



Stable Isotope Geochemistry, Chloride-Bromide Systematics, and the Identification of Sources of Saline Groundwater

Raceland Field, Lafourche Parish, LA

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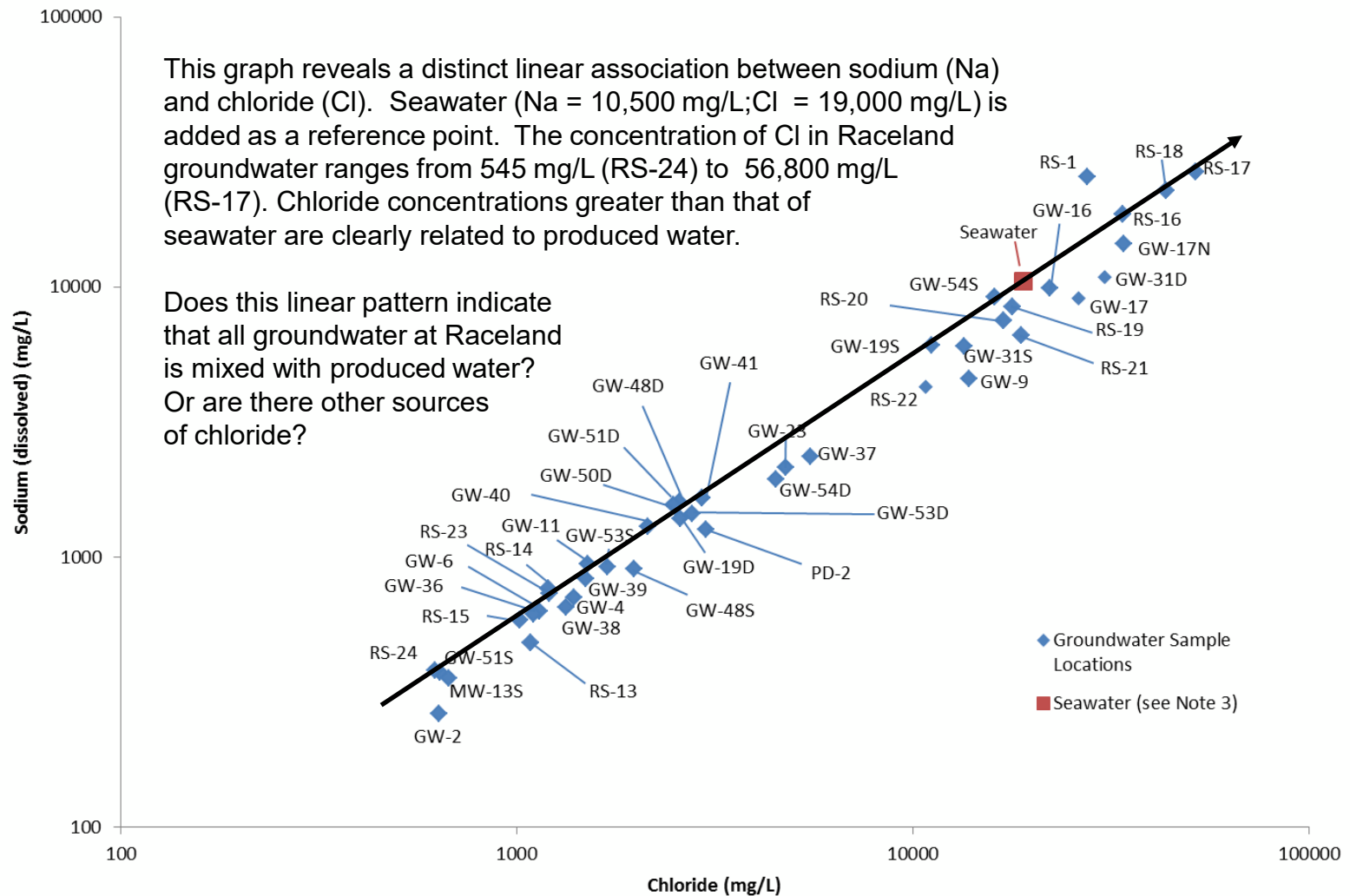
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- Illustrate utility of stable isotope geochemistry and bromide-chloride systematics in identification of source(s) of brine in groundwater
- Explain principles of analysis, using data from the Raceland Oil Field, Lafourche Parish
- Demonstrate that integration of stable isotope geochemistry with bromide-chloride data yields direct and penetrating insight into source(s) of chloride

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- All methods are widely used to identify sources of brine and to model mixing of saline waters and fresh waters.
- Plot standard geochemical relationships for saline solutions
 - X-Y plots (e.g., Na v Cl, Br/Cl v 1/Cl)
 - Identify groups of wells based on geochemical patterns
- Graph ratios of stable isotopes oxygen-18 ($\delta^{18}\text{O}$) and deuterium ($\delta^2\text{H}$, or δD)
 - Identify groupings delineated on X-Y plots
- Graph $\delta^{18}\text{O}$ v Cl or $\delta^{18}\text{O}$ v 1/Cl if there is at least one highly saline end member
 - Look for linear patterns (indicators of different sources of Cl and of mixing)
- Plot strontium isotope ratios v 1/Sr ($^{87}\text{Sr}/^{86}\text{Sr}$ v 1/Sr)
 - Look for clusters or linear patterns and calculate median and interquartile $^{87}\text{Sr}/^{86}\text{Sr}$ ratios



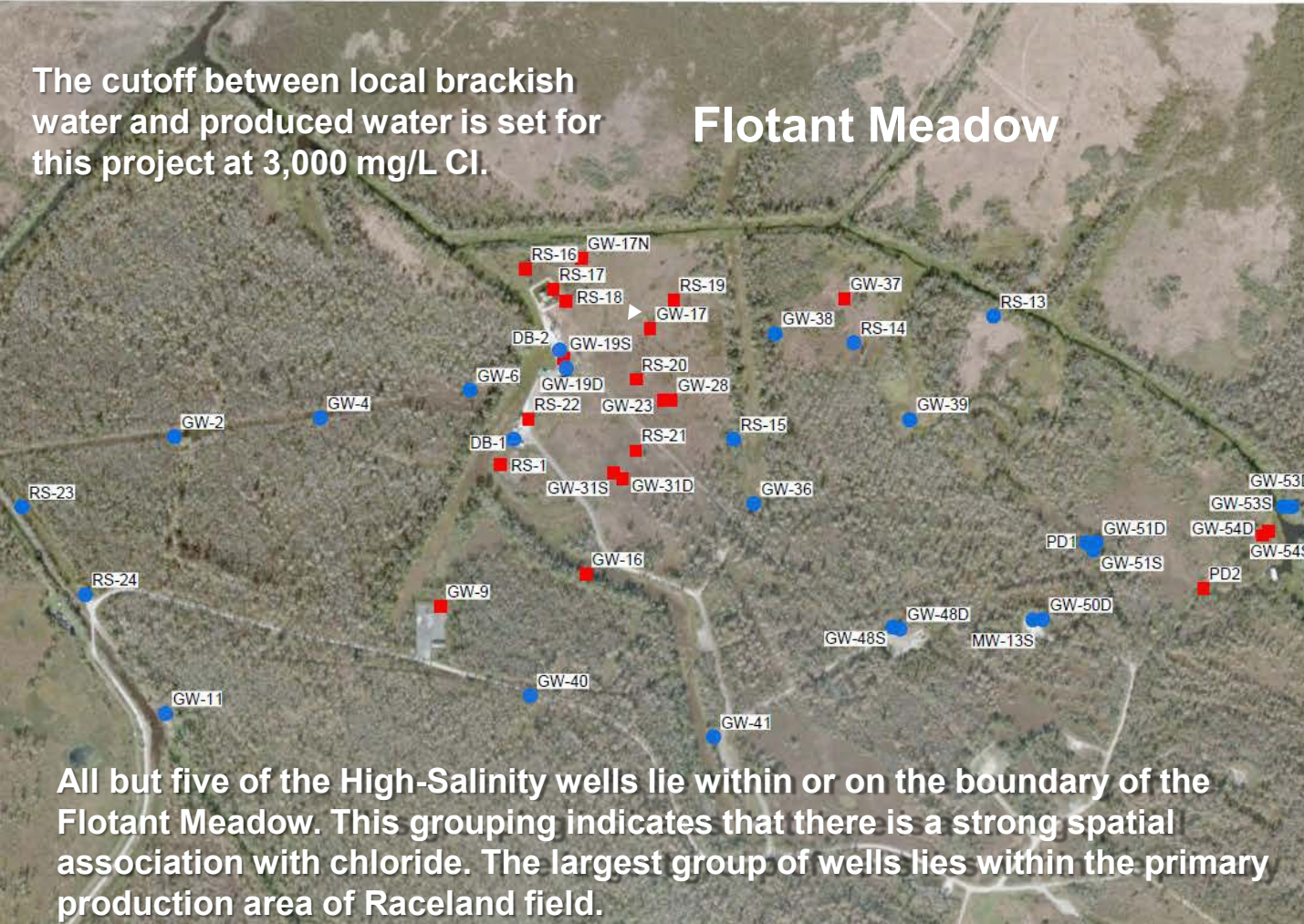
Notes:

1. Data shown are taken from the Conestoga-Rovers & Associates (CRA) database, accessed electronically on 16 March 2015, or provided directly to Geosyntec by Pace Analytical, Isotech Laboratories Inc. (Isotech), and Isotope Tracer Technologies Inc. (IT2).
2. Values for chloride and sodium represent the average concentration based on multiple analytical results, when available.
3. Constituent concentrations for Seawater are provided in Table 2, Composition of Seawater (Hem, 1985).

Wells Representative of High-Salinity Groundwater and Local Brackish Groundwater, Raceland Field, Lafourche Parish

The cutoff between local brackish water and produced water is set for this project at 3,000 mg/L Cl.

Flotant Meadow



LEGEND

- GW-37 HIGH SALINITY GROUNDWATER
- RS-14 LOCAL BRACKISH WATER

NOTES:

1. SATELLITE IMAGERY OBTAINED THRU ESRI ARCGIS ONLINE, WORLD IMAGERY PROGRAM, 2012.
2. EXISTING ICON SOIL BORING WITH WELL LOCATIONS BASED ON COORDINATES PROVIDED IN EXPERT OPINION REPORT (ICON, 2014).

All but five of the High-Salinity wells lie within or on the boundary of the Flotant Meadow. This grouping indicates that there is a strong spatial association with chloride. The largest group of wells lies within the primary production area of Raceland field.

Chloride and Bromide

Periodic Table

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

○ Non Metals ● Noble Gases
● Alkali Metals ● Metalloids
● Alkaline Metals ● Halogens
● Transition Metals ● Other Metals
● Rare Earth Elements

Chlorine (atomic number, 17) and Bromine (atomic number, 35) are members of the Halide Group of elements (Group 17).

The concentration of Cl in seawater is ~19,000 mg/L (536 mMol/L).

The concentration of Br in seawater is ~67 mg/L (0.84 mMols/L)

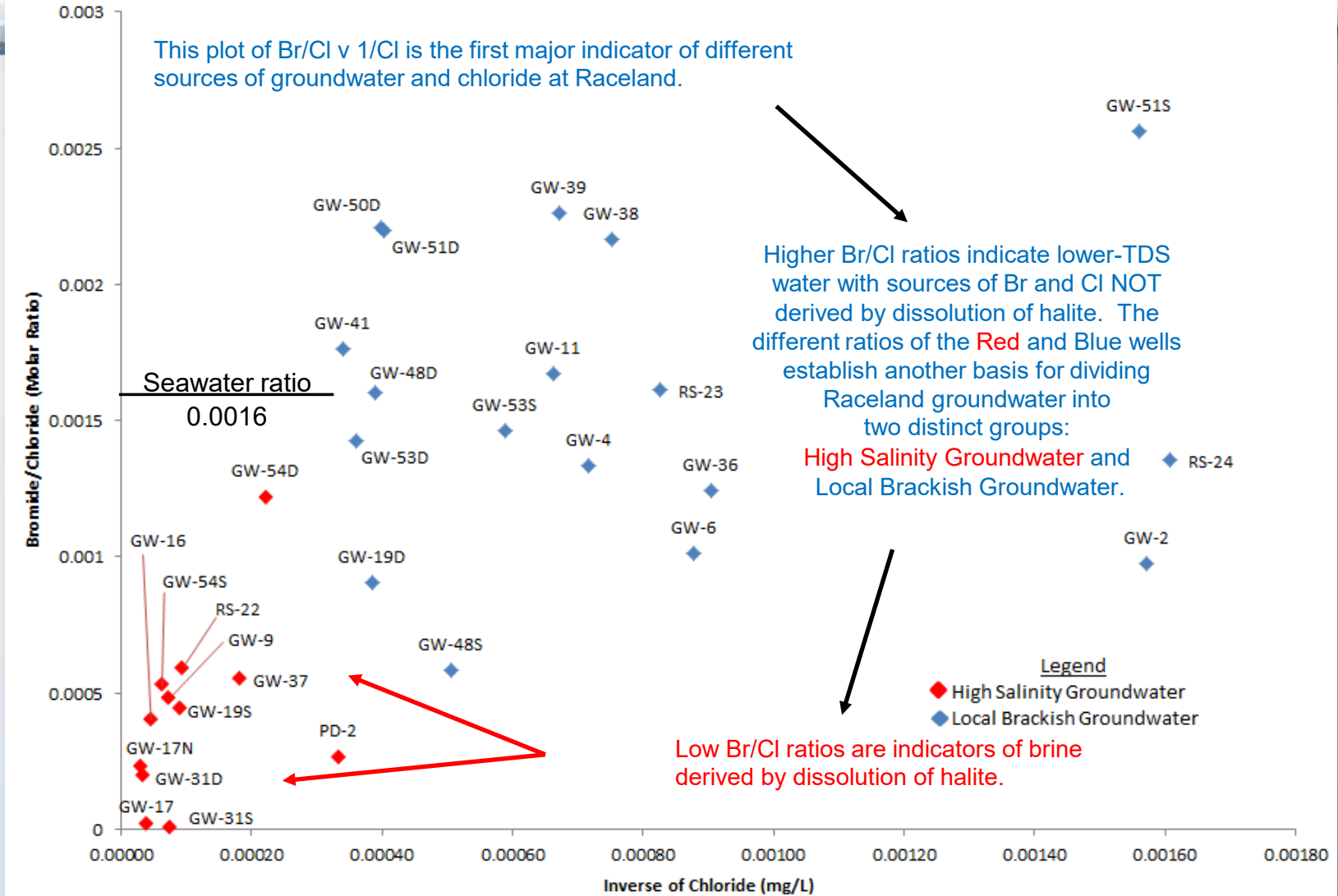
The Br/Cl ratio is used to identify sources of brine in groundwater.

*Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
**Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Bromide-Chloride Systematics

- Br and Cl are important dissolved components of seawater.
- The molar ratio of Br to Cl in seawater is ~ 0.0016 .
- The Br ion is larger than the Cl ion.
- Because of its larger size, Br is not easily incorporated into halite crystals when salt precipitates from highly concentrated brines.
- Because Br remains in solution while halite precipitates, halite contains negligible Br.
- Water that dissolves halite will have Br-to-Cl ratios much lower than the ratio in seawater (0.0016).
- Residual brine, that is, the brine that remains after precipitation of halite, will have a higher Br-to-Cl ratio than seawater.
- Br-to-Cl ratios in rainwater are similar to the ratio in seawater.

Identifying Brine from Halite Dissolution



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2. Values for chloride and bromide represent the average concentration based on multiple analytical results, when available.
3. Bromide was reported as not detected in GW-31S. The value is shown here as one half of the Method Detection Limit.

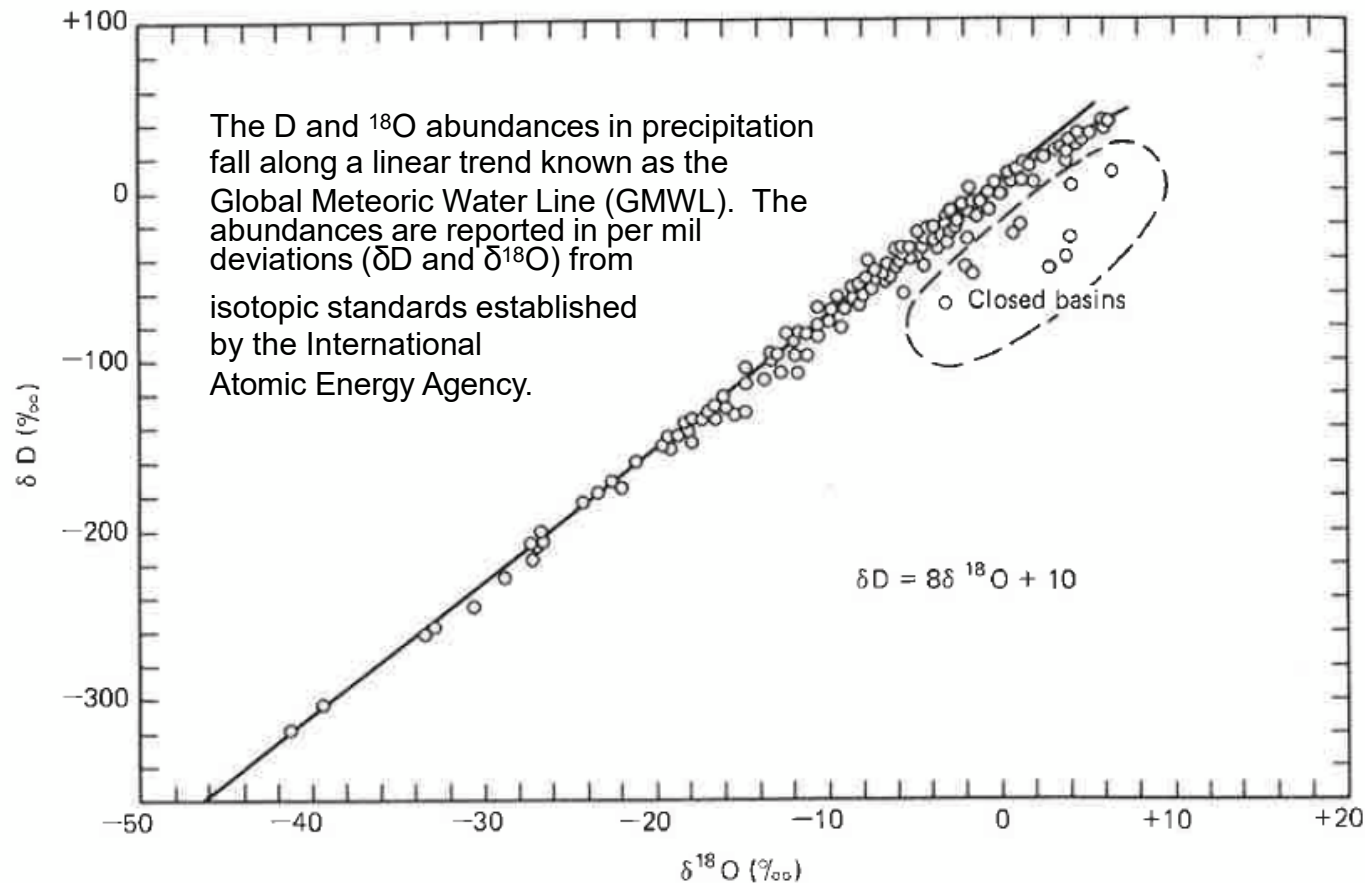


Figure 17-1 Deuterium and ^{18}O variations in rivers, lakes, rain, and snow. (Craig, 1961. Copyright 1961 by the American Association of Science.)

$\delta^{18}\text{O}$ in Global Precipitation

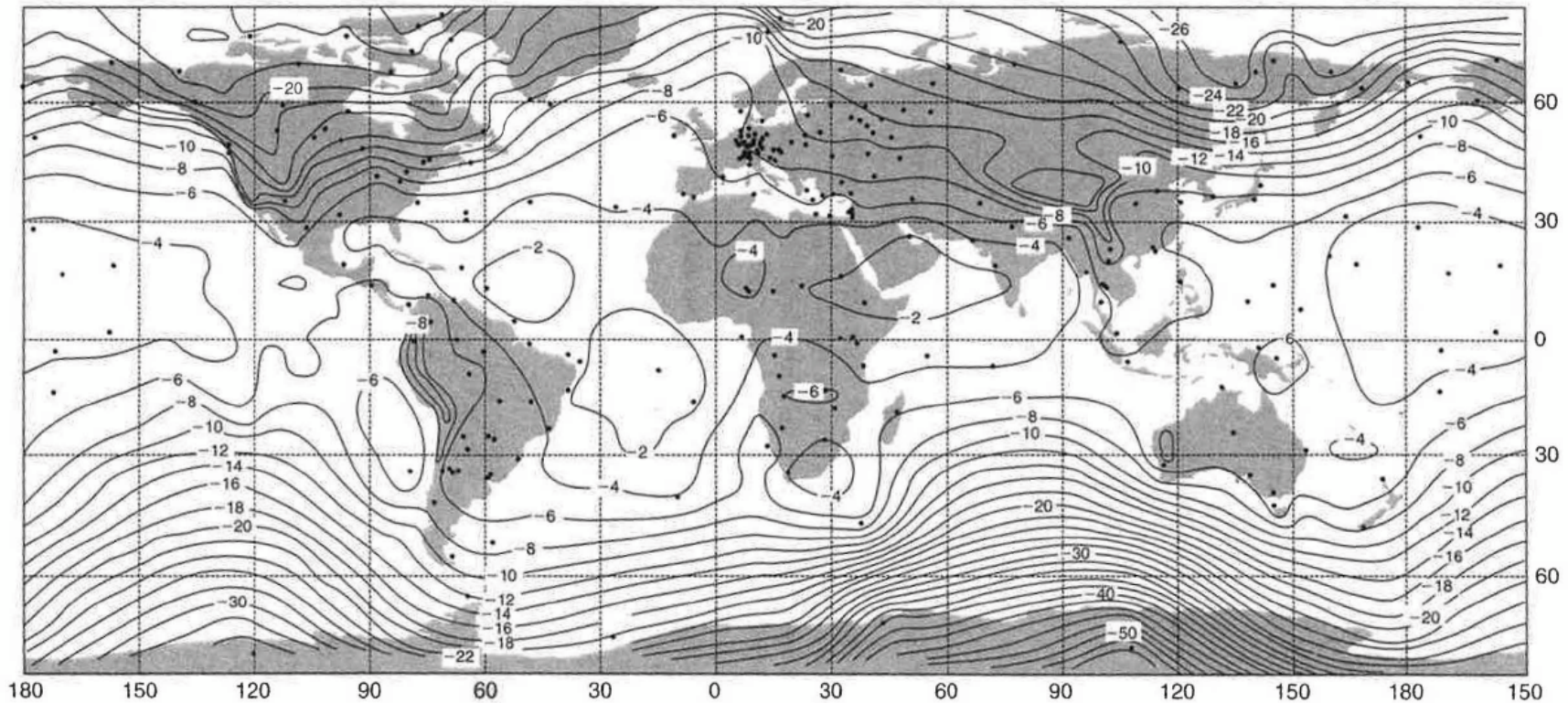


Figure 2.13. The global picture of $\delta^{18}\text{O}$ in precipitation (Clark and Fritz, 1997).

Precipitation becomes more depleted in D and ^{18}O with greater distances north and south of the equator. In the figure above, this is illustrated by increasingly negative $\delta^{18}\text{O}$ values at higher latitudes in the northern and southern hemispheres.

δD and $\delta^{18}O$ in North American Precipitation

North American precipitation becomes increasingly depleted with respect to D and ^{18}O with increasing distance from coastal areas.

The depletion is caused primarily by the “rainout” effect (known as Rayleigh distillation) as moisture-laden air masses move inland from coastlines.

Depletion occurs because the heavier D and ^{18}O isotopes are “rained out” in preference to the lighter ^1H and ^{16}O isotopes of hydrogen and oxygen. As this happens, the amount of D and ^{18}O in precipitation decreases.

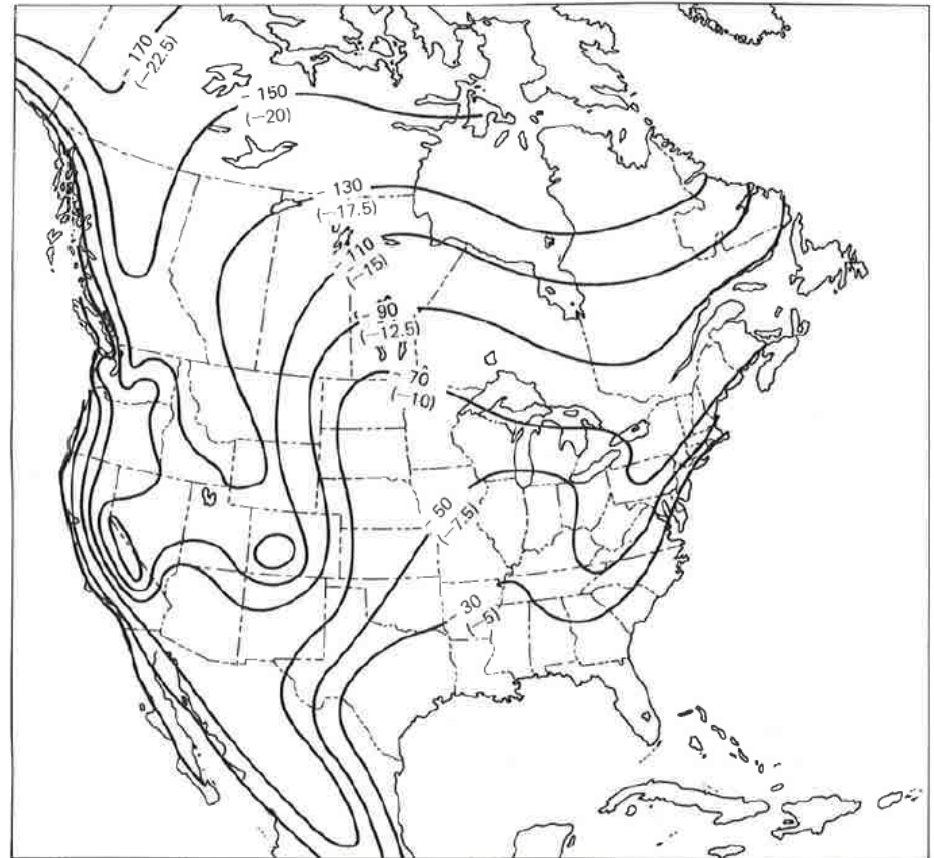
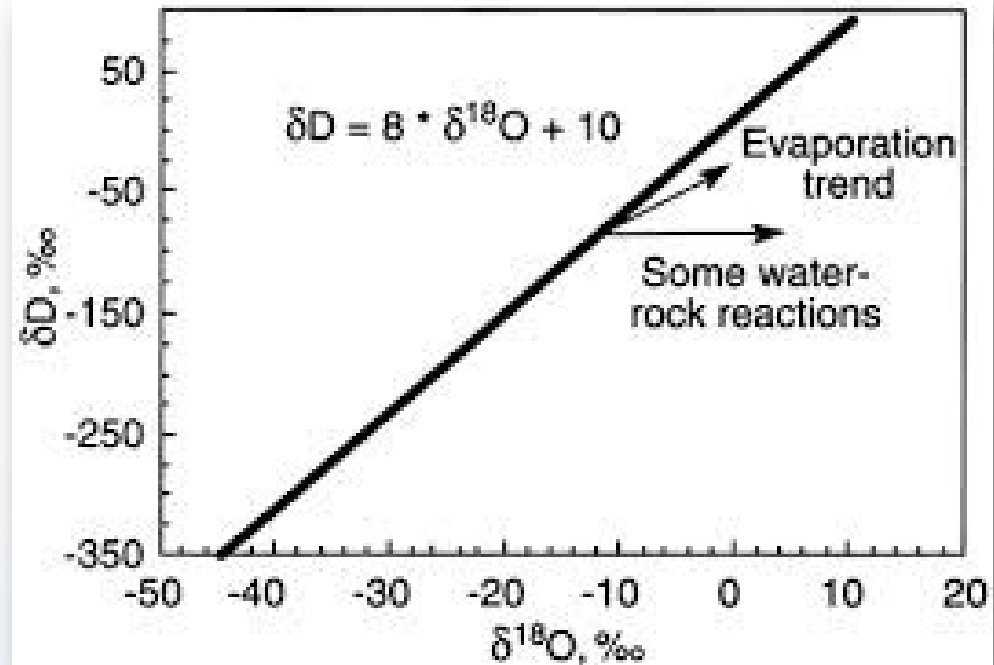


Figure 17-2 Distribution of δD and corresponding $\delta^{18}O$ (in parentheses) in meteoric waters in North America (adapted from Sheppard et al., 1969).

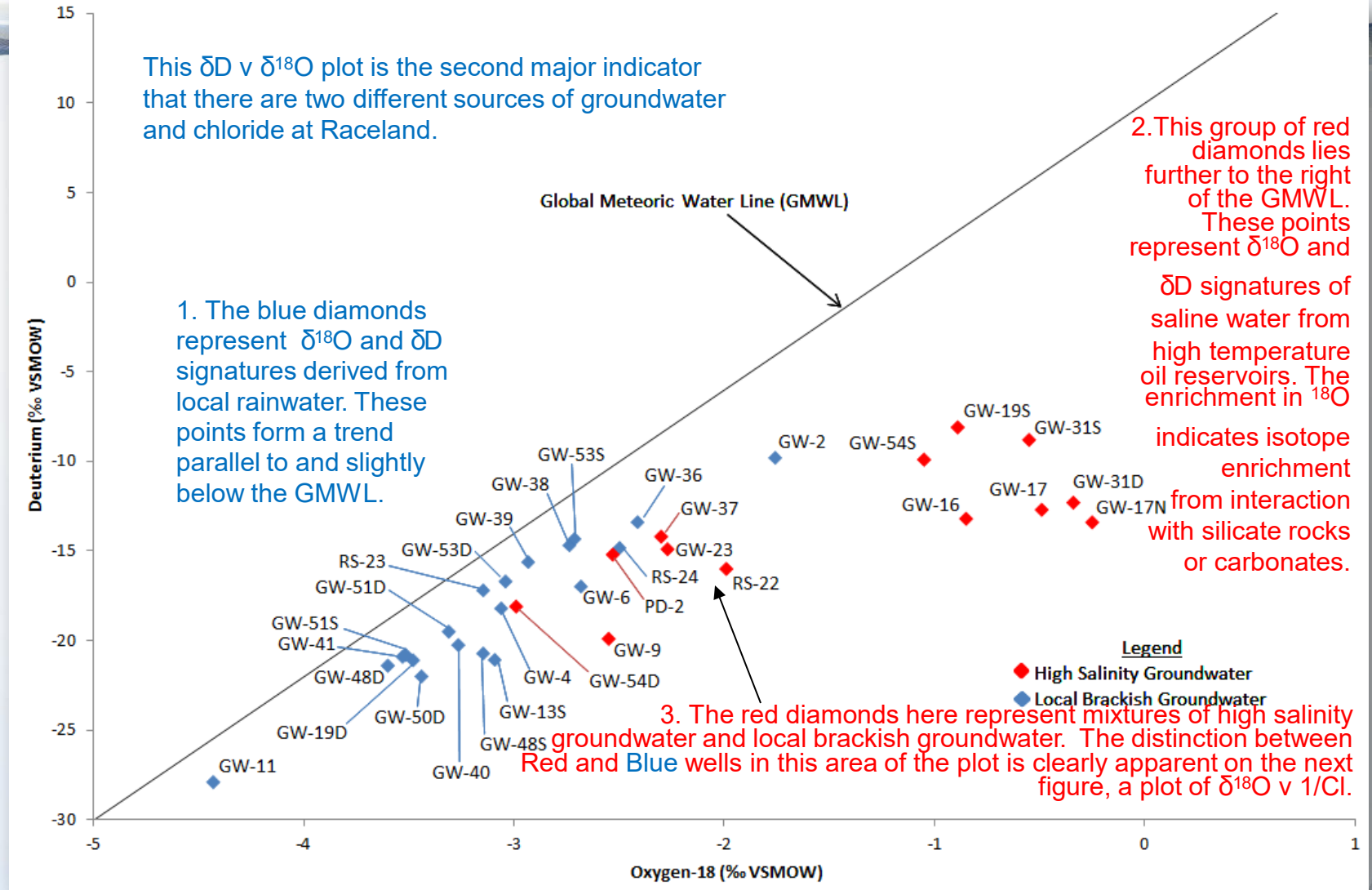
Evaporation and Water-Rock Interactions

Evaporation causes water to become enriched in D and ^{18}O because the process removes the lighter and more abundant ^1H and ^{16}O fractions from water. This causes the δD and $\delta^{18}\text{O}$ signatures of water to shift upward and to the right from the GMWL.

In many high-temperature subsurface environments, water becomes enriched in ^{18}O through interaction with carbonate rocks and silicate rocks. As a result of such exchange, the δD and $\delta^{18}\text{O}$ signatures will plot along horizontal lines to the right of the GMWL. This is typical of produced waters. We see this in the highly saline groundwater of the Raceland field.



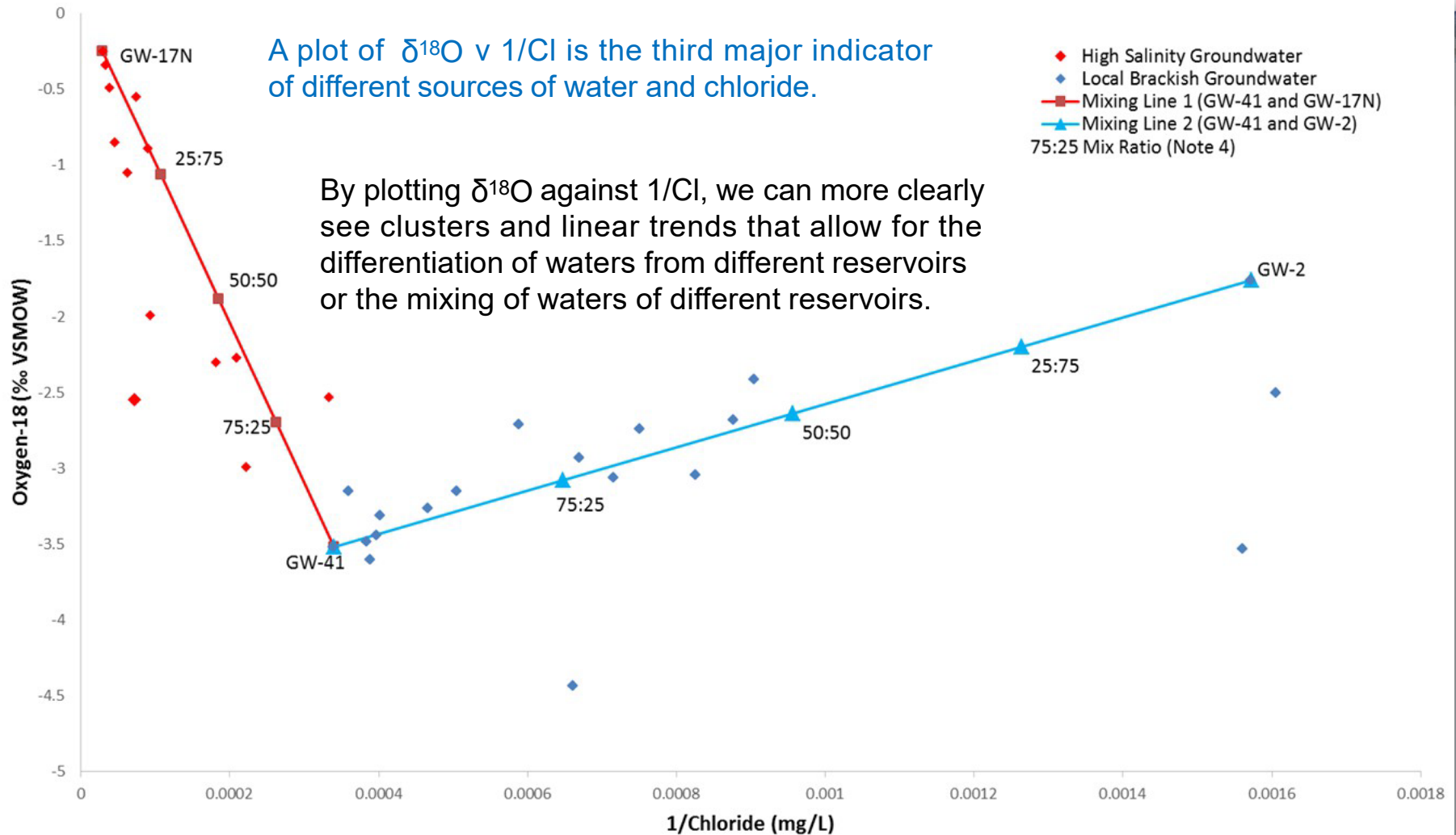
δD and $\delta^{18}O$ of Groundwater at Raceland Field



Not
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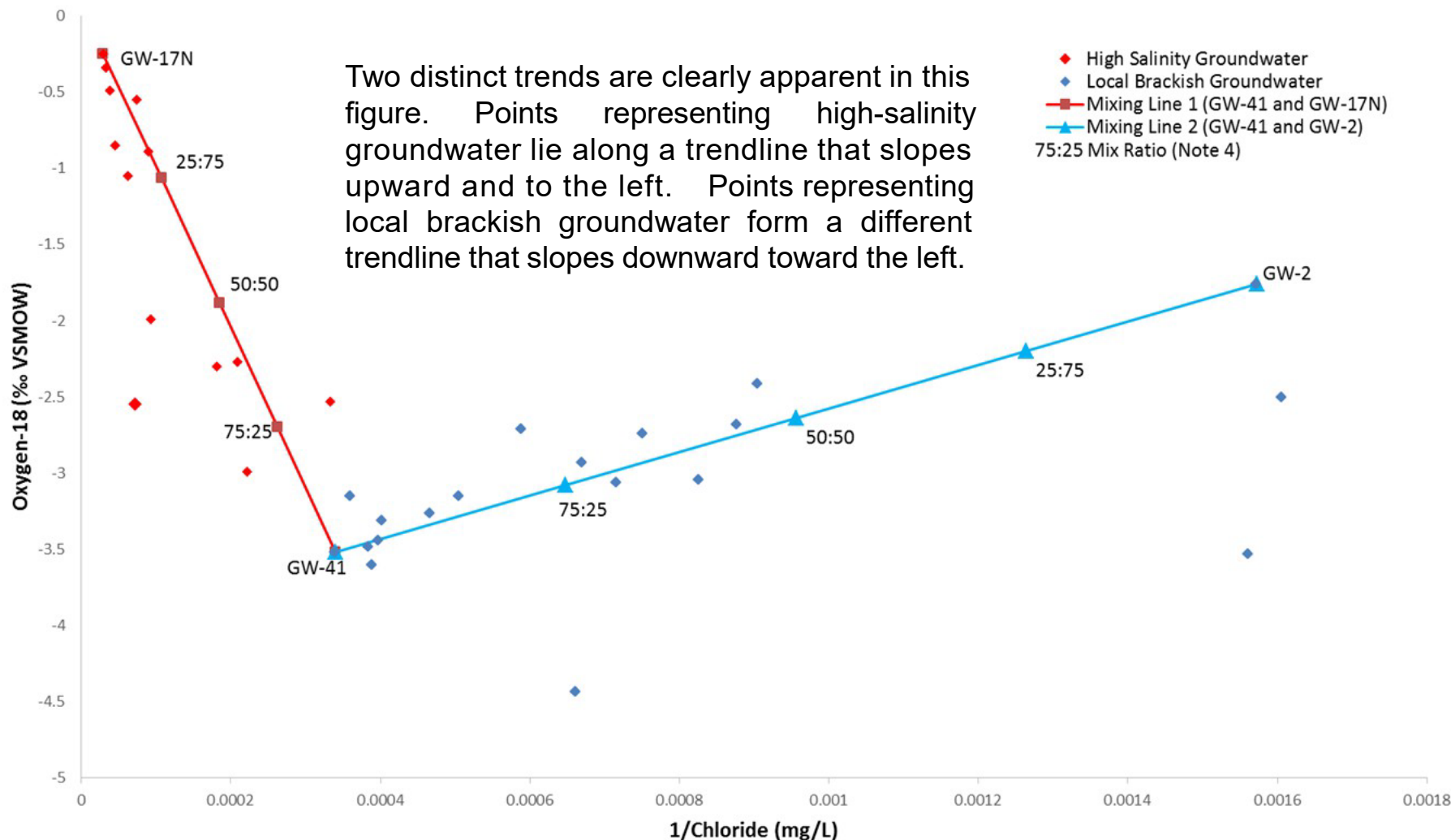
to Geosyntec by Pace Analytical, Isotech Laboratories Inc. (Isotech), and Isotope Tracer Technologies Inc. (IT2).

2. Values for deuterium and oxygen-18 represent the average concentration based on multiple analytical results, when available.



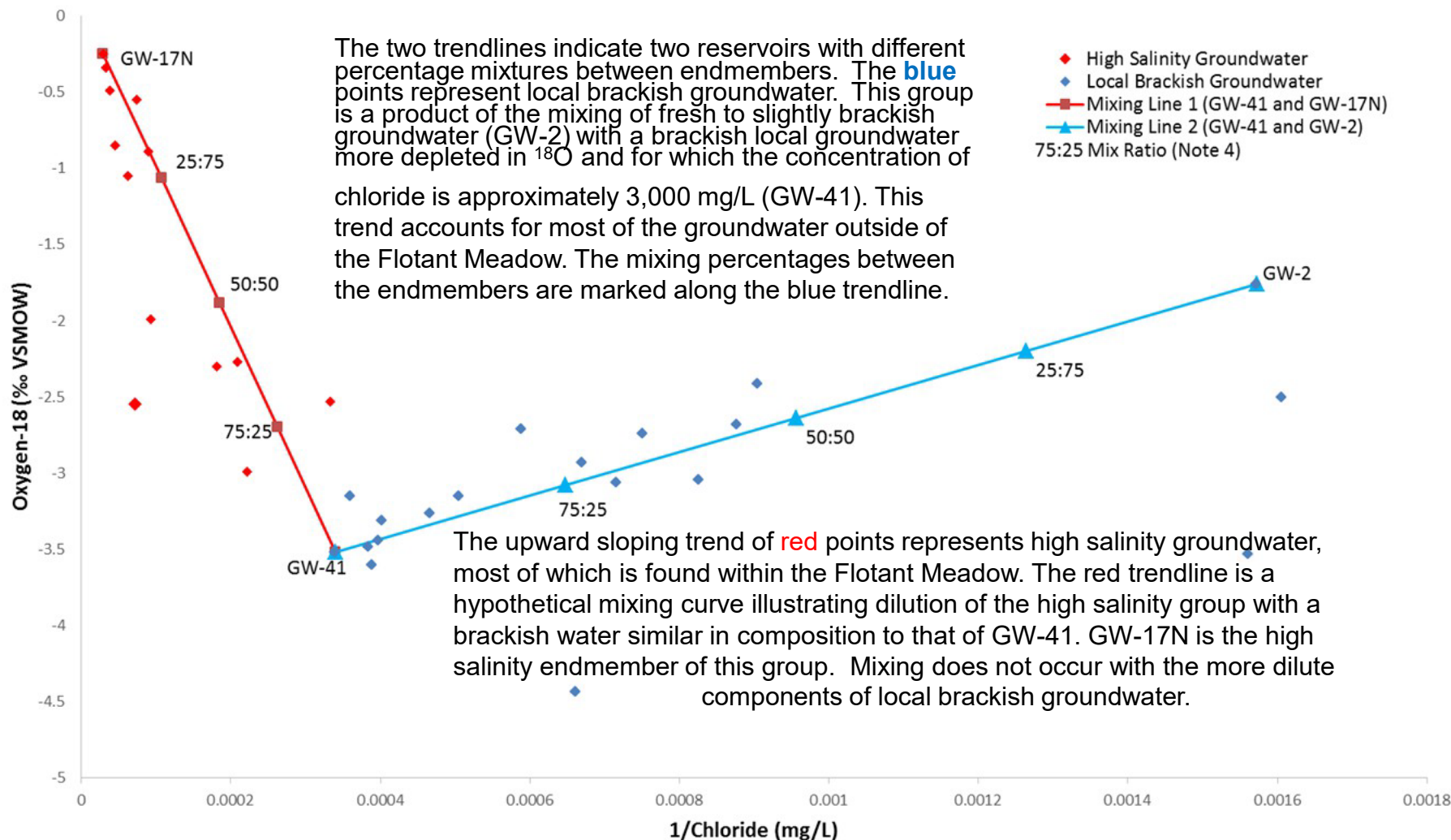
Notes:

1. Data shown is taken from the Conestoga-Rovers & Associates (CRA) database, accessed electronically on 16 March 2015, and provided by Isotech Laboratories Inc. (Isotech).
2. Values for chloride (Cl) and oxygen-18 (O-18) represent the average concentration based on multiple analytical results, when available.
3. mg/L indicates milligrams per liter and ‰ VSMOW indicates Permil Vienna Standard Mean Ocean Water.
4. In the mix ratios, the first number refers to the percentage of GW-41 constituents present in the mixture, and the second number refers to the percentage of constituents from the other well (GW-17N or GW-2).



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Strontium (Sr, atomic number 38) is a member of the Alkaline Earth group of elements (Group 2).

There are four naturally occurring stable isotopes of Sr: ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr .

There are two components of ^{87}Sr : (1) Primordial ^{87}Sr that formed along with the other stable isotopes of Sr 4.5 billion years before present time, and (2) ^{87}Sr formed over geologic time by the radioactive decay of rubidium-87 (^{87}Rb , Group 1, atomic number 37).

It is the “radiogenic” component of ^{87}Sr that is of special significance here, because the production of ^{87}Sr has varied over Earth’s history as tectonism has alternately increased and decreased over hundreds of millions of years.

The ratio of ^{87}Sr to ^{86}Sr in water ($^{87}\text{Sr}/^{86}\text{Sr}$) varies in response to the age of the rocks with which water has been in contact. This ratio is a powerful isotopic tracer of brines and of produced waters from deeply buried oil and gas reservoirs.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Raceland groundwater clearly reveal marked differences in the ratios of produced water and the ratios of local brackish water.

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5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

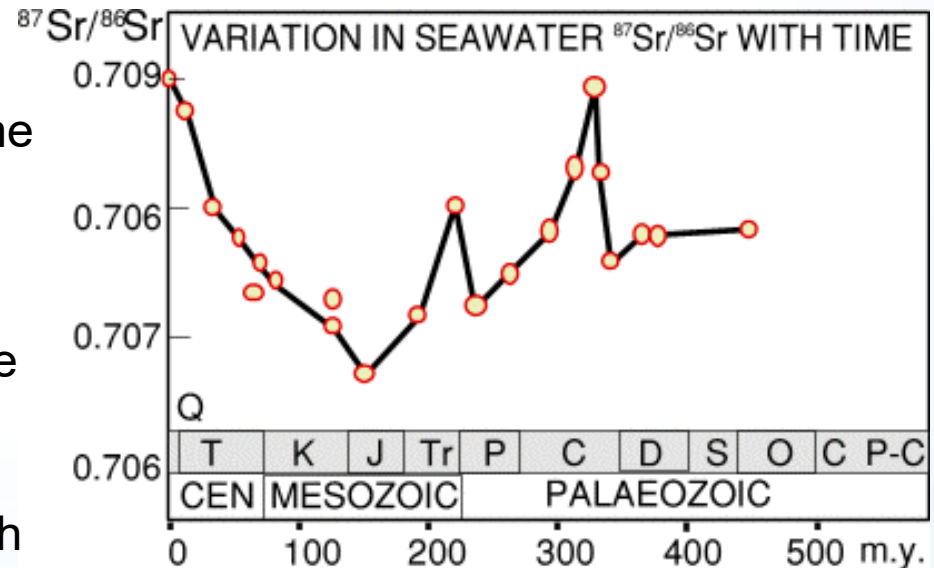
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**Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

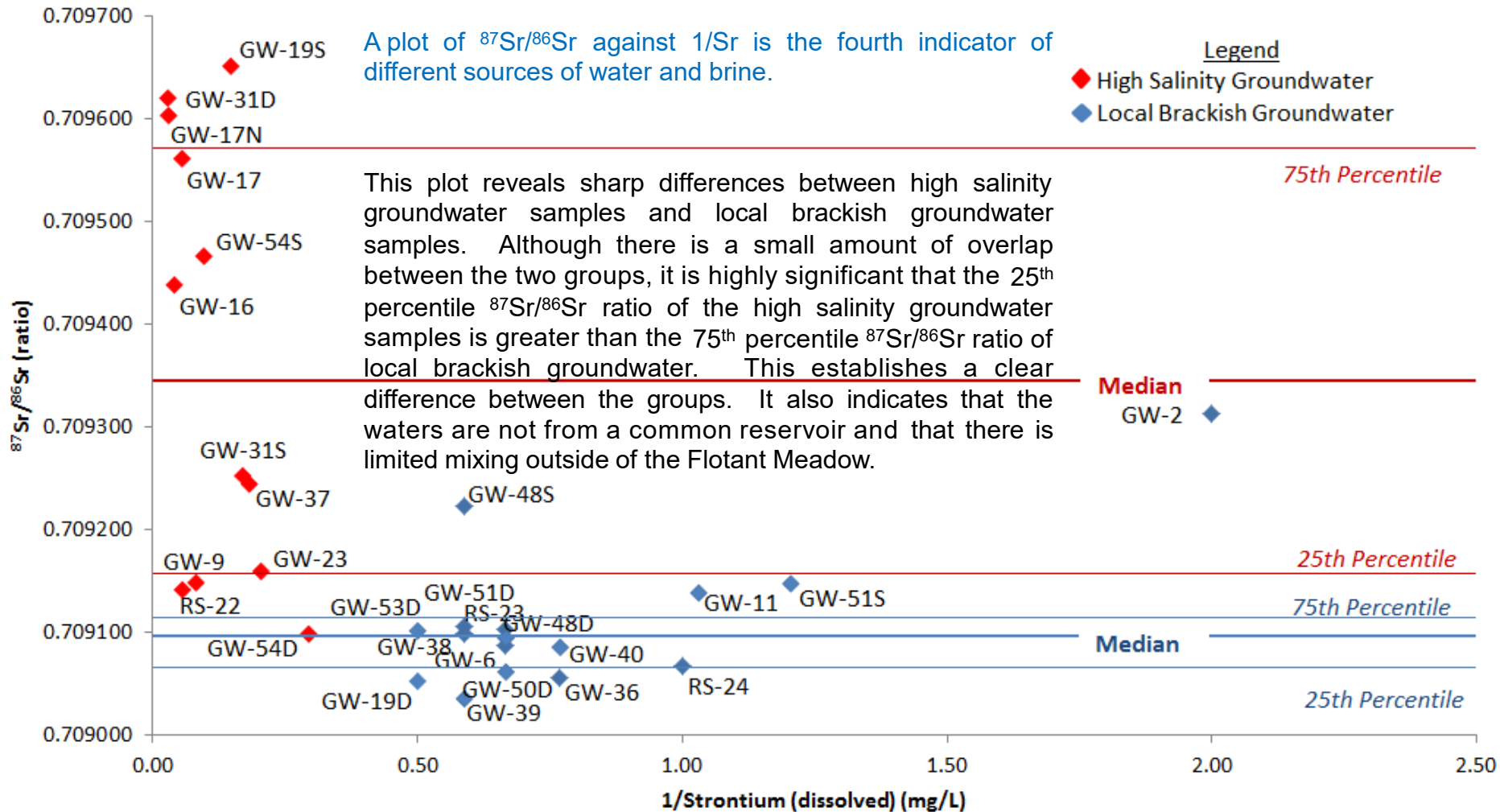
The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in seawater has varied over the last 500 million years (Phanerozoic Era), as shown by the figure on the right.

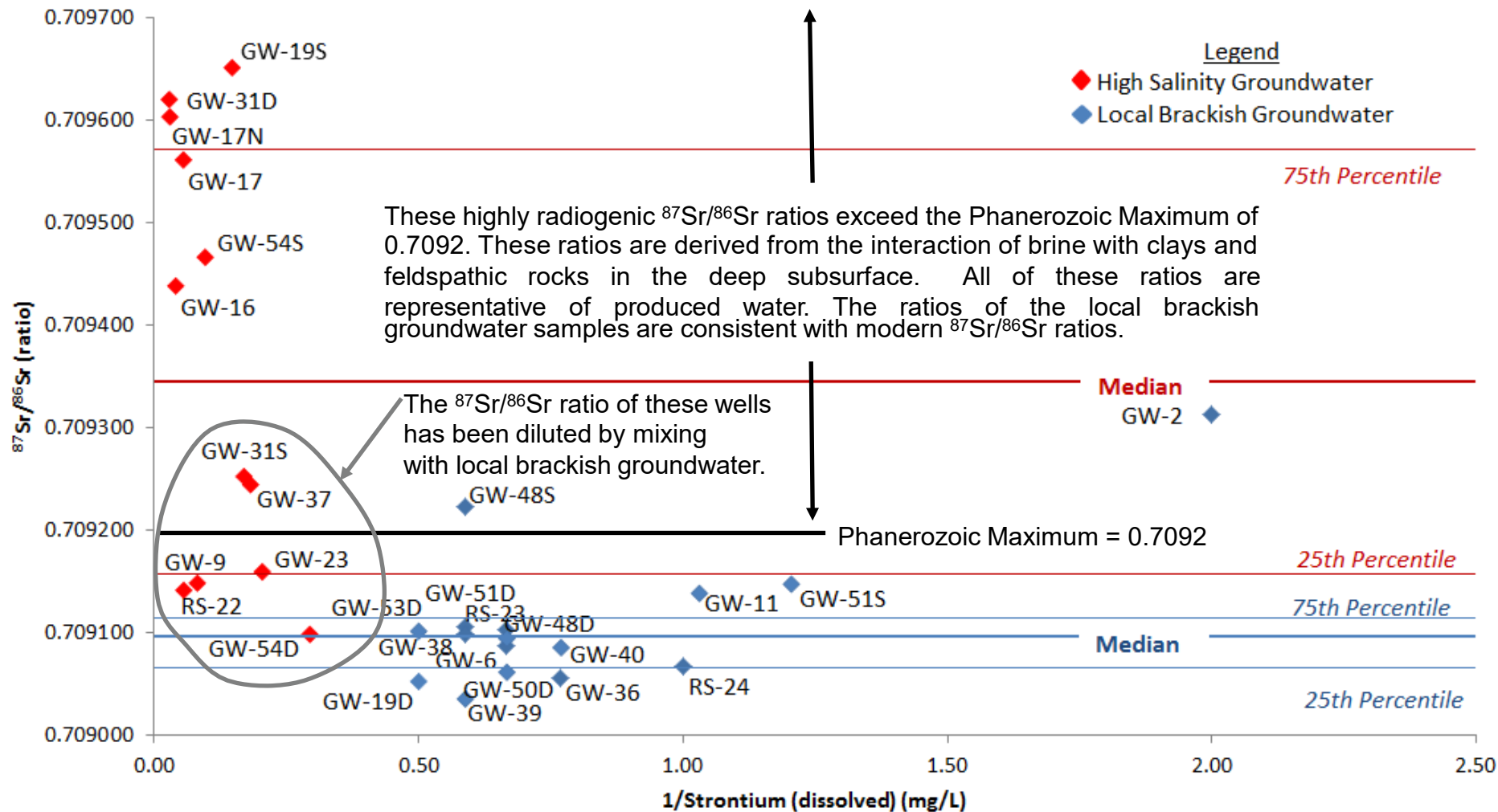
The maximum ratio over this period of time has been 0.7092. This is known as the Phanerozoic Maximum.

Modern ratios in seawater are close to the Phanerozoic Maximum.

Groundwater that has been in contact with rocks rich in ^{87}Rb and radiogenic ^{87}Sr often have $^{87}\text{Sr}/^{86}\text{Sr}$ signatures greater than the Phanerozoic Maximum. This is common among many produced waters, and this is what we see in the highly saline groundwater at Raceland.







- Raceland groundwater can be divided into two groups, based on Cl concentrations:
 - High salinity groundwater
 - Local brackish groundwater
- The highest Cl concentrations are found in the Flotant Meadow. Outside of the Flotant Meadow, high Cl concentrations are found at discrete locations between broad areas where local brackish water predominates.
- The division into the two groups described above is further supported by sharp differences in Br/Cl molar ratios which, for the high salinity samples, are very low and consistent with brine derived from the dissolution of halite.

- δD and $\delta^{18}O$ data indicate that local brackish groundwater plots parallel to and slightly below the GMWL.
- Local brackish water is derived from precipitation.
- Most high salinity samples plot to the right of the GMWL in a location that indicates enrichment in ^{18}O through interaction with carbonates or silicates in deeply buried reservoirs. This is produced water.
- A few high salinity samples outside of the Flotant Meadow plot near local brackish water samples.
- A plot of $\delta^{18}O$ v $1/Cl$ reveals two distinct trendlines:
 - A high salinity trendline, and
 - A local brackish water trendline.

- The two trendlines indicate different sources of water with different sources of chloride.
- The local brackish groundwater trendline indicates mixing between a low-TDS endmember (GW-2) and a higher-TDS but still brackish endmember (GW-41) that is more depleted in ^{18}O .
- The high salinity groundwater trendline is consistent with mixing between a high salinity endmember similar to GW-17N and brackish endmember such as GW-41.
- There is no apparent mixing with the more dilute components of local brackish groundwater.
- Most of the high salinity groundwater is located within the boundaries of the Flotant Meadow.
- There is limited mixing of high salinity groundwater and local brackish groundwater outside of the Flotant Meadow.

- $^{87}\text{Sr}/^{86}\text{Sr}$ ratios also divide Raceland groundwater samples into two groups, with different medians and interquartile ratios.
- The ratios of the high salinity samples indicate a highly radiogenic source of Sr from deeply buried rocks. These ratios are typically greater than the Phanerozoic Maximum of $^{87}\text{Sr}/^{86}\text{Sr}$.
- The ratios of the local brackish water samples are below the Phanerozoic Maximum but within the range of ratios characteristic of modern seawater.
- The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios indicate that produced water is limited primarily to the Flotant Meadow. There is limited interaction between produced water and local brackish water beyond the boundaries of the Flotant Meadow.

- The stable isotope data and the inorganic analytes Br, Cl and Sr establish a firm basis for the following conclusions:
 - There are two groundwater sources at Raceland:
 - High salinity (produced) groundwater, and
 - Local brackish groundwater
 - The signatures of the produced water samples are consistent with groundwater from high-temperature oil and gas reservoirs.
 - The local brackish waters are of meteoric origin.
 - Most of the high salinity groundwater is within the boundaries of the Flotant Meadow.
 - There is limited interaction between high salinity (produced) water and local brackish water beyond the boundaries of the Flotant Meadow.

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