

## Assessing the utility of $\delta^{13}\text{C}$ as a monitoring tool for subsurface $\text{CO}_2$ injections: A hydrothermal experimental approach

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Stable carbon isotopes have been used in previous research as a process and monitoring tool at  $\text{CO}_2$  injection sites, but no experimental laboratory basis exists to validate this practice. We will present carbon stable isotope results from hydrothermal experiments using flexible Au-Ti reaction cells (Dickson cells) that allow for analysis of fluids and gases at in-situ temperatures and pressures. To our knowledge, this is the first time a hydrothermal experimental approach using supercritical (sc) $\text{CO}_2$  has been applied to address this knowledge gap.

We will react a synthetic brine with shale samples and maintain conditions at 100 bar over a range of temperatures applicable to geological sequestration reservoirs. After a period of rock-brine reaction to steady-state conditions, sc $\text{CO}_2$  will be injected into the reactor and both gases and liquids will be periodically sampled for  $\delta^{13}\text{C}$  until isotopic equilibration of the water-rock- $\text{CO}_2$  system has been reached.  $\text{CO}_2$  will be added in excess of brine saturation to ensure the existence of a separate sc $\text{CO}_2$  phase and fluid saturation for the duration of the experiments. The carbon isotopic composition of the brine, injected  $\text{CO}_2$ , and shale (both organic and inorganic C) will be determined prior to the experiments. Using these values, a mass balance approach will be employed to predict equilibrium  $\delta^{13}\text{C}$  values. .

Results will guide interpretations of interactions between injected  $\text{CO}_2$  and dissolved or solid organic carbon phases. Supercritical  $\text{CO}_2$  and DIC phases in all experiments are expected to reach  $\delta^{13}\text{C}$  values consistent with the mass-balance calculations involving inorganic carbon in the reactor. The organic carbon in the shale is not expected to impact values. Observation of deviations between predicted and observed  $\delta^{13}\text{C}$  values will help quantify contributions from constituents of the shale such as carbonates and organic matter. The results of this study will inform the validity of using carbon stable isotopes from both DIC and injected  $\text{CO}_2$  as a process and monitoring tool at carbon sequestration sites.