

PS Measured Water Saturations in Mudstones: Preliminary Evidence for the Introduction of Water Through Drilling and Completion Practices*

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Abstract

Gas-in-place (GIP) models play a critical role in the assessment and valuation of unconventional reservoirs, the quantification of recovered hydrocarbon, completion stimulation, and production modeling. Integral to these models is an accurate quantification of hydrocarbon and water saturations within pores. Standard Gas Research Institute (GRI)-based shale core analysis involves determination of the *in situ* fluid saturations by measuring the amount of water and oil extracted from the sample, often via the Dean Stark method. Reported core water saturations for the Marcellus Shale in southwestern Pennsylvania and northern West Virginia average approximately 30% of the pore volume. However, calculations of cation exchange capacity (CEC) demonstrate that the clays in the reservoir are under-saturated (often >75% desiccated) with respect to water, indicating the clays would absorb water, a phenomenon commonly observed when spraying water on the core surface. Furthermore, the full load of water pumped during completions is rarely captured during the flowback, suggesting its possible uptake by the formation.

In order to understand the nature of water/rock interactions in the Marcellus Shale, several field and lab experiments were conducted on core. Wax-preserved full diameter core were extracted using a Dean Stark apparatus and the fluids were analyzed for oxygen and deuterium isotopes. When these data points are plotted on a $\delta^{18}\text{O}$ and $\delta^2\text{H}$ plot, they follow an evaporation trend that originates at the isotopic signature of the surface waters used in the drilling mud. The same trends can be seen by plotting flowback water isotopes with time. These observations would suggest that some portion of the water extracted during GRI shale core analysis is an artifact of the drilling process and not *in situ*, yielding an underestimation of gas-filled porosity and resultant calculated GIP.

Finally, the fractionation of oxygen and deuterium isotopes may be impacted by present day reservoir temperature, permeability, porosity, clay content, and thermal maturity history, or a combination of these factors. On-going studies are focused on understanding how these factors alter the isotopic signature of the waters extracted from core and during flowback.

Measured Water Saturations in Mudstones: Preliminary Evidence for the Introduction of Water Through Drilling and Completion Practices

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Abstract

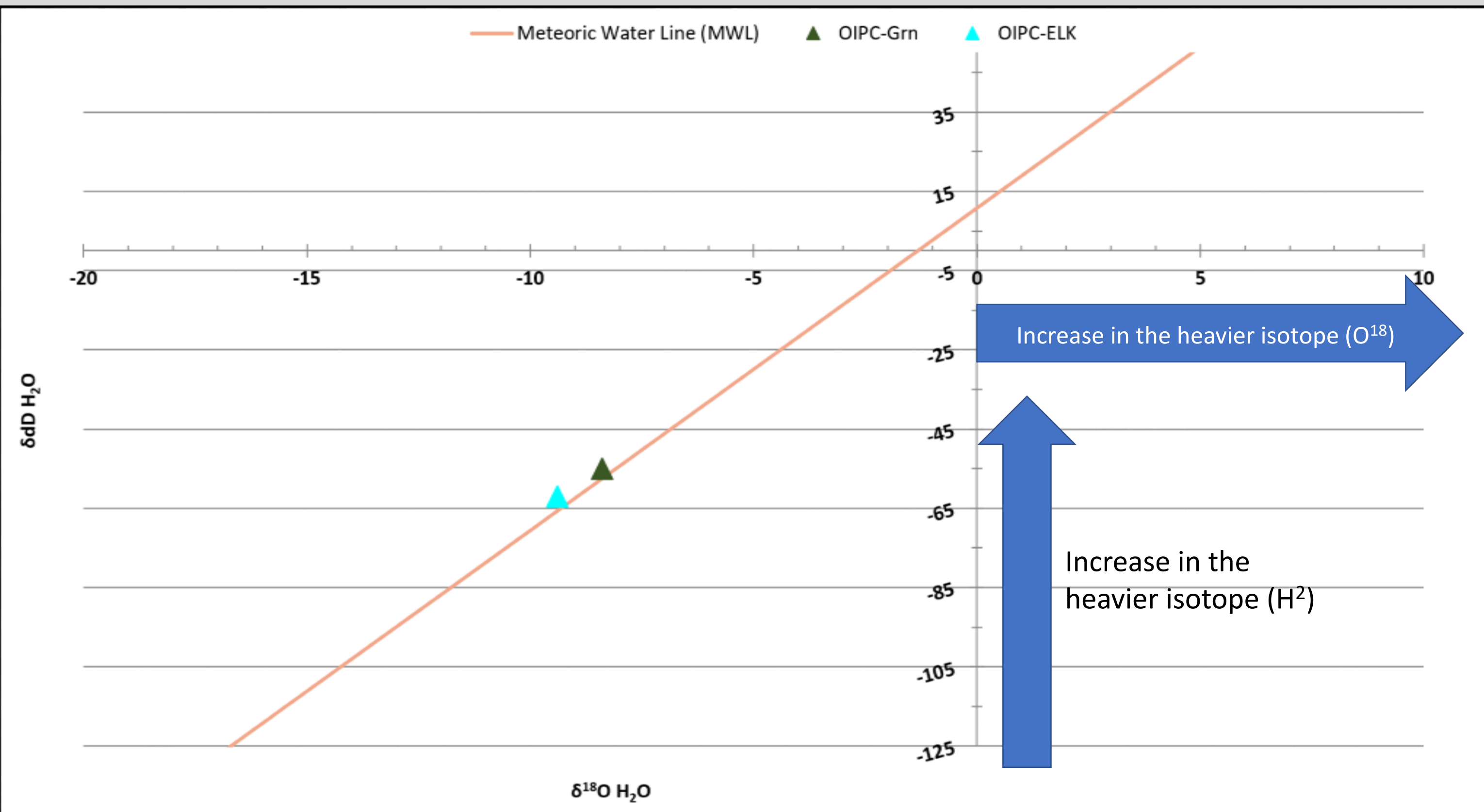
Gas-in-place (GIP) models play a critical role in the assessment and valuation of unconventional reservoirs, the quantification of recovered hydrocarbon, completion stimulation, and production modeling. Integral to these models is an accurate quantification of hydrocarbon and water saturations within pores. Standard Gas Research Institute (GRI)-based shale core analysis involves determination of the in situ fluid saturations by measuring the amount of water and oil extracted from the sample, often via the Dean Stark method. Reported core water saturations for the Marcellus Shale in southwestern Pennsylvania and northern West Virginia average approximately 30% of the pore volume. However, calculations of cation exchange capacity (CEC) demonstrate that the clays in the reservoir are under-saturated (often >75% desiccated) with respect to water, indicating the clays would absorb water, a phenomenon commonly observed when spraying water on the core surface. Furthermore, the full load of water pumped during completions is rarely captured during the flowback, suggesting the uptake of completion fluid by the formation.

In order to understand the nature of water/rock interactions in the Marcellus Shale, several field and lab experiments were conducted on core. Wax preserved full diameter core were extracted using a Dean Stark apparatus and the fluids were analyzed for oxygen and deuterium isotopes. When these data points are plotted on a $\delta^{18}\text{O}$ and $\delta^2\text{H}$ plot, they follow an evaporation trend that originates at the isotopic signature of the surface waters used in the drilling mud and completion fluids. The same trends can be seen by plotting flowback water isotopes with time. These observations would suggest that some portion of the water extracted during GRI shale core analysis is an artifact of the drilling process and not in situ, yielding an underestimation of gas-filled porosity and resultant calculated GIP. Finally, the fractionation of oxygen and deuterium isotopes may be impacted by present day reservoir temperature, permeability, porosity, clay content, and thermal maturity history, or a combination of these factors. On-going studies are focused on understanding how these factors alter the isotopic signature of the waters extracted from core during flowback.

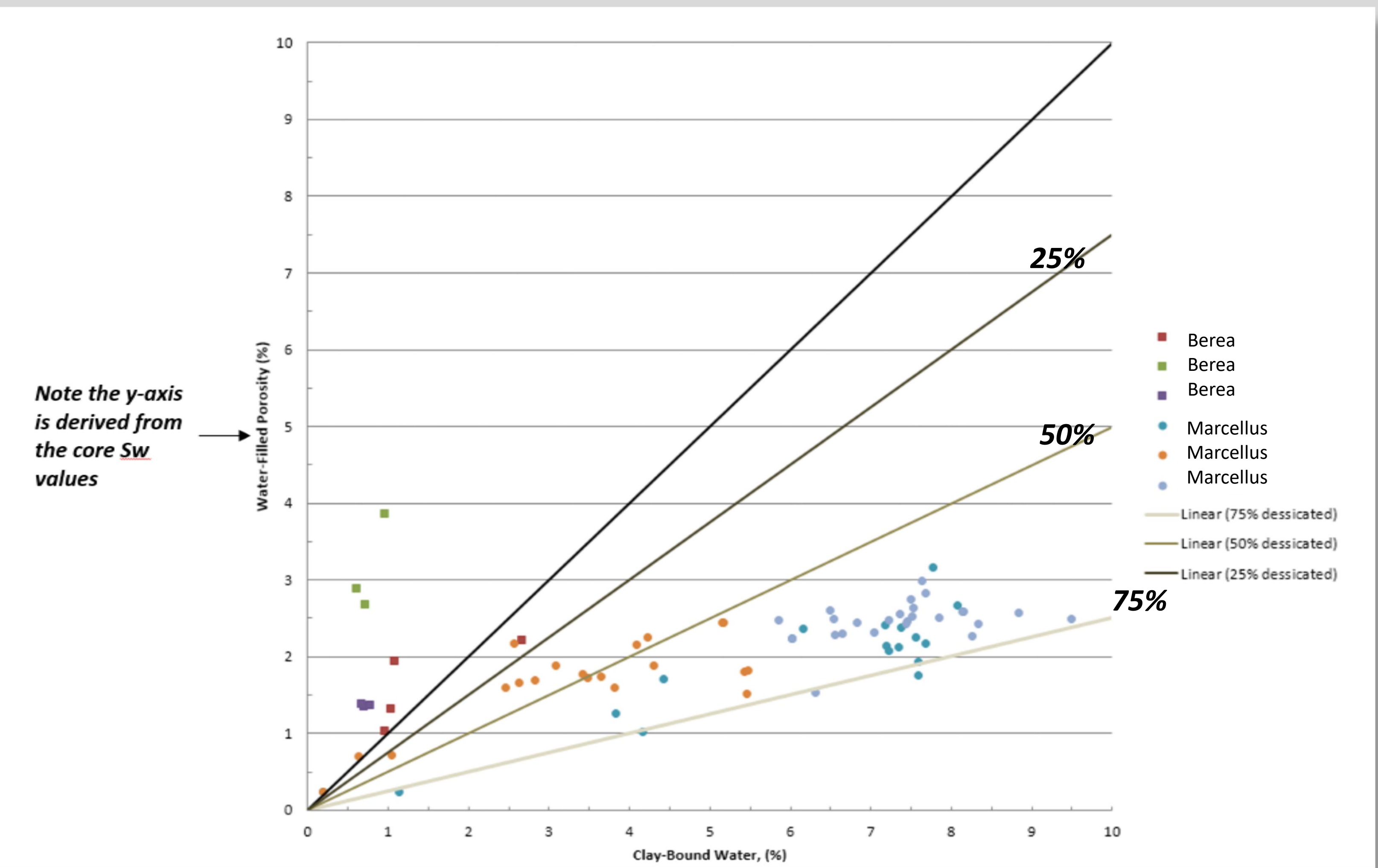
Range of Dean Stark derived values for the Marcellus in SW PA and northern WV

	Sw	So	Sg	Φg
	(% of pore volume)			(% of bulk volume)
No. of datapoints	29	27	30	52
Minimum	14.5	0	35	1
Maximum	61	26	83	8
Average	31	4	66	4.6
Median	28	1	68	5

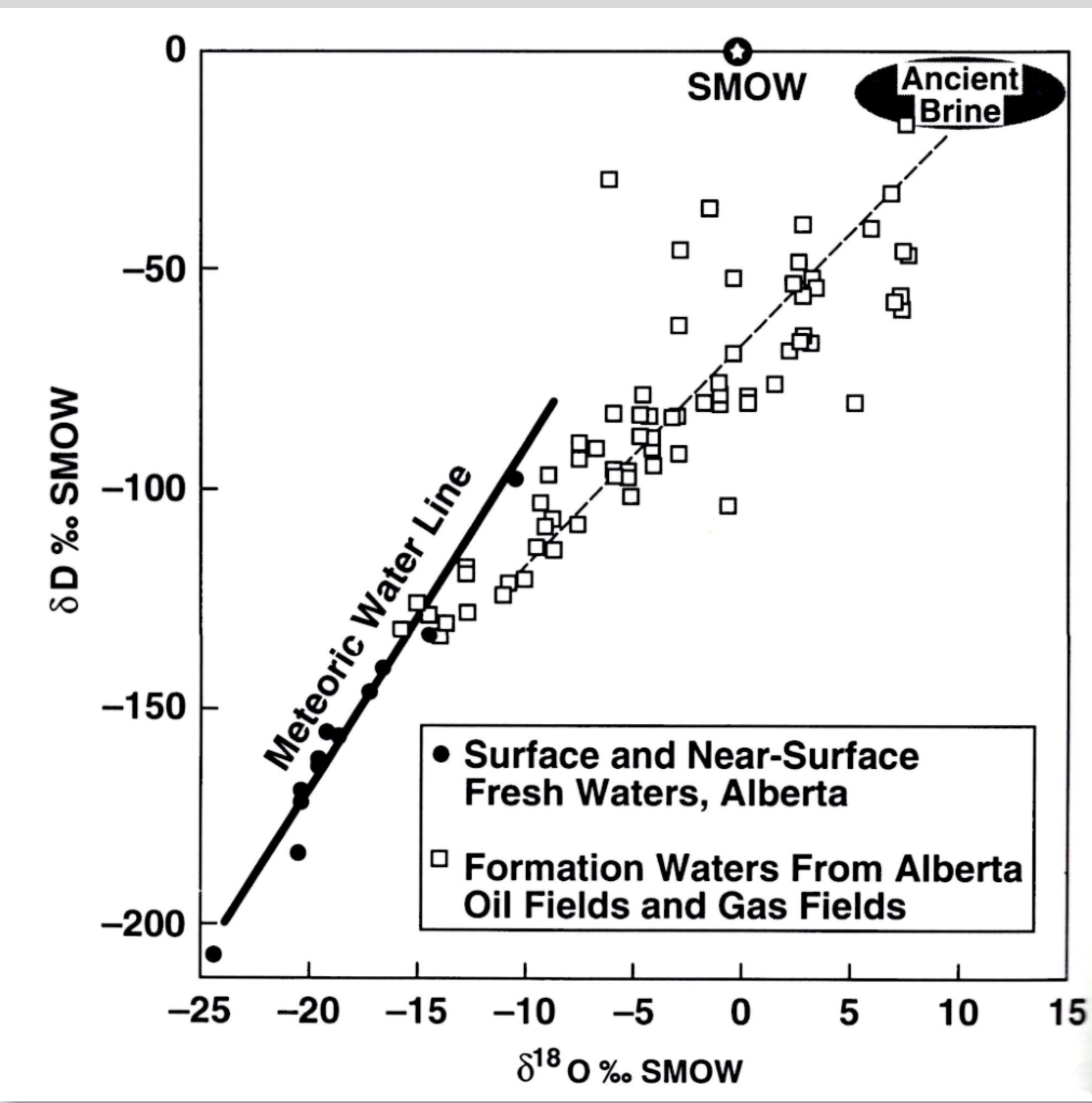
Most of the productive areas of the Marcellus fall in the $Sw \leq 30\%$. Areas that have been structurally compromised fall on the higher end, $Sw \geq 50\%$. The reported Sw values are used to reduce the GIP in these shales.



Surface waters plot along the Meteoric Water Line (MWL). The plot location depends on factors including latitude, longitude, altitude, and climate. As data points trend away from the MWL, the water is evaporating. The slope of the evaporation trend is dependent on the amount of humidity the water has been subjected to.



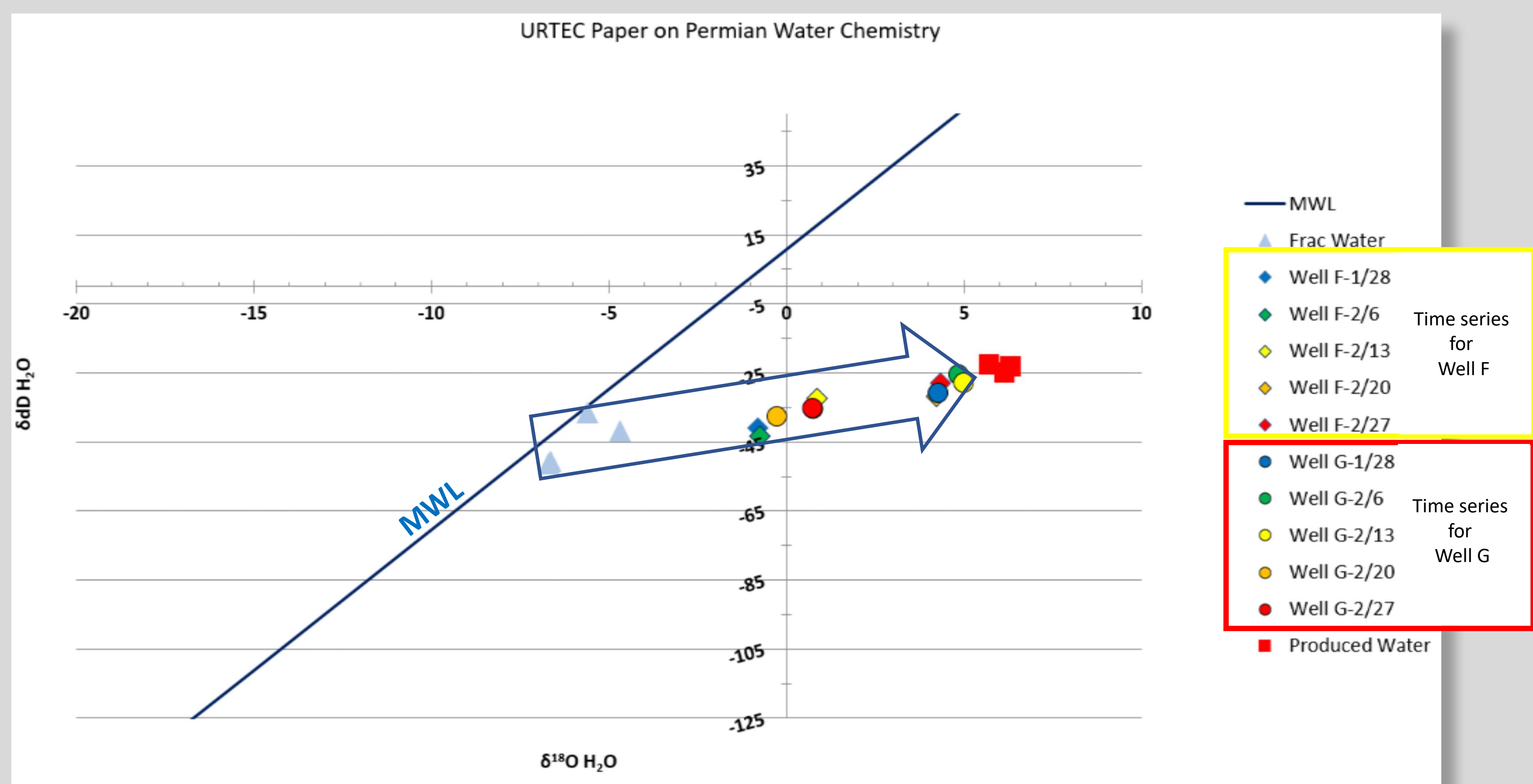
Cation Exchange Capacity (CEC) plots show that the Berea has hydrated clays and movable water, whereas the Marcellus contains desiccated clays indicating they will absorb introduced water.



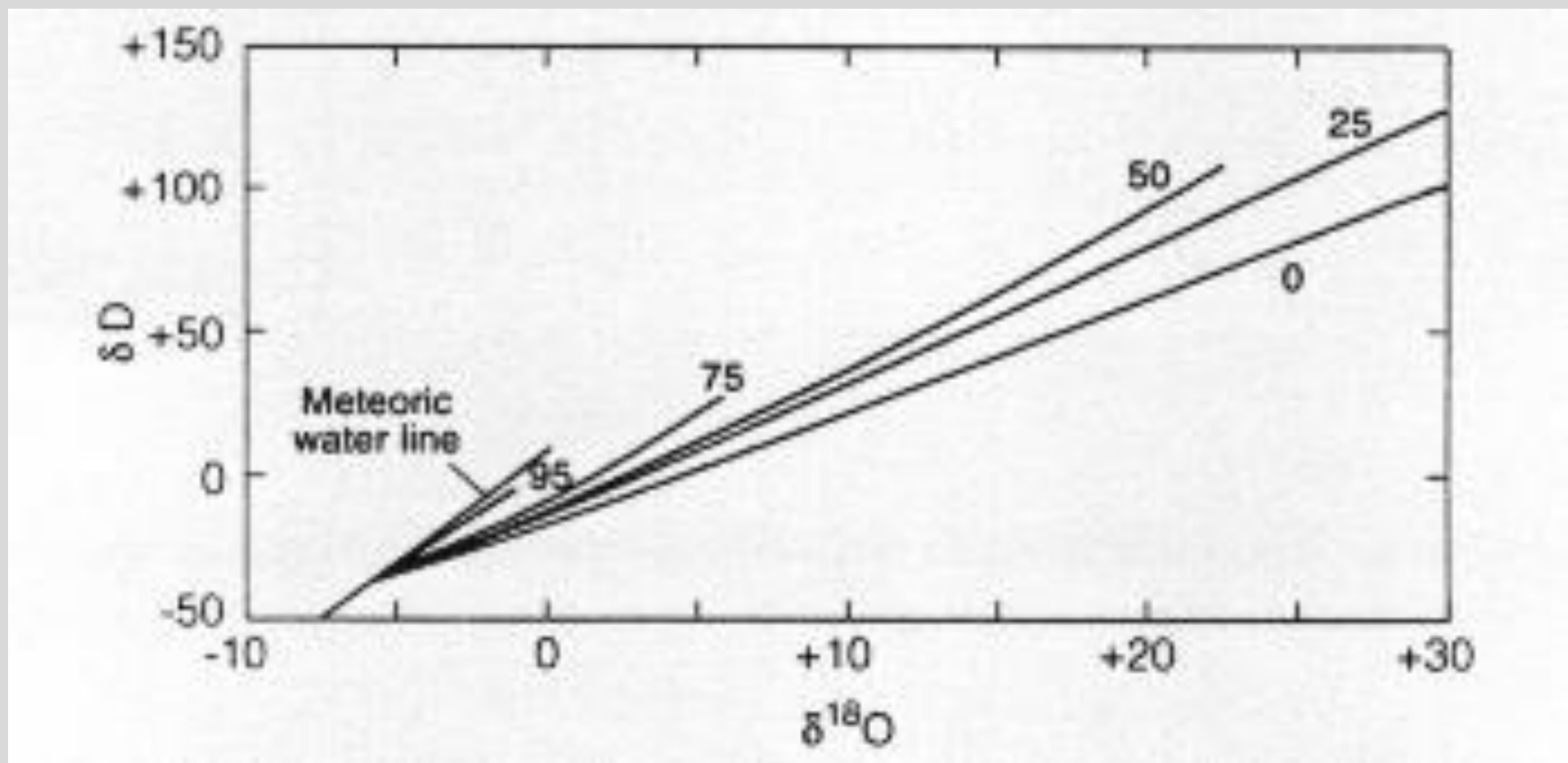
Hitchon and Friedman (1969) sampled surface waters and waters from oil and gas wells from the Alberta Basin, western Canada. This plot demonstrates the proposed relationship between the two sampled datasets and the hypothesized ancient brines within the basin. The oil and gas water brines plot along a mixing trend between the end member surface and basinal brines indicating the amount of mixing between these two end-members.

Allan and Wiggins, 1993

PRODUCED WATER ISOTOPES AND INTERPRETATIONS

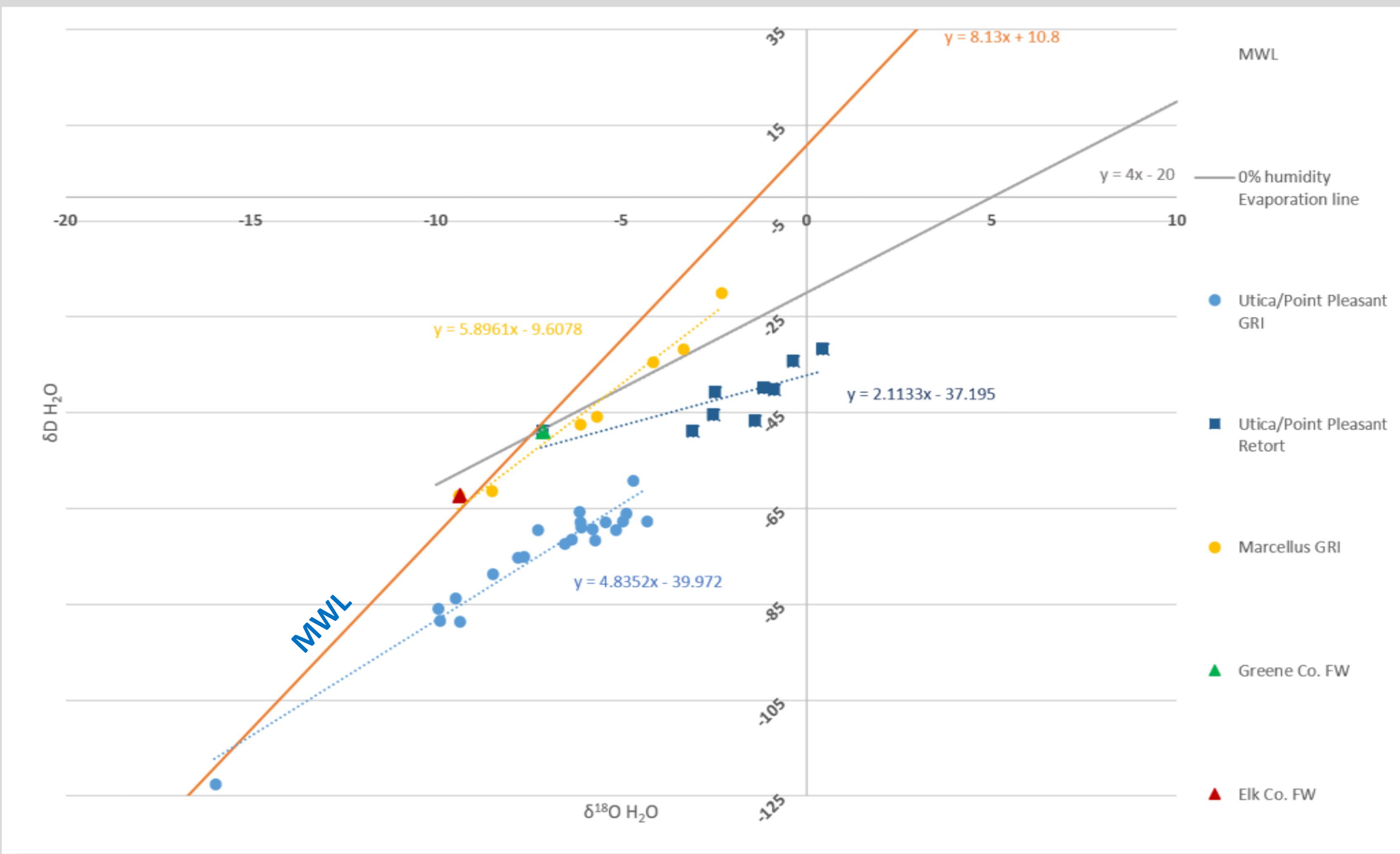


In 2014, Laughland, et al, published a paper (URTeC 1926712) documenting the changes in water chemistry and isotopic concentrations in the Permian Basin. There are two wells on this graph (Well F = diamonds; Well G = circles) plotted over a one month time period. The water used during frac operations lies just off the MWL as blue triangles and the “produced water” plots as red squares. The authors noticed a shift between the frac water and the produced water isotopic signatures. As the wells produced, the isotopic signature shifted to the heavier endpoints. The authors proposed the heavier isotopes of the produced water represented 100% formation water. Given how far to the right the initial flowback datapoints plotted, the authors proposed formation water is produced almost immediately upon flowback.

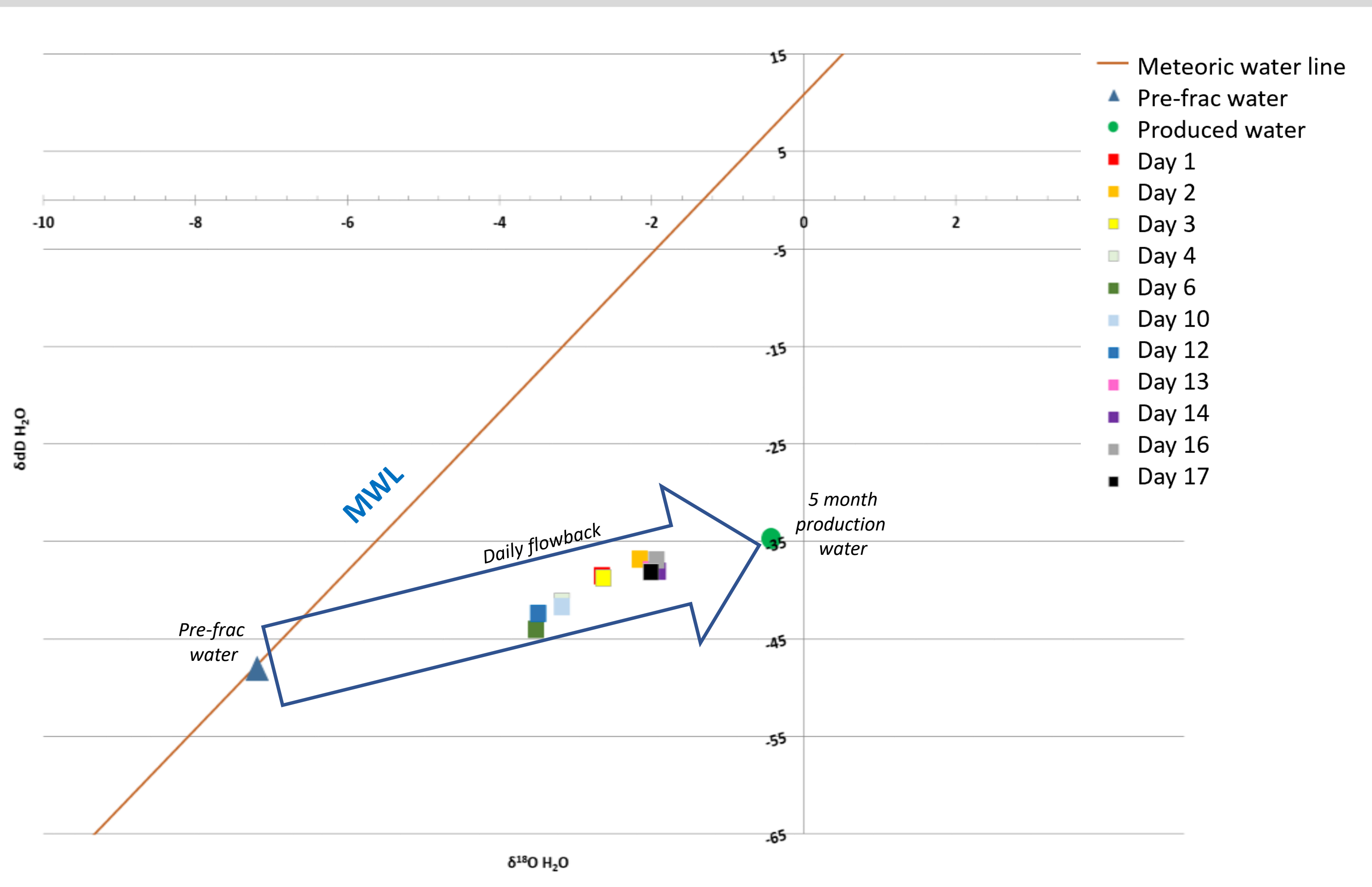


^{16}O and ^1H (the lighter isotopes) preferentially move to a vapor phase during evaporation, whereas ^{18}O and ^2H (the heavier isotopes) tend to stay in the liquid phase. This fractionation causes the isotopes to trend towards the heavier ends of the graph.

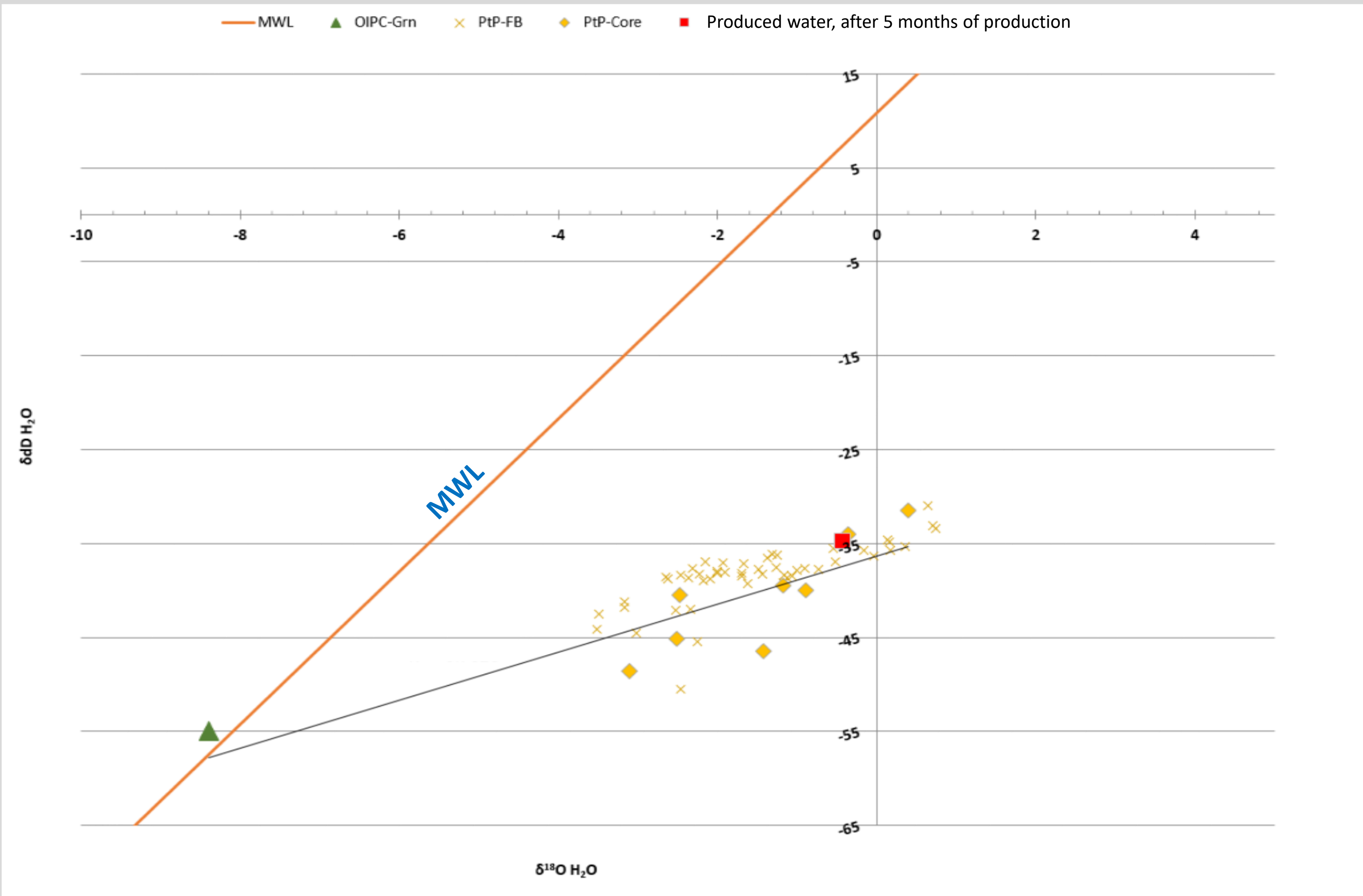
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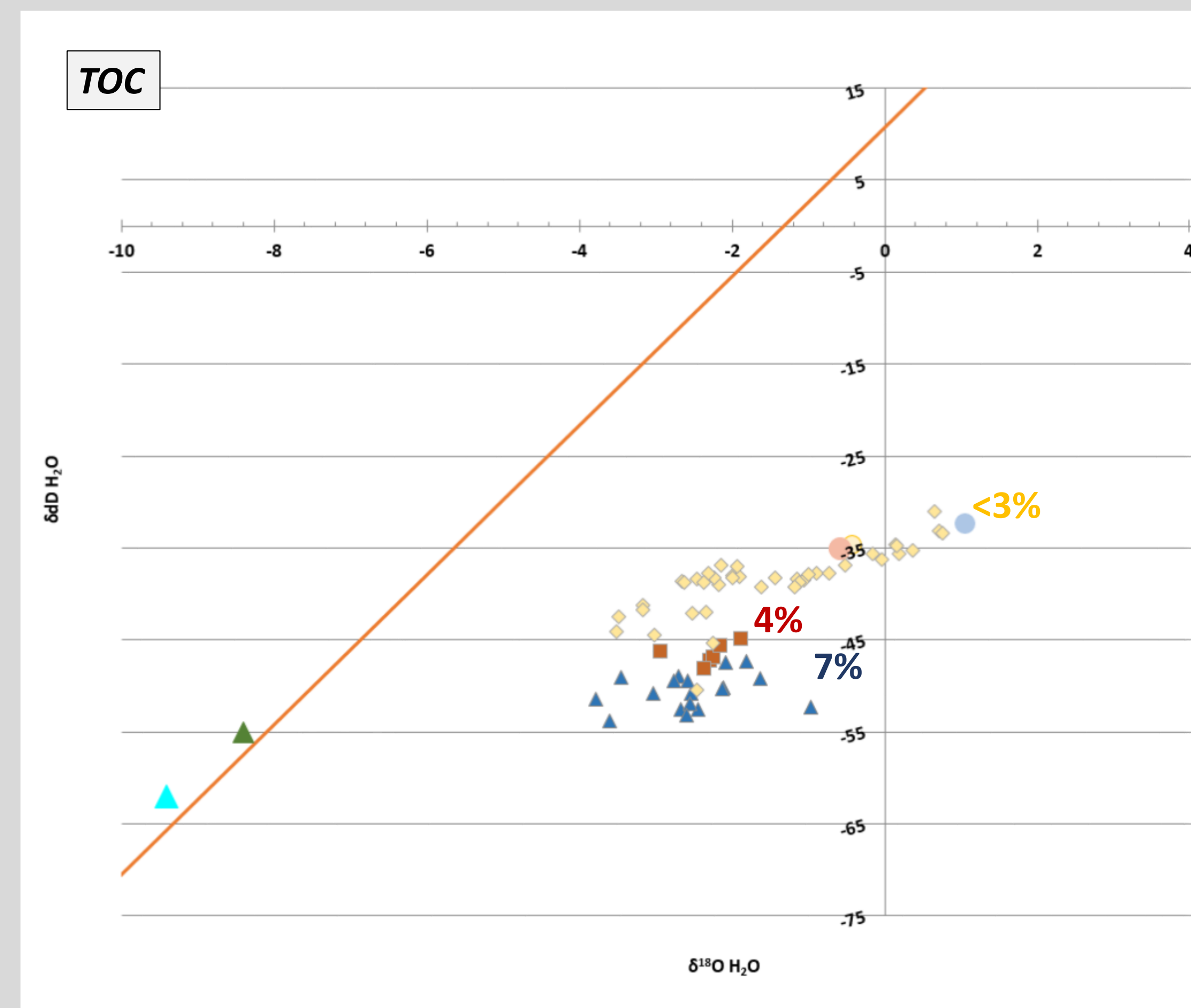
Water from two cores, one Marcellus and the other Point Pleasant, were extracted using GRI (Dean Stark apparatus) and retort methods. The Marcellus core exhibited a strong evaporation trend with one data point showing almost no isotopic fractionation. Published evaporation trends, at the earth’s surface with 0% humidity, have a slope of 4. Various humidities will cause different slopes (between 4 and 8), as shown in the plot above from the USGS. The retort method shows a shallow slope at 2.11. This is most likely attributed to the difference in extraction methods between GRI and retort.



Initial data gathering for the Point Pleasant formation in Greene Co, PA showed a similar trend to the data presented in Laughland, et al, 2014. This gave confidence to implement the next phase of the project which was to determine the end-member from core extracted waters. The core extracted data would give the end member point needed to define the amount of mixing with the production stream.

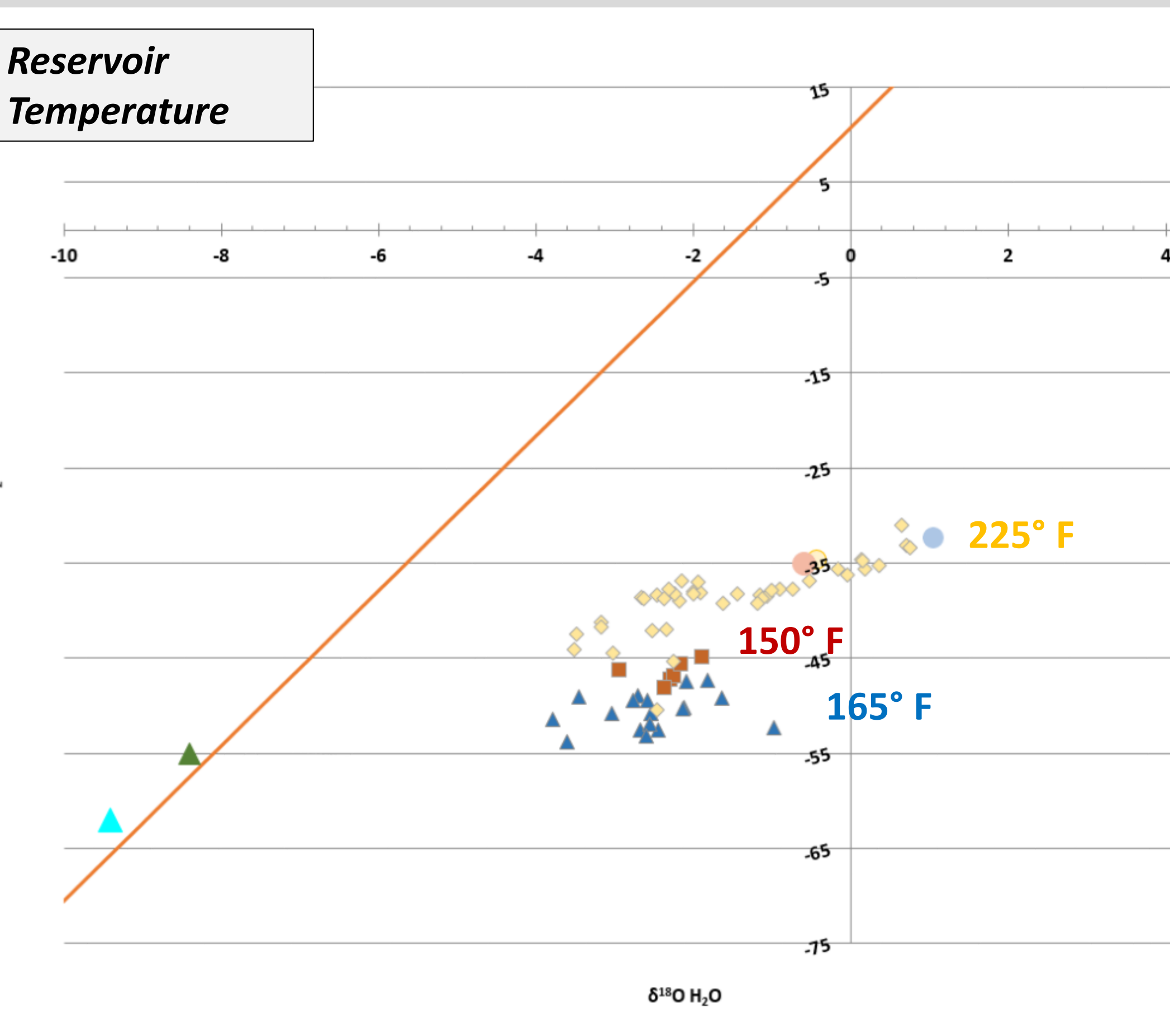
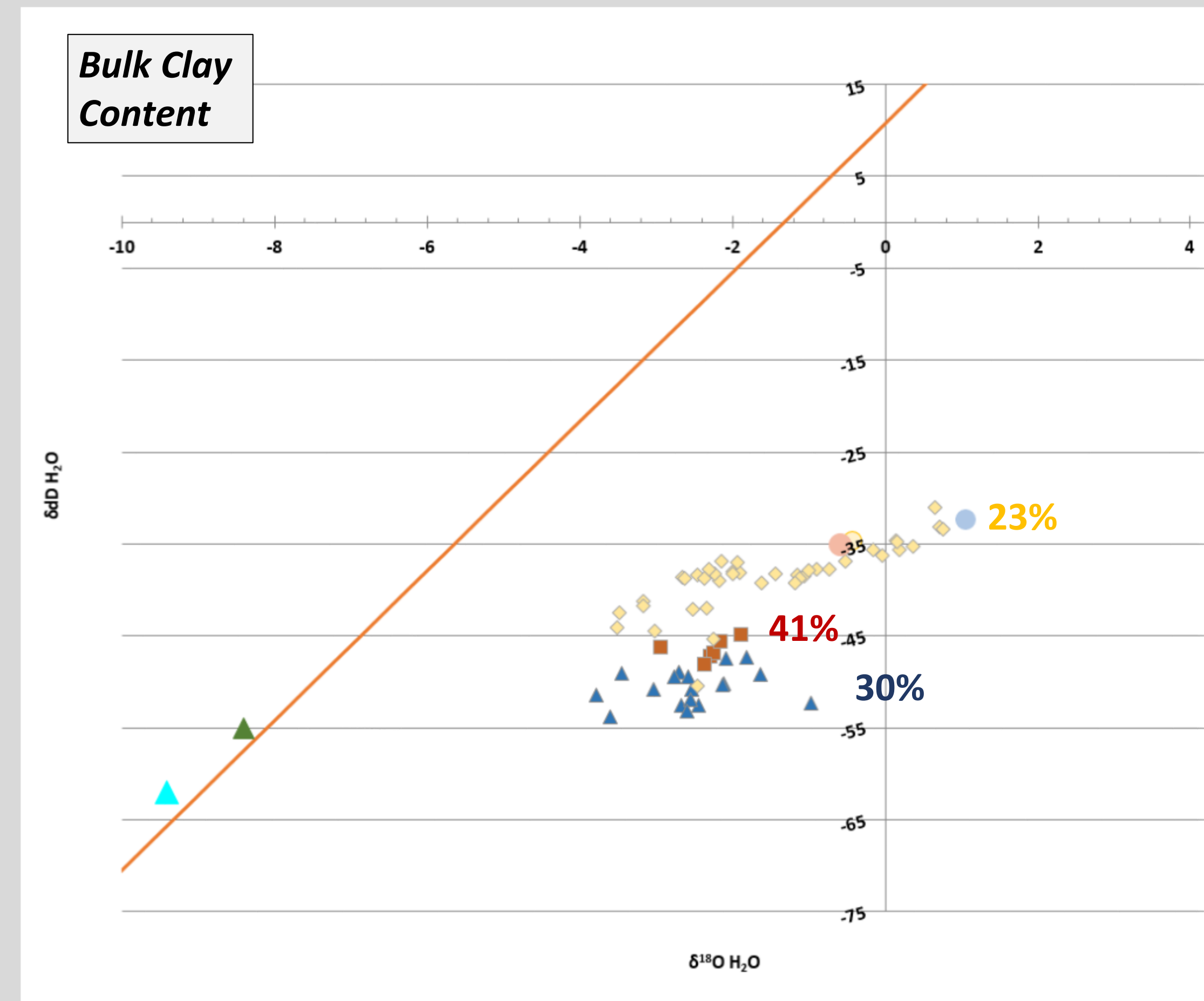


When the flowback water analysis is plotted with the core extracted retort data, it is clear that the flowback and core water exist in the same space on the oxygen and deuterium isotope plot, thereby indicating they have a similar source. This indicates there is no end-member water source in the Point Pleasant; rather the waters have been introduced during the drilling (extracted core water) and completion (flowback water) processes.



In determining the reservoir characteristic with the greatest influence on isotope fractionation of the water, we looked at three distinguishing characteristics of the rocks: TOC, clay content, and reservoir temperature.

The difference in slopes of the isotope fractionation between the three formations is mostly controlled by the change in the deuterium isotope. The graphs show the average value of TOC, bulk clay content, and reservoir temperature for the Marcellus (blue triangles), Genesee (red squares), and Point Pleasant (yellow diamonds). TOC may be influencing the slope of the isotope fractionation since higher TOC content appears to correlate with lighter deuterium isotopes, however no relationship is seen with bulk clay content. This is not intuitive since in the Marcellus and Genesee formations TOC and clay content are inversely related, whereas in the Point Pleasant, the two covary (Blood, 2018). Therefore, further investigation of individual clay components was warranted. Interestingly, the reservoir temperature graph indicates the higher reservoir temperature of the Point Pleasant is causing the reaction to continue. Presumably fractionation continues until water achieves equilibrium with the reservoir temperature.



WATER-ROCK INTERACTIONS

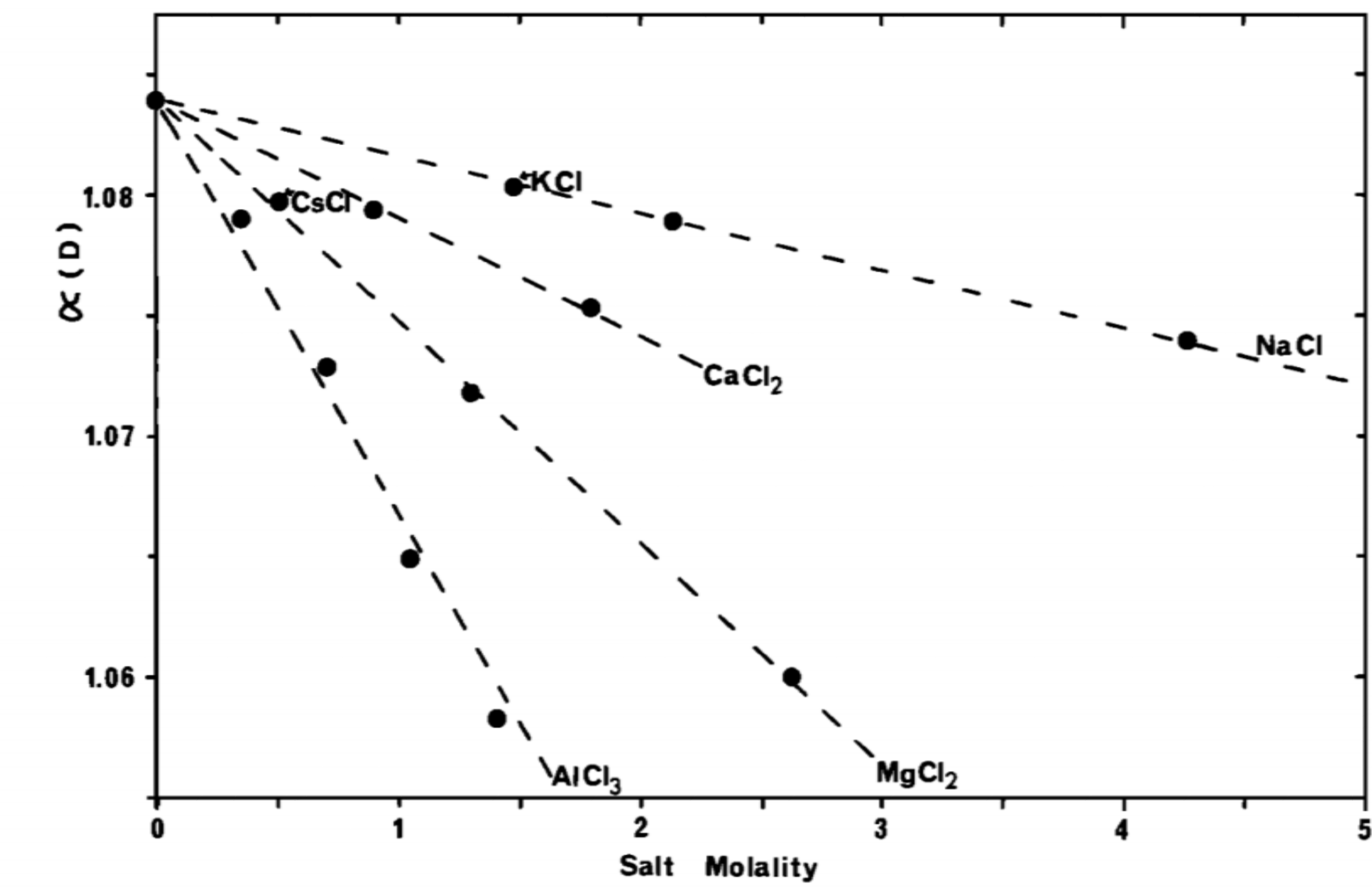
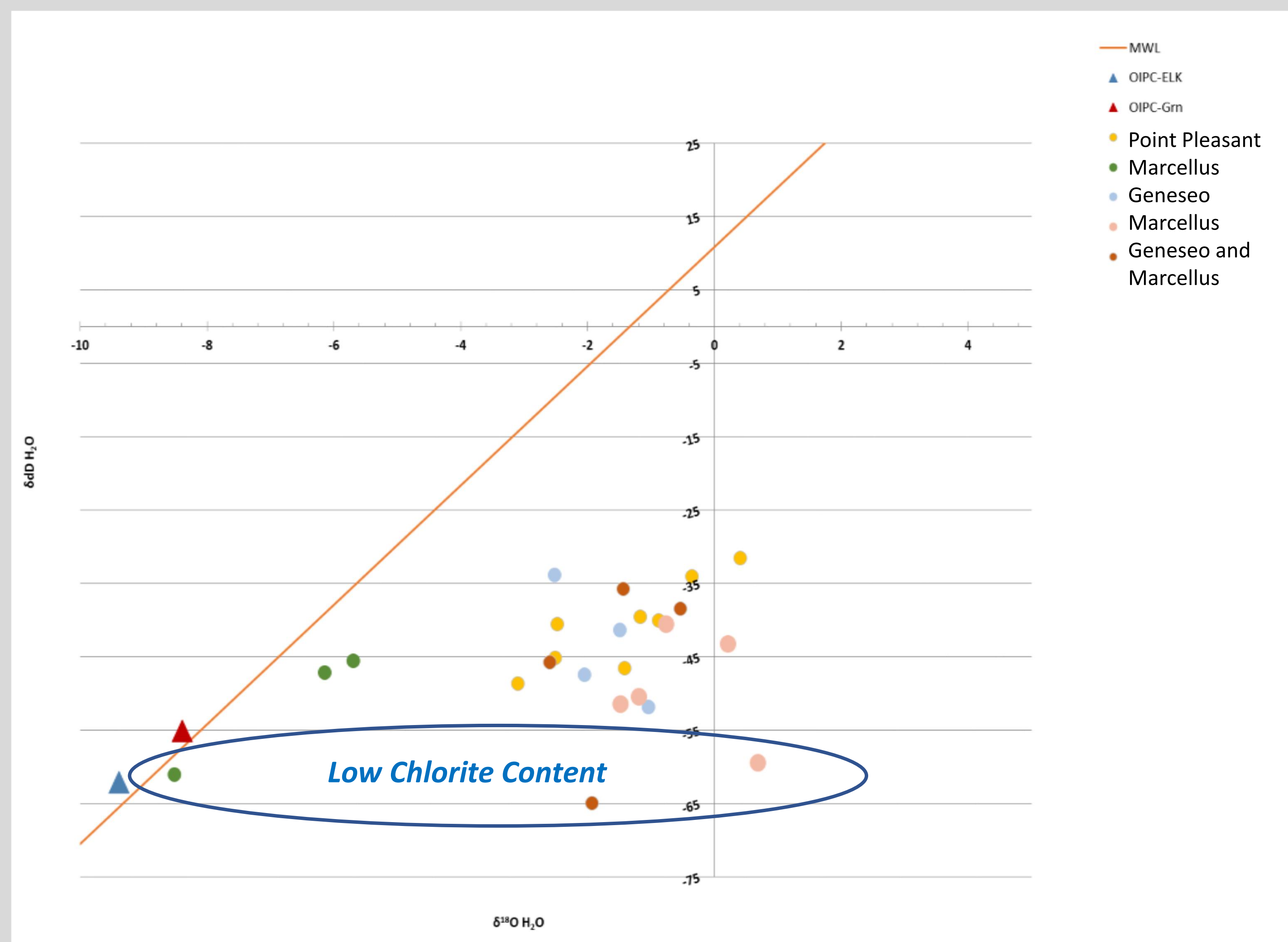


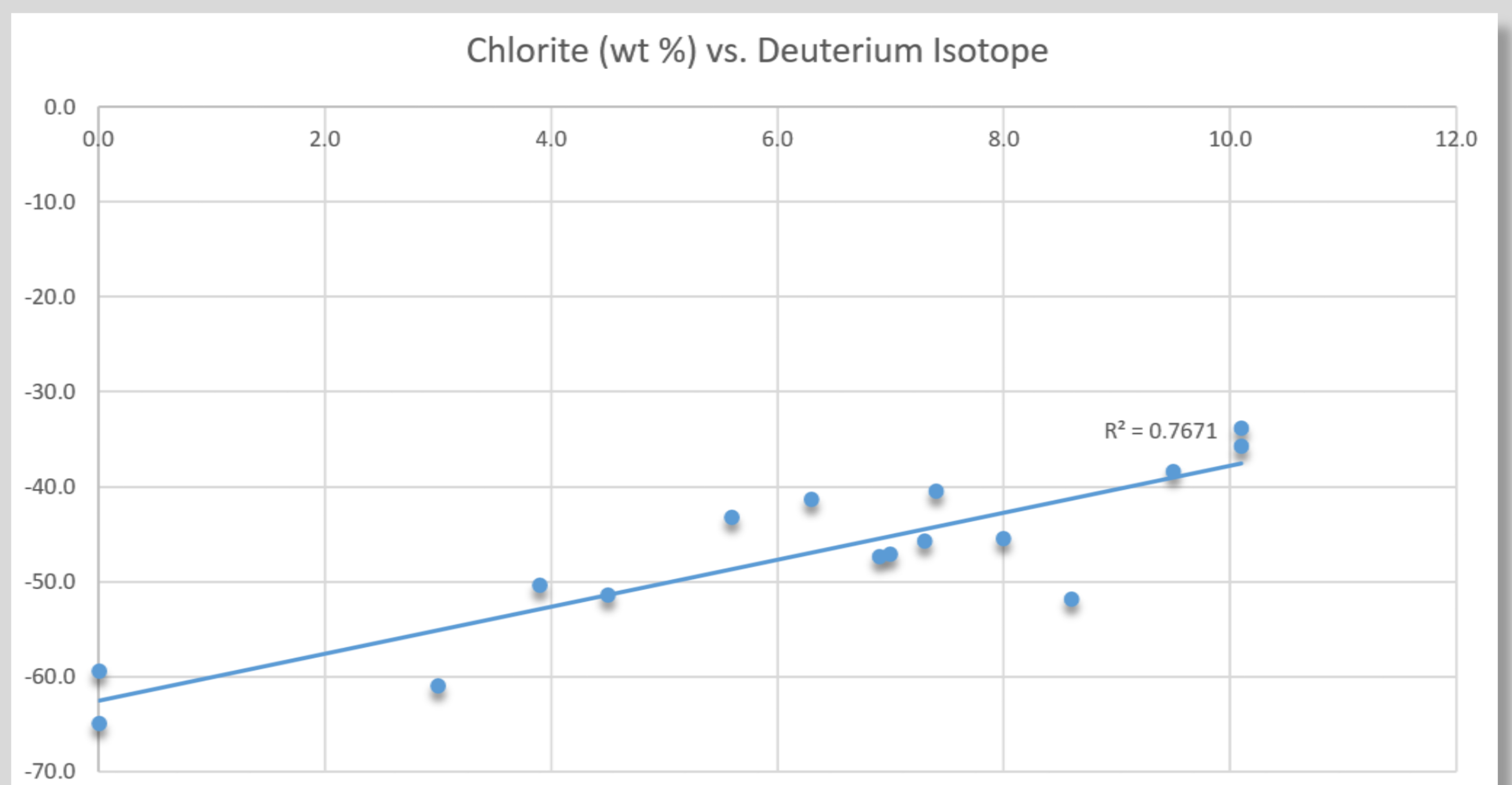
Fig. 5. Plot of deuterium fractionation factor between salt solutions and water vapor for various chlorides versus salt molality.

Water isotope fractionation is impacted by temperature (from evaporation studies of surface waters) and salt concentrations (Stewart and Friedman, 1975). The plot above shows the impact of various salts on deuterium fractionation.

Stewart and Friedman, 1975

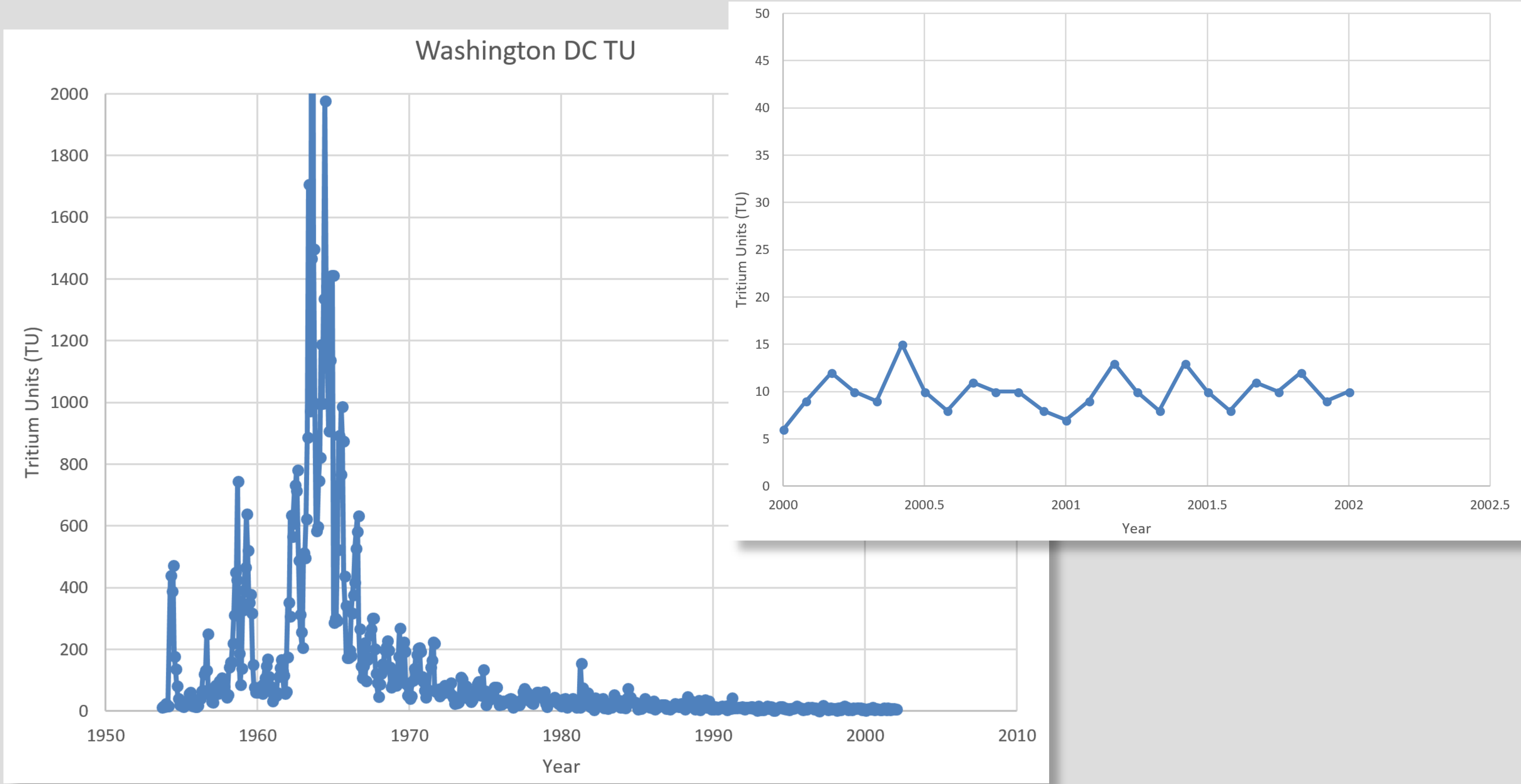


All samples shown on the oxygen vs. deuterium plot above had full XRD analysis completed. The three samples that showed minimal fractionation of the deuterium isotope had the lowest chlorite clay content relative to the remaining samples analyzed (from left to right, 3, 0, 0).



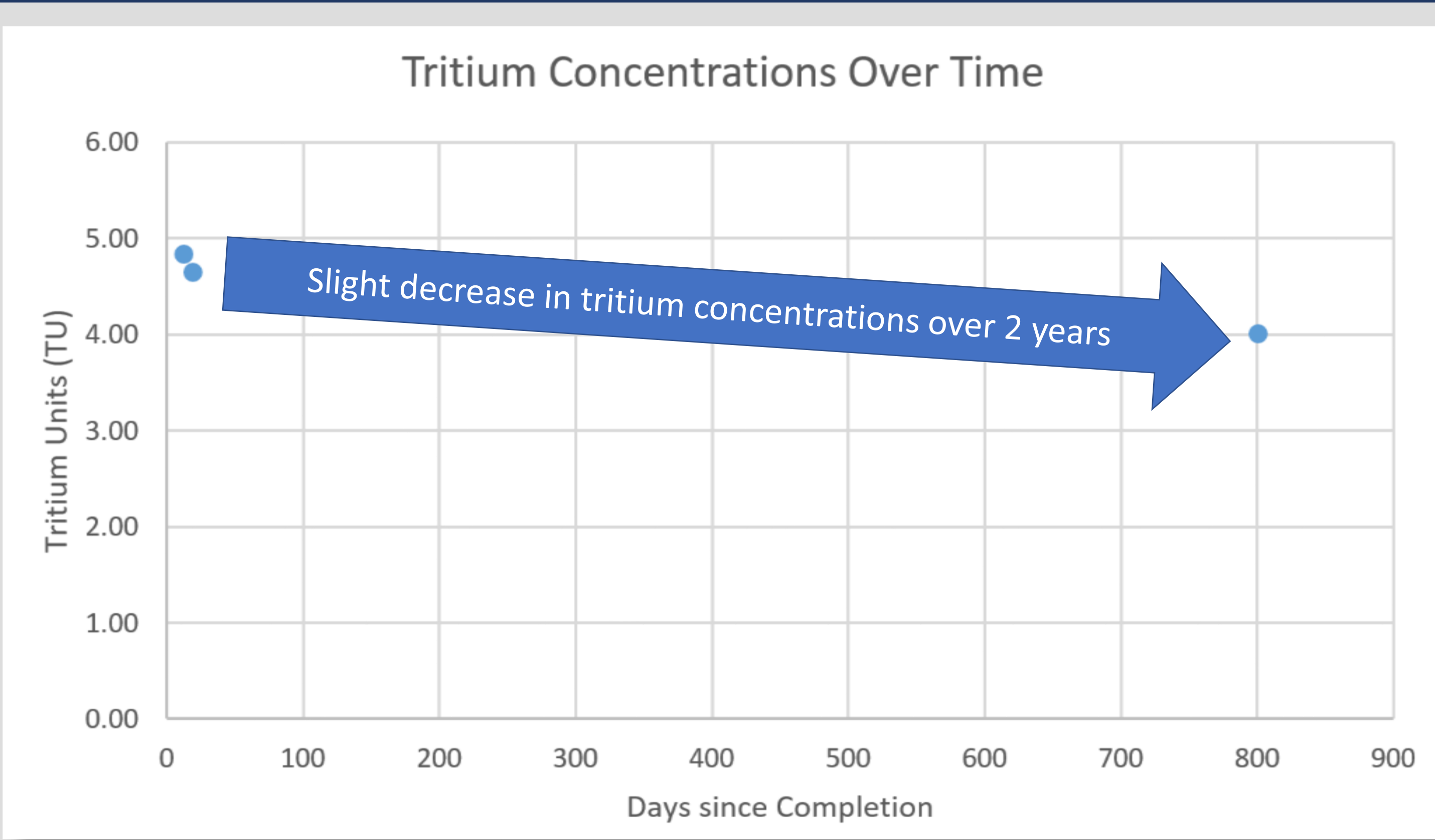
The linear relationship between the amount of chlorite present (in weight percent) and the deuterium isotopic value of the water samples analyzed here yields an r^2 value of 0.77, indicating a strong relationship between these two parameters. Chlorite may be an easy receptor for water, especially if ions exist on the surface of the clay particle due to the dehydration process associated with catagenesis.

TRITIUM ANALYSIS



Atmospheric tritium concentrations have diminished since the peak nuclear bomb testing of the 1960s. Atmospheric tritium concentrations vary depending on location, but they all follow the same diminishing trend. Readings from the years 2000-2002 in Washington DC average approximately 10 tritium units (TU). Measurements in Ottawa continued to show a decline in tritium concentrations after 2002. Presumably, the same decline has occurred in the Appalachian Basin surface waters.

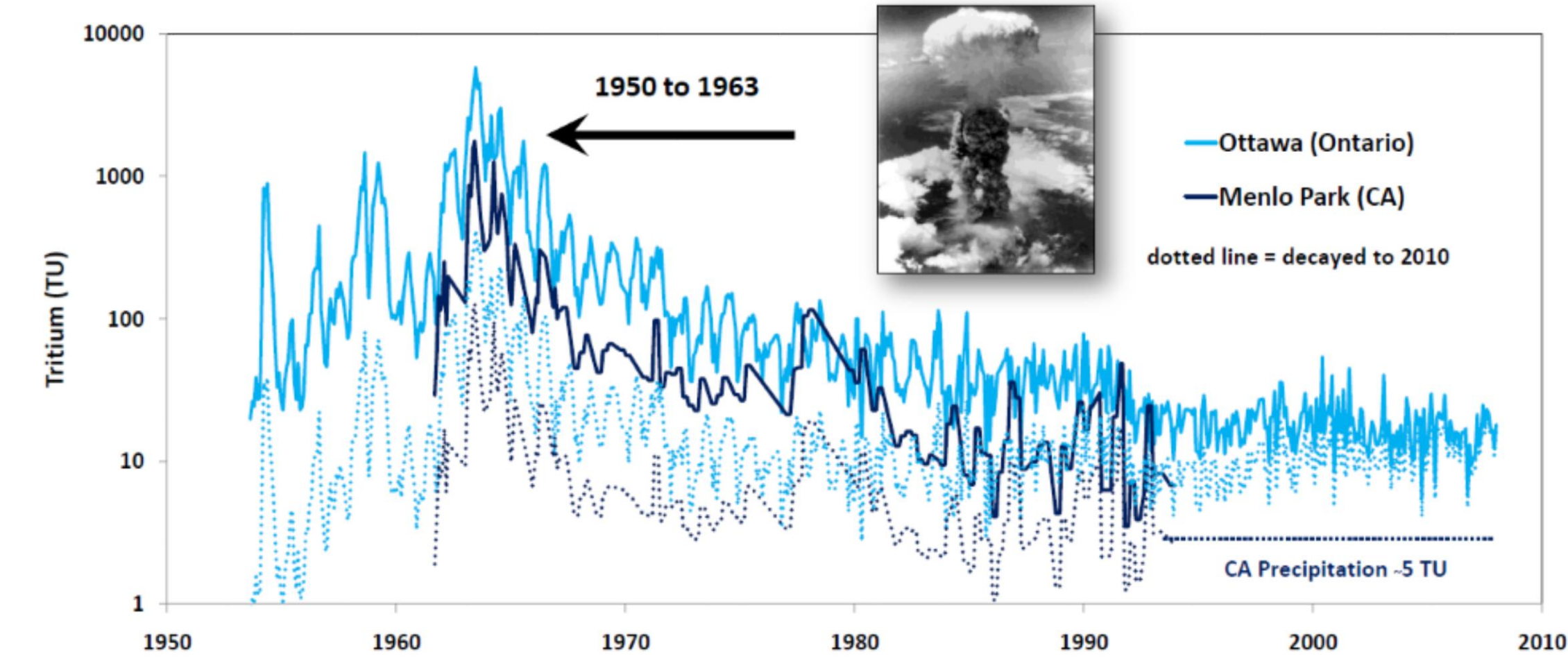
USGS Reston Groundwater Dating Laboratory



Three tritium analysis of two flowing wells. No recycled water was used during completions of these wells. The reservoir targeted by these wells is ~13,500' TVD, with a reservoir pressure in excess of 0.8 psi/ft, thus making connectivity with tritium enriched surface waters very unlikely.

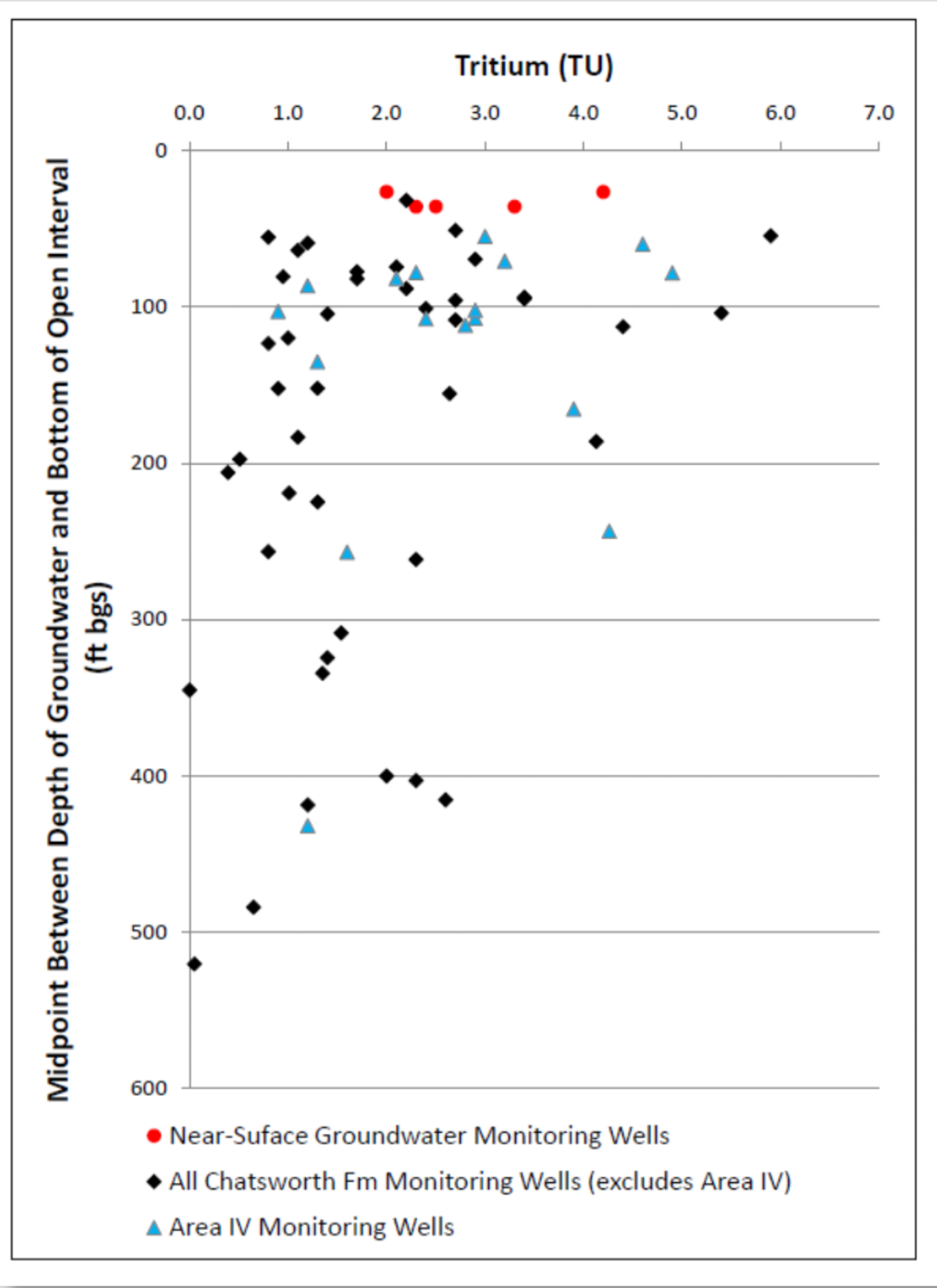
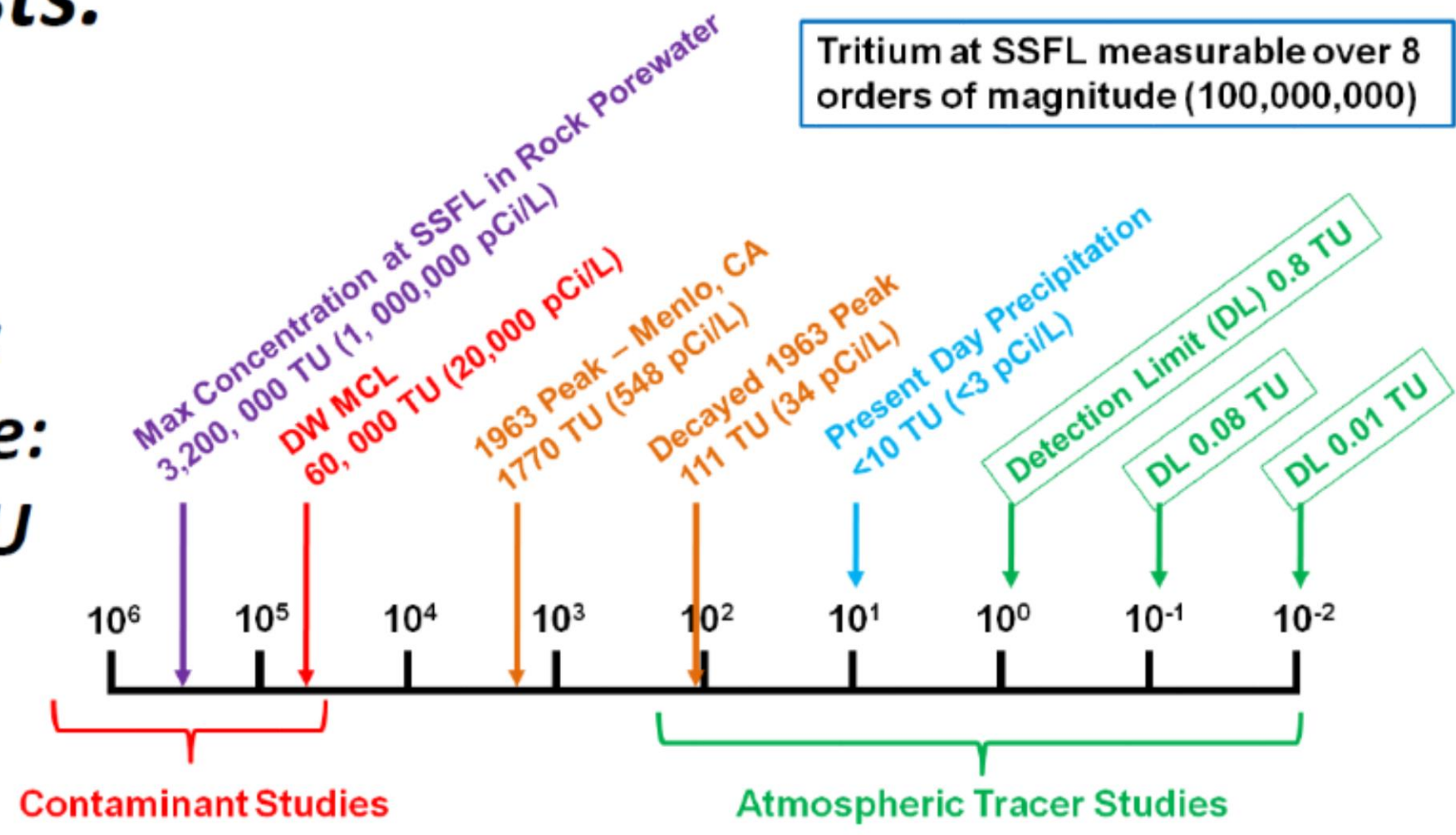
The presence of tritium in produced water is significant given that its short half life (12.43 years) precludes it from being present in such quantities in ancient basin fluids. This suggests the fluids recovered during initial flowback and after two years of production are frac fluids and not basin fluids.

Tritium occurs in rainfall



Tritium in rainfall caused by atmospheric nuclear tests.

Atmospheric tritium range: 10^2 to 10^{-2} TU



As interaction with mobile groundwater decreases with depth, tritium concentrations also fall.

University of Guelph and Groundwater U., Atmospheric Tritium is a Groundwater Tracer, Santa Susana Field Laboratory