

## Geochemistry of Flowback Fluids from the Utica Shale in Eastern Ohio

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Flowback fluids were collected from two Utica/Point Pleasant shale hydraulic fracturing sites in eastern Ohio. The northern site was in the wet gas zone, while the southern site consisted of four wells on the same pad in the dry gas zone. Samples of input fluids also were collected before and during hydraulic fracturing. Flowback fluids are Na-Ca-Cl brines with total dissolved salt (TDS) concentrations that increase over several months from ~ 100 to 200 g/L. The slightly higher TDS of the dry gas fluids are in part due to recycled flowback used as input fluids. Concentrations of most major ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Sr}^{2+}$ , Fe, Mn, Cl, Br) are similar for the five wells sampled, although small but systematic changes occur in the major element ratios over time. Most notably, an increase in the Sr/Cl ratio corresponds to an increase in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the fluids, suggesting interactions with a more radiogenic Sr source in the subsurface. Trace metal concentrations (Li, Rb, Y, Mo, Zr, Ru, Rh, Ag, Te, Cs, La, Ce, Gd, Yb, Lu, W and Cr) follow a similar trend as the major elements, though concentrations are approximately two to five fold higher in the four dry gas wells than the wet gas well, suggesting greater accessibility to and reactions with clay minerals. Input water chemistry exerts an important control on the Sr and Ba concentrations in flowback water. High  $\text{SO}_4$  in the input fluids used for hydraulically fracturing the wet gas well leads to precipitation of barite-celestite in flowback fluids.

Water oxygen ( $\delta^{18}\text{O}$ ) and hydrogen ( $\delta\text{D}$ ) isotopes for input (source) fluids fall on the Global Meteoric Water Line (GMWL). Flowback fluids from all five wells are relatively enriched in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  compared to the input, suggesting reaction and isotopic exchange with carbonates, mixing with in situ brines, or fractionation due to imbibition in the rock.

Water-rock interaction experiments were conducted to determine the source of solutes in the flowback fluids. Mass balance calculations suggest that solutes in a liter of flowback fluids are derived from interactions with approximately 5 to 100 kg of rock in the subsurface.