

Modeling shallow groundwater geochemistry and carbon isotopes: Test of methodology for CO₂ storage evaluation at an EOR site, West Texas, USA

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**Katherine D. Romanak
Rebecca C. Smyth
Changbing Yang
Susan D. Hovorka**



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Romanak, K. D., Smyth, R. C., Yang, C., and Hovorka S. D.

KINDER MORGAN

Gulf Coast Carbon Center, Bureau of Economic Geology, Jackson School of Geosciences, The University of Texas at Austin, P.O. Box X, Austin, TX, 78713, USA

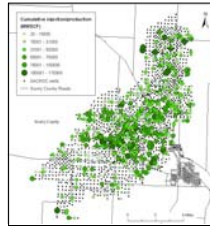
Introduction

Capture and storage of industrial CO₂ in subsurface geologic sinks (depleted oil and gas reservoirs and deep brine formations) is a strategy for mitigating global warming. The U.S. Dept. of Energy National Energy Technology Laboratory (NETL) is funding research through the Regional Carbon Sequestration Partnership program to monitor carbon storage sites and verify that injected CO₂ remains in the subsurface (Litnyski et al., 2006). The SACROC oil field in Scurry County, TX, is one of the field-experiment sites within the NETL Southwest Partnership (Brian McPherson, PI). Kinder Morgan Co. operates SACROC, where CO₂ has been injected for enhanced oil recovery (EOR) since 1972. Our goals are to (1) assess interaction between shallow groundwater and CO₂ injectate and (2) test low-cost methods of monitoring shallow groundwater at CO₂ sequestration sites. GCCC researchers collected Dockum aquifer samples and are utilizing carbonate system parameters to conduct geochemical mixing, reaction, and stable isotope models in order to identify geochemical anomalies relative to regional trends and identify sources of CO₂ in groundwater near SACROC.

Background

Why SACROC?

- The Scurry Area Canyon Reef Operators Committee (SACROC) unitized oil field has the longest history of CO₂ injection for EOR in the world (fig. 1).
- Since 1972, 150 million metric tons (MMt) of CO₂ has been injected at SACROC; 75 MMt has been recovered/recycled. The balance may be permanently sequestered in or near the injection zone.
- CO₂ injection history provides the opportunity to look for injectate CO₂ in shallow groundwater above SACROC and to test stable carbon isotope methodologies for monitoring shallow groundwater above sequestration sites.

Fig. 1. SACROC CO₂ injection map.

Water Sampling

- BEG monitored shallow Dockum groundwater (50- to 500-ft-deep private water wells) near SACROC between July 2007 and November 2008.
- BEG and TWDB (<http://www.twdb.state.tx.us>) water samples (fig. 2) collected inside SACROC are compared with samples from outside SACROC to assess potential impacts on freshwater resources by CO₂ injection operations.
- Geochemical data are from the fresh to slightly saline Dockum Formation, Permian-age evaporite horizons, and brine from the 6,000- to 7,000-ft injection/production zone.



Fig. 2. Surface geologic units and water-well sample locations around the SACROC oil field.

Geologic unit key:

P = undifferentiated Permian; TrD = Triassic Dockum
P-Eo = Paleocene-Eocene Ogallala; Q = undiff. Quaternary

Geochemical Influences

- Potential sources of CO₂ in Dockum groundwater include (1) CO₂ injected into production zone, (2) degassing from rock-water reactions, and (3) CO₂ produced from microbial activities (fig. 3).
- Additional geochemical influences are (1) mixing with Permian evaporite waters along a well-documented Permian dissolution zone (i.e., Dutton, 1989) and (2) infiltration of produced brine formerly stored in unlined surface pits.

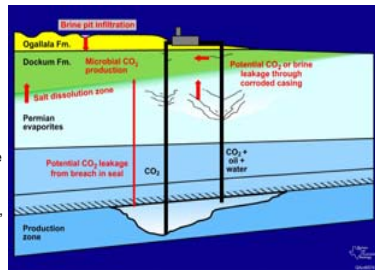


Fig. 3. Schematic cross section of study area (not to scale).

Major Element Geochemistry

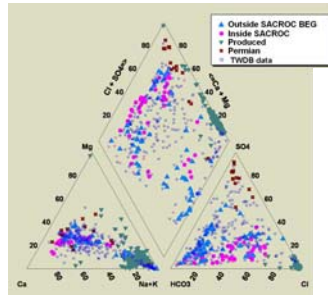


Fig. 4. Piper diagram of (1) Dockum chemistry outside and inside SACROC, (2) Permian groundwater, (3) produced brine, and (4) regional TWDB data.

- Distribution of anions shows that Dockum water outside SACROC trends toward Permian (CaSO₄) compositions and water inside SACROC trends toward produced water (NaCl) compositions.
- Mixing of Dockum freshwater with Permian and oil reservoir brine has influenced Dockum geochemistry. Greater influence from reservoir brine occurs inside SACROC. Otherwise, there is no large-scale distinction between Dockum samples collected inside SACROC and regional geochemical trends.
- Groundwater mixing, cation exchange, and dedolomitization are major geochemical processes controlling Dockum groundwater compositions.

Modeling Carbonate Geochemistry

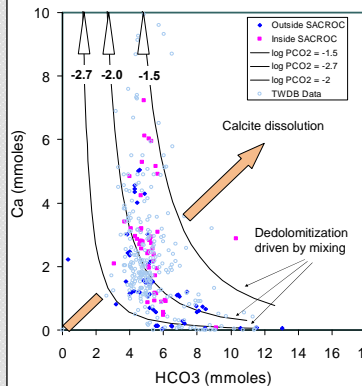
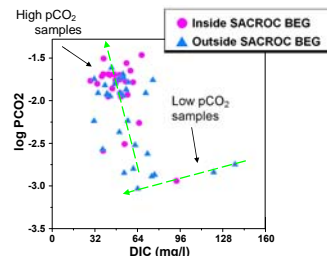


Fig. 5. Modeling of carbonate processes: calcite dissolution and dedolomitization.

- Dedolomitization [Ca²⁺ + CaMg(CO₃)₂ = Mg²⁺ + 2CaCO₃] of aquifer carbonate caused by mixing of Dockum water with Permian water dominates the system.
- Data fit modeled curves for dedolomitization (log pCO₂ = -1.5, -2.0, and -2.7 shown) but do not fit the modeled trend for calcite dissolution [CO_{2(aq)} + H₂O + CaCO₃ = Ca²⁺ + 2HCO₃⁻], which is a common effect of CO₂ gas in freshwater aquifers (orange arrow in fig. 5).
- Modeled rock-water reaction progress is toward high Ca²⁺ and low HCO₃⁻. Data trend from pCO₂ of about 10^{-2.7} to 10^{-1.5} with increased reaction, suggesting that CO₂ is being added to the system.
- Again, there is no distinction between samples collected inside versus outside SACROC.

Fig. 6. Analyzed DIC vs. calculated log pCO₂ for selected GCCC samples.

- A few samples with low pCO₂ (Ca²⁺ < 0.3 mmol/L; fig. 5) show decreasing dissolved inorganic carbon (DIC) with decreasing pCO₂ (fig. 6), as would be expected for degassing during dedolomitization in an open system where CO₂ is free to diffuse.
- Samples with high pCO₂ (Ca²⁺ > 0.3 mmol/L; fig. 5) show increasing pCO₂ with decreasing DIC, an indication of gas buildup (Back et al., 1983) by either (1) a closed system where degassing CO₂ is trapped or (2) input of microbial or injectate gas.

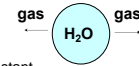
CO₂ Source Identification Modeling

- We used stable carbon isotope ratios of carbon sources (table 1), the PHREEQC numerical code, and mass balance equations (after Appelo and Postma, 2005) to (1) model isotopic trends during dedolomitization under open and closed systems and (2) identify the most likely source of CO₂ in the Dockum aquifer.

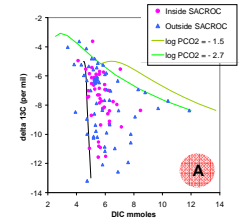
Table 1. Measured carbon isotope ratios for various carbon end members.

A. Open-system degassing

- CO₂ source is degassing during dedolomitization.
- Green lines = model output for constant pCO₂. Isotopic trends for low-pCO₂ samples (fig. 6) can be explained by this process in which rate of CO₂ production = rate of diffusion.
- Black line = model output for slightly increasing pCO₂. Isotopic trends for degassing in which rate of CO₂ production < diffusion may explain the remainder of the data.

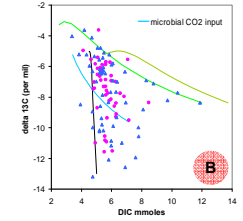
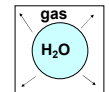


| End member | δ ¹³ C Range |
|-------------------------------|-------------------------|
| Injectate CO ₂ gas | 0 to -6 |
| Natural CO ₂ gas | -23 to -29 |
| Carbonate | -2 to -8 |
| Dockum water | -4 to -13 |
| Permian water | -8 to -10 |
| Produced water | +1 to +9 |



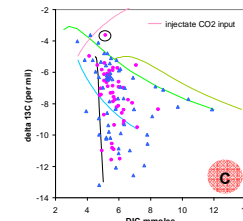
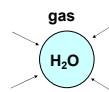
B. Closed system

- Increasing pCO₂ where CO₂ production >> diffusion.
- CO₂ source is microbial and originates from within the system (blue line in fig. 7B). Modeled trend shows that introduction of microbial gas is possible but not necessary to explain the data.



C. Open system with outside CO₂ source

- pCO₂ increases owing to external source of CO₂: injectate from EOR activities.
- CO₂ source is injectate and originates from outside the system (pink line in fig. 7C). Modeled trend shows that introduction of injectate gas is possible but not necessary to explain the data. One sample (circled) lies in the field of potential impact.

Fig. 7. pCO₂ systems and their related isotopic trends.

Conclusions

- In a system where dedolomitization is dominant over calcite dissolution, carbon isotopes have limited use for identifying injectate CO₂ in shallow groundwater.
- The composition of most Dockum samples collected above the SACROC CO₂ injection site can be explained by open-system dedolomitization without the addition of injectate or microbial gas.
- The geochemical similarity between Dockum aquifer samples collected inside SACROC and regional groundwater chemistry, is additional evidence for minimal to no impact from CO₂ injection practices at SACROC.
- One sample shows possible impact from injectate CO₂, however, complex water mixing relationships may play a role.

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