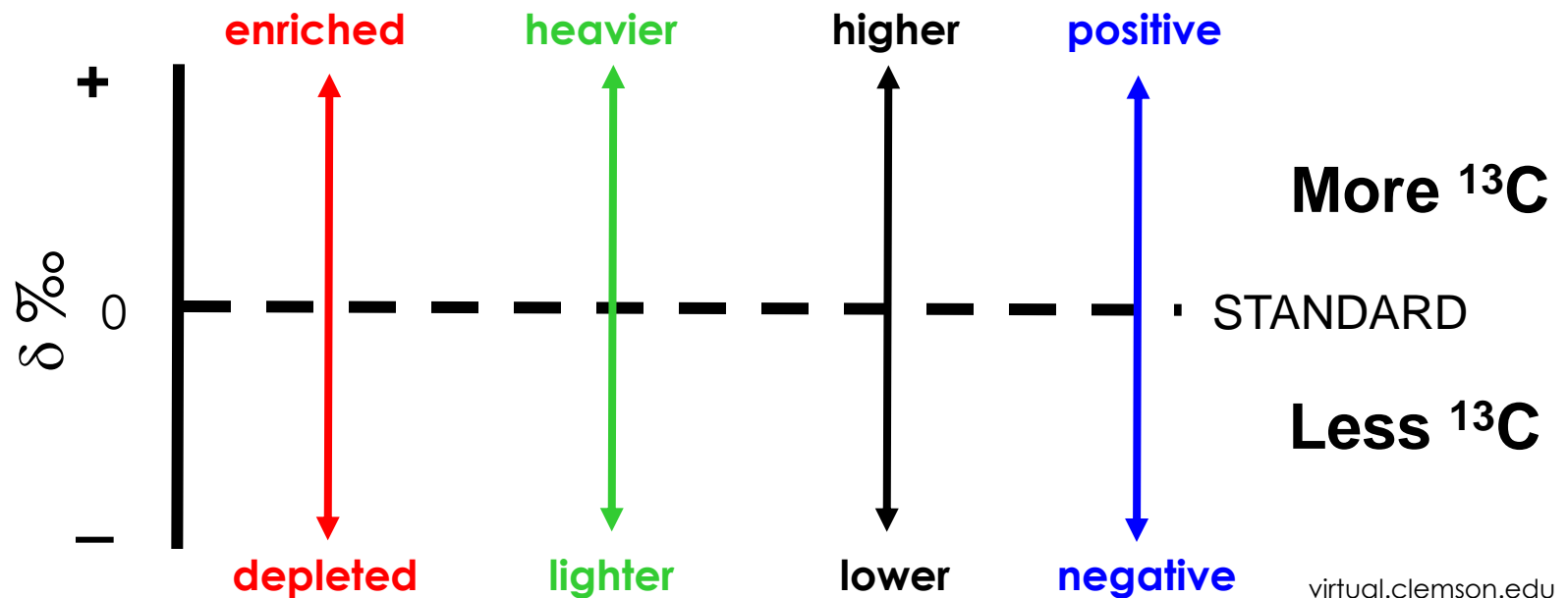


$$\delta = \delta(\text{‰}) = (R_{\text{sample}}/R_{\text{standard}} - 1) * 1000$$

R = rare isotope/abundant isotope

δ (del) Notation

Here's some often-used nomenclature – they are descriptions against the PDB standard



virtual.clemson.edu

Cretaceous Peedee Belemnite (PDB)

- Belemnite is a cephalopod.
- A limestone found in South Carolina.
- The measurement standard (depleted).



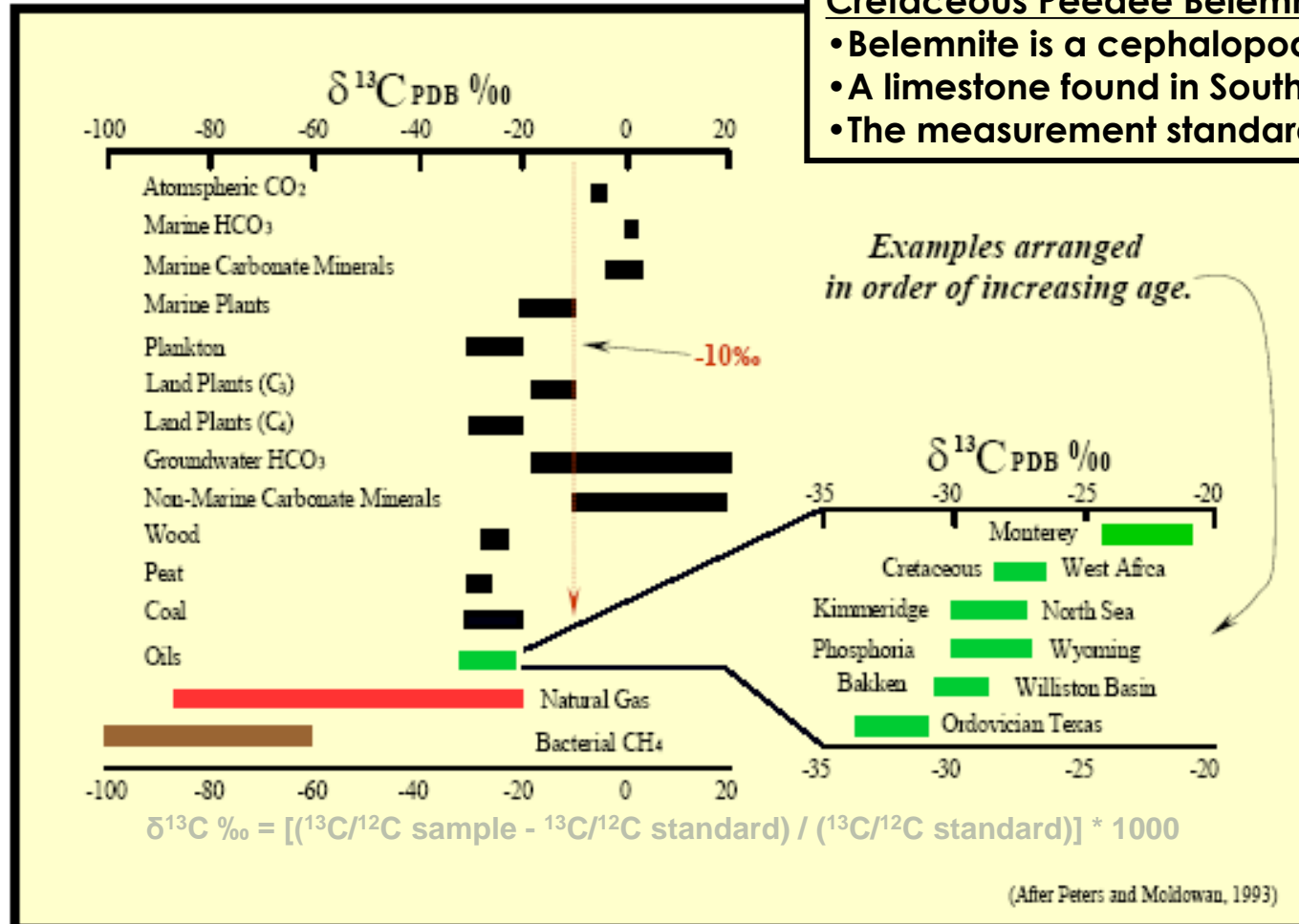
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Stable Carbon Isotope Ratios

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Cretaceous Peedee Belemnite (PDB)

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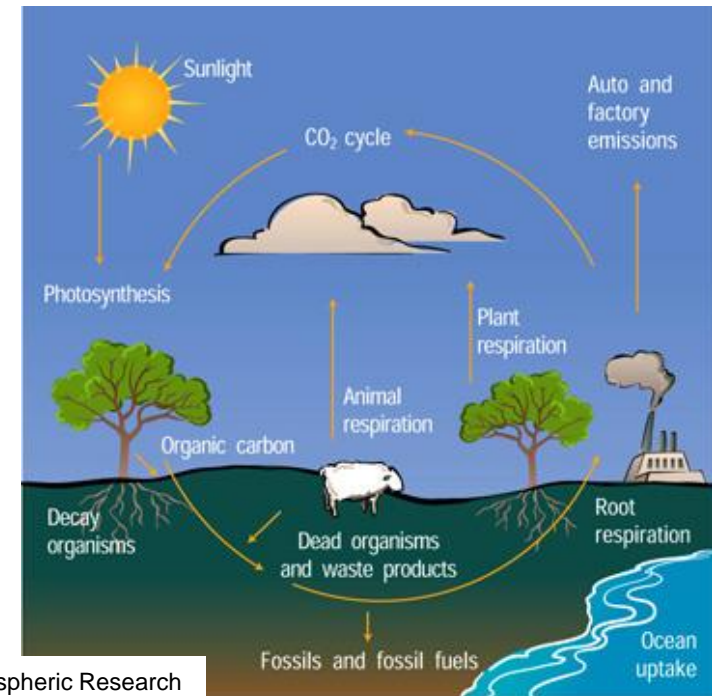


Isotopes can record carbon fixing in the carbon cycle through fractionation.

- In petroleum systems – How do ^{12}C & ^{13}C signatures develop?
 - **Kinetic Isotope Effect**
 - Bond-Making and Bond-Breaking Chemical Reactions.
 - **Equilibrium Isotope Effect**
 - Heavier Isotope is concentrated in compounds bound most strongly.
 - **Biological Isotope Fractionation**
 - Carbon fixes during photosynthesis.
 - Methanogenesis favors lighter products.

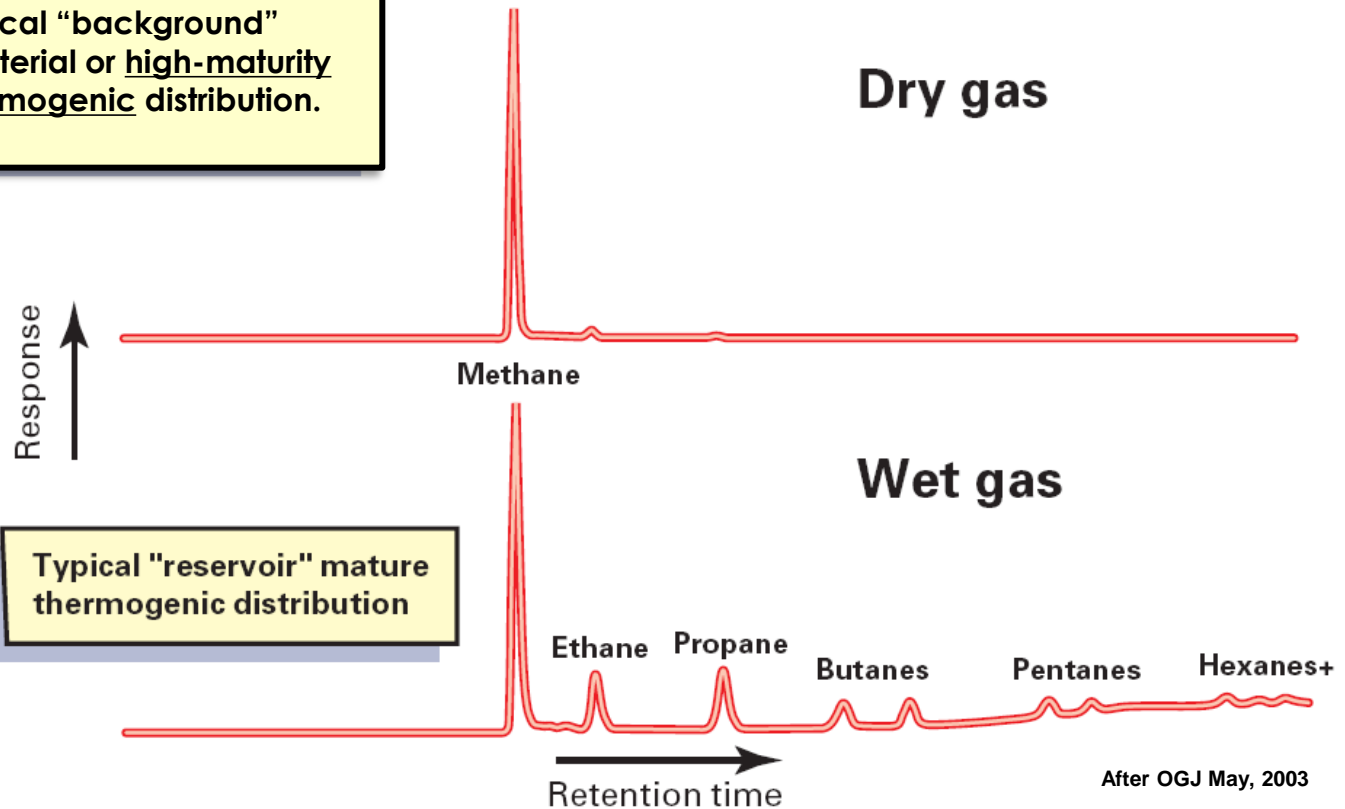
Under increasing thermal stress (burial) hydrocarbon gas generally gets heavier isotopically. Reversals can occur. We are interested in these reversals.

The Carbon Cycle



Hydrocarbon Dry and Wet Gas Compositions

Typical “background”
bacterial or high-maturity
thermogenic distribution.



We can measure the carbon isotopic concentration of any of these molecular components against our PDB standard.

Enough Chemistry!

What About the Applications?

- Isotopic analyses of mud stream and production gases to evaluate the character of reservoir hydrocarbons.

There are many potential uses for these data.

- **Thermal Maturity at which the gas was generated.**
 - **Shale Gas with no migration can be proxy for source rock maturity.**
 - **Mis-matched maturity between rock and gas indicates migration.**
- Reservoir Continuity
 - Allocation of produced fluids
 - Compartmentalization of reservoir HCs
- Determination of seal competency.
- Migration and Charge Analysis



Mud Gas
Sampling
Manifold

Mud Gas Isotope Analysis - Methane Isotopes

Uinta Basin
Utah, USA

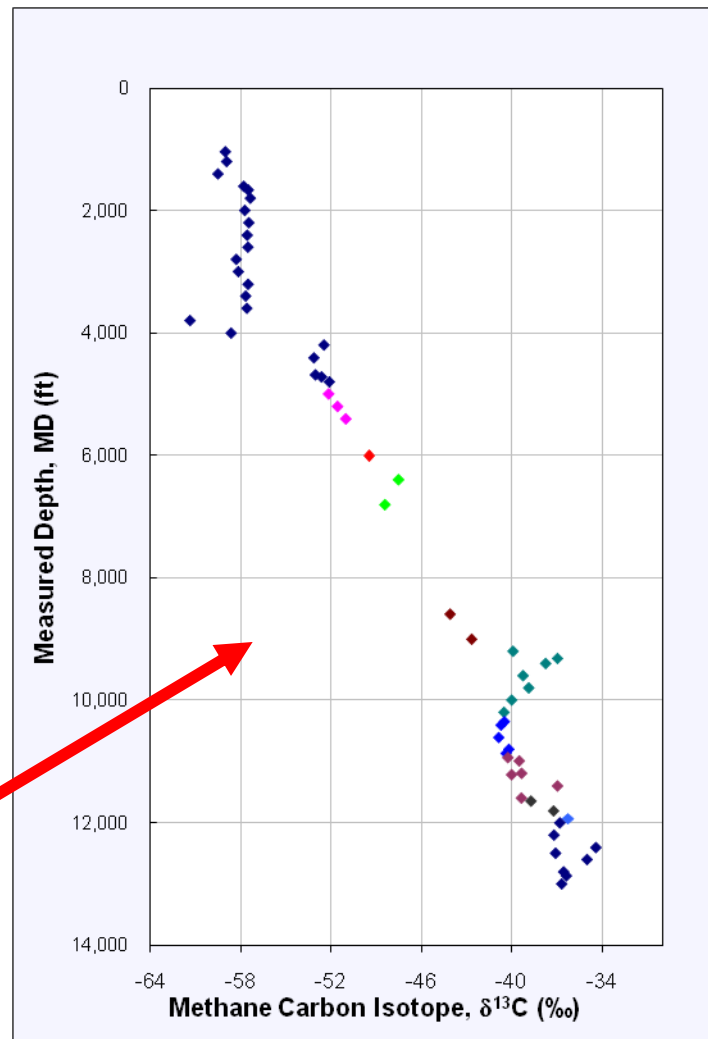
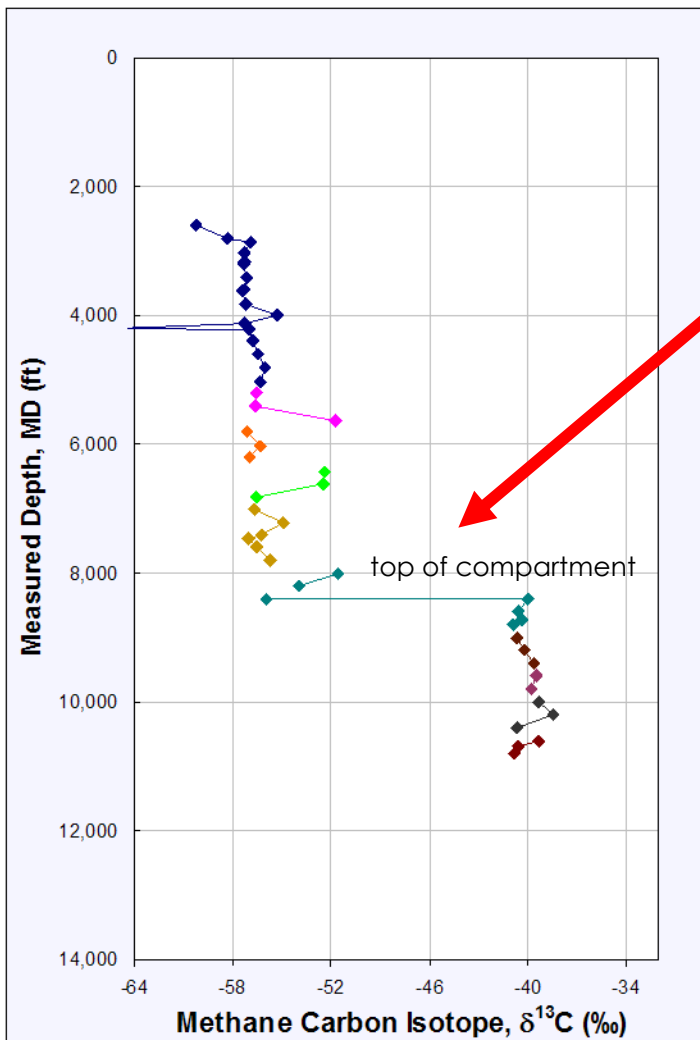


Dolan et.al., AAPG Poster 2007

Competency of Seal/Compartments

Discrete seal is indicated in this Uinta Basin example. Separate and distinct isotopic methane values indicates completion strategy.

If a competent seal is not present the fluids will exhibit a more gradual isotope (maturity) profile. Conduction may be heat transfer mechanism.

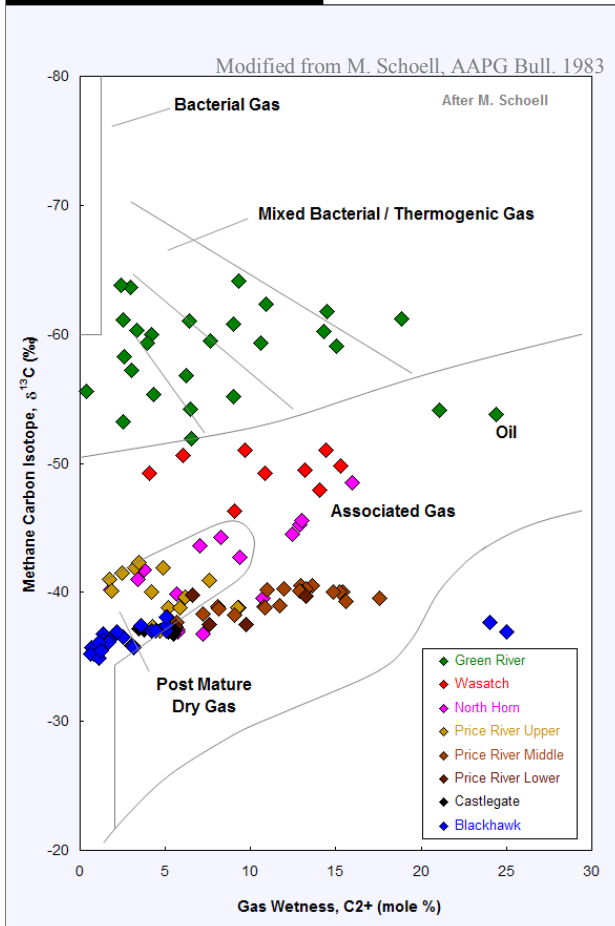


Mud Gas Interpretive Plots

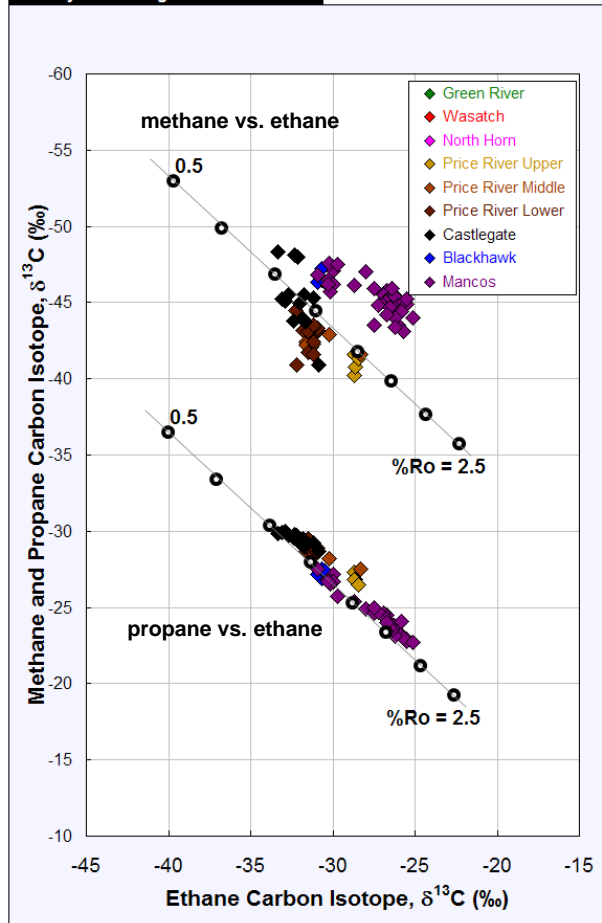
Gas Classification & Maturity

Dolan et.al., AAPG Poster 2007

Genetic Gas Classifications



Maturity and Mixing Plot



Classification

- Bacterial versus Post Mature Dry Gas
- Wetness plot allows oil associated gases to be classified.
- Methane isotope signature very distinguishable

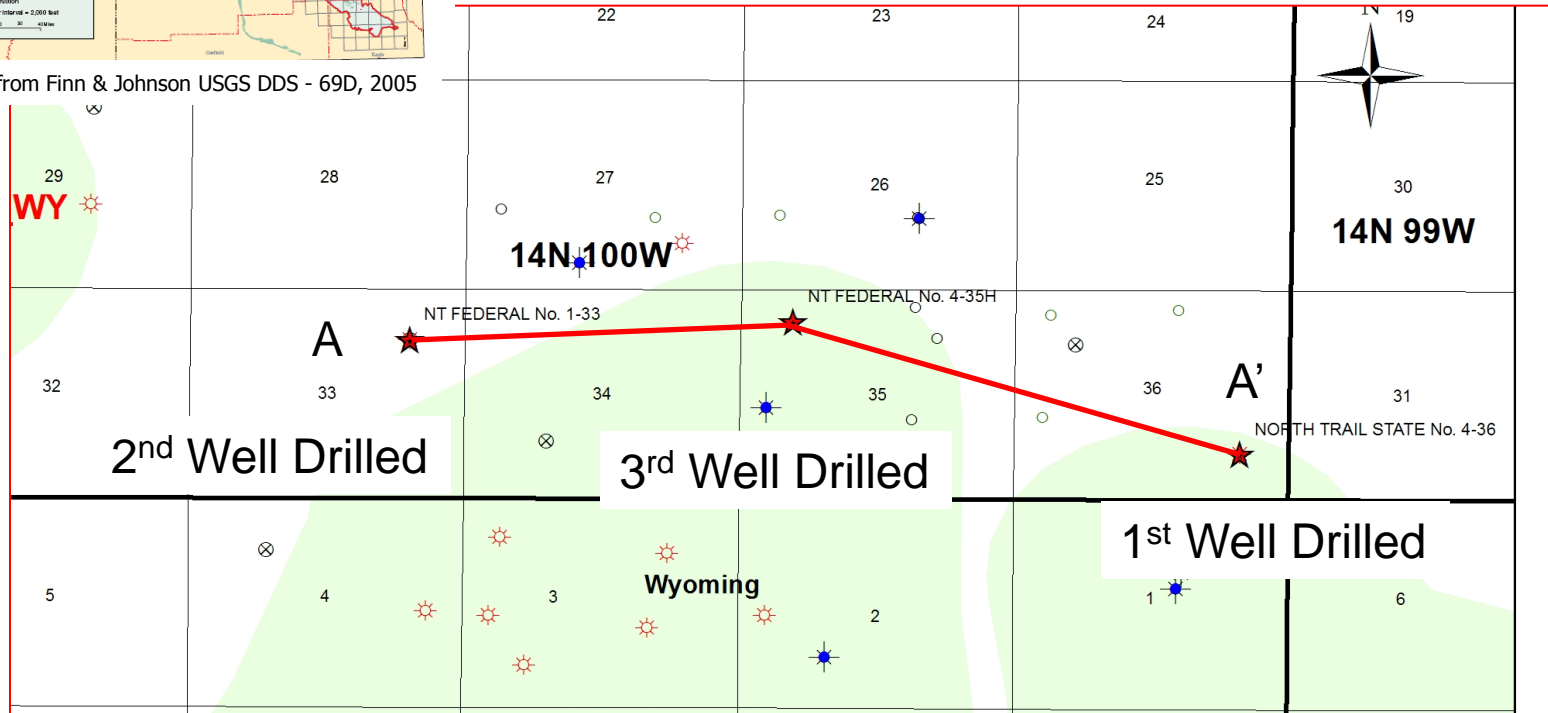
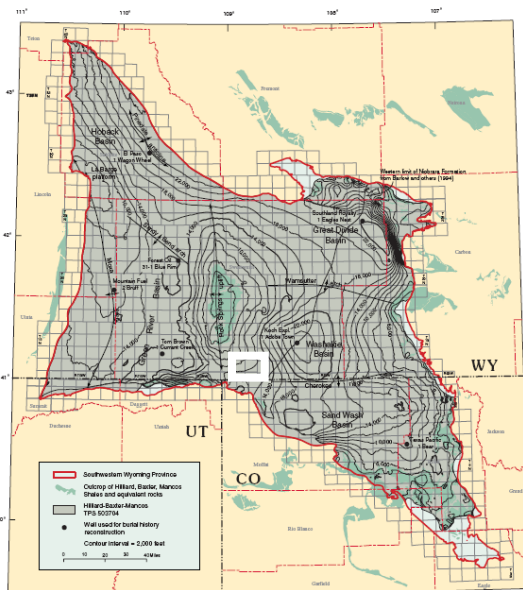
Maturity

- Maturity indicates the maximum temperature/time to allow generation of HCs
- Calibrated to Basin specific gases

Applications

- Migration of gas into fractured shales may exhibit different maturity signature (higher) than reservoir rock.
- Extremely cost-efficient way to quickly ascertain maturity in the system.
- Hydrocarbon charge timing interpretations can be made in other reservoir intervals.

Location of three well program in the Vermillion Basin, Wyoming USA



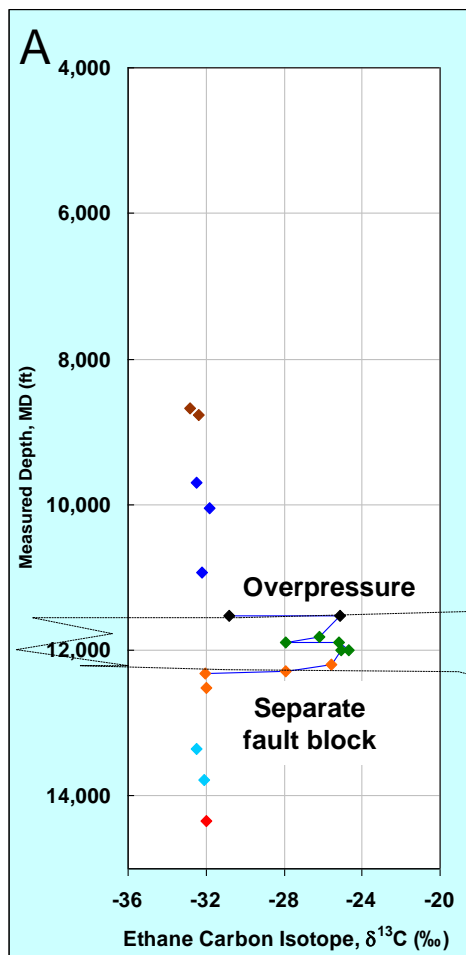
Vermillion Basin, Wyoming, USA

Baxter Shale Charge System is Isotopically Distinct



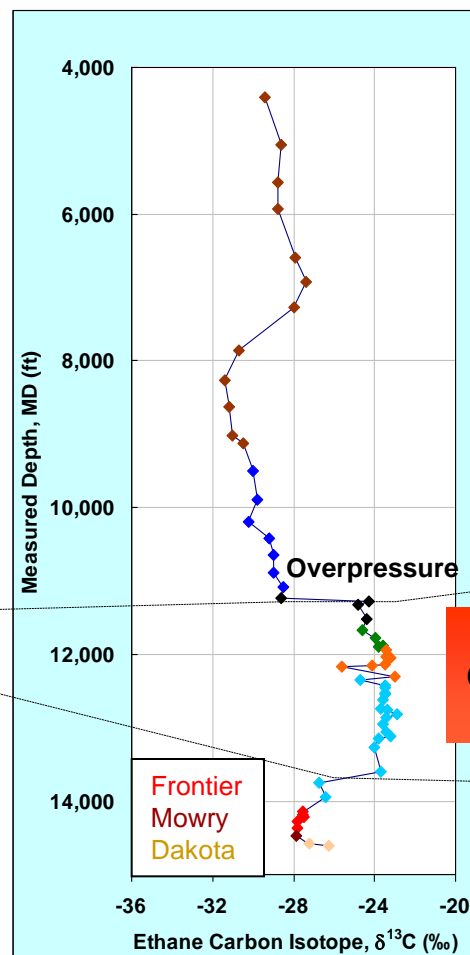
Dolan et al., AAPG Poster 2007

2nd Well Drilled



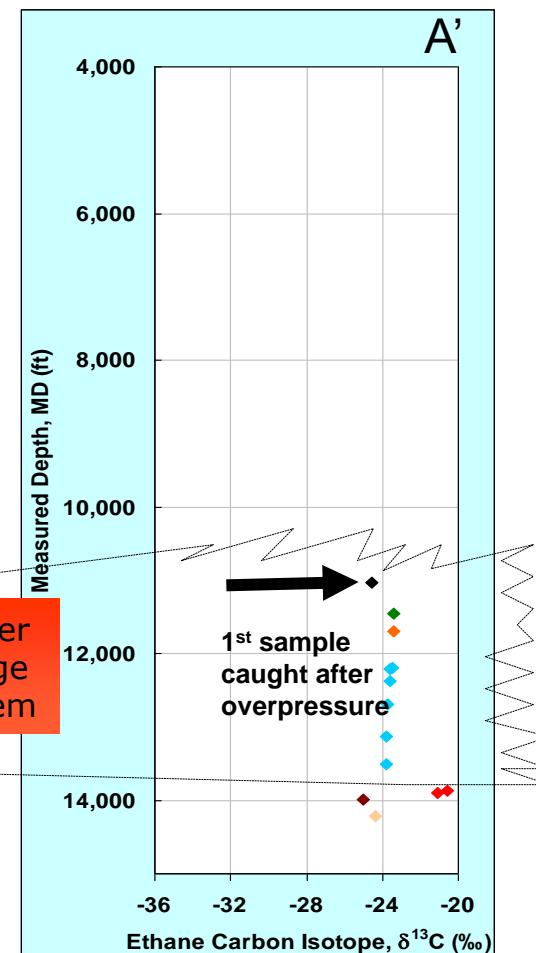
North Trail 1-33

3rd Well Drilled



North Trail 4-35

1st Well Drilled

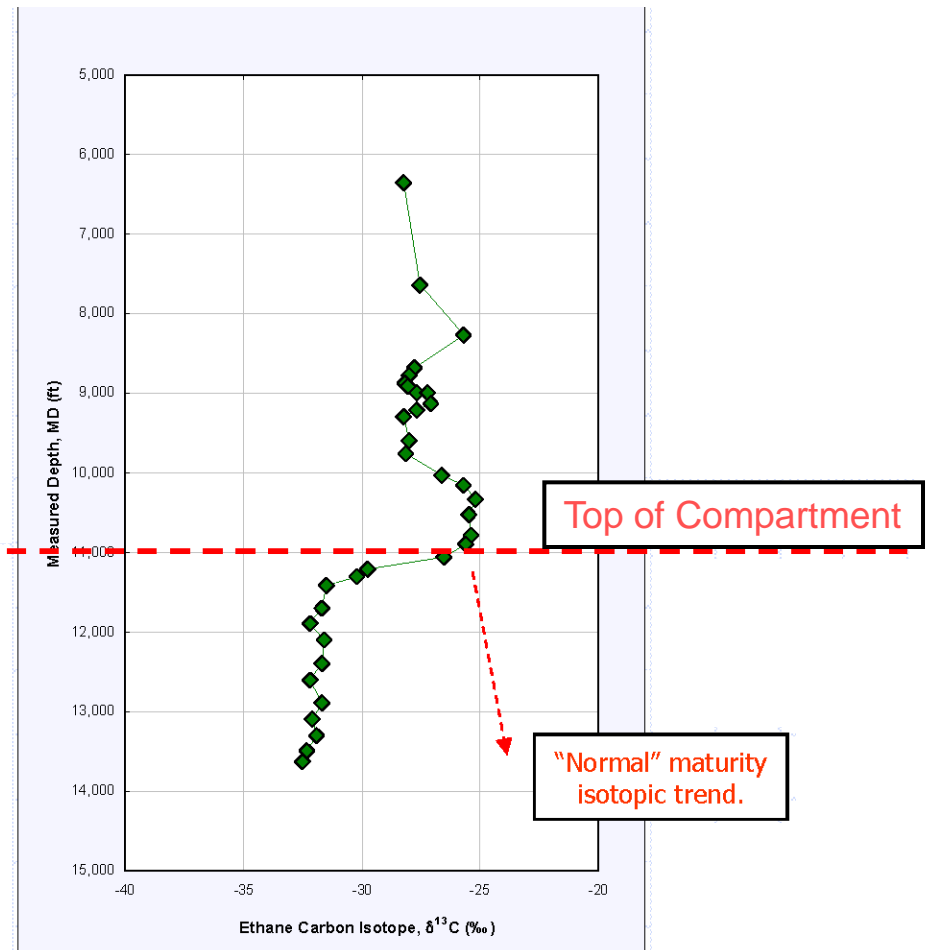
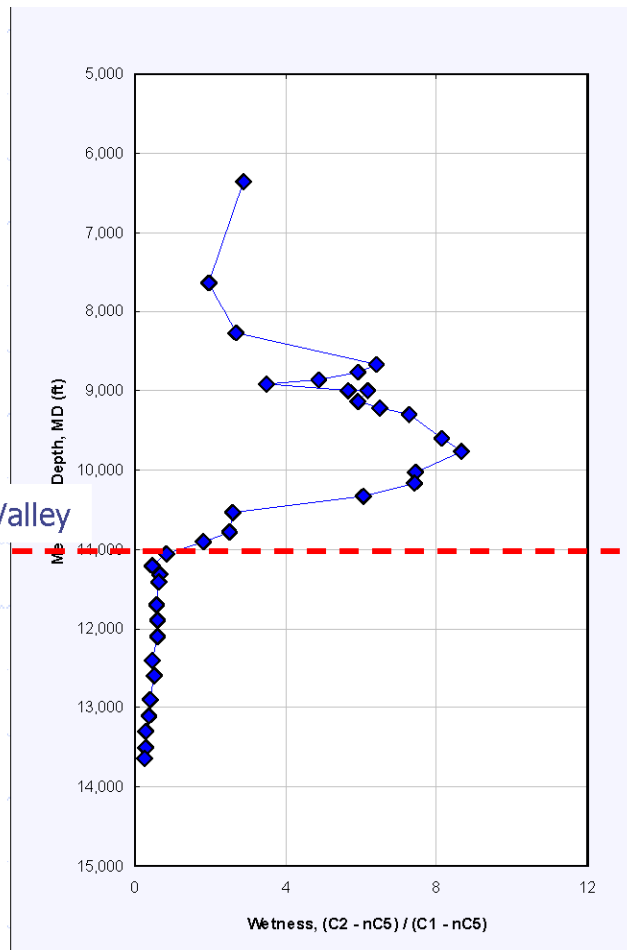


North Trail 4-36

Baxter Charge System

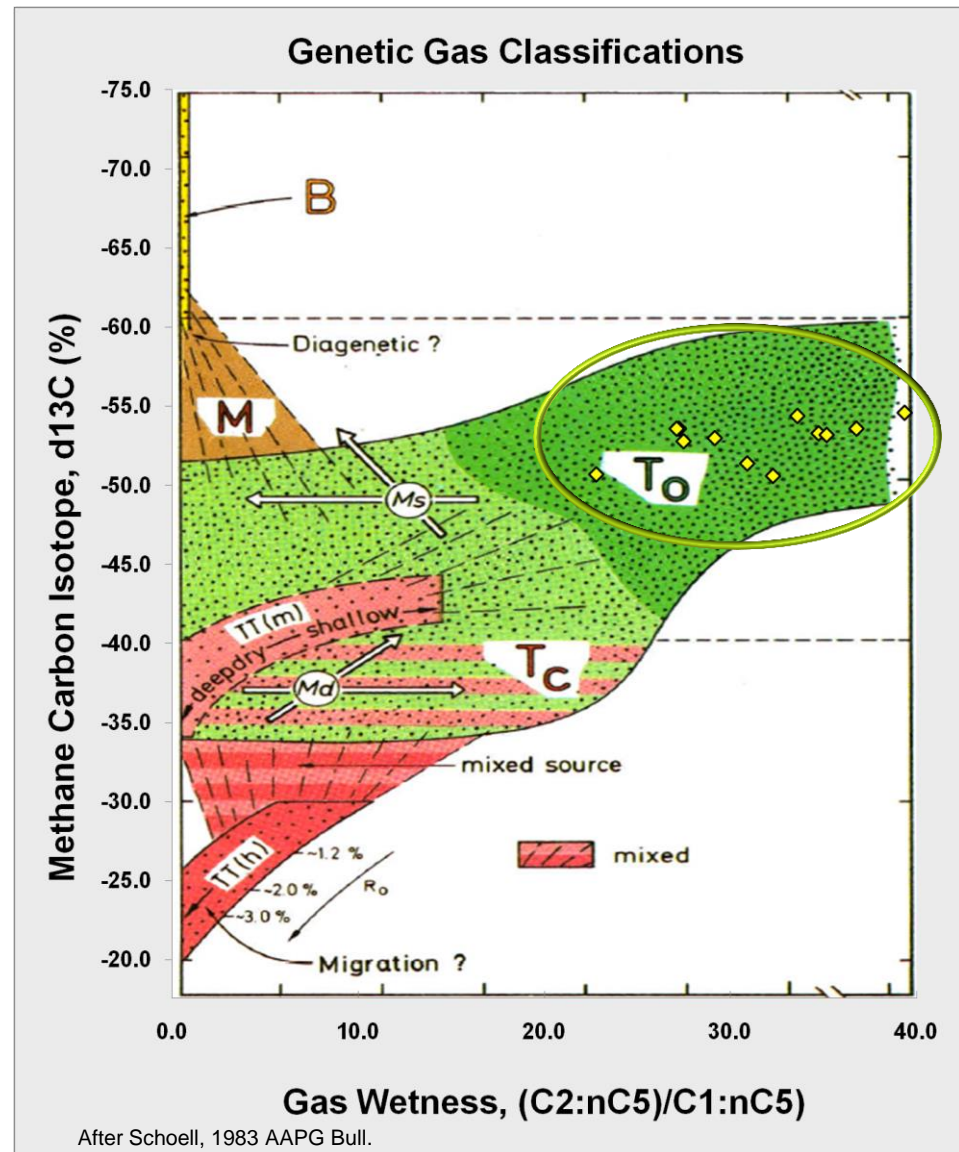
Mud Gas Ethane Isotope “Reversals” (Haynesville Example)

Bossier / Cotton Valley
Haynesville



Resolute Example – Powder River Basin

- This is a plot that helps to classify the Genetic Gas Classification.
- The gases are plotted wetness vs. Methane Carbon Isotope
- This plot was developed (and redeveloped) by Martin Schoell and published in 1983.
- The REN are clearly classified as Oil Associated Gases.
- This plot can also distinguish biogenic methane, post-mature dry gases and the mixed signatures among them.
- All samples are gases generated in liquid phase (oil) maturity. Should characterize as oil associated gas.

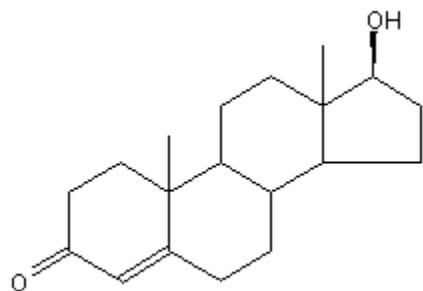
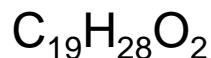


Presentation Summary

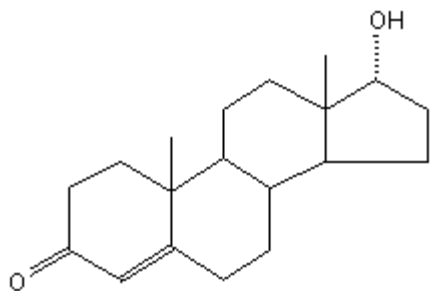
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Isotopes in the News

Floyd Landis and the Tour de France

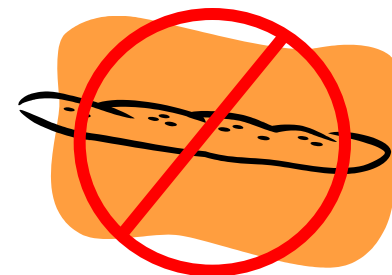


Testosterone



Epitestosterone

17Alpha-hydroxyandrost-4-en-3-one



Carbon and Diet

- **Testosterone/Epitestosterone imbalance – not good, Floyd**
 - Both naturally occurring steroids.
 - Stereo-isomers
 - The molecular concentration imbalance that was measured is bad news for Floyd.
 - Balance those isomers!
- **Stable Carbon Isotopes**
 - Biotic reactions will thermodynamically favor the lighter isotope (^{12}C) in the products.
 - When Floyd (or anybody) produces testosterone a distinct isotopic signature is seen (you are what you eat!).
 - Synthetic testosterone is produced from phytosterol precursors in yams and soy from particular climatic regions. Primarily C3 plants. The subtle variations in isotopic signature are easily distinguishable in the western industrial diet (C4 plants).
- **Did Floyd eat a loaded baguette?**