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A Geochemical Analysis of Produced Water in the Permian Delaware Basin, West Texas

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Abstract

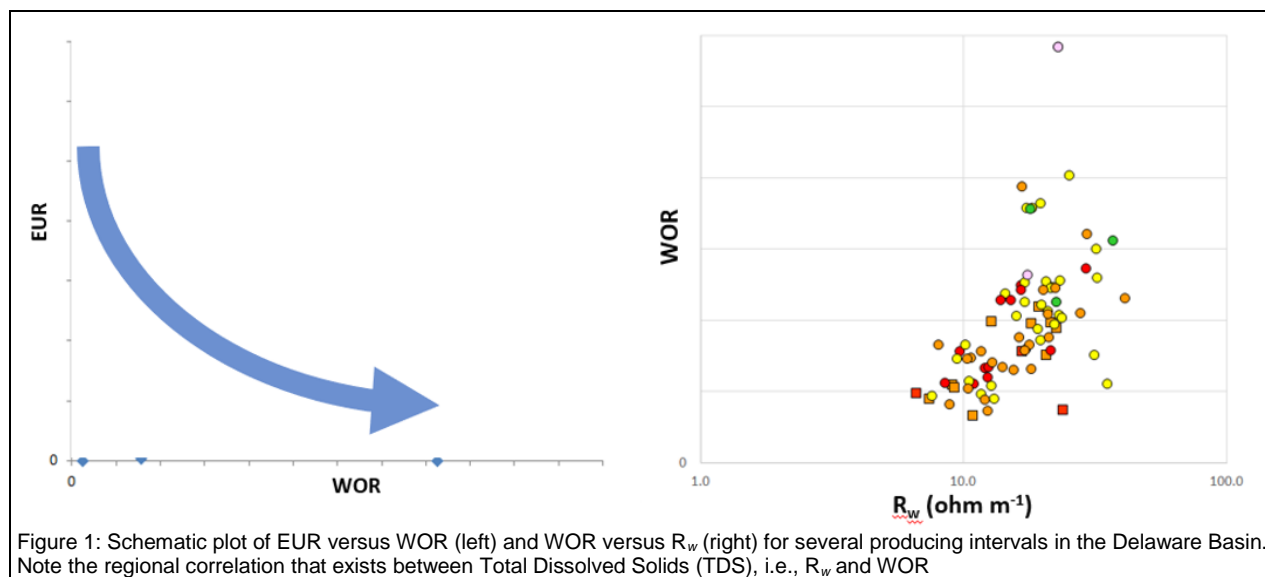
The Permian Delaware Basin (DB) is one of the most desirable regions for production of unconventional oil in the United States. While extended horizontal wells, stimulated with hydraulic fracturing, can recover economic volumes of oil in the DB, this production is often associated with large volumes of produced water (PW). Relatively high water-oil ratios (WORs) can erode the value of producing wells. This of course begs the questions: where is the water coming from and why is so much being produced? This study shows that the PWs are primarily *in-situ* Wolfcamp shale formation water and not water associated with hydraulic fracturing or well completions. This conclusion is based on the observation that the Wolfcamp shale formation water has an oxygen isotopic composition of $\sim 6.5 \pm 0.5$ ‰ (SMOW) and a salinity of ~ 23 kppm. These oxygen isotopic data and salinities are consistent with illite-water equilibrium at peak burial conditions.

However, in some areas of the DB, PWs have much higher salinities (~ 50 - 125 kppm). The PWs also have a characteristic geochemical fingerprint of highly radiogenic $^{87/86}\text{Sr}$ ratios of ~ 0.7085 - 0.7095 . The source of this highly radiogenic strontium is believed to be the Salado salt in the overlying shallow Ochoan evaporites, with $^{87/86}\text{Sr}$ of ~ 0.7090 - 0.7095 . Dissolution of the Ochoan evaporites and salt is the likely source of high salinity brines in Guadalupian and Leonardian age sands and silts within the DB. These high salinity PWs are mixtures of Wolfcamp formation water and dissolved Ochoan evaporites and salt that infiltrated deep into the DB during uplift of the western edge of the DB. Uplift was closely related to the formation of the "Alvarado Ridge", beginning at ~ 20 Ma, with peak uplift at ~ 7 to 4 Ma, creating conditions hydrologically favorable for ingress of the high salinity brines deep into the DB. Due to the high illite content in the Wolfcamp shale, the shale-silt interface likely behaved as a clay membrane. Differences in salinity (up to ~ 100 kppm) between shales and sands/silts created gradients in ion and water activity (a_w) across the interface. These gradients resulted in the diffusion of ions from high salinity sands/silt (low a_w) into adjacent shales with low salinity and high a_w . Where shales have not equilibrated with high salinity sands/silts, the water saturation (S_w) in the Wolfcamp shale would remain high and the resultant WOR would also be high. The ion diffusion model predicts co-current flow of oil and water out of the shale. This may explain why oil production in the DB produces so much water.

Why Study Water when all you want is Oil?

Much of the oil production in the DB is associated with high water-to-oil ratios (WORs), which may adversely impact the well EUR (Figure 1; left) of a well and due to additional costs of water disposal,

ultimately well economics. At present, it is not possible to predict a well or pad WOR pre-drill and WOR continues to be de-risked with the drill bit.



The WOR and PW salinity appear to be correlated across the DB (Croft et al., 2018; Figure 1). Many questions arise from the apparent correlation of WOR and R_w in PWs from the DB. For example, where does the produced water come from? Is it local or exogenous and why do WOR and R_w vary across the DB? A better understanding of the source(s) of PWs in the DB and what controls the R_w -TDS relationships in PWs in all the producing lithofacies may provide better formation evaluation of S_w and hence S_{oil} and lead to petrophysical workflows that may de-risk future acreage for WOR using fewer appraisal wells.

Fingerprinting Major Ion Geochemistry of Produced Waters in the Delaware Basin

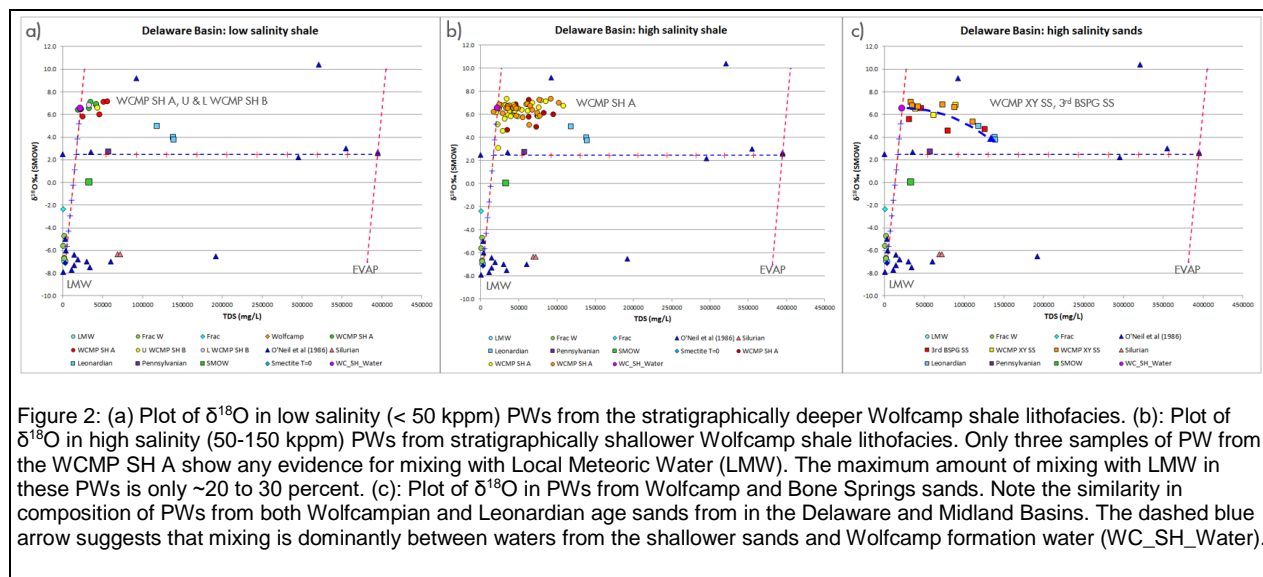
The PWs were collected at the well head and/or separator, mostly as PWs associated with stable production. In some cases, wells were sampled relatively early in their production history and included flowback waters that were part of the well cleanup process after hydraulic fracture stimulation. Radar plots were constructed for the PW samples according to the lithofacies from which they were produced. No obvious differences were observed that would readily distinguish different sources for the PWs. The largest variability that is observed is in their Cl/SO_4^{2-} and Ca/SO_4^{2-} ratios. In addition, PWs from the deep Wolfcamp shales (Upper and Lower WCMP SH B) are relatively low TDS brines, with salinities <50 kppm. Their Cl/SO_4^{2-} ratios are all < 10,000 and their Ca/SO_4^{2-} ratios are consistently ~1000. All shales and sands that are stratigraphically above the Upper WCMP SH B have much higher TDS values, with salinities ranging from ~50 to 125 kppm. They also have much higher ratios of Cl/SO_4^{2-} (>10,000) and their ratios of Ca/SO_4^{2-} are all relatively low, <1000. Apart from the obvious differences in the salinity of PWs from deeper shales and more shallow shales and sands, the only features that might distinguish potential sources of water are their TDS values and the Cl/SO_4^{2-} and Ca/SO_4^{2-} ion ratios.

Oxygen Isotope Systematics of Produced Waters in the Delaware Basin

A geochemical fingerprint commonly used to distinguish potential sources of water and mixing relationships between different sources of water are the oxygen and D/H isotopic composition of the water. The oxygen isotopic composition is usually denoted as $\delta^{18}O$ and is the ratio of $^{18}O/^{16}O$ in H_2O , relative to that in a standard. The isotopic standard for water is Standard Mean Ocean Water (SMOW), for which the $\delta^{18}O$ and D/H ratios are, by definition, zero. Since water may be considered a universal solvent, it is also an excellent means by which to characterize rock-water interactions. Such processes might be

dominated by mixing of different sources of water and/or water-rock. We interpret the TDS and oxygen isotope compositions of PWs using the framework adopted by Bryndzia and Fay (2016).

PWs from the deepest shale lithofacies in the DB are all relatively dilute brines with TDS values of 50 kppm or less and have a very tight distribution in $\delta^{18}\text{O}$ of $\sim 6.5 \pm 0.5$ ‰ (Figure 2a). There is no evidence for any mixing with LMW in this data, suggesting that the water compositions are dominated by Wolfcamp shale formation water. If this interpretation is correct, it also suggests that the $\delta^{18}\text{O}$ of Wolfcamp shale water is in the range of $\sim 6.5 \pm 0.5$ ‰. Figure 2b shows PWs from stratigraphically shallower sands and shales which have TDS contents that range from the same low TDS values in Figure 2a to much higher salinities having TDS values of ~ 120 kppm. Notably, this is the same range of salinities that are observed in sands and silts from this stratigraphic interval in the DB Figure 2c.



The $\delta^{18}\text{O}$ -TDS data in Figure 2c suggests that there is mixing between formation waters in the Wolfcamp and Bone Springs sands with formation water derived from deeper Wolfcamp shales (dashed blue arrow in Figure 2c). Two important points are implied by this suggestion. First, the formation brines in the shallower sands and silts are not as enriched in $\delta^{18}\text{O}$, with oxygen isotopic compositions approaching ~ 4 ‰. Second, the higher TDS of brines in these shallower formations suggests that the increase in TDS is due to the dissolution of evaporite minerals. Only mixing between Wolfcamp shale PWs and the Leonardian age waters are consistent with the observed trend. The Leonardian age formation waters in Figure 2c are from the Midland Basin study by Engle et al. (2016).

Modeling the Oxygen Isotopic Composition of Formation Water in the Wolfcamp Shale

We tested the hypothesis that the oxygen isotopic composition of PWs in the Wolfcamp shale reflects the isotopic composition of water derived from smectite to illite diagenesis i.e., assuming oxygen isotope equilibrium between water and illite. To test this hypothesis, we have adopted the oxygen isotope smectite-illite-water model of Suchecki and Land (1983; Figure 3), who used it to model the isotopic composition of water, smectite and illite in the Great Valley Sequence in California.

We assumed an average thermal gradient of 27.5 °C/km and a maximum burial depth of 5000 m, with 100% smectite as the initial mixed layer clay (MLC) composition and 10% smectite component in the final MLC. As the smectite was deposited in a marine environment it is reasonable to assume that the initial oxygen isotopic composition of the water in equilibrium with smectite was sea water, with $\delta^{18}\text{O}$ of SMOW, i.e., 0 ‰. The initial oxygen isotopic composition of the smectite is 20 ‰ (Suchecki and Land, 1983).

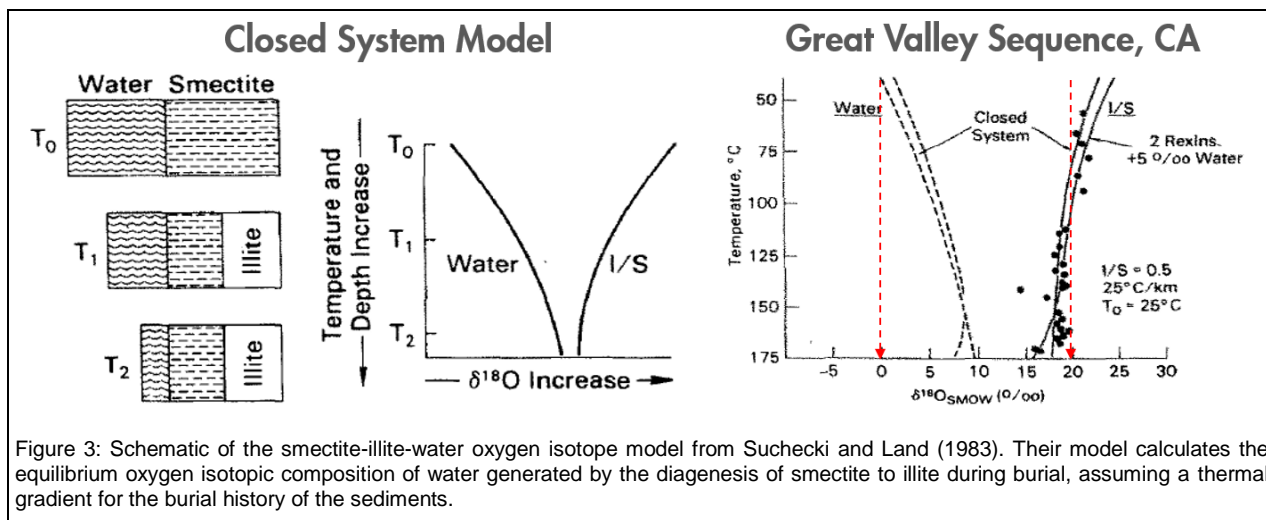


Figure 3: Schematic of the smectite-illite-water oxygen isotope model from Suchecki and Land (1983). Their model calculates the equilibrium oxygen isotopic composition of water generated by the diagenesis of smectite to illite during burial, assuming a thermal gradient for the burial history of the sediments.

Model assumptions include:

- 1) Closed system behavior, i.e., no water leaves the system from one iteration step to the next
- 2) Initial $\delta^{18}O$ in pore fluids is ~ 0 ‰ (SMOW) with $\delta^{18}O$ in smectite ~ 20 ‰ (Figure 3, red dashed arrows)
- 3) Estimate changes in $\delta^{18}O$ of pore fluid using equilibrium fractionation of $\delta^{18}O$ between illite and water, based on different volume fractions of smectite undergoing conversion to illite (Figure 3, left)
- 4) Each time step, i.e., Time, Temp and Depth, estimate $\delta^{18}O$ in pore fluid which is then used in the next iteration of the diagenetic reaction of the remaining smectite fraction to illite (repeated twice per time step)

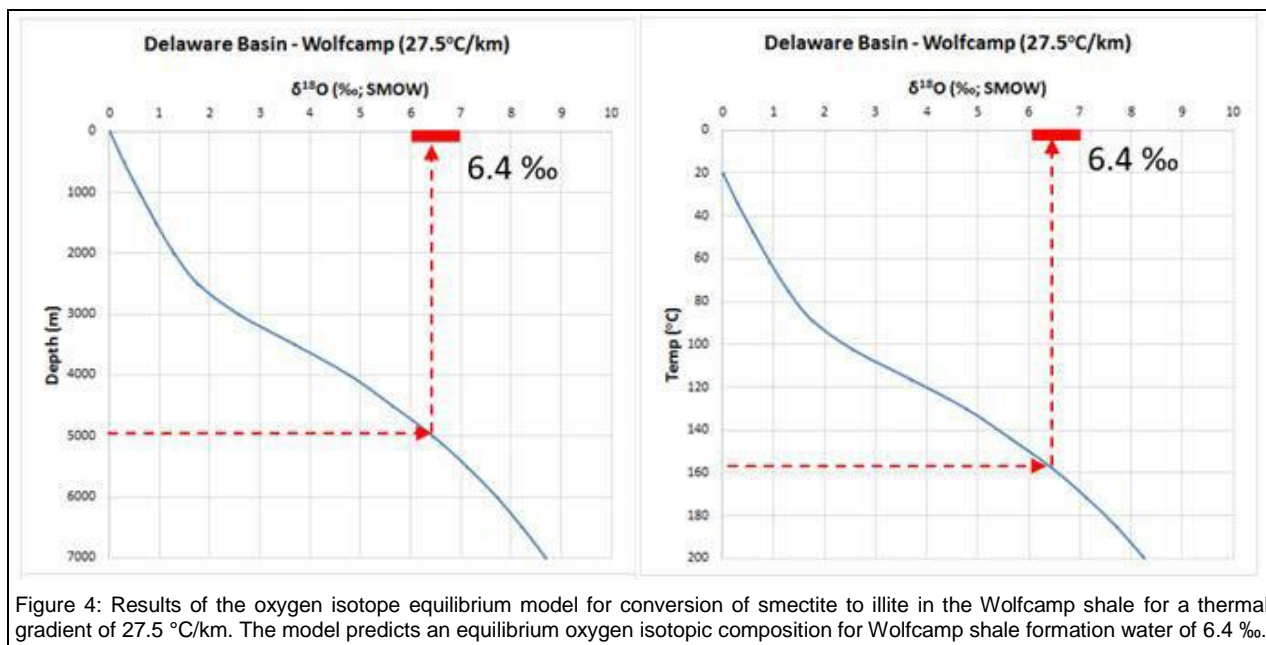


Figure 4: Results of the oxygen isotope equilibrium model for conversion of smectite to illite in the Wolfcamp shale for a thermal gradient of 27.5 °C/km. The model predicts an equilibrium oxygen isotopic composition for Wolfcamp shale formation water of 6.4 ‰.

To calculate the oxygen isotopic composition of water in equilibrium with illite, we used the oxygen isotope equilibrium model for illite-water from Sheppard and Gilg (1996; Equation (1):

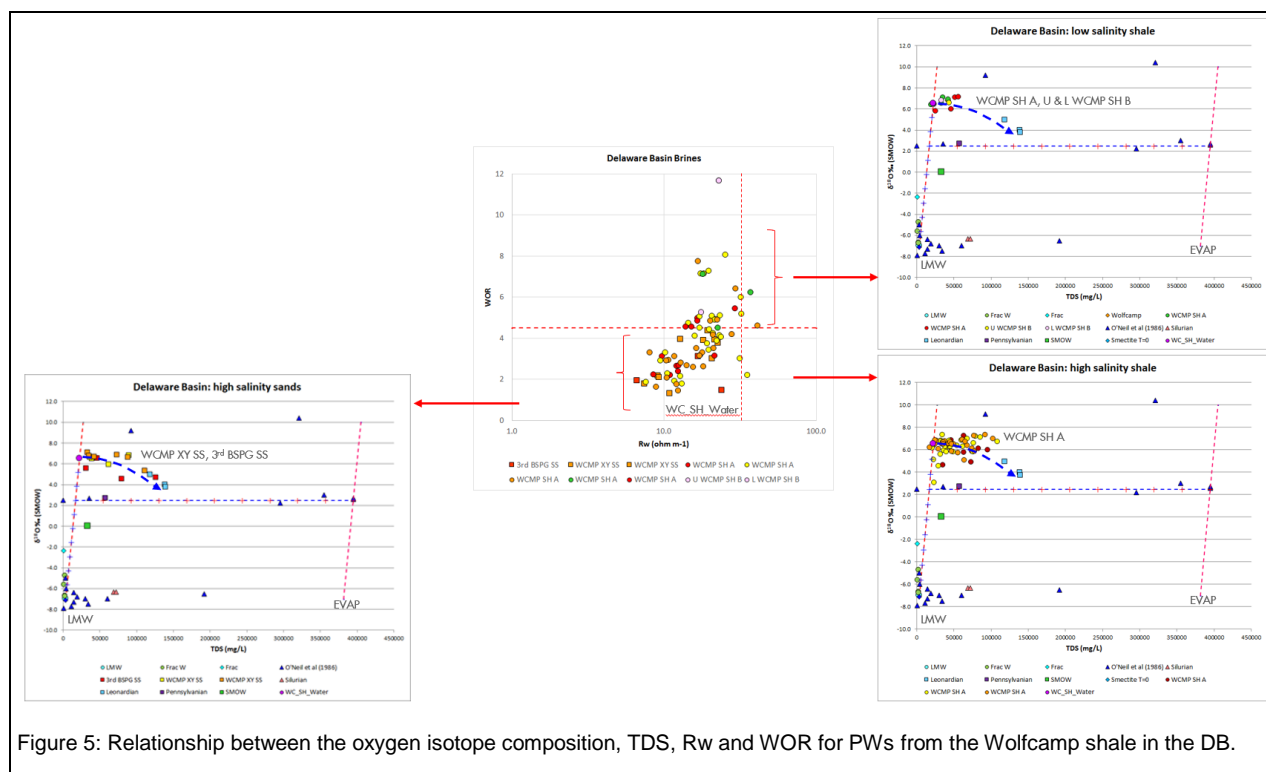
$$1000 \ln \alpha_{\text{illite-water}} = 2.39 \cdot (10^6 T^{-2}) - 3.76 \quad (1)$$

The model was run from 25 °C through to a final temperature of 200 °C. Results of one model scenario are shown in Figure 4.

Results and discussion

Our results showed that the oxygen isotopic composition of Wolfcamp shale water is not very sensitive to the assumed thermal gradient used in the calculation. Assuming a thermal gradient of 25°C/km, resulted in a maximum burial temperature of 145°C and a predicted oxygen isotopic composition of water in the Wolfcamp shale of ~6.5 ‰. Confirmation of our oxygen isotope modeling of Wolfcamp shale water recently became available from a time series of water analyses on PW from one of Shell's DB wells. The TDS values stabilized at ~45 kppm after almost a month of sampling, while the $\delta^{18}\text{O}$ of the PWs had a consistent value of 6.4 ‰. These field data are in excellent agreement with our smectite to illite equilibrium oxygen isotope model for water in the Wolfcamp shale. We conclude that this is the isotopic composition of formation water in the Wolfcamp shale.

In the DB, R_w (an indication of TDS), appears to be correlated with the WOR. Shales that appear to have equilibrated with sands have high TDS and low WOR (Figure 5). Low WORs (<4.5; dashed red line in center) are associated with PWs from sands and shales that have high TDS (bottom left and bottom right). High WORs (>4.5) are almost exclusively associated with low salinity shales (top right) and confirm that relatively high WOR PWs are produced from the deeper Upper and Lower WCMP SH B shale, with an oxygen isotope signature that is dominated by water generated through smectite diagenesis. Low WOR PWs have higher salinities and clearly contain components of shallow Ochoan evaporites. The data



in Figures 1 and 5 support our hypothesis that interaction of dense, high TDS brines with Wolfcamp shale formation waters derived from smectite to illite diagenesis are the cause of the observed TDS and WOR relationships in the DB.

Conclusions

Oil production from the Wolfcamp shale in the Delaware Basin (DB) of west Texas is often associated with high water to oil ratios (WORs). Low WORs are associated with PWs from sands and shales that have high salinities (50-125 kppm). High WORs are almost exclusively associated with deeper, low salinity shales (Upper and Lower WCMP SH B).

The results of an equilibrium oxygen isotope fractionation model between water and illite, produced by smectite diagenesis during burial, predicts that the oxygen isotopic composition of water in Wolfcamp shale evolved from $\delta^{18}\text{O}$ of 0 ‰ at T_{initial} (100% smectite), to ~ 6.4 ‰ at T_{final} (~ 90 % illite) and produced a formation brine with salinity of ~ 23 kppm. Confirmation of our oxygen isotope model was recently provided by oxygen isotope analyses from a time series of PW samples from a WC shale well in the DB. Based on their oxygen isotopic composition and salinity, most PWs in the DB appear to be mixtures of Wolfcamp shale formation water with variable proportions of dissolved shallow Ochoan evaporites and Salado salt. The PWs have a characteristic radiogenic strontium isotope signature, with $^{87/86}\text{Sr}$ isotope ratios of ~ 0.7085 to 0.7095 , much more radiogenic than late Permian sea water (0.7070). The most likely source of the radiogenic strontium is the overlying shallow Salado salt deposits, having $^{87/86}\text{Sr}$ isotope ratios of ~ 0.7090 to 0.7095 .

Uplift of the DB may have been synchronous with the formation of the “Alvarado Ridge”, a pronounced tectonic feature that extends from southern Wyoming to northern New Mexico. The “Alvarado Ridge” formed at ~ 20 Ma, with maximum uplift occurring at ~ 7 to 4 Ma (Eaton, 1987). Uplift of the western part of the DB was accompanied by tilting of permeable sands and silts that helped to establish hydrogeological conditions favorable for dense saline brines to enter deep into the DB.

Variations in WOR, salinity and R_w observed across the DB are a natural consequence of osmosis and diffusion processes across the interfaces between permeable sands and silts and shale. Shales that appear to have equilibrated with high salinity sands all have higher salinities and lower WOR. In the case of the oil bearing Wolfcamp shale, ion diffusion is into the Wolfcamp shale while the driving force for water is to move into the high salinity sands and silts where the activity of water is lower. Both water and oil will, therefore, flow in the same direction. This process, referred to as co-current flow, is opposite to the counter-current flow of water and gas in the case of gas shales. Co-current flow of oil and water may help to explain why oil production in the Wolfcamp shale in the DB is associated with relatively high WOR.

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