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# **Isotopic Tracers of Groundwater Contamination: Techniques, applications and considerations**

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# Talk structure

- Background related to hydraulic fracturing and the relationship to groundwater resources
- Why should isotopic tracers be employed for determining the origin, and controls on, groundwater composition?
- Use of O, H and Sr isotopes to trace natural water bodies
- Introduction of  $^3\text{H}$ - $^3\text{He}$  and  $^4\text{He}$  techniques to monitor evolution in groundwater age
- $^{13}\text{C}$  systematics to constrain the origin of methane in groundwaters
- Limitations and recommendations

# Background

- A requirement exists for the implementation of techniques that verify and insure that groundwater is not contaminated as a result of hydraulic fracturing.
- Groundwater contamination can derive from numerous sources which may carry a distinct “fingerprint” that allows for identification of the source of contamination or the process which gave rise to the contamination. With respect to hydraulic fracturing, direct and indirect pathways could be investigated anytime contamination is alleged:
  - Direct contamination –unconventional gas or fracturing fluids migrating into groundwater and degrading water quality. While EPA's 2004 study and others have found no direct contamination from the hydraulic fracturing process itself, the breakdown of operational safeguards, e.g. lack of well bore integrity, surface spills, etc. may present pathways.
  - Indirect contamination – e.g. migrating fluids drive (bio)geochemical processes that result in the release of contaminants to the groundwater or naturally occurring species present in groundwater at concentrations that exceed threshold values.
- Isotopic techniques can identify the source of contamination and yield information on process such as redox or chemical evolution, mixing and migration.
- The chemical composition of relevant end members (groundwaters, produced waters, and fracturing fluids) are needed to make best diagnostic use of isotope or other geochemical techniques.

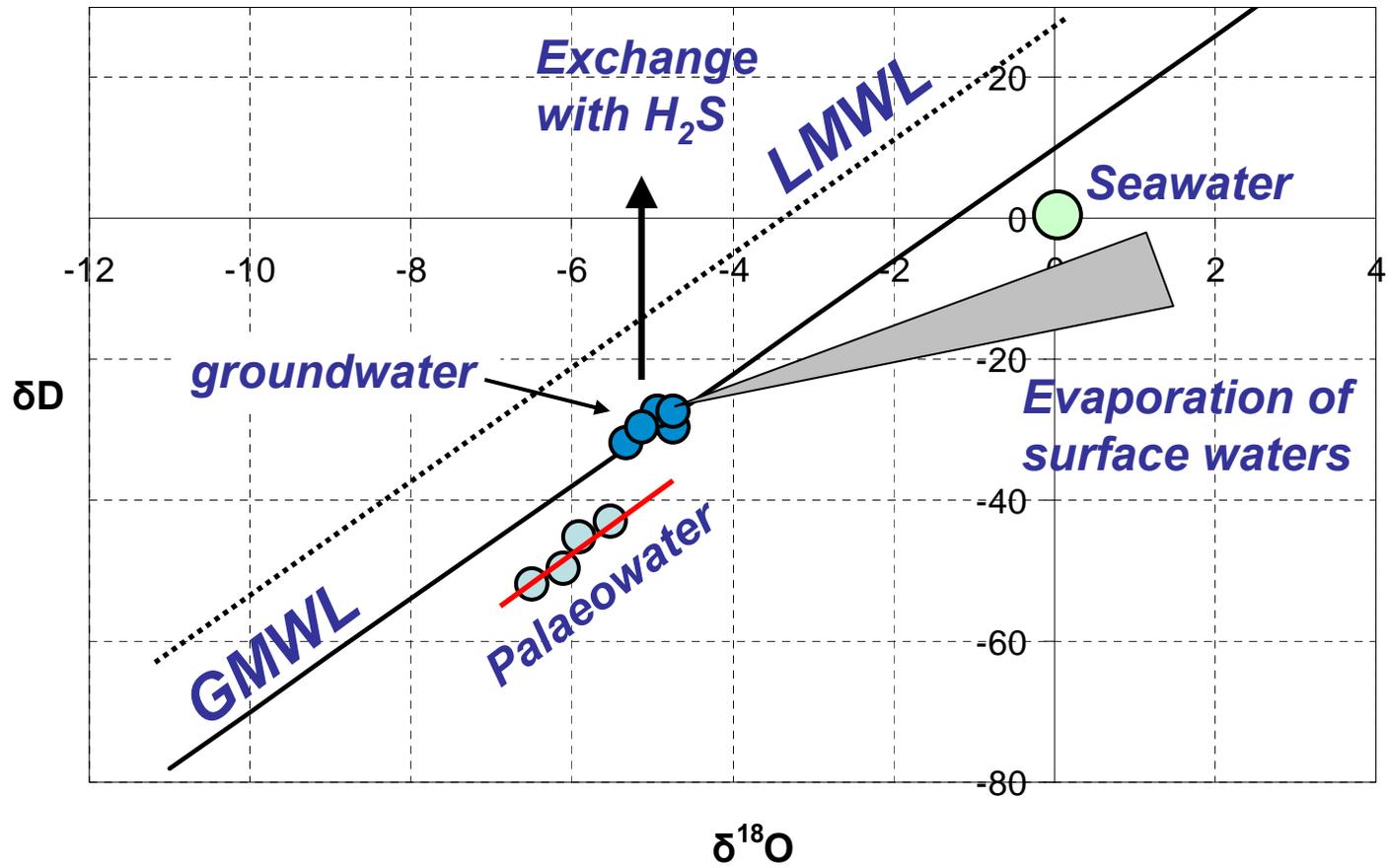
# Why use isotopic tracers?

- Major-ion chemistry of natural and injected fluids may not differ sufficiently enough for identification of the source(s) of materials present in groundwaters.

Isotopic tracers allow for:

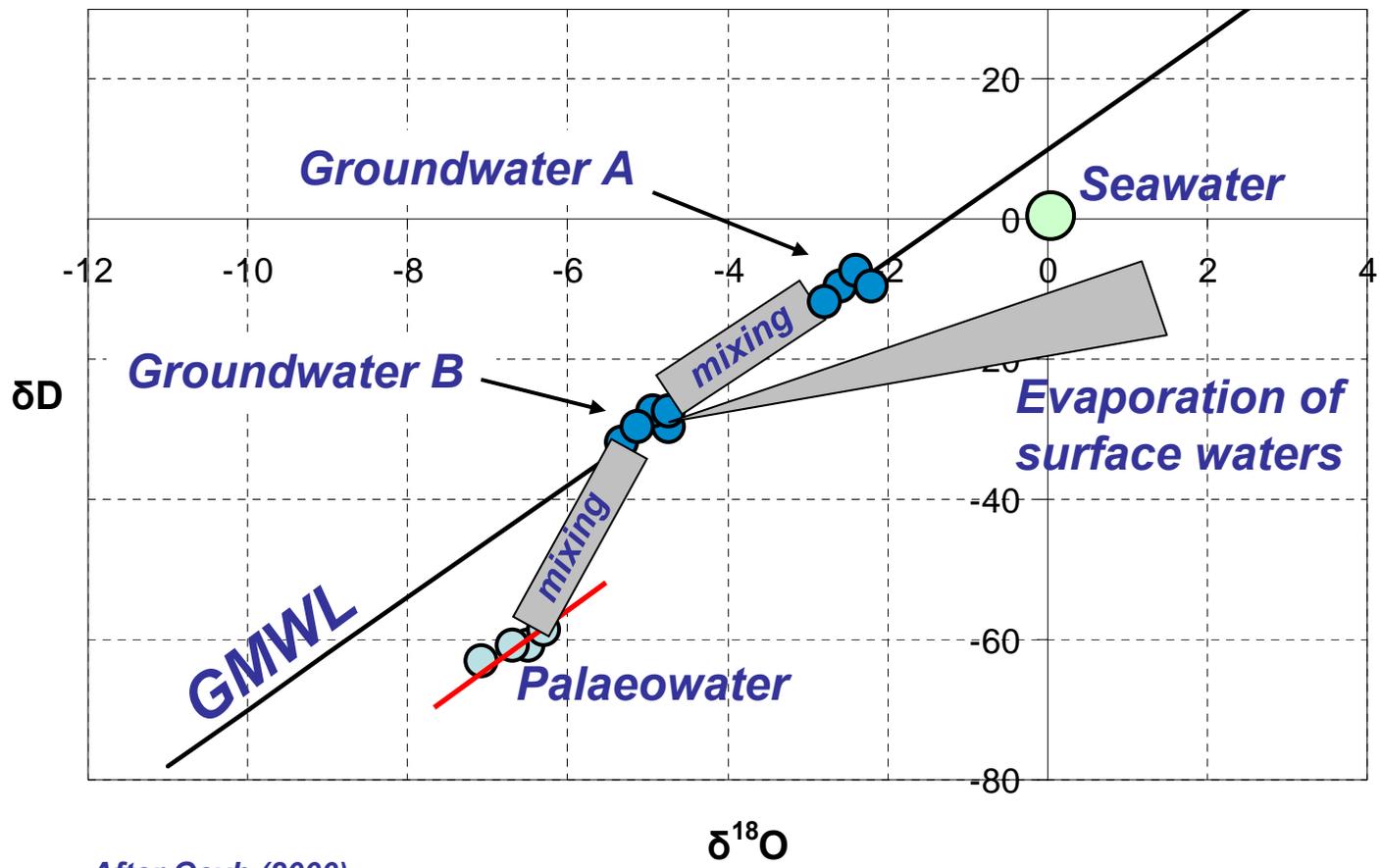
- Identification of naturally occurring surface-water contributions.
- Identification of mixing of different groundwater bodies.
- Identification of contributions and identification of the source of natural gas to shallow groundwaters.
  - Is this a result of the migration from shales as a direct result of hydraulic fracturing or is this naturally present e.g. through the biological production of methane in shallow groundwater?

# Natural water compositions



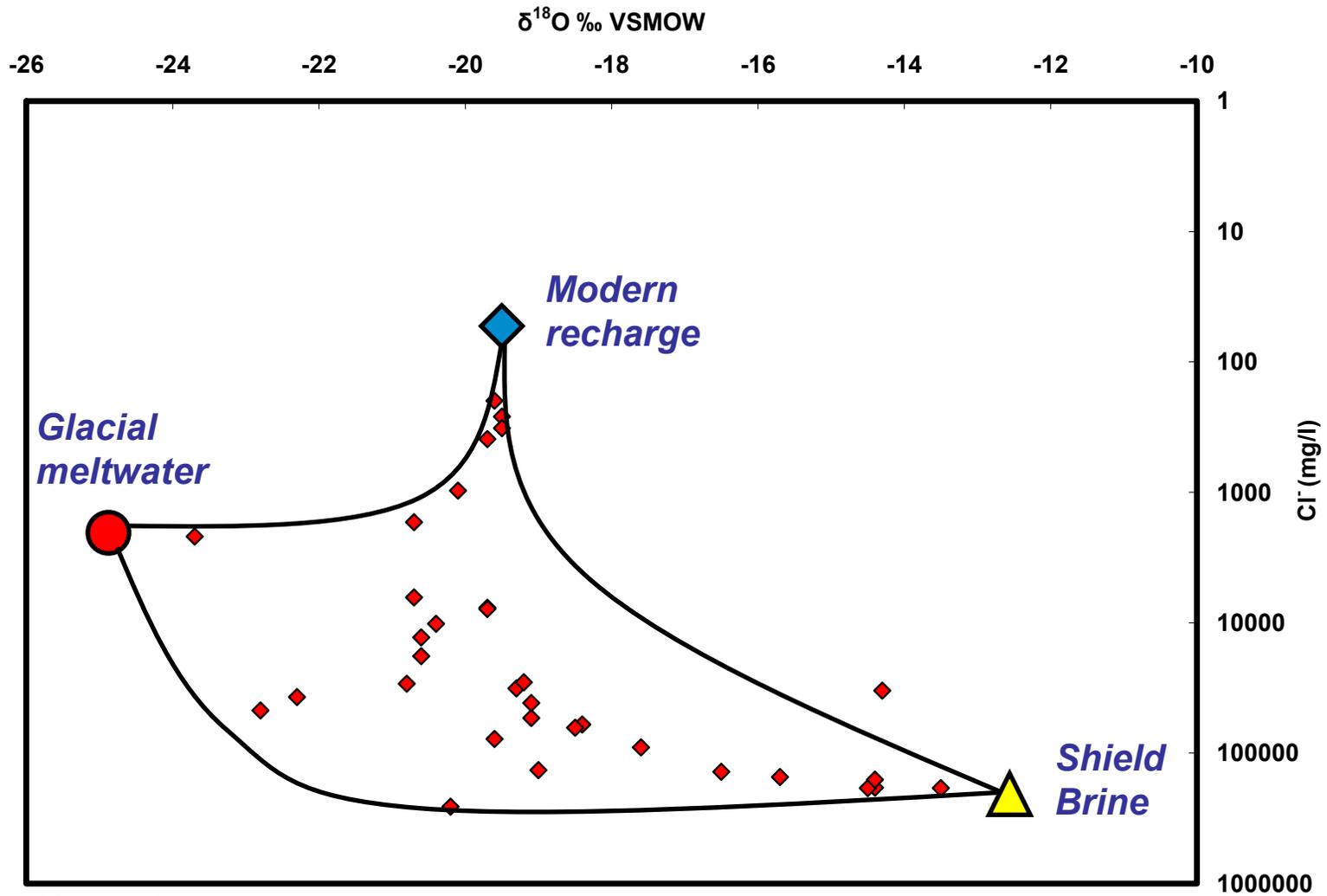
After Geyh (2000)

# Elucidating mixing processes



After Geyh (2000)

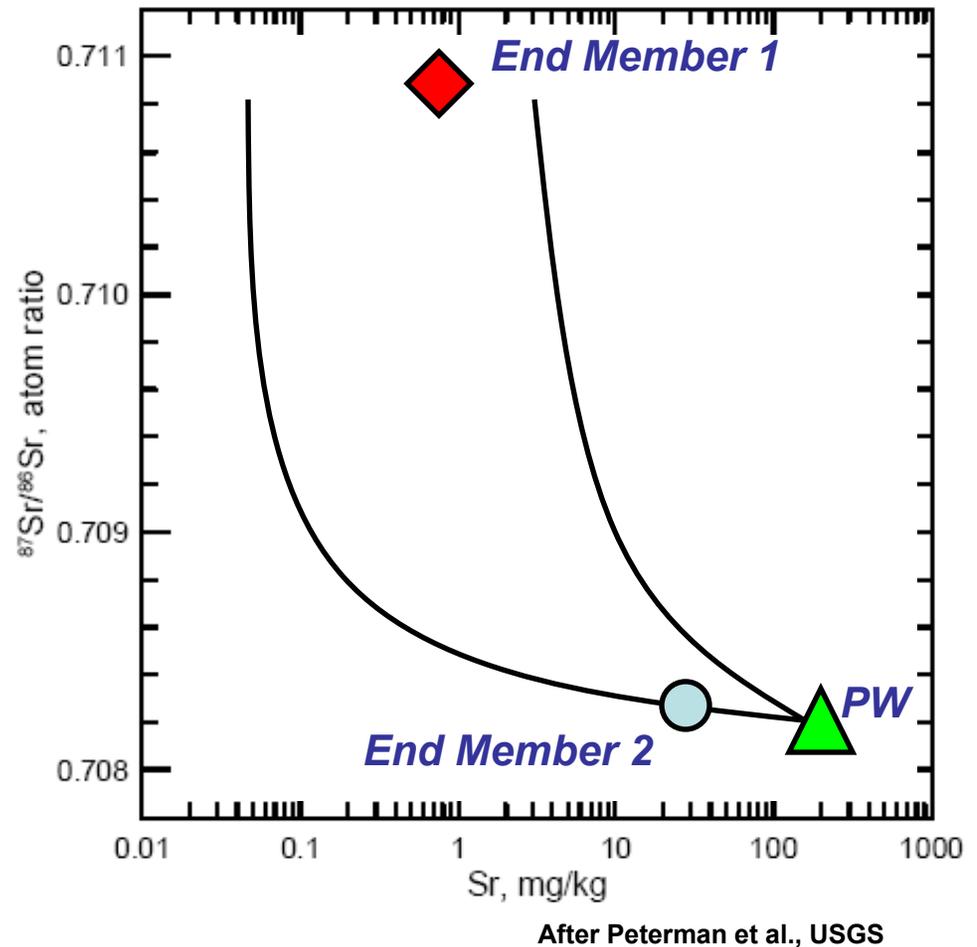
# Groundwater Mixing



After Douglas et al., 2000

# Resolving small contributions

- Formation waters typically have higher Sr concentrations compared to surface waters and shallow groundwater.
- When Sr isotopic compositions vary between different water bodies, Sr isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) provide a sensitive indicator of presence of low concentration differently sourced fluids.



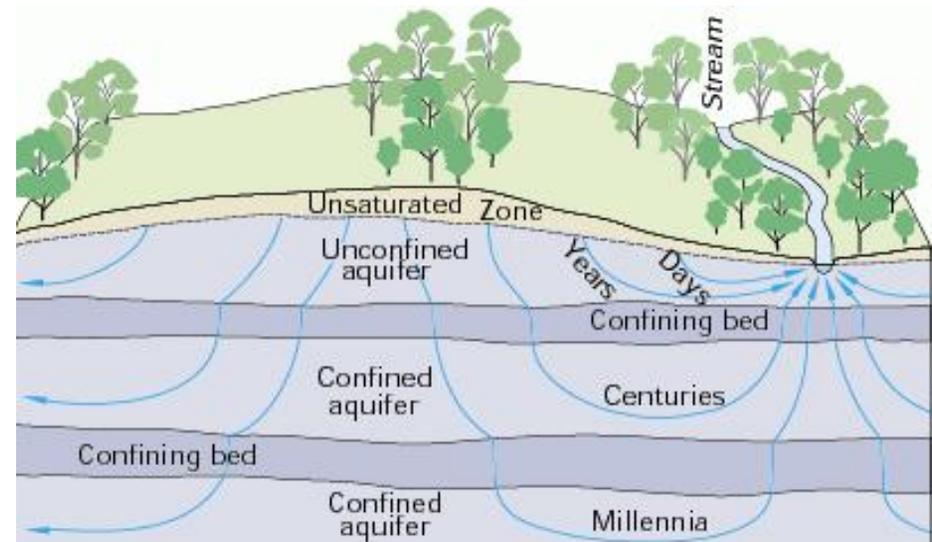
# Groundwater age

## Tritium-<sup>3</sup>He

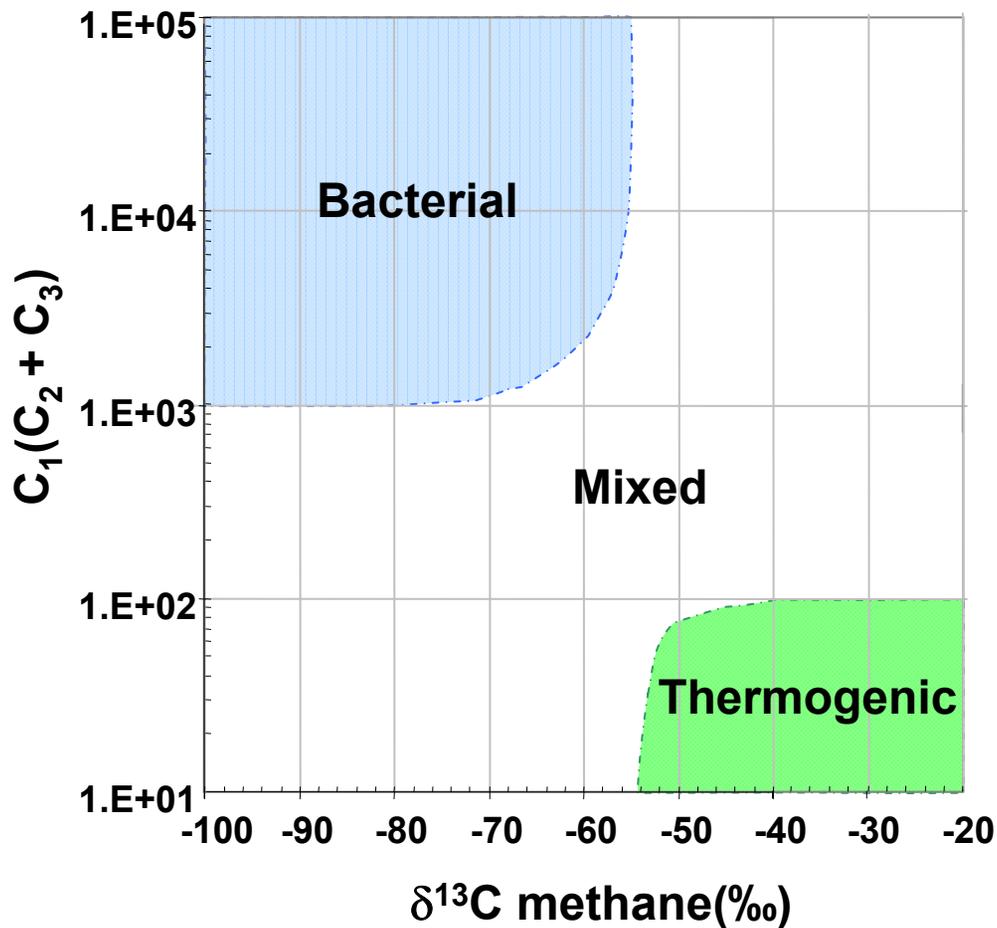
- Directly incorporated into water molecule.
- Decays to <sup>3</sup>He,  $t_{1/2} = 12.43$  yrs.
- GW < 60 years.

## <sup>4</sup>He

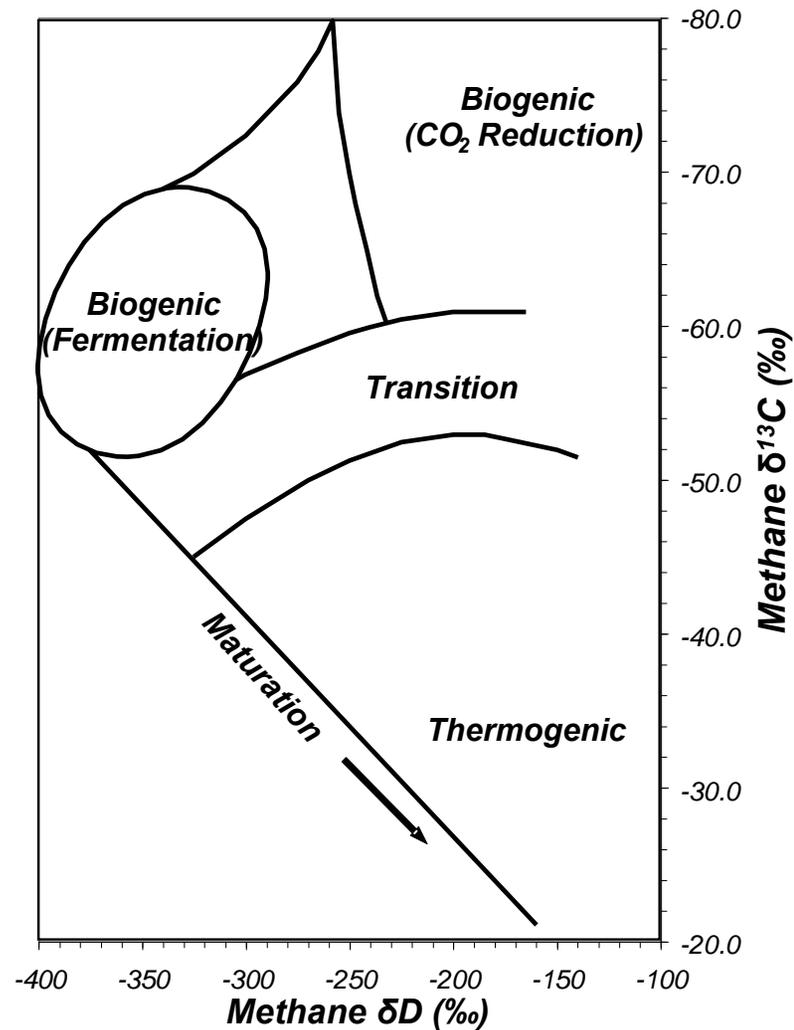
- Radiogenic He produced by U and Th decay from crustal minerals and atmosphere.
- Used to identify older GW (100's – 100,000's years).



# Examples of Biogenic vs. Thermogenic Gas Interpretation Schemes



After Bernard, 1978



After Rice, 1993

# Technical Summary

- There is a need to establish natural baseline conditions to assess deviations from the natural system.
- Major-ion chemistry alone may not yield definitive results as to the source(s) of any identified deviations.
- The application of multiple isotope systems allows for a more robust and comprehensive assessment of potential sources of contamination and allows for quantitative estimates of the contribution of these sources to be made.
- Sampling of potential end member fluids (surface waters, groundwaters and introduced fluids used during the fracturing process) may provide important compositional information that could prove useful when attempting to identify the existence and/or source of any perceived contamination.