

## Geochemical Analysis of Returned Treatment Waters (RTW) associated with shale gas production in the Appalachian Basin (USA) and Deep Basin (Canada): Potential use of Total Dissolved Solids (TDS) and Oxygen isotope data for assessing Water:Rock ratios and Stimulated Rock Volume (SRV)

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### Summary

The Marcellus gas shale and Duvernay liquid rich shale are attractive targets because of their relatively high hydrocarbon saturations  $S_{g-MARC} \sim 0.8 - 0.9$  and  $S_{HC-DVRN} \sim 0.7 - 0.8$ , respectively. The implied very low water saturations ( $S_w \sim 0.1-0.3$ ) confirm that these shales are dehydrated and contain no mobile water. When exposed to dilute meteoric water during hydraulic fracture stimulation the shale undergoes spontaneous imbibition, resulting in a coupled osmosis and diffusion process that imbibes most of the injected water. Only  $\sim 10-20$  vol. % of the residual treatment water (RTW) is recovered from Marcellus wells, and  $\sim 20-50$  vol. % of the residual treatment water (RTW) is recovered from Duvernay wells. RTW tends to be highly saline, increasing over production time, and often with TDS contents exceeding 250-300 kppm.

Recently published data for Marcellus flow back brines by Rowan et al. (2015) shows that the RTW are isotopically enriched relative to injected local meteoric water (LMW) used in hydraulic fracture (HF) stimulation with  $\delta^{18}O \sim -1$  to  $-3$  ‰ vs.  $-9.5$  ‰ for LMW (SMOW). The cause of the enriched oxygen isotopic signature has been attributed by some as being due to dissolution of salts in the Marcellus shale matrix. However, the RTW that has equilibrated with the Marcellus shale matrix is under-saturated with respect to halite.

Based on geochemical analysis of hundreds of proprietary brine samples, an alternative interpretation is proposed for the origin of high salinities in RTWs associated with gas production in the Marcellus and Duvernay Fms. When plotted in the ternary NaCl-MCl<sub>2</sub>-H<sub>2</sub>O system (where  $M=Ca^{2+} + Mg^{2+} + Ba^{2+} + Sr^{2+}$ ), compositions of flow back brines from 55 Marcellus wells show a remarkably uniform composition with NaCl:MCl<sub>2</sub> of 57.8:42.2, indicating that their compositions are controlled by equilibration with the shale matrix. The Duvernay shale in the Deep Basin of Alberta Canada indicates very uniform NaCl:MCl<sub>2</sub> of  $\sim 70:30$  also suggesting that RTW compositions are also controlled by equilibration with the shale matrix.

Published oxygen isotope and TDS data from Marcellus RTW have been used to model the Water:Rock ratio (W:R) based on exchange between LMW and the shale matrix. An “open system” model has been used to estimate the W:R as this best approximates a single batch of fluid passing through the hydraulically fractured subsurface, consistent with the process of injection and flow back.

Application of the oxygen isotope model to RTW associated with the Duvernay Fm., from Deep Basin in Alberta Canada, shows similar oxygen isotope enrichment for the highest TDS and lowest inferred W:R ratios. The oxygen isotope-TDS signatures observed in some of the Deep Basin RTW allows for the fingerprinting of formation waters from stratigraphically deeper formations. These have enriched oxygen isotopic signatures ( $\sim +5$  ‰; SMOW) and very high TDS contents of  $\sim 250$  kppm. Their presence in Duvernay produced waters is an indication of breakthrough from these deeper and more saline formations.

The new oxygen isotope model allows for the estimation of the W:R ratio in RTW from their TDS contents and  $\delta^{18}O$  values. The W:R ratio is a proxy for Surface Area and Stimulated Rock Volume (SRV), since the most enriched and highest TDS brines have the lowest W:R ratios i.e., more exchange higher TDS and heavier  $\delta^{18}O$ . For the Marcellus

shale for example, the model shows that to produce RTW with the most enriched oxygen isotopic signature (-1 to -3 ‰; SMOW) and highest TDS, ~325 kppm, implies a W:R ratio of ~0.02. This W:R ratio is almost identical to that proposed by Stewart et al. (2015) based on their analysis of Strontium isotopes in Marcellus flow back brines. The Duvernay flow back brine mixtures have enriched oxygen isotopic signatures (~+5 ‰; SMOW), very high TDS contents of ~300 kppm and the lowest inferred W:R ratios. For the Duvernay shale the W:R ratio is as low as 0.001 for some produced water samples

## Introduction

The source of high TDS residual treatment waters (RTW) associated with shale gas production is a contentious topic, with little consensus as to the source of the high TDS brines and how they might have formed. Several authors e.g., Dresel and Rose (2010), Haluszczak et al. (2013) and Rowan et al. (2015) have proposed, based on Cl/Br vs Na/Br data, that the Marcellus RTW shows geochemical evidence for having formed from evaporitic brines in which halite saturation had been exceeded. In some instances, Marcellus flow back brines show evidence for having been contaminated by halite derived from the Salina Salt, particularly where the Marcellus shale Fm is structurally proximal and/or juxtaposed against the Salina Salt due to structural deformation as a result of Appalachian tectonism (Bryndzia and Ash, 2015).

The dominant ion components in RTW are Na<sup>+</sup> and Ca<sup>2+</sup> ions (Bryndzia, 2012; Engelder et al., 2014 and Bryndzia and Ash, 2015) common interlayer cations associated with original smectite clay minerals typical of marine shale. Diagenesis of smectite to illite during burial and compaction produces illite, in which the K<sup>+</sup> ion replaces the Na<sup>+</sup> and Ca<sup>2+</sup> interlayer cations. S<sub>w</sub> in mature gas shales is very low with S<sub>w</sub> ~0.1 to 0.2, due to the removal of fresh water, both through membrane filtration and evaporative transport processes associated with compaction and thermal maturation of kerogen. The end-result of this dehydration process is geochemically indistinguishable from that of advanced seawater evaporation. The remaining ions and low water saturation form hydrophilic ion complexes that are most likely associated with maintaining charge balance on clay mineral surfaces formerly satisfied by van Der Waals bonding by hydrogen in water. It is the interaction of these hydrophilic ionic complexes with fresh fracture fluids that results in strong diffusion and osmosis gradients being established between freshly created matrix surfaces and dilute fluids in the fracture. Water is strongly imbibed into the shale matrix via capillary action while ionic diffusion results in the RTW in the hydraulic fracture becoming progressively more saline (Engelder et al., 2014).

Another characteristic of RTW is their enriched oxygen and deuterium isotopic compositions relative to that of LMW which is commonly injected fresh surface waters used in HF stimulation of unconventional source rock reservoirs (Rowan et al., 2015). Other more conventional oil and gas plays that utilize hydraulic fracturing such as the Permian Basin of Texas, also utilize aqueous and isotope geochemistry to examine fluid movements in and between reservoirs and faults in the subsurface. Laughland et al. (2014) used ionic and H<sub>2</sub>O isotopic compositions to show that formation water was mixing from two zones in wells with problematically high water cuts, and that these high water cuts appeared to be associated with a fault system observed on micro seismic and seismic surveys. In this paper, we develop an oxygen isotope exchange model based on published TDS and oxygen isotope data for RTW associated with Marcellus gas production from two areas in PA. Using this model, we estimate water:rock ratios (W/R) implied by the sampled RTW compositions. This model is then applied to interpret the source of produced waters that have unique isotopic and aqueous geochemical signatures to that normally produced as RTW from light oil production in the Duvernay Fm in the Deep Basin area of Alberta, Canada.

## Theory

The hypothesis that we tested is that the oxygen isotopic composition and salinity of Marcellus RTWs is a function of the W/R ratio that hydraulic fracture (HF) fluids are exposed to in the subsurface i.e., more exchange → higher TDS and heavier δ<sup>18</sup>O in RTW. The profile of the dashed green line in Figure 2 was our first indication that we are most likely dealing with an exchange/mixing process between shale matrix and water from injected HF.

We base our model on a simple mass balance exchange between LMW and illite, the most common phyllosilicate in the thermally mature Marcellus gas shale. We have estimated the isotopic fractionation factor ( $1000 \ln \alpha$ ) for oxygen isotope exchange between water-illite, based on the data of Sheppard and Gilg (1996; Table 1). The initial

$\delta^{18}\text{O}$  value we have assumed for the Marcellus shale is +16.5 ‰, the average of values reported for marine shale in Savin and Epstein (1970). Input parameters are summarized in Table 1.

Table 1: Input parameters for estimating W/R in RTW from both the Marcellus and Duvernay shale Formations

Formation	Temp (°C)	$1000 \ln \alpha$	$\delta^{18}\text{O}$ (‰; SMOW) LMW
<b>Marcellus</b>			
SW PA	75	-17.40	-9.5
NC PA	65	-15.96	-9.5
<b>Duvernay</b>	115	-19.62	-17.0
$1000 \ln \alpha_{\text{illite-water}} = -2.39 \cdot 10^6 \cdot T^{-2} - 3.76$			

Oxygen isotope exchange between the shale matrix and HF fluid may be modeled as either an open or closed system. An open system is one in which the fluid makes a single pass through a given volume of rock, whereas in a closed system the fluid is able to exchange many times with the same rock volume. We have modeled the exchange of HF fluid with the shale matrix as an open system process since the HF fluids literally do make a single pass through the system prior to flow back and clean-up of wells. The simple mass balance relationship that we have used to estimate the W/R ratio based on isotopic exchange of oxygen between rock and water is given by equation 1, taken from Taylor (1979).

$$\frac{W}{R} = \ln \left[ \frac{\delta_w^i + \Delta - \delta_r^i}{\delta_w^f - (\delta_r^f - \Delta)} \right] \quad (1)$$

Where:  $W$  indicates the mass of water involved and  $R$  the mass of rock involved;  $w$  and  $r$  represent *water* and *rock*, respectively, and the superscripts  $i$  and  $f$  denote the *initial* and *final* isotope ratio.  $\Delta = \delta_r^f - \delta_w^f$ .

## Examples

The results of our modeling for two examples including the Marcellus gas producing areas in PA and Duvernay condensate areas in Kaybob, Alberta are presented in Figure 3. Both open and closed system models are shown in Figure 3. The oxygen isotopic composition of RTW from Duvernay production in Alberta is clearly more enriched than the RTW from Marcellus, but this enrichment is, in part, temperature controlled. The model in Figure 3 would also suggest that the range of  $\delta^{18}\text{O}$  in RTW for both Marcellus and Duvernay produced water may be due to a much lower W/R ratio. In other words, it appears that the RTW associated with highly enriched  $\delta^{18}\text{O}$  in RTW has exchanged with a much larger rock volume. To test this hypothesis further, we interpolated reported TDS and model W/R ratios for RTW from Rowan et al. (2015). The results be discussed in the presentation.

## Conclusions

We have demonstrated that the composition of RTW associated with production from unconventional shale reservoirs appears to be controlled by equilibrium between injected HF water and the shale matrix. It is also the shale matrix, dominated by illite in mature to over-mature shales, that controls the isotopic enrichment and high TDS contents observed in RTW. Data from both the Marcellus and Duvernay shale formations are consistent with this interpretation. A model based on the oxygen isotopic composition of the RTW and its TDS permits an estimate to be made of the W/R, a direct indication of the total surface area of stimulated shale that the HF injected water has been in contact with. This surface area is therefore a direct proxy for SRV.

The routine geochemical analysis of RTW provides a rapid and inexpensive surveillance strategy for monitoring RTW associated with production from unconventional reservoirs. Using previously established formation and RTW isotopic compositions i.e., baseline, any breakthrough of extraneous brines that might occur from breaching aquifers or other sources of water, would be readily apparent in real time. This kind of information potentially impacts many aspects of disposal and/or reuse of produced RTW in subsequent completions. For example, it would not be prudent to re-inject high TDS RTW in subsequent completions if the possibility existed that the HF fluids could reach halite saturation in the sub surface, resulting in impaired production and potentially requiring expensive remediation in the future.

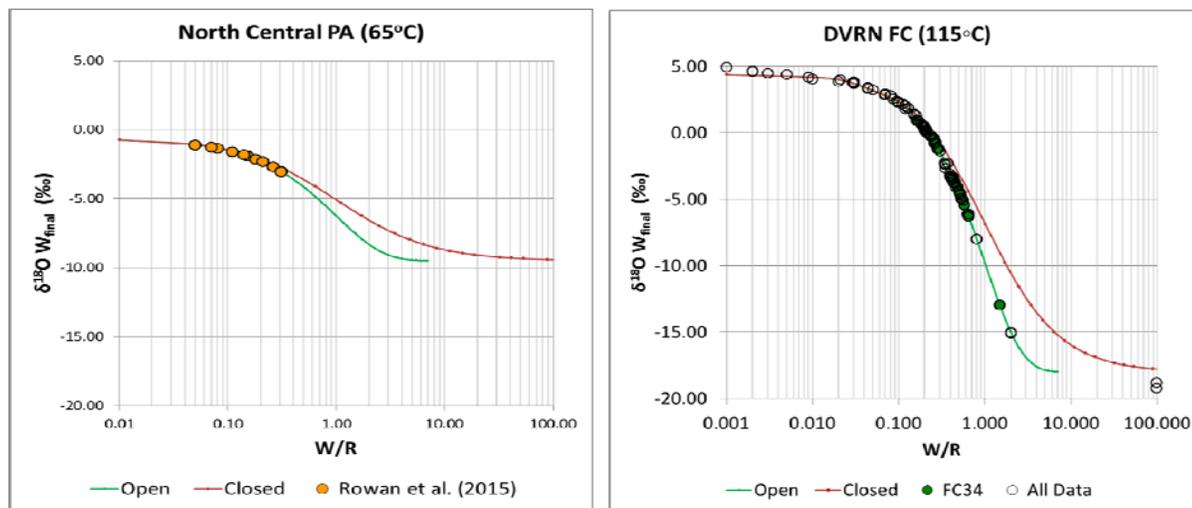


Figure 3: Estimated W/R ratios calculated using the data in Table 1 and oxygen isotope data for Marcellus RTW from Rowan et al. (2015) and Duvernay well flowback water sample data.

## Acknowledgements

A more complete discussion of this work is available in Bryndzia and Fay (2016). Reprinted with permission from URTeC.

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