



New data for C-isotope fractionation between dissolved inorganic carbon and CO_{2(g)} at elevated temperatures relevant to CO₂ storage

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Geochemical monitoring concepts for CO₂ injection projects associated with carbon capture and storage (CCS) rely on field- and laboratory data to describe the fate of CO₂ in the subsurface. In this context, stable carbon isotope investigations have proven as valuable tools when investigating processes involved between dissolved inorganic carbon (DIC) and CO₂. However, during the migratory path of the injected CO₂, isotope fractionation may occur, which needs to be accounted for when data from samples obtained during monitoring programs are interpreted. Since stable carbon isotope fractionation within the carbonate system also depends on pH, all probable pH regimes within the potential CO₂-migratory path must be considered. Close to the CO₂ injection well, for instance, pH levels in the reservoir tend to decrease and hence the dominant carbon isotope fractionation will occur between H₂CO₃^{*} and CO_{2(g)}. However, fractionation factors for this stage are only reliable up to about 60°C. This poses a problem since CO₂-reservoirs often encompass higher temperatures. Further away from an injection well, near-neutral pH levels are often observed, for example, when elevated carbonate concentrations are present in the fluids. In this case isotope fractionation between HCO₃⁻ and CO_{2(g)} can be expected, however fractionation data is only reliable up to 70°C (Myrntinen et al., 2012).

New investigations therefore are conducted with analogue fluids (with up to 1 mol/L C, using NaHCO₃ as carbon source) to measure the relation between elevated temperatures (up to 120°C), pressure (pCO₂= 60 bar) and stable carbon isotope fractionation factors between DIC and CO_{2(g)} at various pH levels. Since, for isotope and DIC analyses, only the bulk parameter of DIC can be measured, a mixed fractionation effect between the present DIC species and the gaseous CO₂ may occur. For instance, at temperatures between 20 and 120°C, isotope measurements reveal δ¹³C_{DIC-CO₂} differences (ε) that decreased from 3.2 to 2.5 with increasing temperature. These results indicate that C-isotope fractionation occurred between CO_{2(g)} and a mixture of H₂CO₃^{*} and HCO₃⁻.

These investigations form the basis for further experiments at various pH levels to investigate the DIC-CO_{2(g)} isotope fractionation-shift from an H₂CO₃^{*} dominant regime to one of HCO₃⁻ dominance at elevated temperatures. These results aim to improve the accuracy with which the isotopic composition of CO₂ can be used to trace injected gas. They also lay foundations for interpreting geochemical reactions induced by CO₂ migration in the subsurface.

References:

Myrntinen, A., Becker, V., Barth, J.A.C., 2012. A review of methods used for equilibrium isotope fractionation investigations between dissolved inorganic carbon and CO₂. *Earth-Science Reviews*, 115(3): 192-199.