Laboratory CO_2 flow experiments to model hydrochemical and mineralogical changes in the Arbuckle aquifer during CO_2 storage

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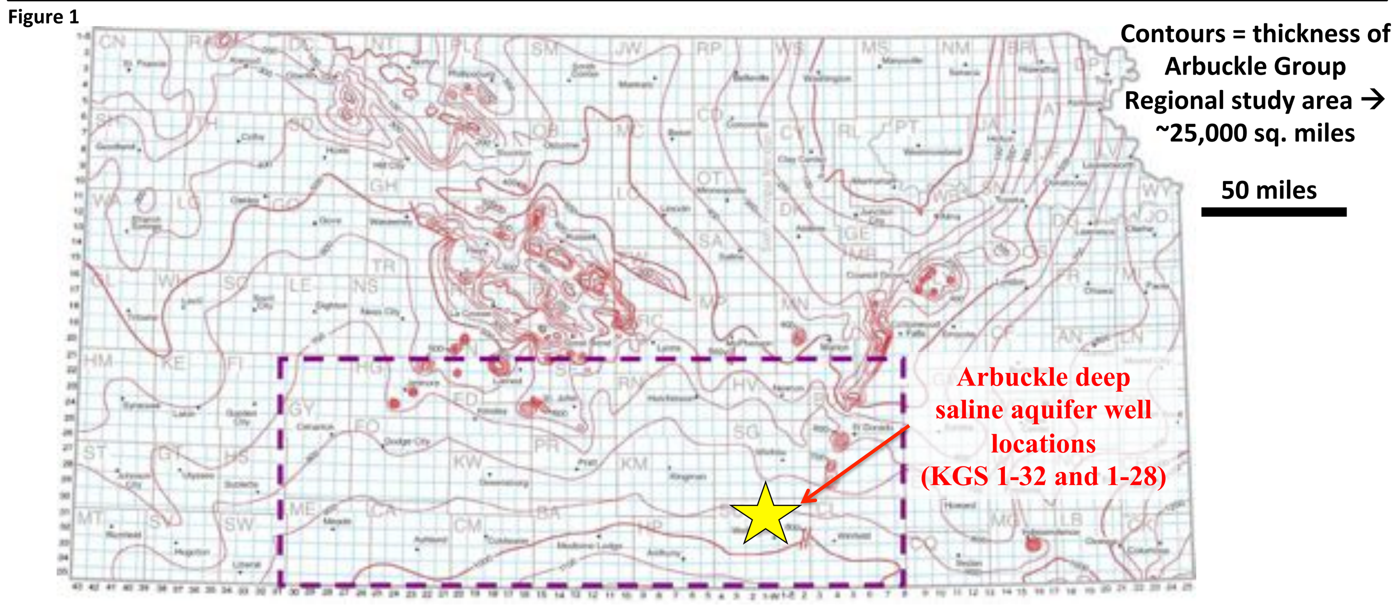
Introduction

- Geologic sequestration of CO_2 has been targeted as a way to mitigate future release of this green house gas
- Deep saline aquifers are the most appealing geologic formations for sequestration because they are unfit for drinking and usually isolated from fresh water sources
- Secure, long term storage involves mineralization reactions that require the presence of certain minerals in the core rocks and ionic species in formation waters to facilitate precipitation in presence of supercritical CO_2
- Arbuckle aquifer in SC Kansas has been targeted for this CO_2 sequestration project
- Water samples have been analyzed from 8 drill stem tests (DST) (3677`, 4182`, 4335`, 4520`, 4876`, 4927`, 5036`) and 1 swab test (5010`) in the Mississippian and Arbuckle aquifers and analyzed for hydrogeochemistry
- 1600 feet of core was taken from well KGS 1-32 for mineralogical investigation
- Core samples have been analyzed with X-ray diffraction, thin section petrography and scanning electron microscopy
- Supercritical flow-through experiments at the National Energy Technology Laboratory (NETL, Pittsburgh) provide experimental data to constrain geochemical models, providing geochemical dissolution, mobilization and precipitation kinetics
- Hydrogeochemical and mineralogical data allow for comprehensive reservoir characterization to be utilized in a CMG-GEM CO_2 injection simulation

Objectives

- Characterizing the Arbuckle core mineralogy and describing key porosity and mineral textures that could promote reaction fronts within formation rocks
- Describing the evolution and hydrogeochemistry of the Arbuckle aquifer and examining how it will change in presence of CO_2
- Understanding experimentally what happens when supercritical CO_2 reacts with existing brine and how it could change the core mineralogy to promote mineral sequestration of CO_2

Well Locations and Local Geology



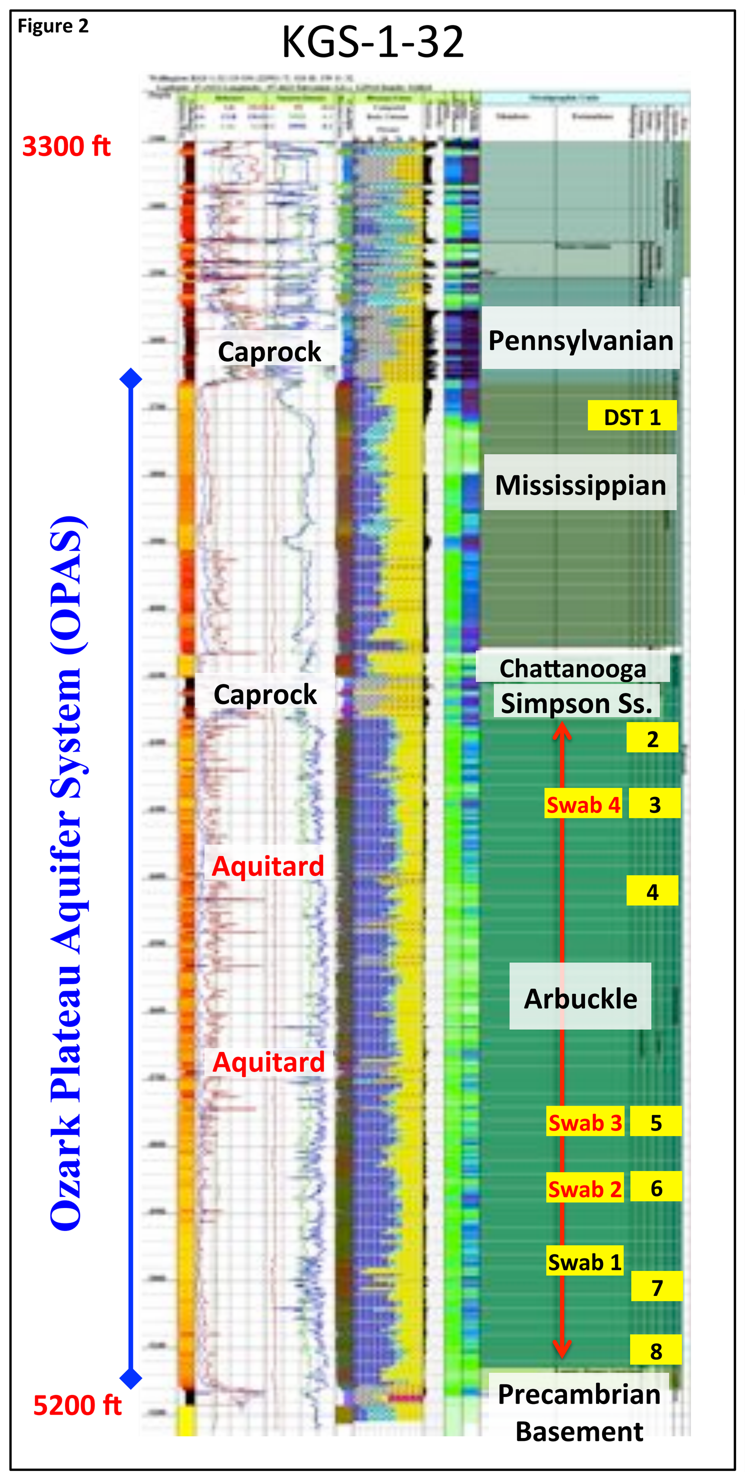


Figure 1: Contour map of the Arbuckle group thickness in Kansas and regional study area (purple rectangle). Experimental wells KGS 1-32 and 1-28 located in the Sedgwick Basin are 4 miles north west of Wellington, KS (yellow star). *Map courtesy of the Kansas Geologic Survey.*
Figure 2: Well log of the Arbuckle and Mississippian aquifers from KGS 1-32 experimental well, Sumner Co., KS. DST and swab sample depths are labeled. Total depth in KGS 1-32 is ~5200`.
Figure 3: Whole core section (4684-4686`) from KGS 1-32. Notice large vugs and heterogeneity throughout the core (photos taken on-site during February 2011).

- Arbuckle is the lower part of the Ozark Plateau Aquifer System which includes the freshwater Ogallala aquifer
- Arbuckle Group rocks are late Cambrian to early Ordovician in age consisting generally of porous dolomitic carbonates with interbedded shaley aquitards
- The Arbuckle is overlain by the Simpson sandstone and the Chatanooga shale (absent in KGS 1-32, present in 1-28). Economically important Mississippian oil reservoir lies above them
- Two wells (KGS 1-32 and 1-28) were drilled 2000` apart in the Wellington field, Sumner Co, SC Kansas (figure 1)
- The wells extend through the entire Arbuckle formation and into the Precambrian granite bedrock below (figure 2)
- Salinity values in the aquifer range from 30,000 to 120,000 ppm

Arbuckle Core Mineralogy

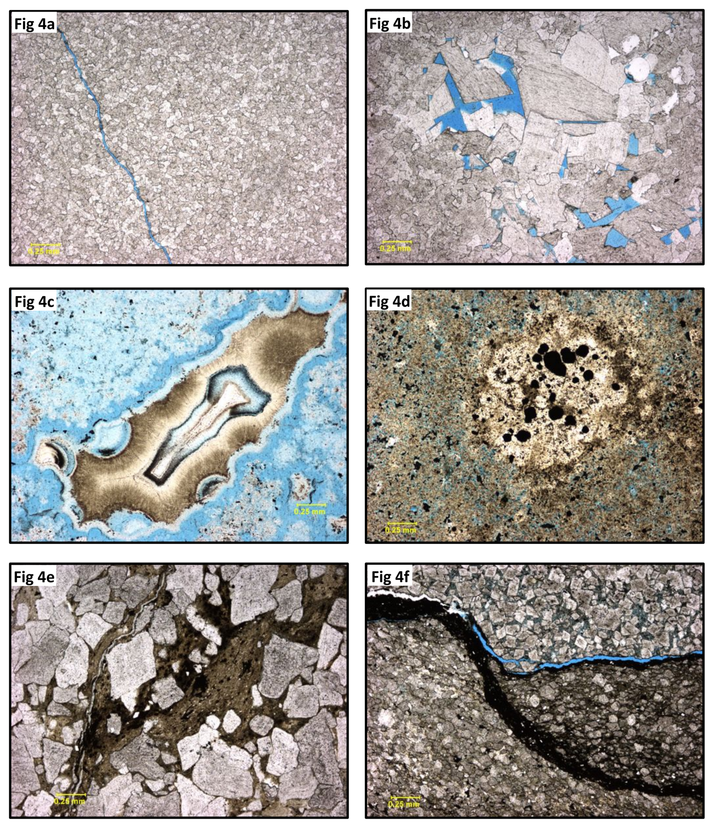


Figure 4: a) 4187.2 in pl; Dolomite replacement mosaic with presence of micro-fracture. **b)** 4923.7` in pl; Large dolomite crystals filling pore space in fine grained replacement mosaic. **c)** 4955.85` in pl; Chalcedony filling pore surrounded by porous silica texture. **d)** 4515.5` in pl; Chert nodule with pyrite(?) in moderately porous dolomite/chert with pyrite(?). **e)** 4570.1` in pl; Fracture filled with argillaceous material and pyrite(?). Healed fractures could be preferential reaction zone. **f)** 4388.8` in pl; Fracture filled with pyrite(?) in brecciated zone.

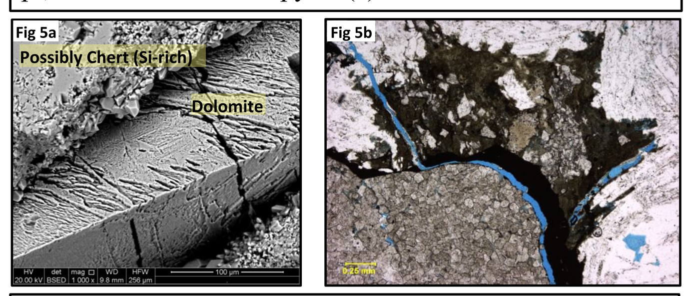
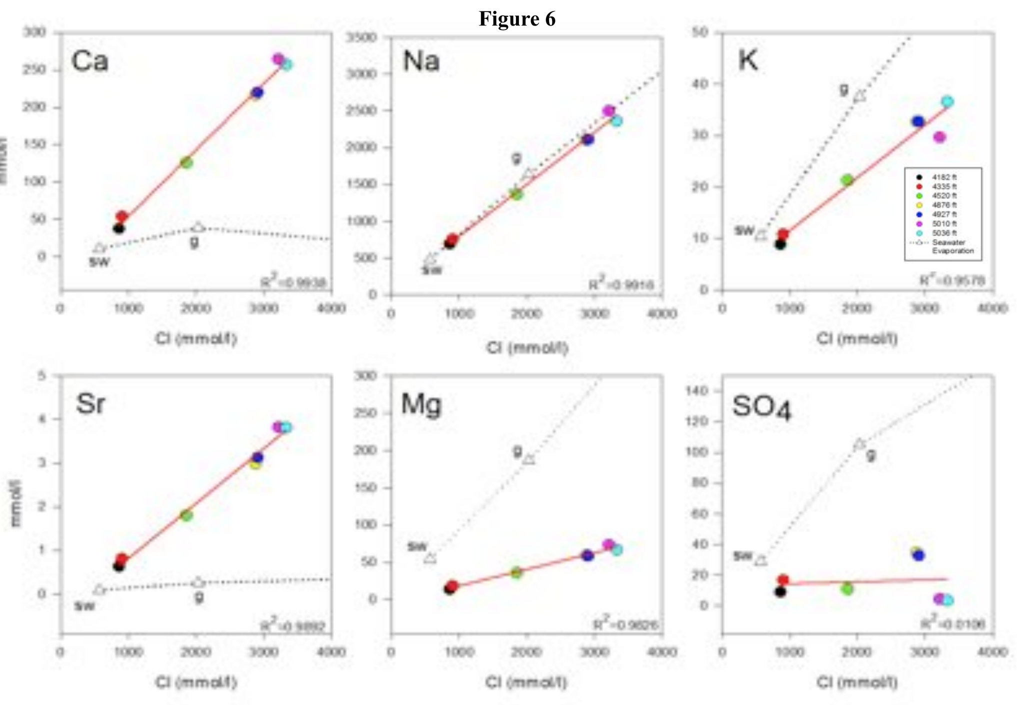


Figure 5: a) Scanning electron micrograph of plug 31-19 (4977`). Dolomite-chert contact could be a potential reaction site with preferential dissolution of dolomite and formation of fractures along reaction fronts. **b)** Thin section of 19-41 (4504`) showing complexity of chert/carbonate boundary.

Hydrogeochemistry of Arbuckle Aquifer



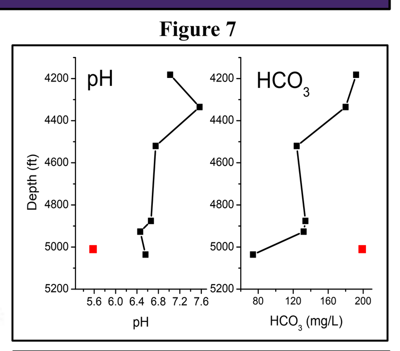


Figure 6: Chloride ratios with specific ions within the Arbuckle compared to modern seawater evaporation curve. They show evaporative enrichment with depth, coupled with diagenetic alterations. **Figure 7:** pH and HCO_3^- decrease with depth in the Arbuckle. Red symbol represents swab 1.

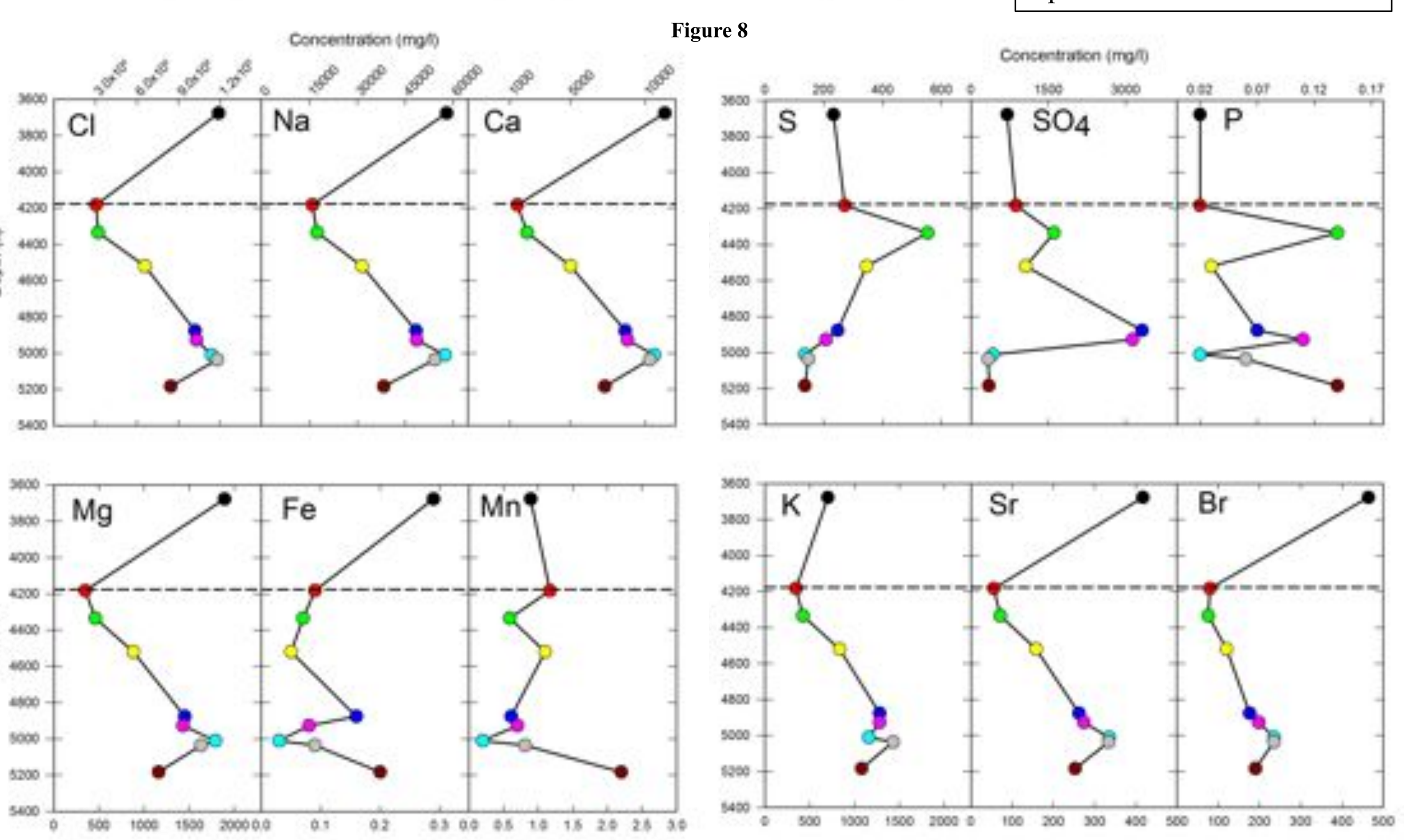
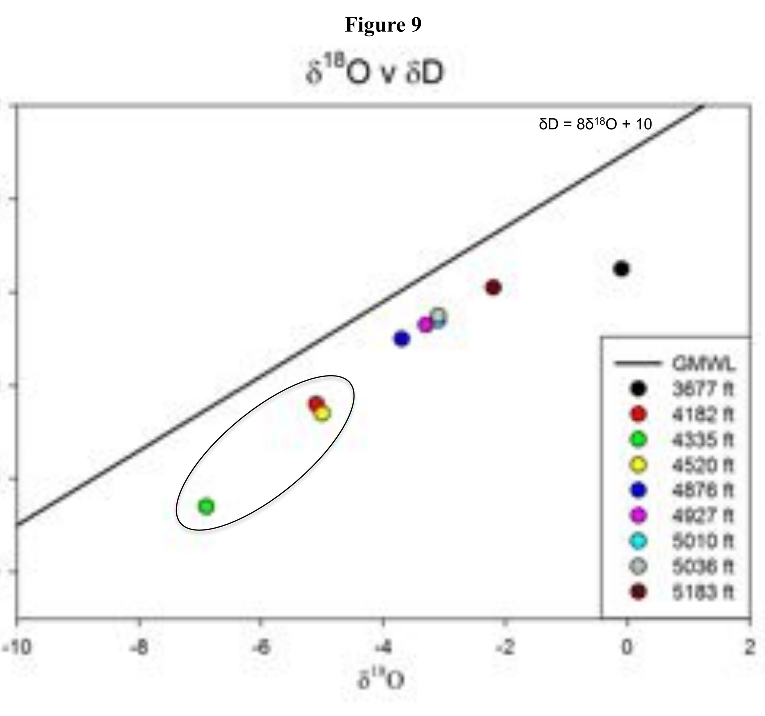
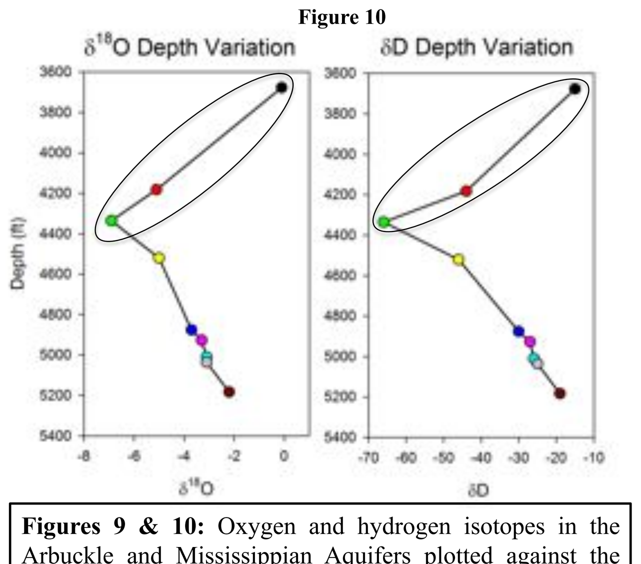


Figure 8: Depth profiles of major elements in the Mississippian and Arbuckle aquifers. Mississippian chemistry (black circle) is distinct from Arbuckle. Within the Arbuckle major species (Cl, Na, Ca, Mg, Sr, K, Br) increase linearly with depth which is typical of saline aquifers. Redox sensitive species (SO_4, P, Fe, Mn) show fluctuations with depth that is presumed to be the result of microbial metabolism. Porosity and NMR logs suggest a hydrologic baffle exists at ~4300`, limiting the connectivity between upper and lower zones. Oxygen isotope data add weight to this hypothesis.

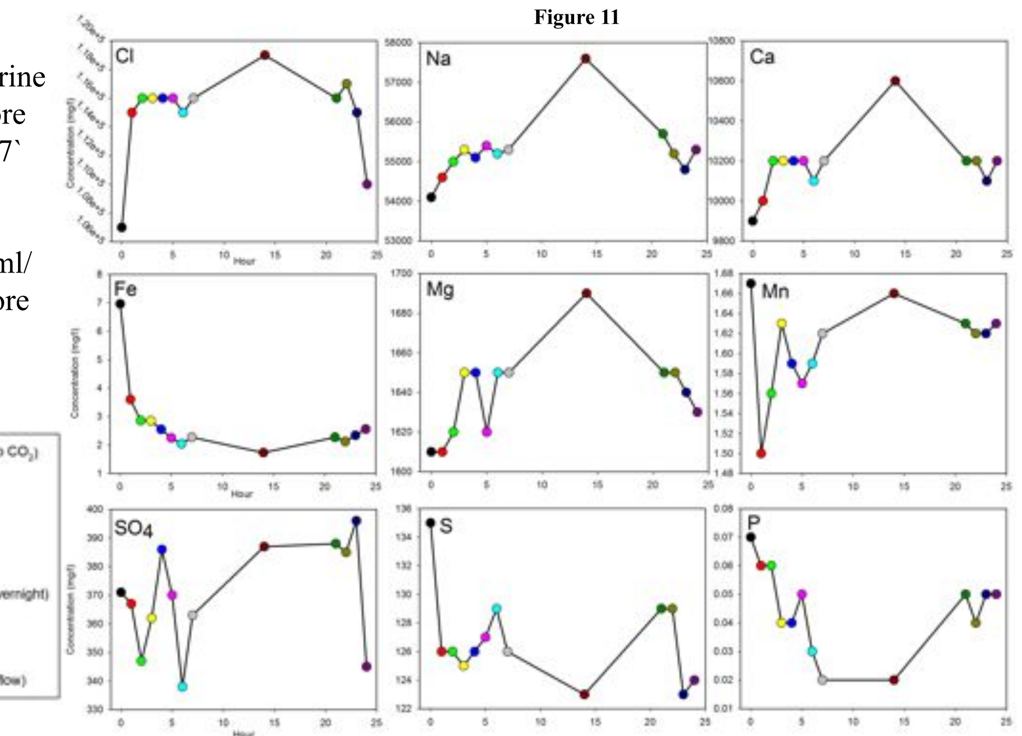


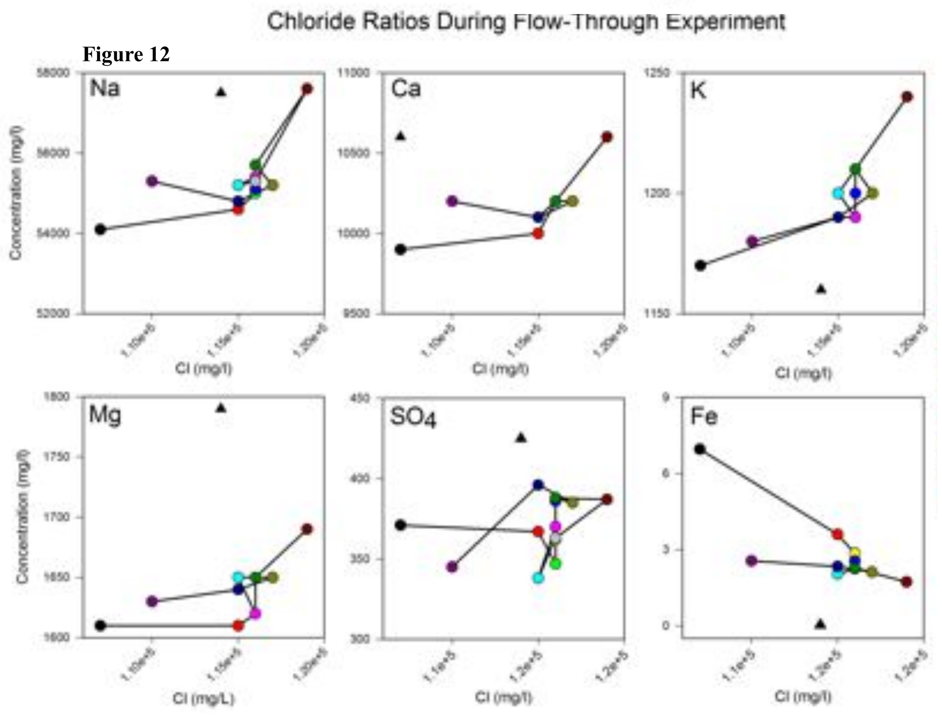


Figures 9 & 10: Oxygen and hydrogen isotopes in the Arbuckle and Mississippian Aquifers plotted against the GMWL (**Fig 9**) and with depth (**Fig 10**). Shows $\delta^{18}O$ enrichment with depth. Variation at 4182 and 4335 ft could signify geologic baffle zone between upper and lower Arbuckle units. Communication between Mississippian and upper Arbuckle likely.

Supercritical Flow-through Experiment

- Core Flow System 839z instrument was used to flow brine and CO_2 through formation core from the injection zone at 4977`
- Confining pressure 2100 psi; T= 40°C
- Brine only was flowed at 0.2 ml/min for 13 hours to saturate core (hour zero)
- CO_2 was introduced with brine at 1 ml/min (hour 1)
- Effluent collected hourly for analyses ('hour 14' is an average of over night brine + CO_2 flow)





- **Figure 11:** Time series (24 hour) analysis for CO_2-brine flow-through experiment using formation water (swab 1; 5000-5020') and using core from 4977`
- The values for pre flow brine were either higher (SO_4, S, Mg, Ca, Na) or lower (Cl, Fe, Mn, P). The difference in brine compositions could be due to contamination or chemical changes prior to CO_2 introduction
- **Figure 12**: Chloride ratios plotted against major reactive elements for the 24 hour flow through experiment
- Decreases in Cl during hour zero and hour 24 suggest the brine was diluted, while the over-night sample has been affected by evaporation
- Fe and K concentrations increased relative to the pre-flow brine composition (black triangle) while other species decreased in this Fe dominated system
- Longer flow experiments could show changing reaction rates

Conclusions

- The hydrogeochemical facies in the Arbuckle is majorly Na-Ca-Cl type, showing increasing concentrations of the same with depth. Average salinity of the injection zone formation water is of the order of 116,000 ppm Cl
- Major cations and anions show increasing concentrations with depth (eg. Na, Cl, SO_4, Ca and Mg), consistent with seawater evaporation and diagenetic changes
- Oxygen and hydrogen isotopes suggest upper and lower Arbuckle are separated by a low porosity 'baffle' zone
- Mineralogical analyses suggest extensive small and large scale heterogeneity with major mineralogy being dominated by dolomitic limestone with frequent cherty nodules and infillings. Microfractures and discontinuous argillaceous zones were marked all through the 1600 ft core
- Heterogeneity of the core and proportion of chert increases with depth through the proposed injection zone. Visible porosity increase with depth in the core.
- SEM micrographs of the core plugs show clear interface between chert and dolomite where fractures could develop with accentuated dissolution reactions
- Flow-through experiments of 4977` core plug showed variable responses for major species involved over a 24 hour period. At the first 5 hours Ca, Cl, Mg, Na and SO_4 increased while Fe and S decreased which followed the same trend with the only difference being Mn going into solution more rapidly. The next 8 hours demonstrated SO_4, Fe and S to be increasing in solution while Ca, Cl, Na, Mg, K and Mn decreased. Investigation is ongoing on the effect of high SO4 and Cl in the system on dissolution kinetics and extent of carbonate mineralization in the injection zone
- Overall conclusion is, with possible reactions inferred in the injection zone and their rates obtained, carbonate aquifers with high salinity can prove effective in sequestration but special attention needs to be imparted towards intricate textural relations and water chemistry
- There is no immediate sign of water quality degradation of the shallow aquifer due to injection

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