

Geochemical Resource Characterization of Alberta Groundwater

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Project Goals:

- 1) To determine the baseline quality of Alberta groundwater.**
- 1) To determine the distribution and sources of possible contaminants (in particular methane).**
- 1) Relate those contaminants to groundwater ages in order to quantify timespans required for contaminants to buildup or degrade along groundwater flow paths.**

Methane in Alberta Groundwater?



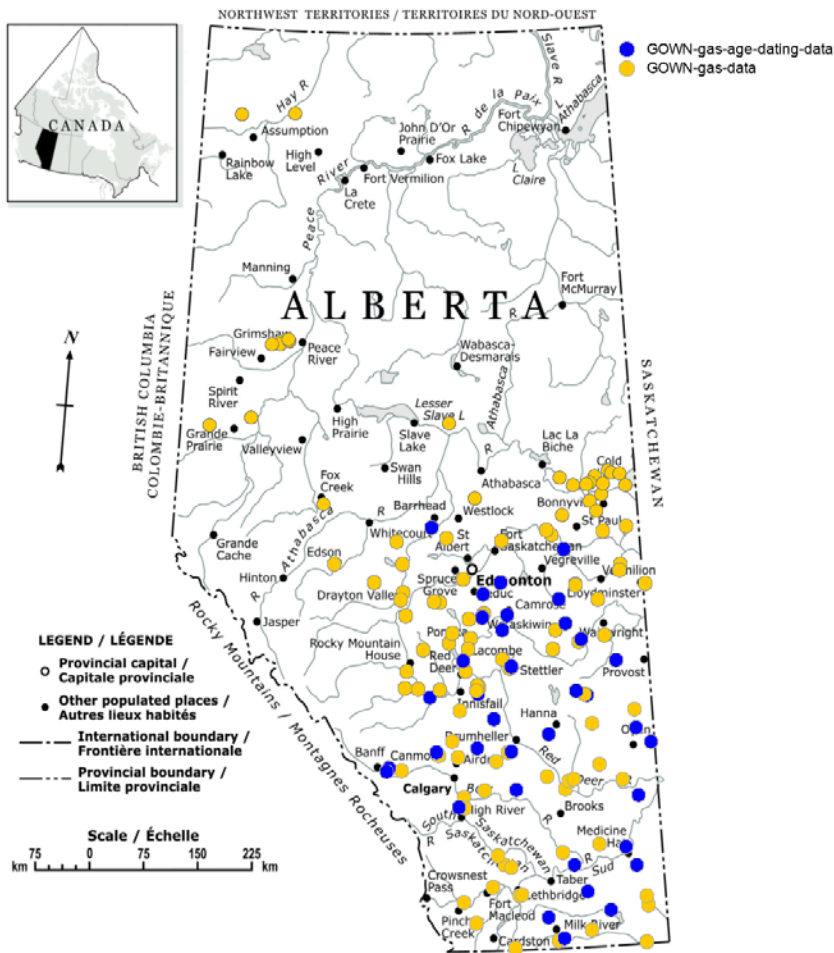
- 1) Is methane present?
- 2) How much?
- 3) What's it doing there?
 - a. Was it generated in situ?
 - b. Has it migrated?
(result of anthropogenic or non-anthropogenic activity)?

Approach:

Using samples collected from Alberta Environment's Groundwater Observation Network (or GOWN) we:

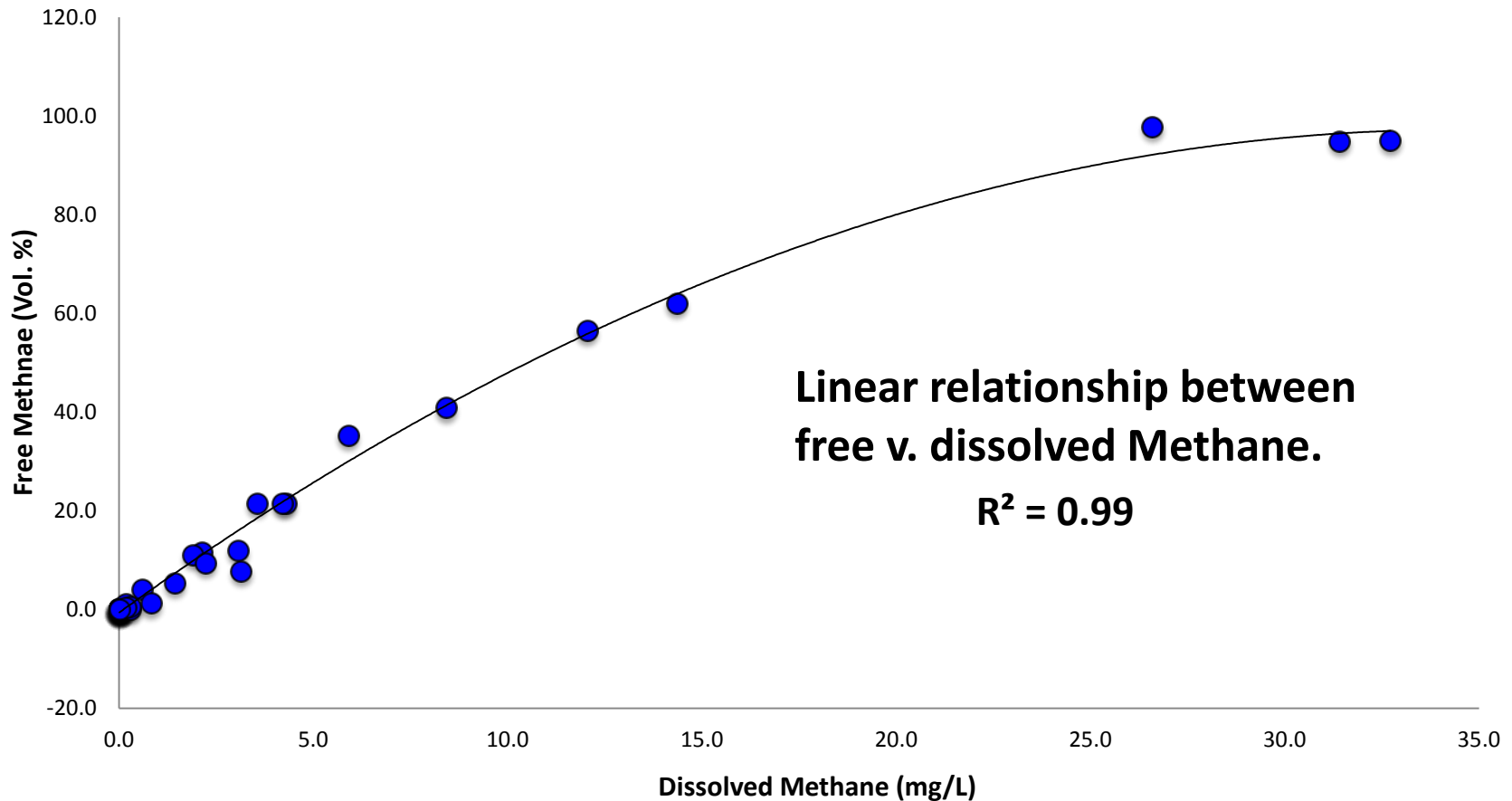
- 1) Determined concentration of dissolved inorganic constituents (in particular NO_3^- and SO_4^{2-}).
- 1) Determined concentration of dissolved and free gas (in particular methane).
- 1) Stable isotope analysis of 1) and 2) above.
- 1) Age dating of water using tritium and carbon-14.

Samples Collected



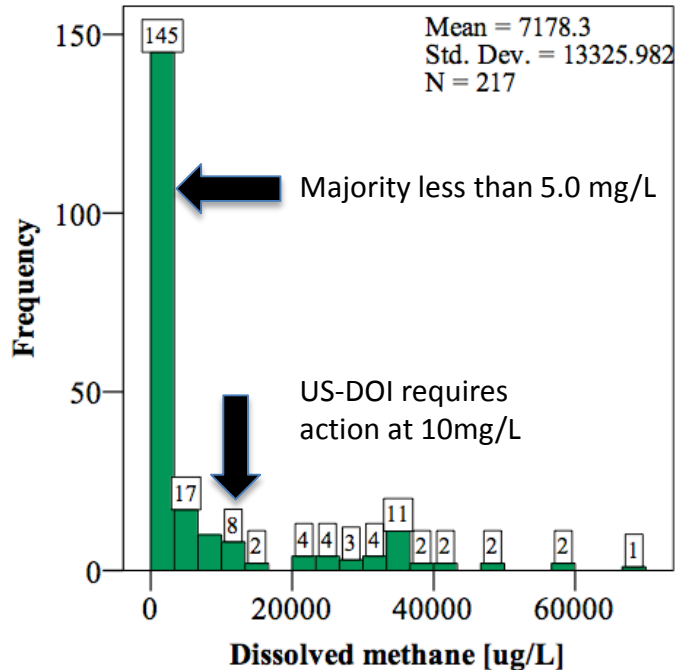
- Gas and water samples from 185 GOWN wells for chemical and stable isotope analysis.
- Water samples from a subset of 66 GOWN wells for Carbon-14 and Tritium.
- Methane observed in 183 of 185 wells sampled.

Methane in Groundwater (2015/16)

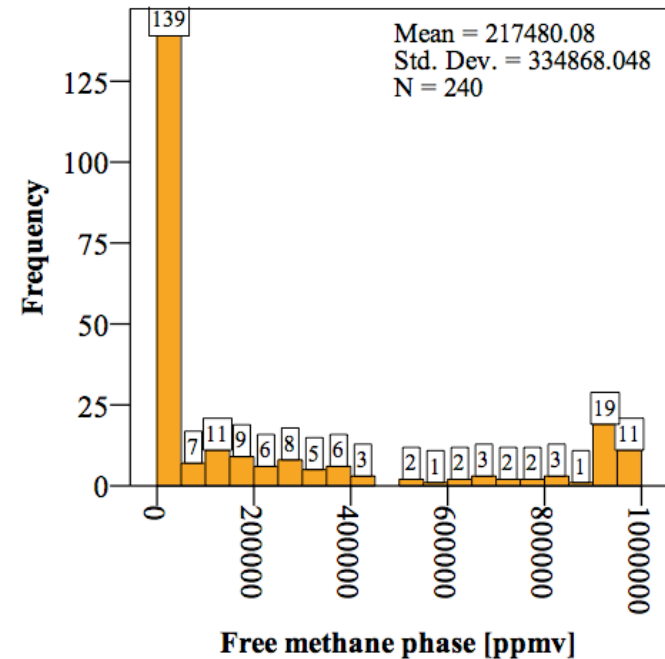


Methane in GOWN Wells

Dissolved Methane

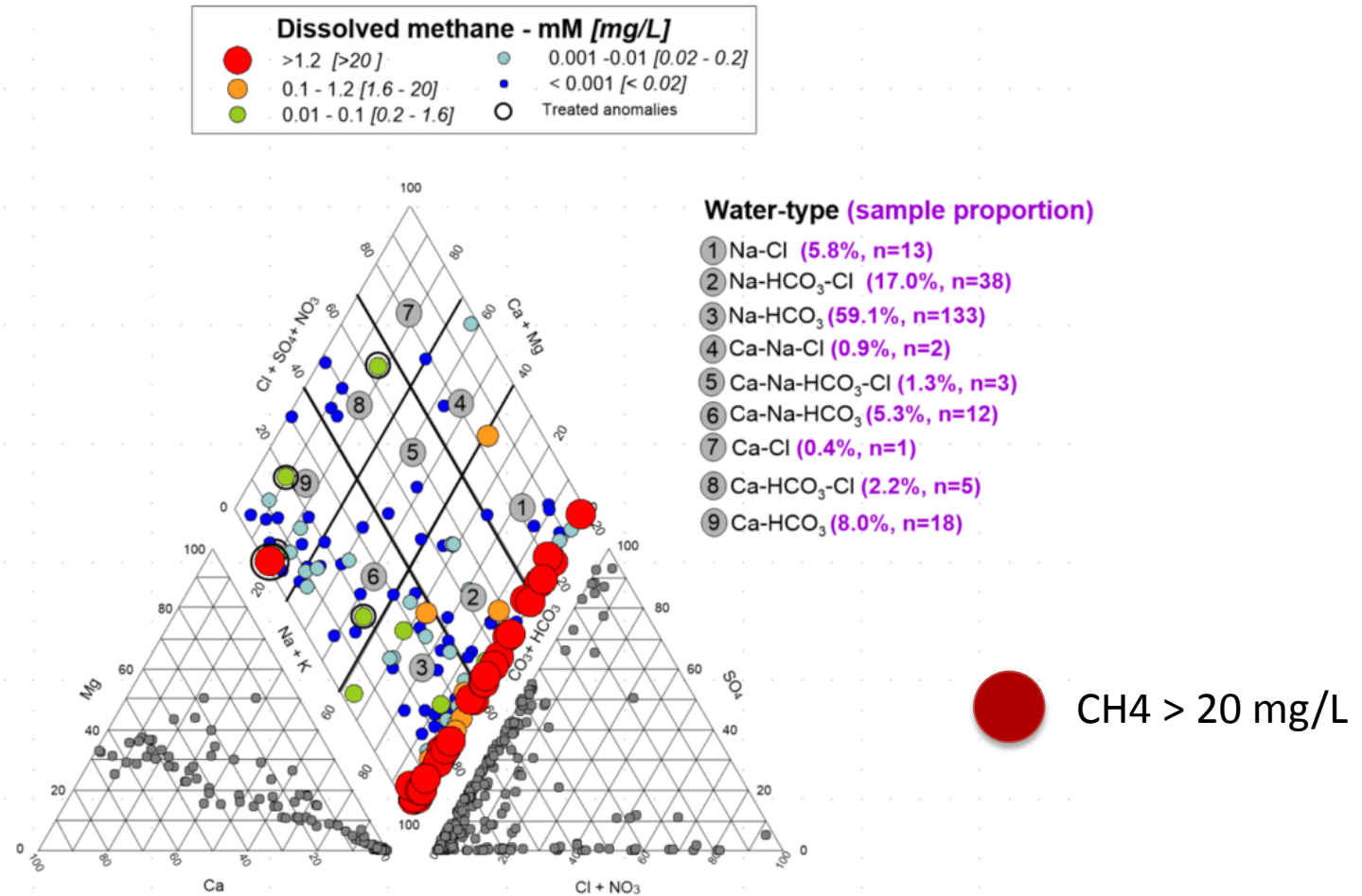


Free Gas Methane



In spite of being ubiquitous, majority of samples have only small amounts of methane present.

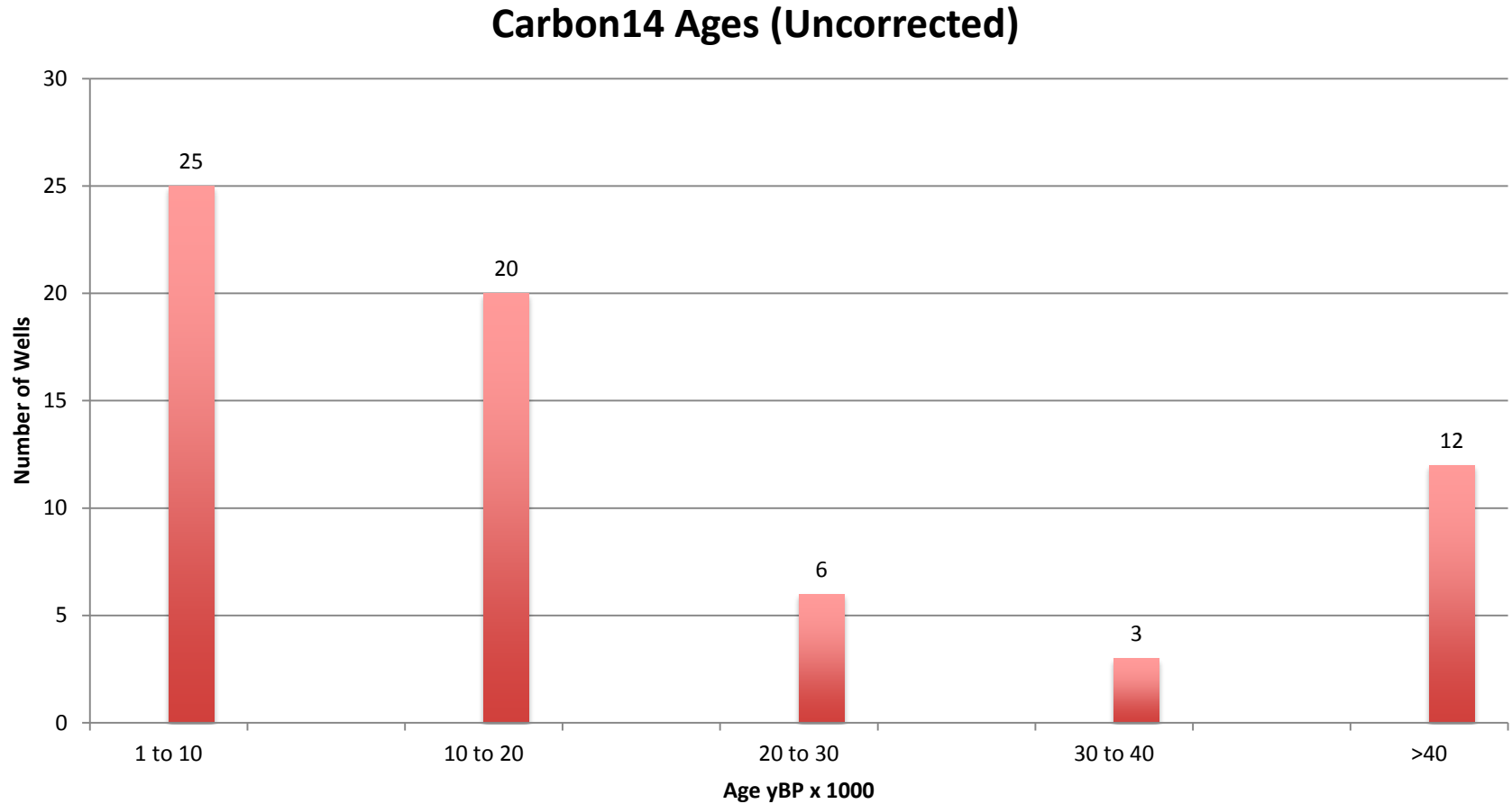
Methane and Water Type



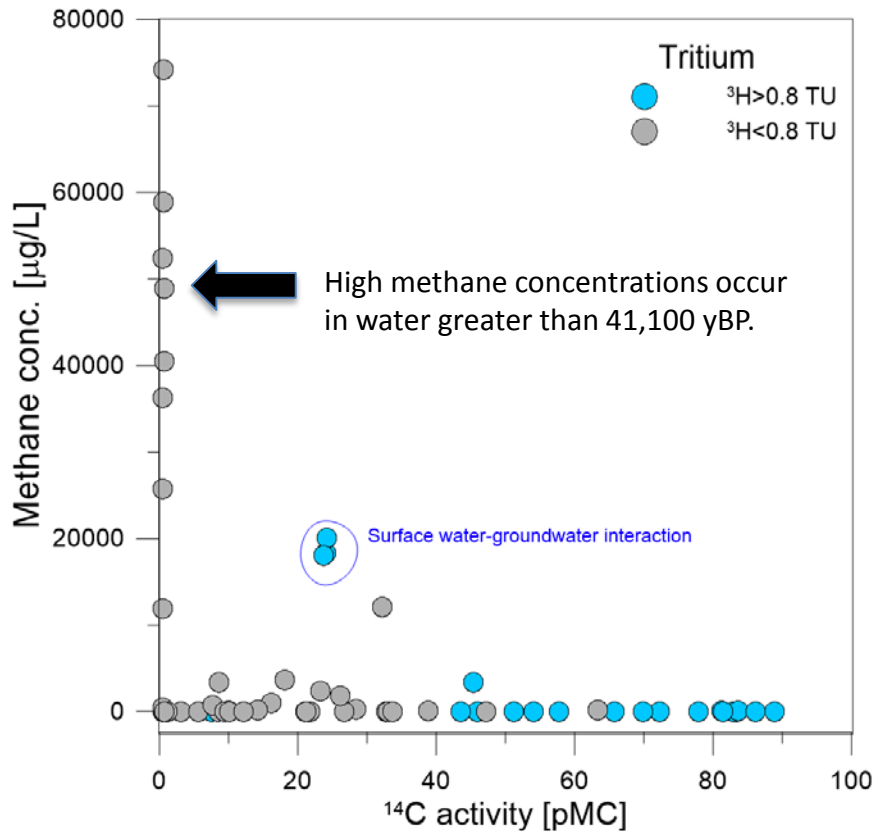
Tritium and Carbon-14 Age Data (72 samples from 66 wells)

	Radiocarbon analyses (^{14}C)	Tritium analyses (^3H)
Samples	72 (10 samples = DL)	72 (50 samples = DL)
Detection Limit	>41,100 yBP	<0.8 TU
Range	from 945 to 41,024 yBP	from 1.0 to 23 TU
Median	11,494 yBP	6.2

Carbon-14 Age Data (N=66)

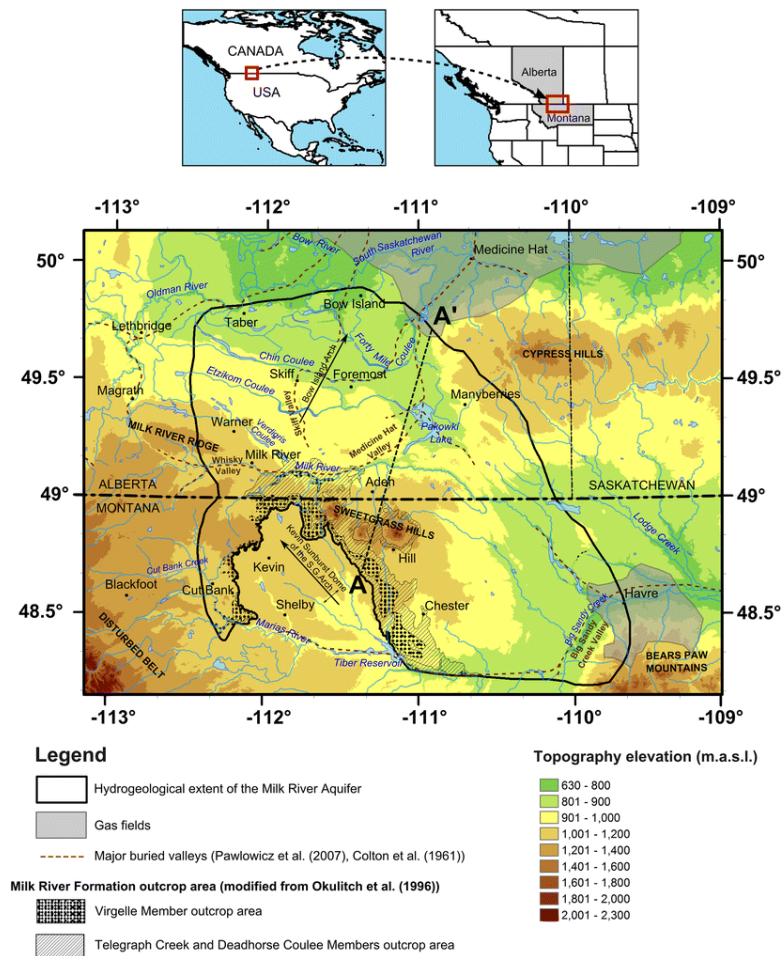


Dissolved Methane v. Age



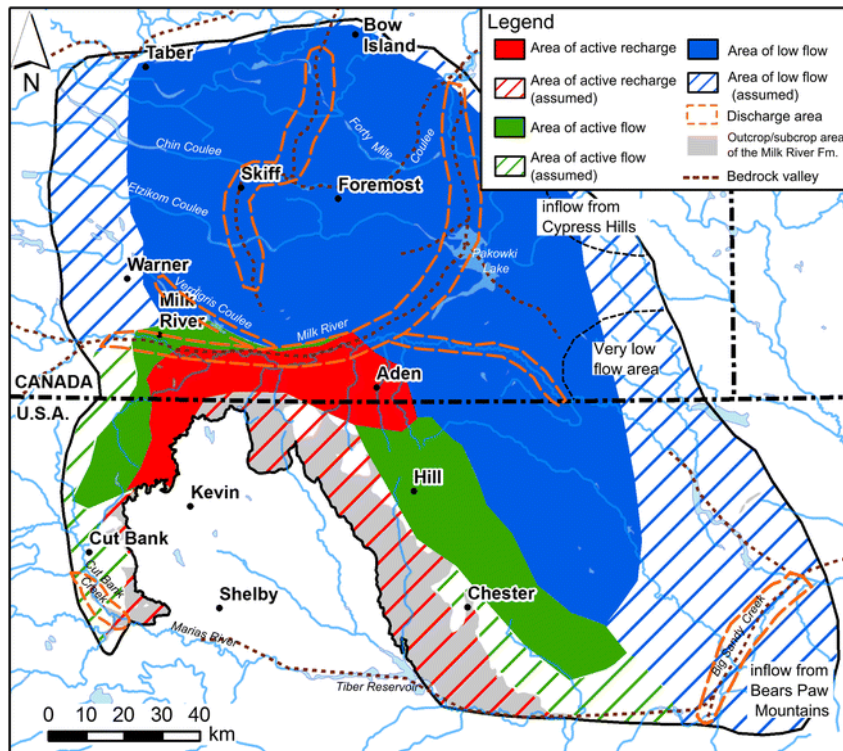
- Highest methane concentrations corresponds to groundwater with ^{14}C -DIC $< 1\%$ modern carbon (pMC) or to age greater than 41,100 years before present (yBP).

Spatial relationship between methane occurrence, water-type and age within an aquifer (e.g. Milk River)



From Petre et al (2016), Hydrogeol J. 24:1847-1871

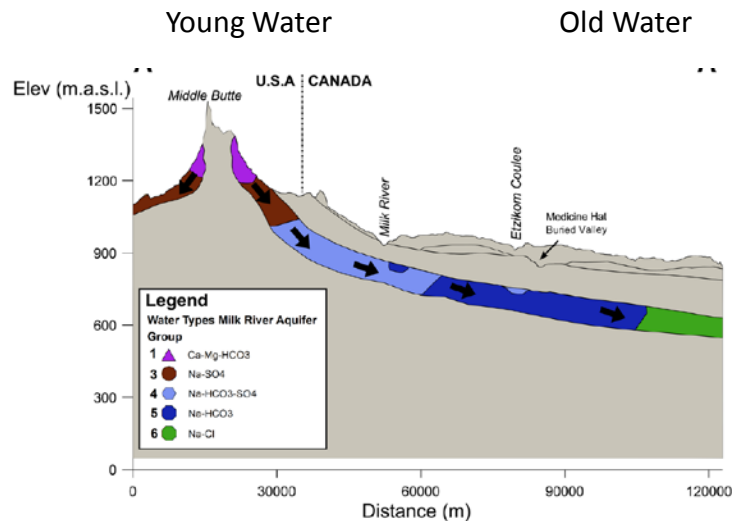
Spatial relationship between methane occurrence, water-type and age within an aquifer (e.g. Milk River)



- Distance from area of recharge to northern limit is approximately 100km.
- Within the aquifer, water flows north from area of recharge (red zone) along the Canada/US Border.

From Petre et al (2016), Hydrogeol J. 24:1847-1871

Spatial relationship between methane occurrence, water-type and age within an aquifer (e.g. Milk River)

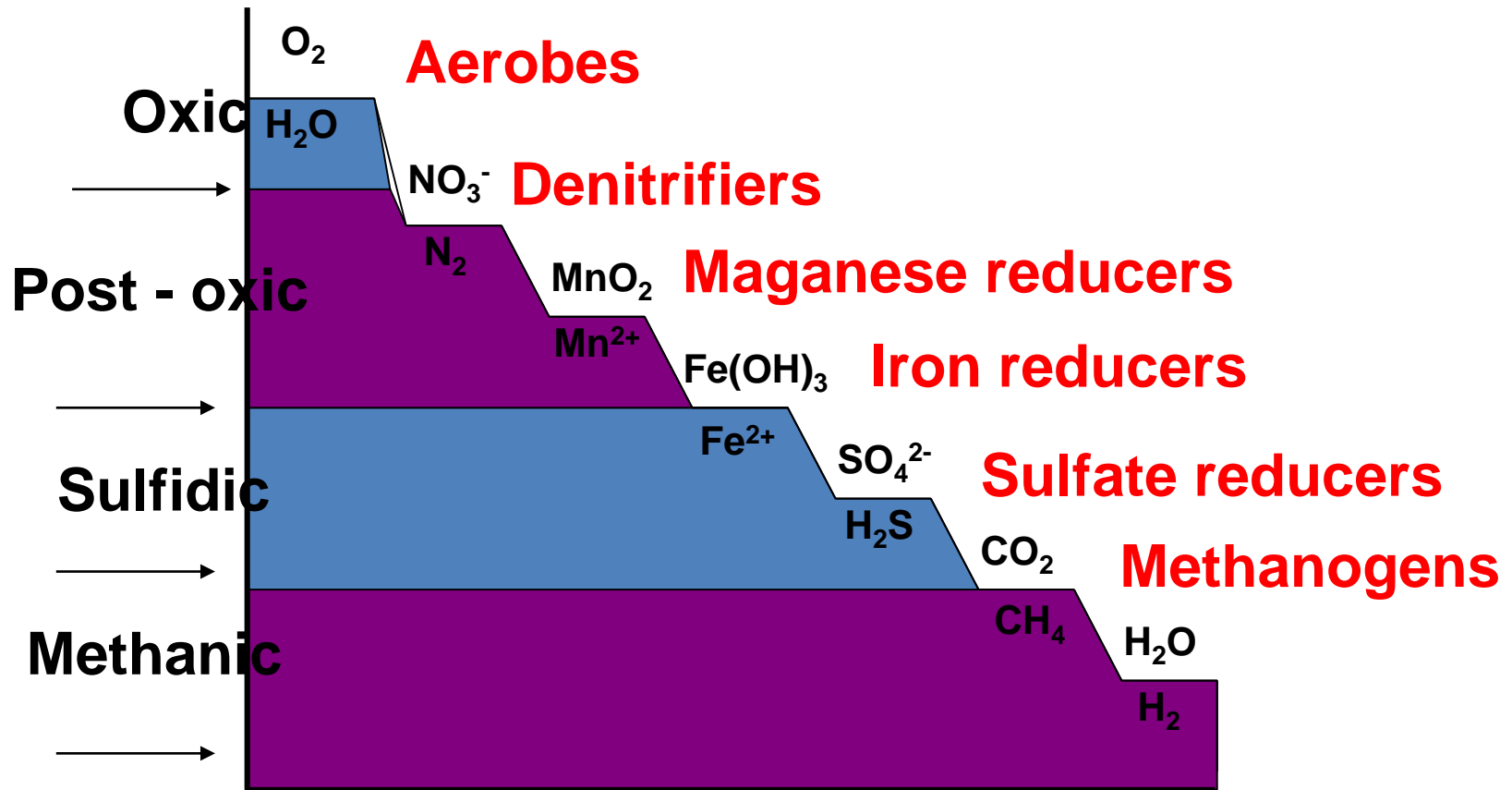


- Significant changes in water chemistry occur as water moves away from area of recharge.
- Water gets older moving away from area of recharge.

From Petre et al (2016), Hydrogeol J. 24:1847-1871

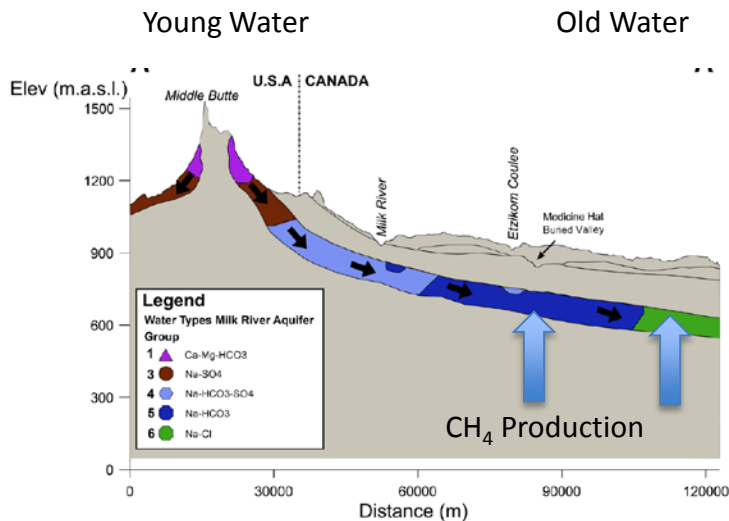
The Redox Ladder Concept

Changes in water chemistry can be explained in part using the redox ladder concept. Methanogenesis cannot occur until sulfate is consumed.



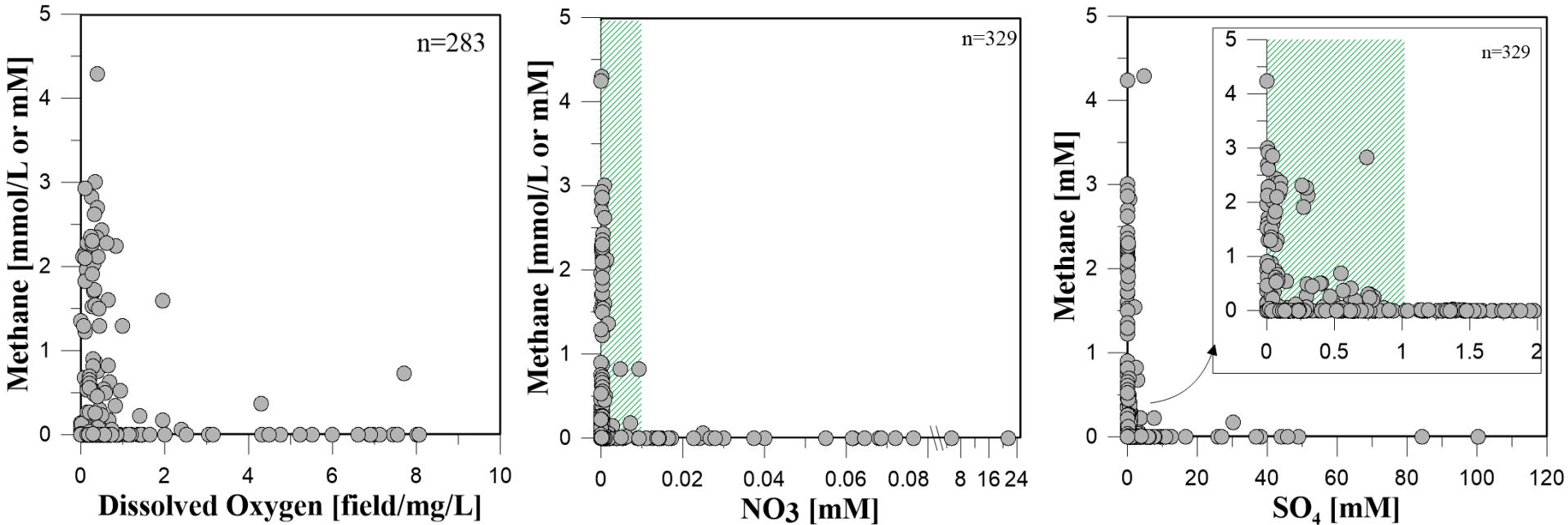
Spatial relationship between methane occurrence, water-type and age within an aquifer (e.g. Milk River)

- Methane production would be expected to occur in Na-HCO₃ and NaCl water types.



Modified from Petre et al (2016), Hydrogeol J. 24:1847-1871

GOWN data adheres to redox ladder concept, i.e. we find methane where we expect to find it.



Elevated methane concentrations in GOWN wells found only when:

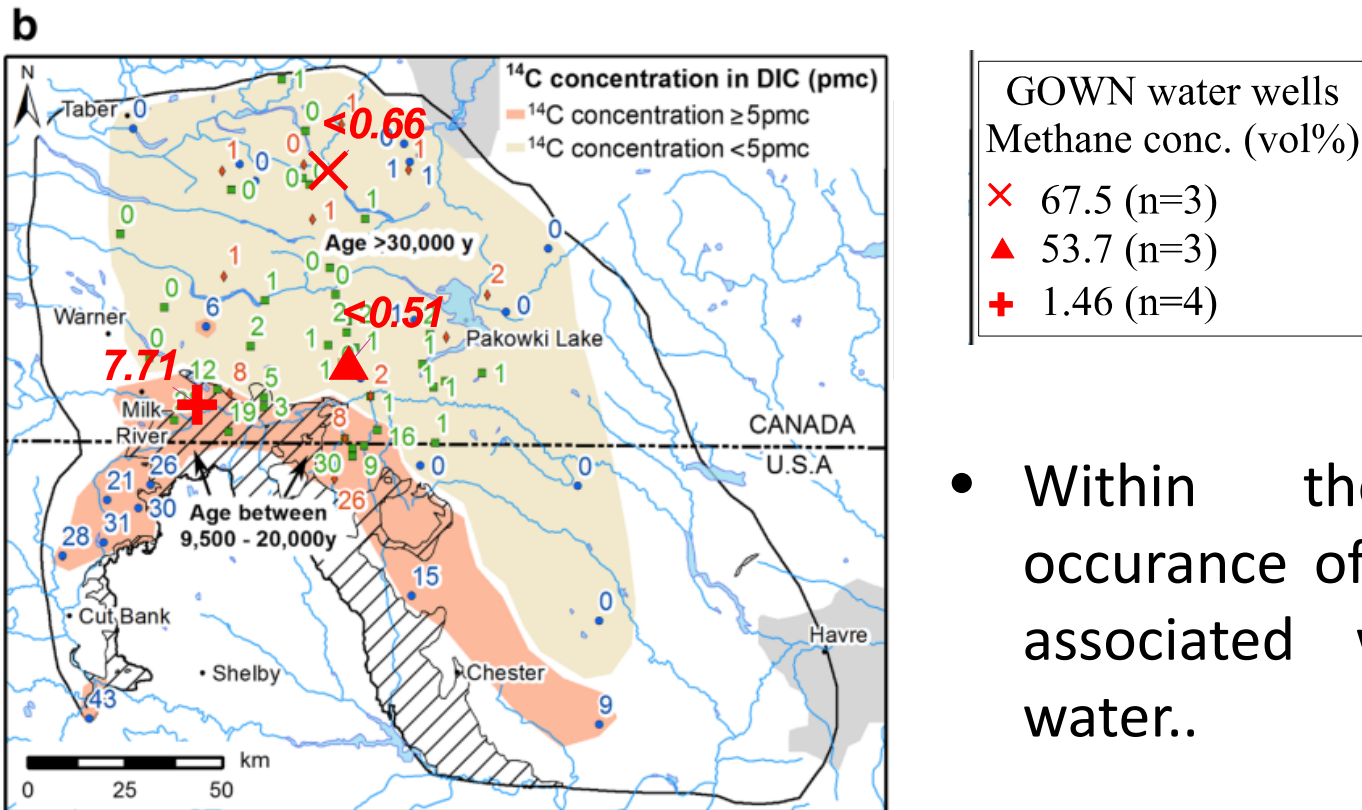
- a. dissolved **oxygen** is negligible
- b. dissolved **nitrate** is negligible
- c. dissolved **sulfate** is negligible

Groundwater Age Dating (Carbon-14):

Highest methane production observed in older water and in the absence of sulfate.

<u>GOWN#</u>	<u>CH4 (ppmv)</u>	<u>14C (yr BP)</u>	<u>Water Type</u>
214	70	11062	Na-SO4
113	227	18629	Na-SO4
265	254	7585	Na-HCO3
140	1013	8950	Na-HCO3
972	166654	19676	Na-HCO3
989	222000	>41700	Na-Cl
381	951088	>41700	Na-HCO3-Cl
439	974140	>41700	Na-HCO3-Cl

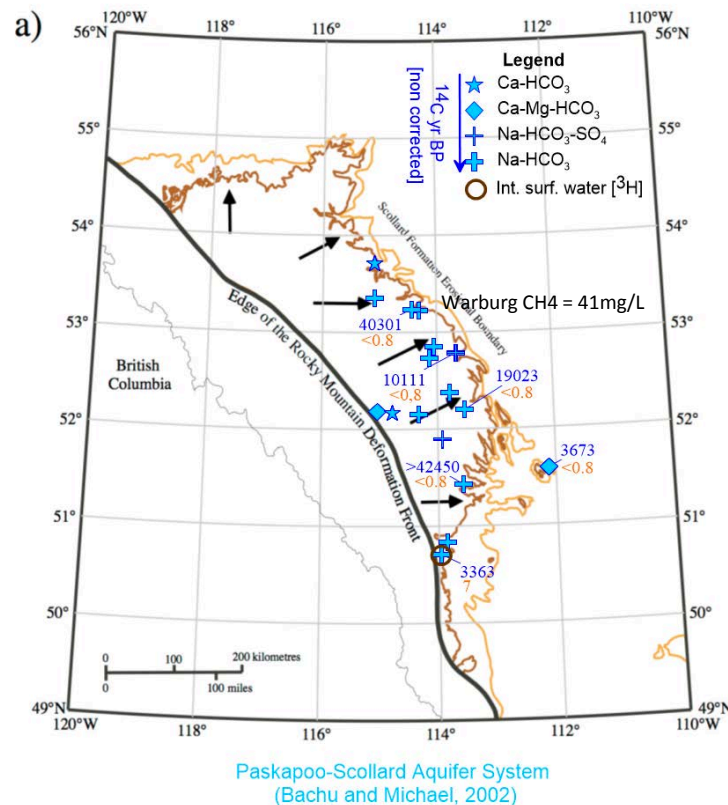
Milk River Aquifer (Our Carbon-14 and Methane Data)



- Within the aquifer, occurrence of methane is associated with oldest water..

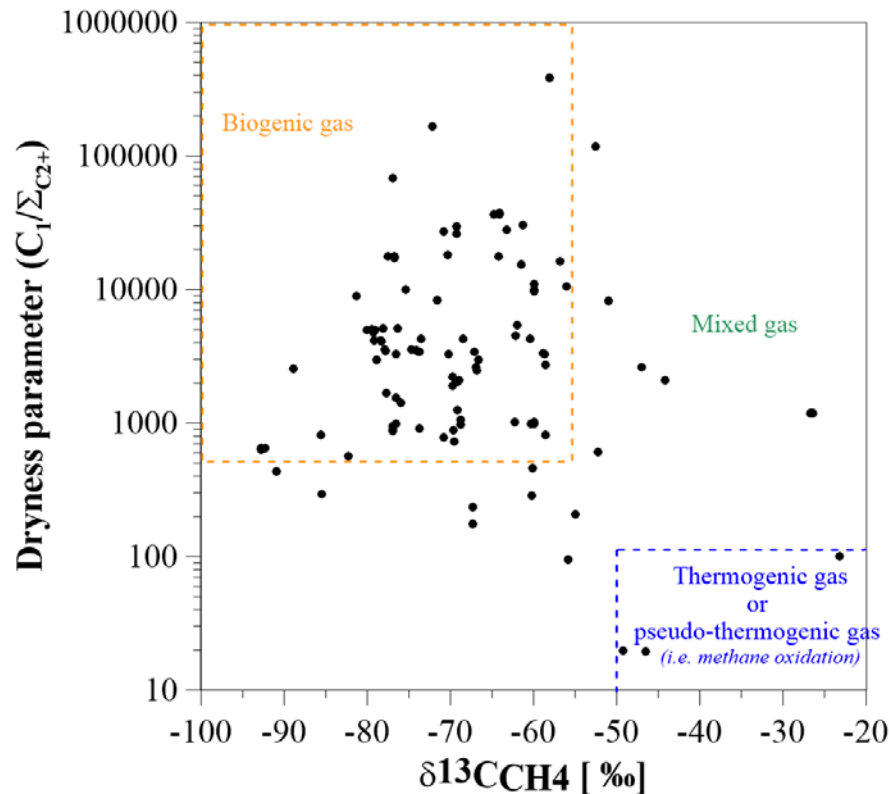
Modified from Petre et al (2016), Hydrogeol J. 24:1847-1871

Spatial relationship between water-type and age within an aquifer (e.g. Paskapoo)



- Within the Paskapoo, water chemistry and age change as water moves away from areas of recharge.

Stable isotopes provide evidence of methane of a largely biogenic origin in GOWN wells.

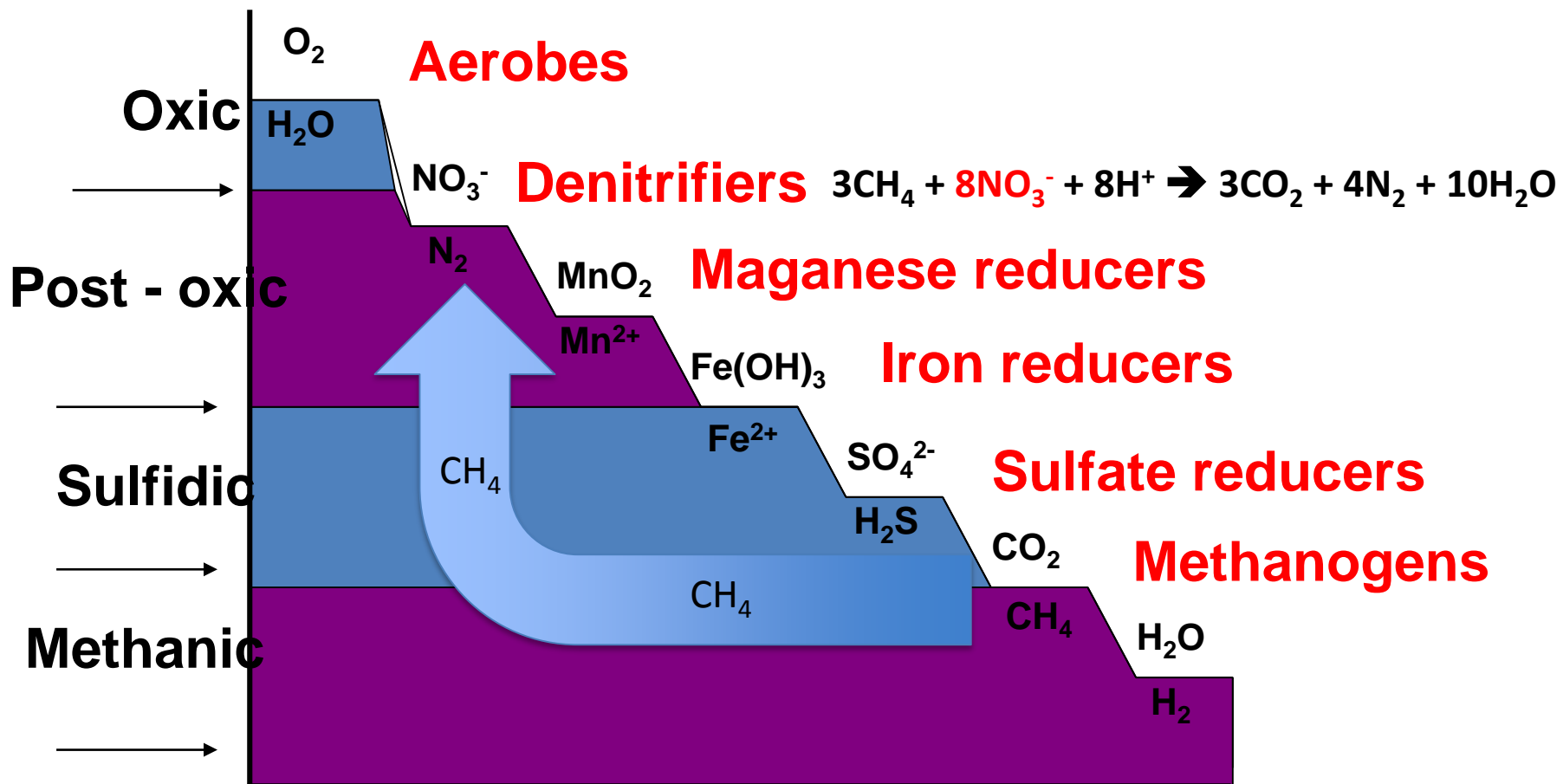


-consistent with a
biogenic origin

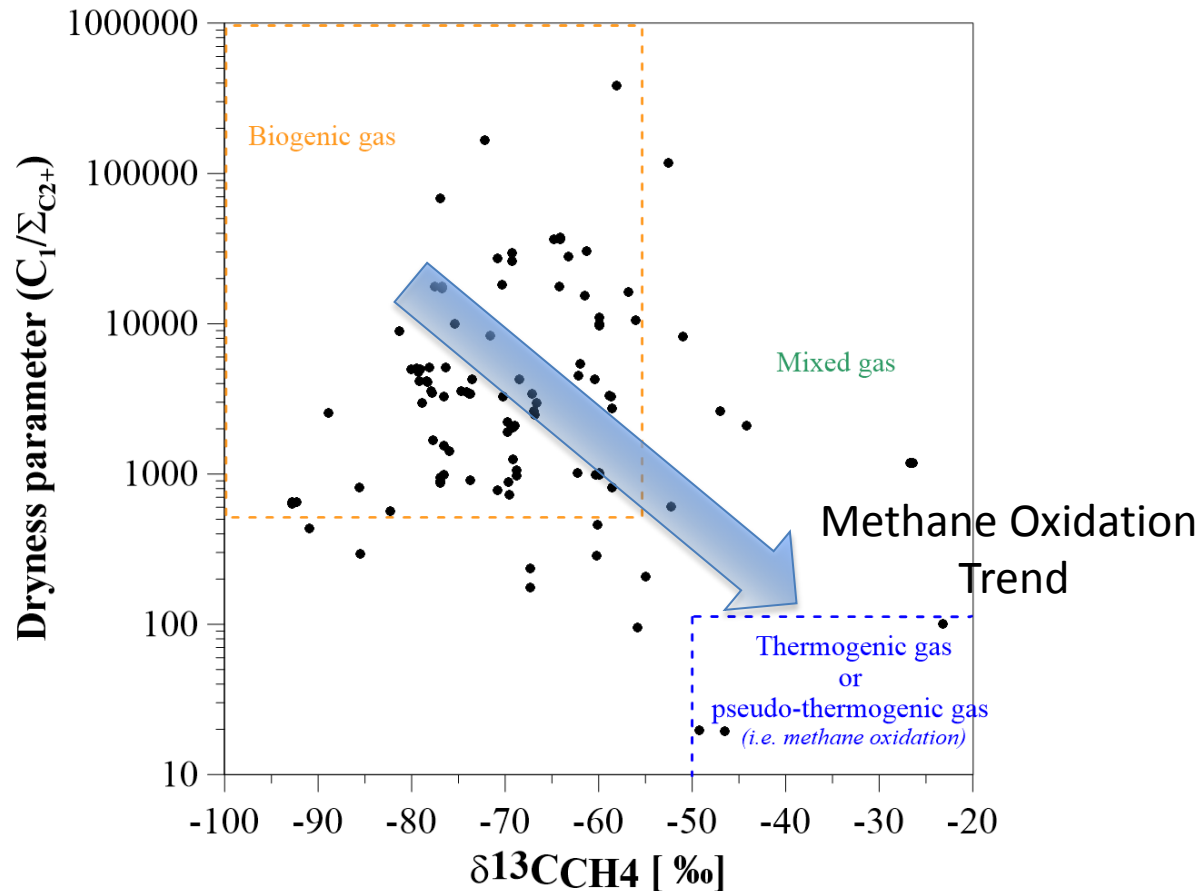
-only very few
samples indicate
**mixed gas or
possible
thermogenic origin.**

The Redox Ladder Concept

The migration of methane further up the redox ladder leads to oxidation (e.g. by nitrate):



Methane Isotope Oxidation Trend (GOWN Wells)



Future Work (?)

- 1) Krypton-81 age dating of water samples greater than 41,000 yBP.
- 1) Metagenomics (RNA and DNA) to identify presence of methanogens and pathways of methane formation.

Thank you!

- Questions?