FLUID EVOLUTION IN CAMBRIAN-ORDOVICIAN KNOX GROUP RESERVOIRS

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Carbonate strata in the Cambrian-Ordovician Knox Group, where buried to 2,500 ft. or deeper in the Appalachian and Illinois Basins of Kentucky, are being investigated as a potential reservoir for geologic carbon storage. Analyses of archived formation water chemistry data show that Lower Ordovician and older reservoirs, including Knox Group reservoirs, are less saline than would be predicted by salinity trends in Silurian and younger reservoirs. Less saline water in the Knox Group suggests the possible influence of meteoric water, but it is not clear whether the meteoric water originated as "old" meteoric water that penetrated exposure surfaces during or shortly after Knox deposition or relatively "young" meteoric water that infiltrated along structural highs, such as the Cincinnati Arch. Distinguishing the causal mechanism is critical as infiltration of "young" meteoric water from the Cincinnati Arch into the deeper basin would imply that injected CO_2 could migrate the opposite direction to the surface driven by buoyancy forces.

The role of the Cincinnati Arch in fluid evolution in Knox Group reservoirs was investigated using bulk and isotopic (d^{18}O-H_2O, dD-H_2O) chemistry measurements from two geographic areas along the Cincinnati Arch representing structural culminations where Knox Group reservoirs are shallowly buried. The areas include the Jessamine Dome of north-central Kentucky and Nashville Dome of Tennessee. In addition, the age of Knox groundwater in the two areas was estimated using chlorine-36 measurements.

Most of the groundwater samples came from upper Knox Group carbonates (Beekmantown Dolomite and Chepultepec Dolomite) at depths of less than 100 to approximately 2,500 ft. below ground surface. Salinities were similar between the Jessamine and Nashville Dome areas and ranged from 467 to 8,189 mg/L, TDS. Most groundwater was NaCl-rich, but also included $NaHCO_3$-and $CaHCO_3$-rich groundwater. Chloride:bromide ratios in the Jessamine Dome area ranged from 39 to 292 and most values were on or close to a trajectory suggesting dilution of a parent marine water. The d^{18}O-H_2O and dD-H_2O measurements, however, were on or close to the meteoric water line for the Jessamine (d^{18}O= -7.3 to -8.1 per mil, dD= -41 to -57 per mil) and Nashville Dome (d^{18}O= -5.9 to -6.4 per mil, dD= -34 to -36 per mil) areas. Collectively, the data in both areas support substantial dilution of Knox groundwater, having a likely marine provenance, by meteoric water.

Similar chloride concentrations between the Jessamine (11- 1,300 mg/L) and Nashville Dome 15- 1,500 mg/L) areas suggest they were similarly influenced by meteoric flushing. The similarity diverged, however, when the ratio of chlorine-36 to stable chlorine (^{36}Cl/Cl) was measured. Chlorine-36, produced largely in the atmosphere by cosmic ray interactions with argon-40, has a half-life of approximately 301,000 years. Upon entering the groundwater system as precipitation, the ^{36}Cl/Cl in meteoric water generally declines with time and along the flow path. Ratios of ^{36}Cl/Cl for the Nashville Dome area ranged from 160 to 709 (n= 7) with most ratios being slightly less than the value for meteoric water before nuclear testing (400). This suggests that dilute Knox groundwater in the Nashville Dome area is relatively young meteoric water. Jessamine Dome $^{36}Cl/Cl$ ratios, in contrast, were markedly lower and ranged from 1 to 176 (n= 6) with five ratios being less than 6. Compared to the calculated secular $^{36}Cl/Cl$ ratio of 9 for a carbonate reservoir, this suggests that most of the sampled Knox groundwater in the Jessamine Dome region has attained secular equilibrium. One implication of this finding is that, although dilute, Knox groundwater in the Jessamine Dome region is possibly older than 1.5 million years old.

The $^{36}Cl/Cl$ measurements thus suggest that, despite similar structural and stratigraphic settings and similar aqueous chemistry, upper Knox aquifers in the Nashville Dome and Jessamine Dome areas were infiltrated by meteoric water at significantly different times. Substantiation of this interpretation would benefit, however, by comparison with a different dating method, such as ^{81}Kr (half-life= 229,000 years), as the low $^{36}Cl/Cl$ ratios in the Knox in the Jessamine Dome area could reflect mixing with groundwater from other reservoirs.