Stable Isotopes as Natural Tracers

Using Established Technologies in Unconventional Ways

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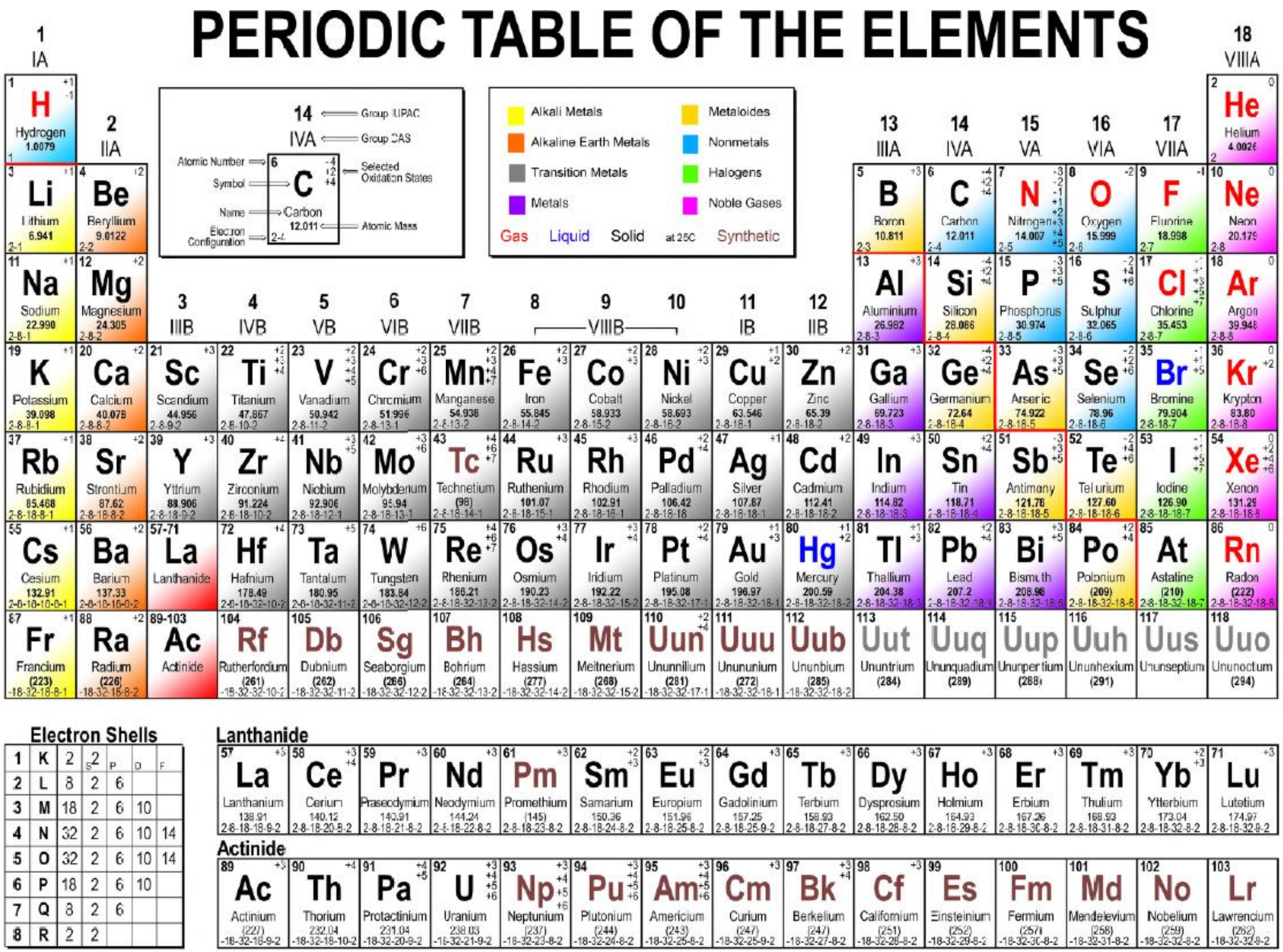
Outline

- 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!

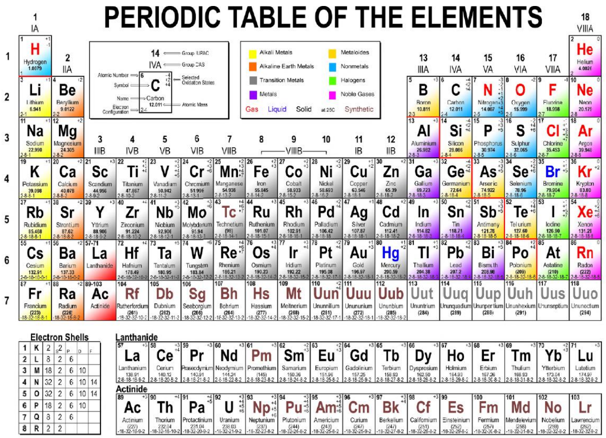


http://www.sciencegeek.net/tables/tables.shtml

What is an Isotope?

•Many basic chemistry texts do not challenge the assumption that atoms of a given element are alike. **<u>THEY ARE NOT.</u>**

•About a century ago, chemists were shocked to learn that all elements are very nearly the same but exhibit slight differences.



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**.

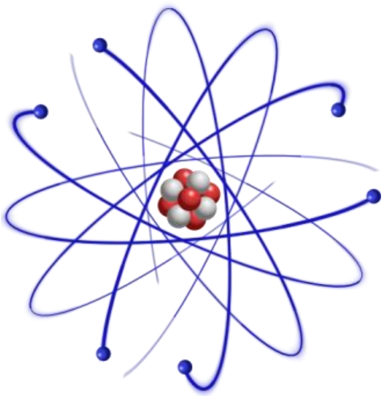
Number of protons + Number of neutrons = atomic mass (or weight)

Let's just talk about Carbon!

Modified from Krauskopf & Bird, 1995 Intro. to Geochem. pp 241

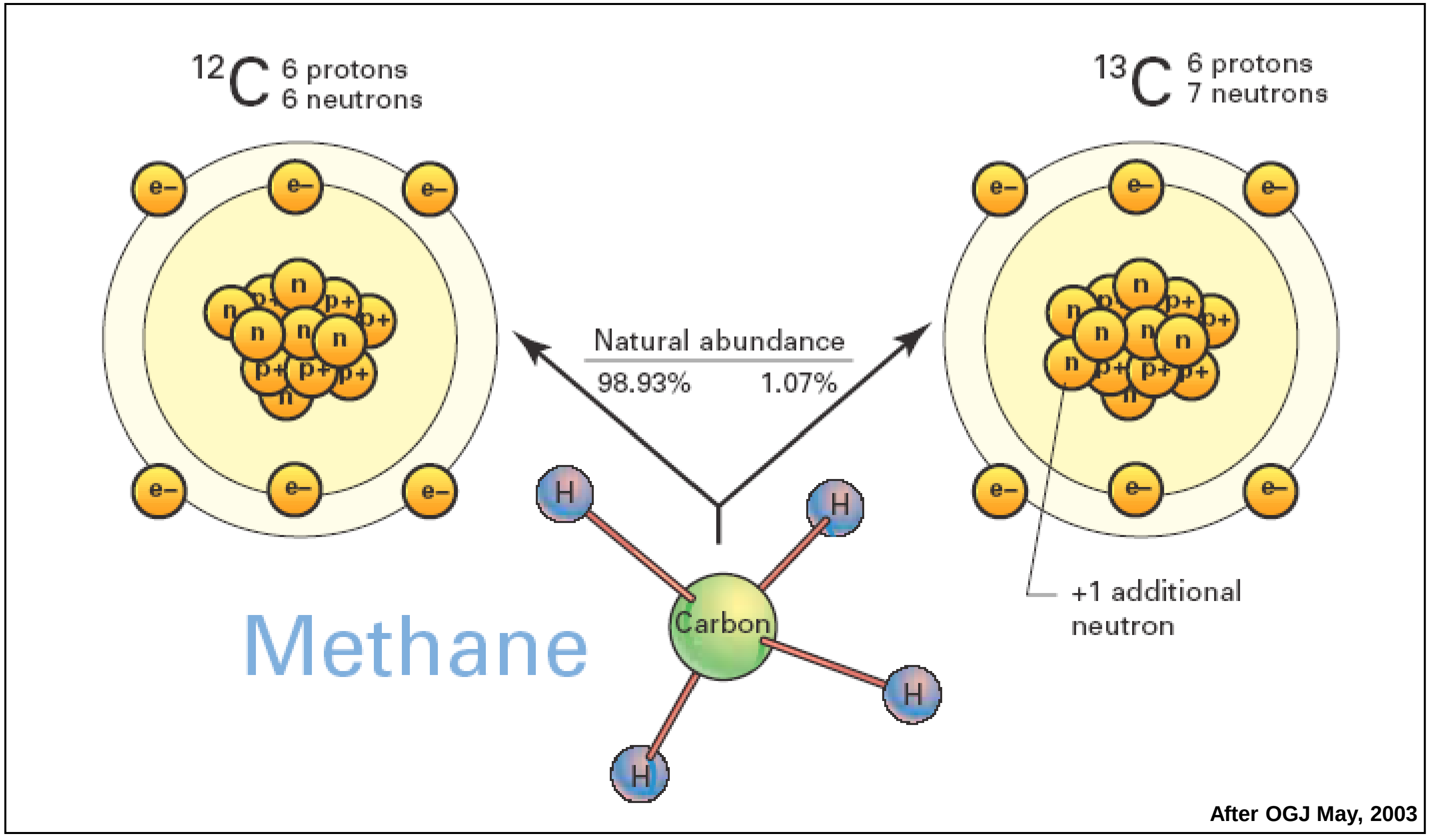
Stable vs. Radiogenic Carbon Isotopes

- ^{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

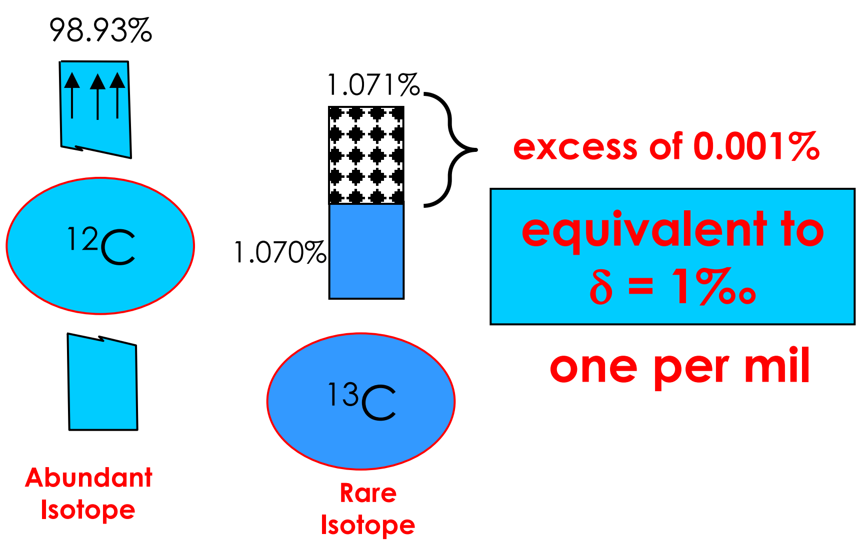
Stable Carbon Isotopes



δ (del) Notation

Natural Abundance (%)

These are defining nucleus-level variations in Carbon



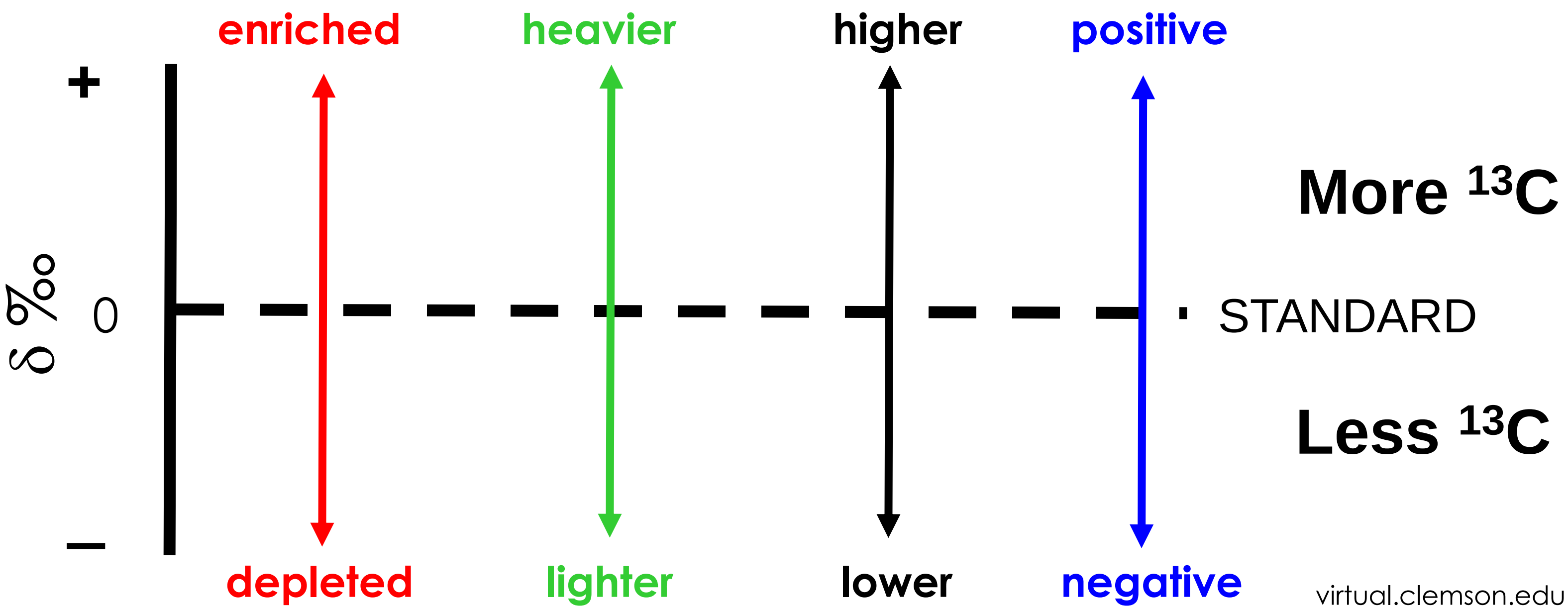
$$\text{del} = \delta(‰) = (R_{sample}/R_{standard} - 1) * 1000$$

R= rare isotope/abundant isotope

Modified from: http://www.whoi.edu/

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).**

Modified from: http://www.whoi.edu/

Stable Carbon Isotope Ratios

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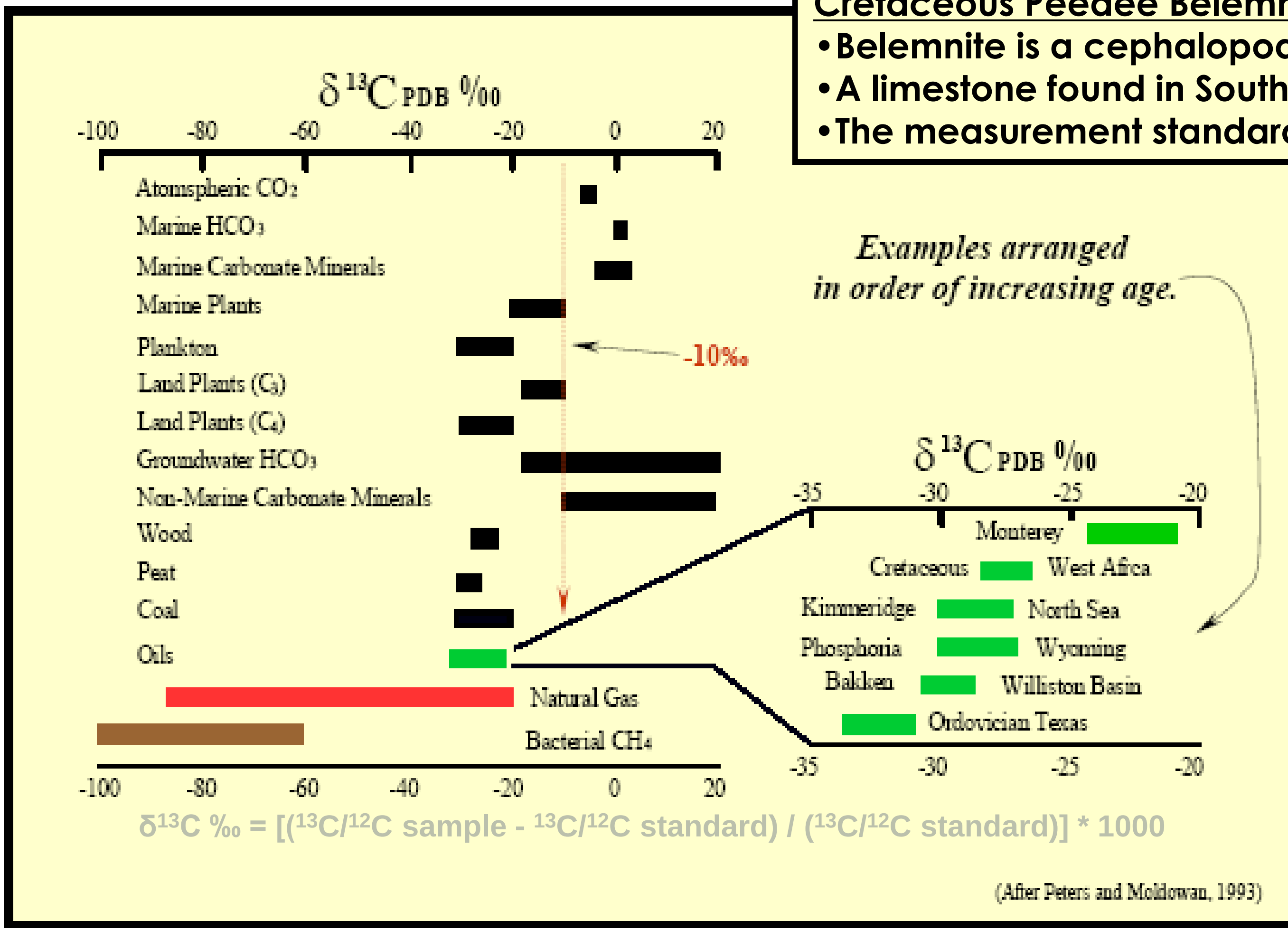
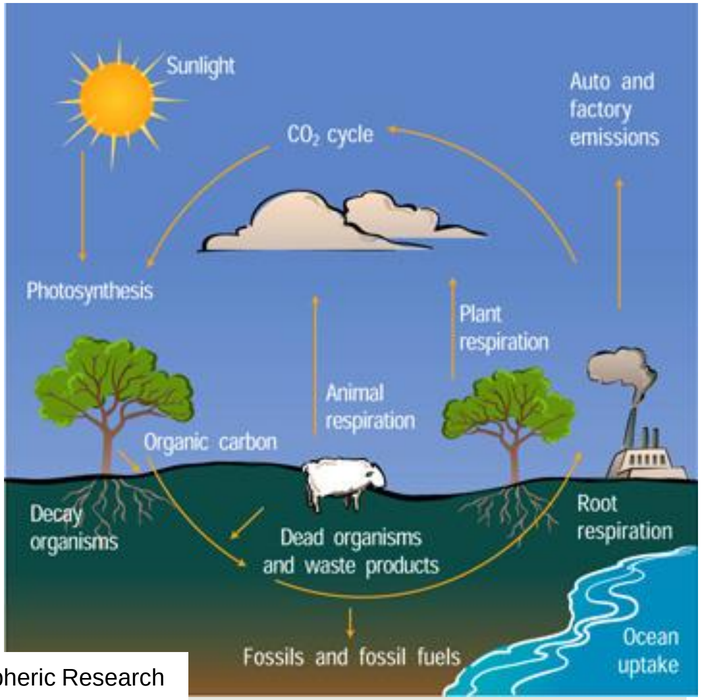


Isotopes can record carbon fixing in the carbon cycle through fractionation.

- 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.

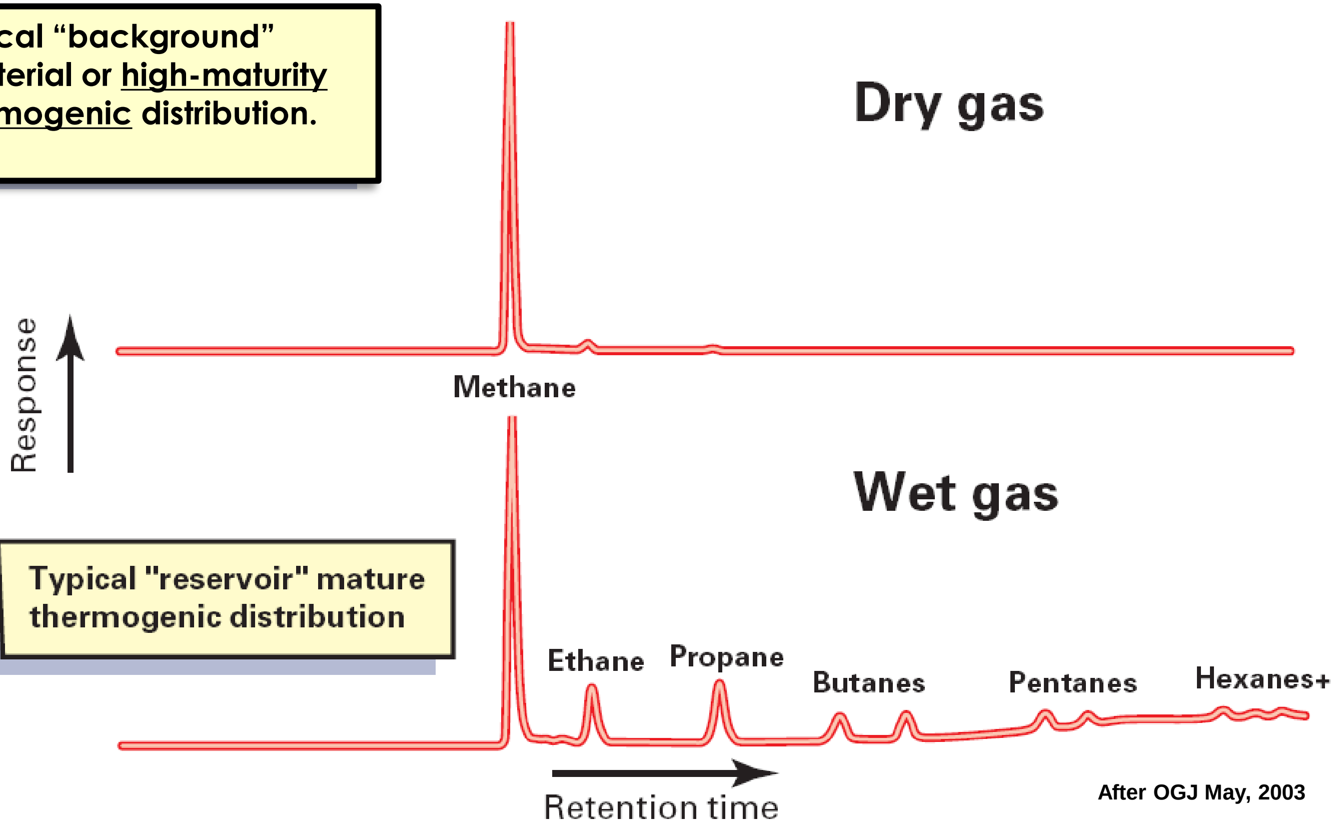
The Carbon Cycle



National Center for Atmospheric Research

Hydrocarbon Dry and Wet Gas Compositions

Typical "background" bacterial or high-maturity thermogenic distribution.



Typical "reservoir" mature 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.

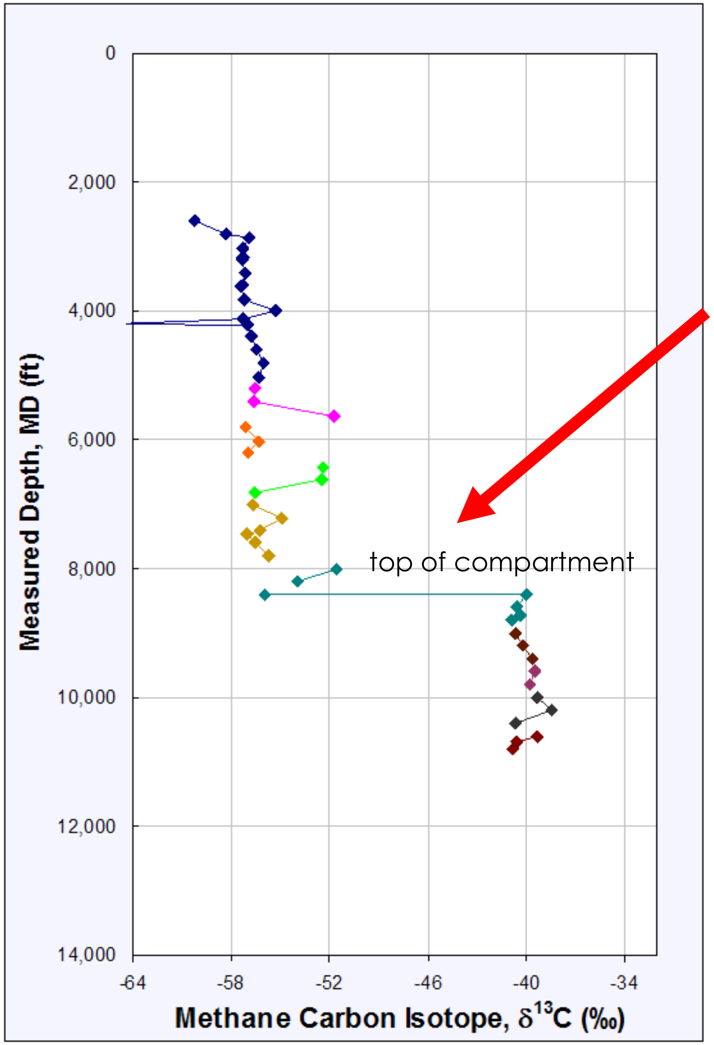
- **Thermal Maturity at which the gas was generated.**
  - **Shale Gas with no migration can be proxy for source rock maturity.**
  - **Mis-matched maturity between rock and gas indicates migration.**
- Reservoir Continuity
  - Allocation of produced fluids
  - Compartmentalization of reservoir HCs
-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

Mud Gas Sampling Manifold

Mud Gas Isotope Analysis - Methane Isotopes

**Uinta Basin
Utah, USA**

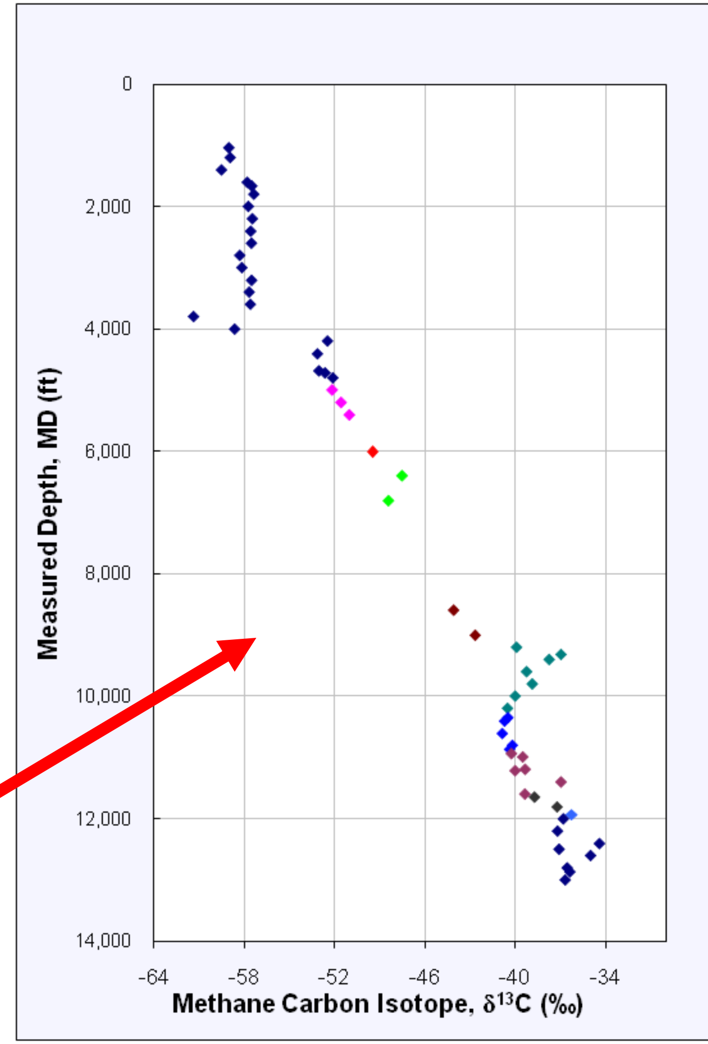
Dolan et.al., AAPG Poster 2007



Competency of Seal/Compartments

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

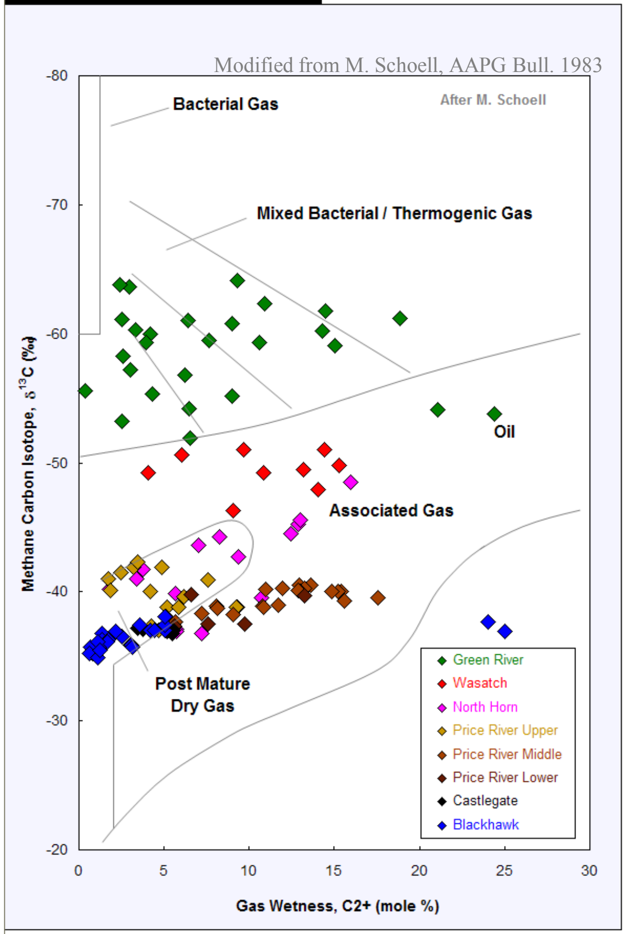
If a competent seal is not present the fluids will exhibit a more gradual isotope (maturity) profile. Conduction may be heat transfer mechanism.



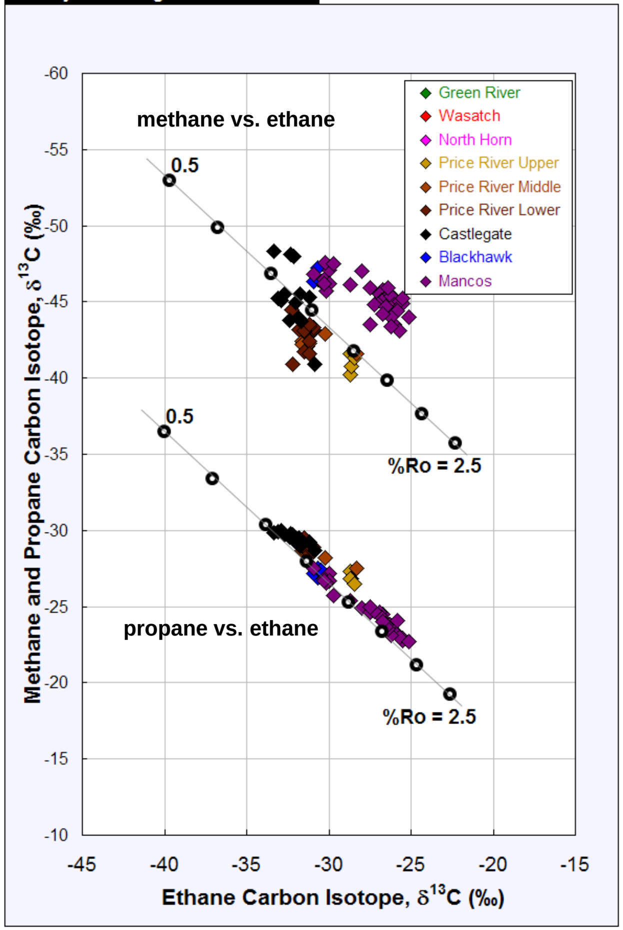
Mud Gas Interpretive Plots
Gas Classification & Maturity

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

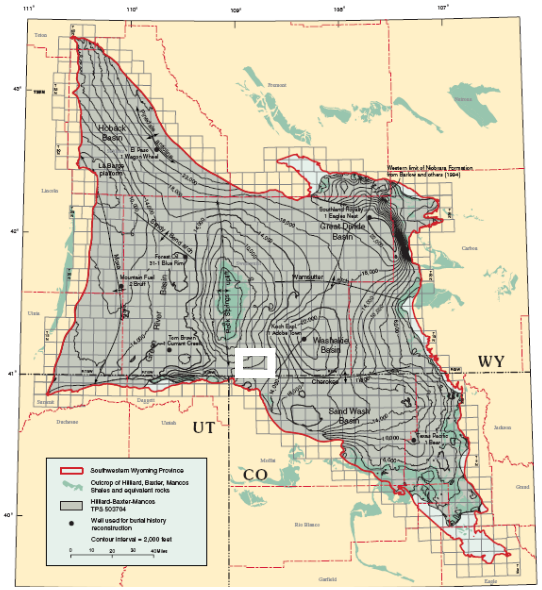
--Calibrated to Basin specific gases

Applications

•Migration of gas into fractured shales may exhibit different maturity signature (higher) than reservoir rock.

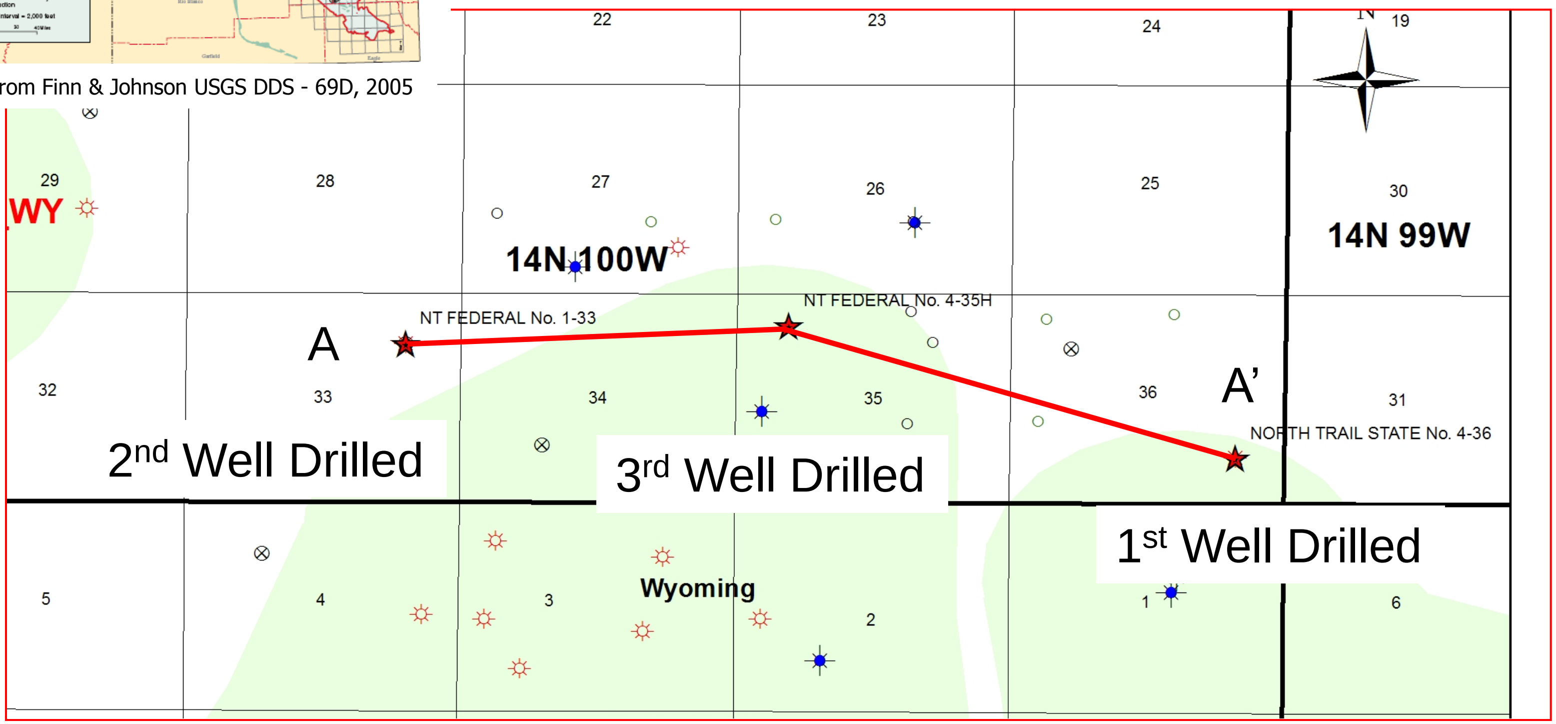
•Extremely cost-efficient way to quickly ascertain maturity in the system.

•Hydrocarbon charge timing interpretations can be made in other reservoir intervals.



Modified from Finn & Johnson USGS DDS - 69D, 2005

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



Vermillion Basin, Wyoming, USA
Baxter Shale Charge System is Isotopically Distinct

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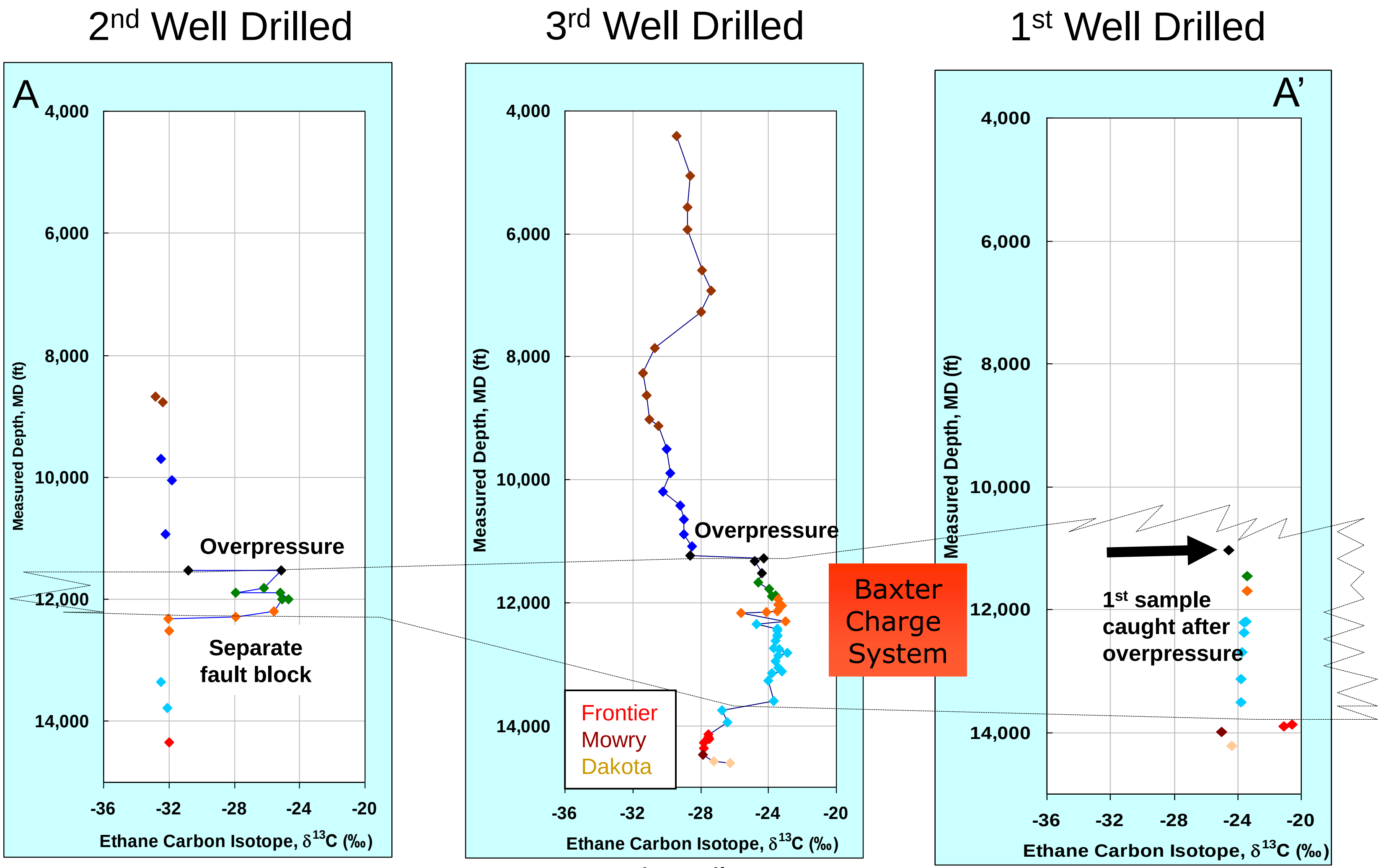
Dolan et.al., AAPG Poster 2007

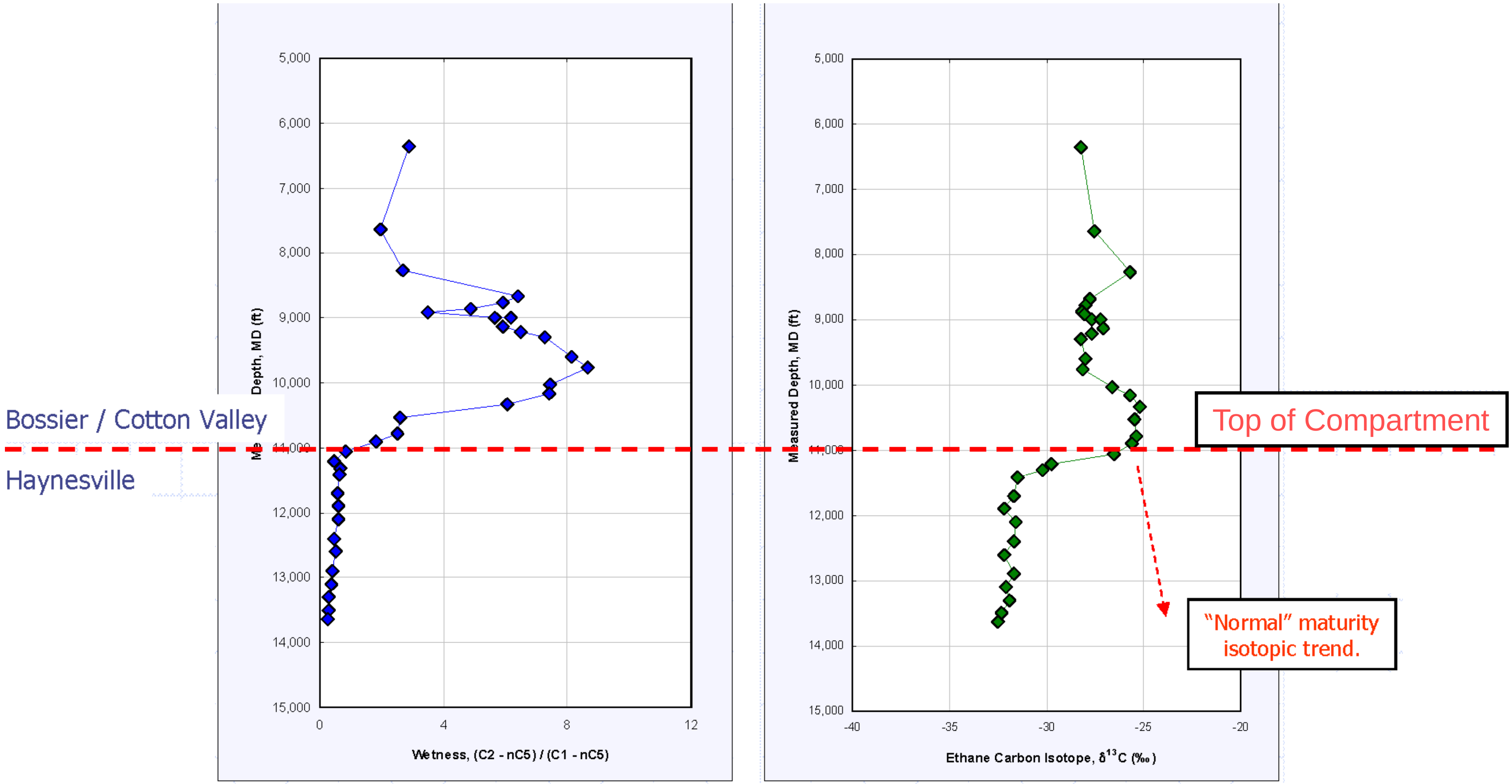


North Trail 1-33

North Trail 4-35

North Trail 4-36

Mud Gas Ethane Isotope "Reversals" (Haynesville Example)



Adapted from GeoMark, 2008

Resolute Example – Powder River Basin

•This is a plot that helps to classify the Genetic Gas Classification.

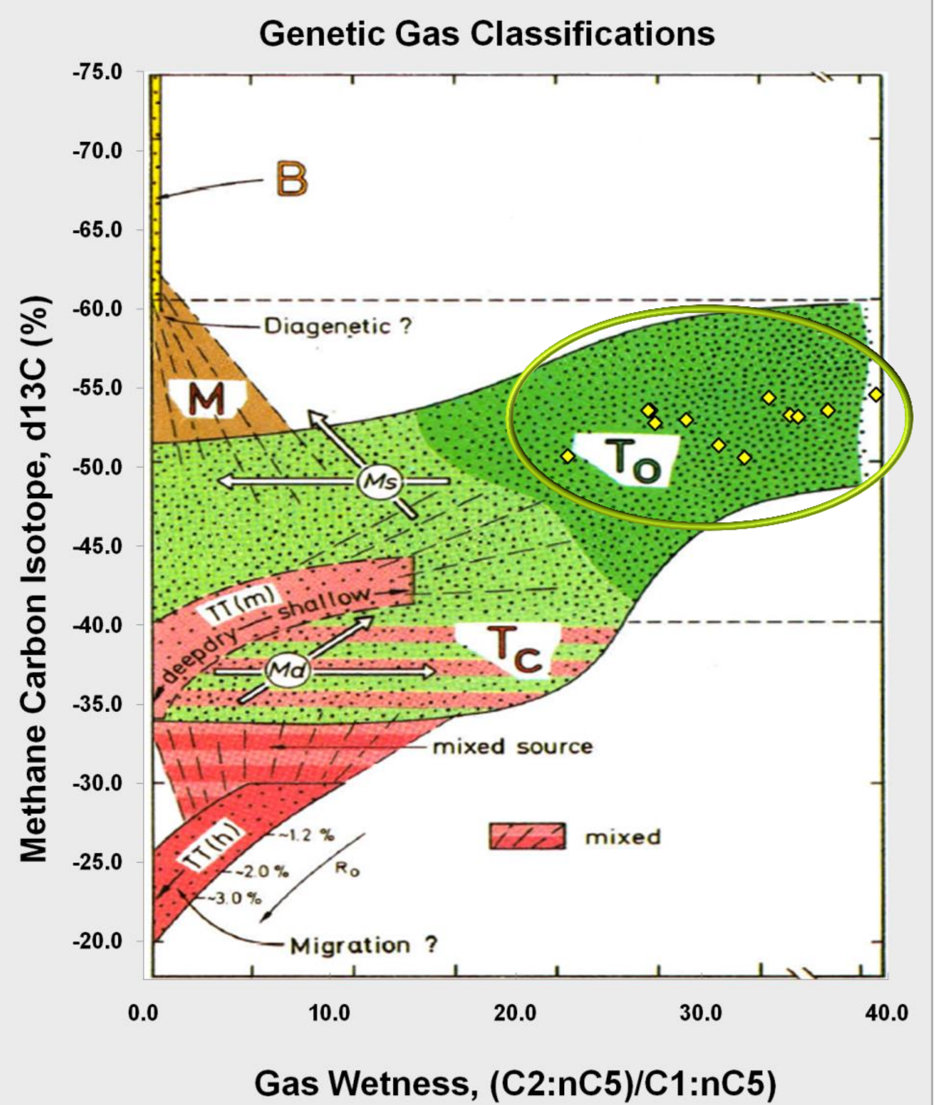
•The gases are plotted wetness vs. Methane Carbon Isotope

•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.



After Schoell, 1983 AAPG Bull.

Presentation Summary

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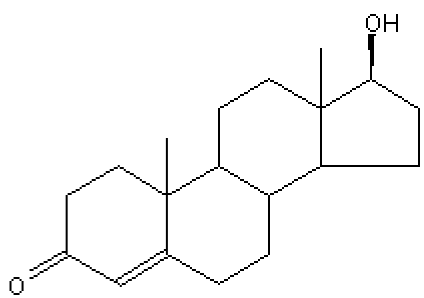
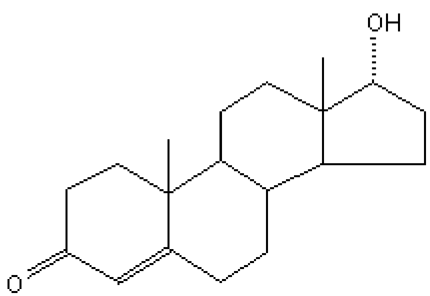
Isotopes in the News

Floyd Landis and the Tour de France

$C_{19}H_{28}O_2$

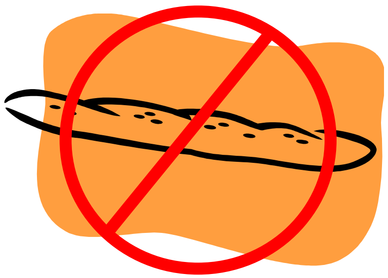


Testosterone



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?