

## Introduction

Capture and storage of industrial CO<sub>2</sub> 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 CO<sub>2</sub> remains in the subsurface (Litynski 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 CO<sub>2</sub> has been injected for enhanced oil recovery (EOR) since 1972. Our goals are to (1) assess interaction between shallow groundwater and CO<sub>2</sub> injectate and (2) test low-cost methods of monitoring shallow groundwater at CO<sub>2</sub> 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 CO<sub>2</sub> in groundwater near SACROC.

## Background

### Why SACROC?

- The Scurry Area Canyon Reef Operators Committee (SACROC) unitized oil field has the longest history of CO<sub>2</sub> injection for EOR in the world (fig. 1).
- Since 1972, 150 million metric tons (MMt) of CO<sub>2</sub> has been injected at SACROC; 75 MMt has been recovered/recycled. The balance may be permanently sequestered in or near the injection zone.
- CO<sub>2</sub> injection history provides the opportunity to look for injectate CO<sub>2</sub> in shallow groundwater above SACROC and to test stable carbon isotope methodologies for monitoring shallow groundwater above sequestration sites.

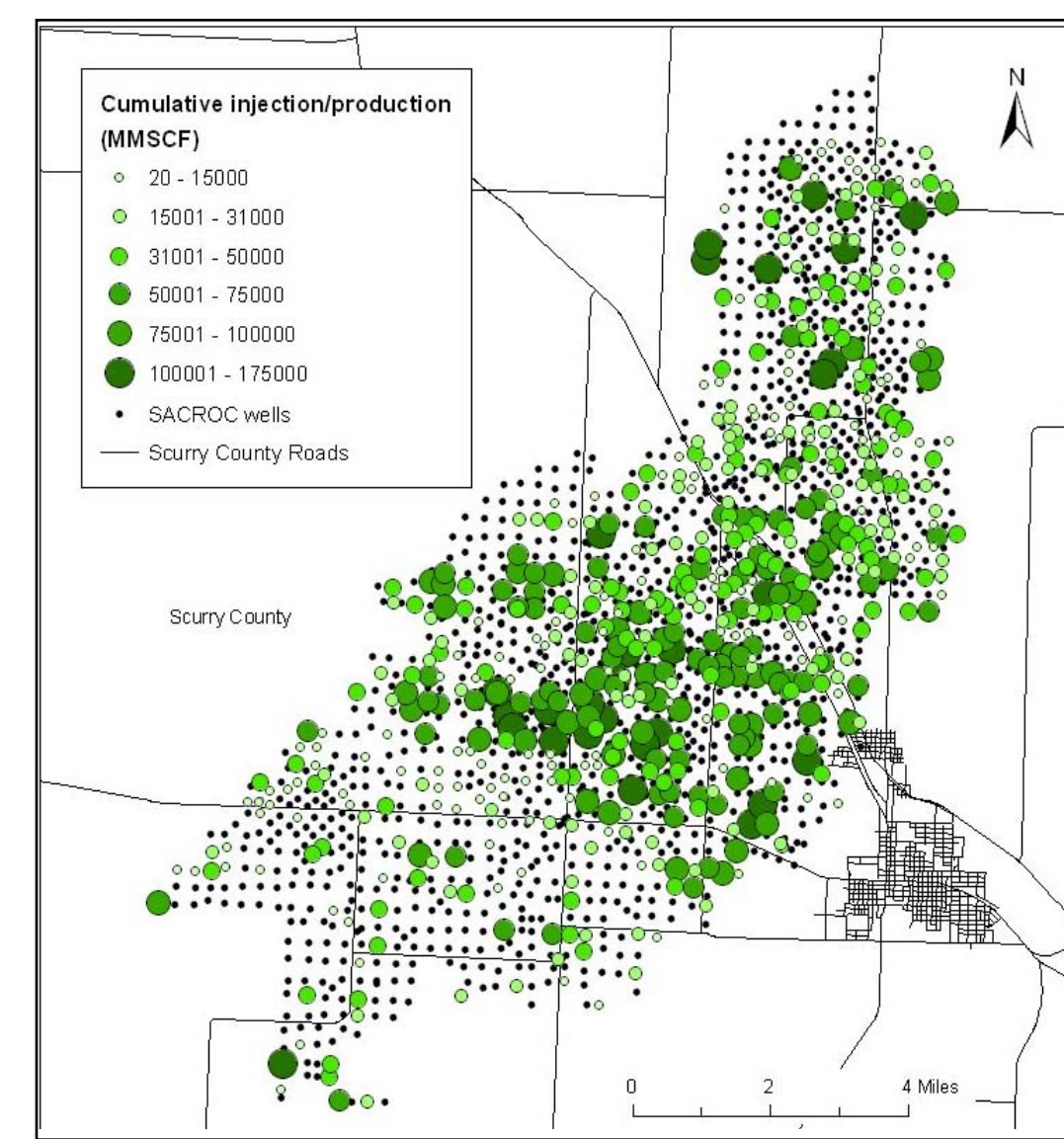


Fig. 1. SACROC CO<sub>2</sub> injection map.

### 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 CO<sub>2</sub> 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.

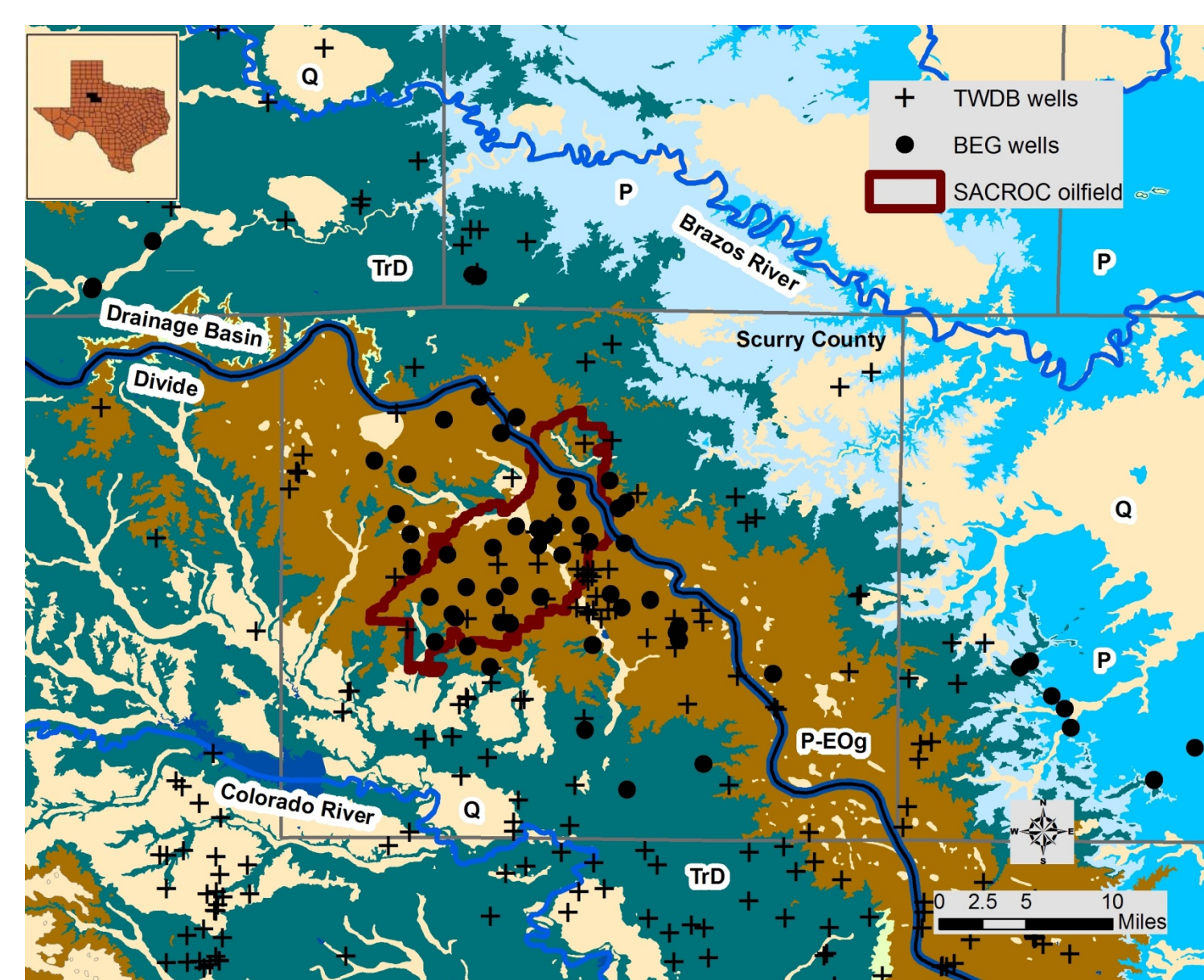


Fig. 2. Surface geologic units and water-well sample locations around the SACROC oil field.

**Geologic unit key:**  
P = undifferentiated Permian; TrD = Triassic Dockum  
P-Eo = Paleocene-Eocene Ogallala; Q = undiff. Quaternary

### Geochemical Influences

- Potential sources of CO<sub>2</sub> in Dockum groundwater include (1) CO<sub>2</sub> injected into production zone, (2) degassing from rock-water reactions, and (3) CO<sub>2</sub> 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.

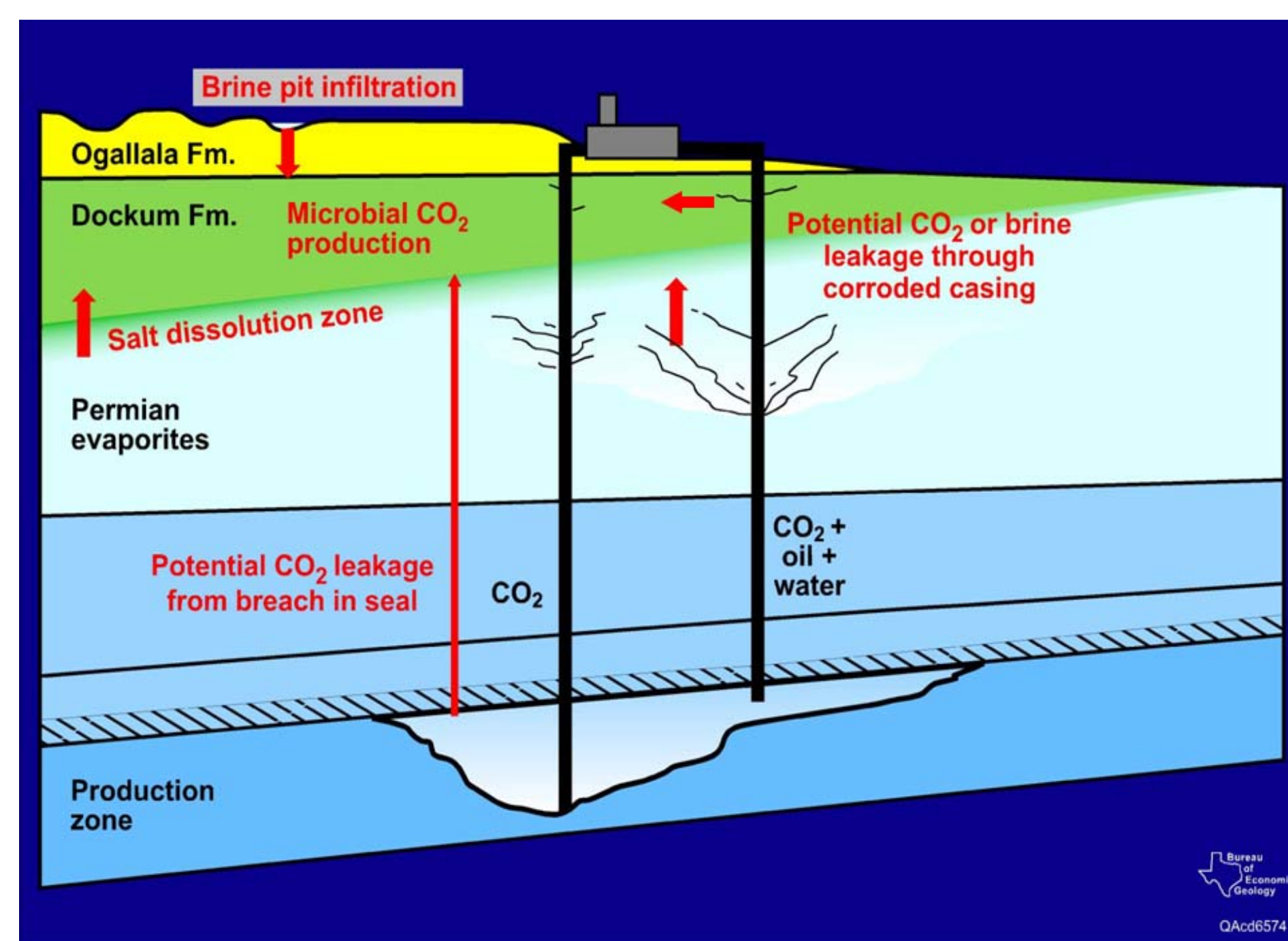


Fig. 3. Schematic cross section of study area (not to scale).

## 3. Major Element Geochemistry

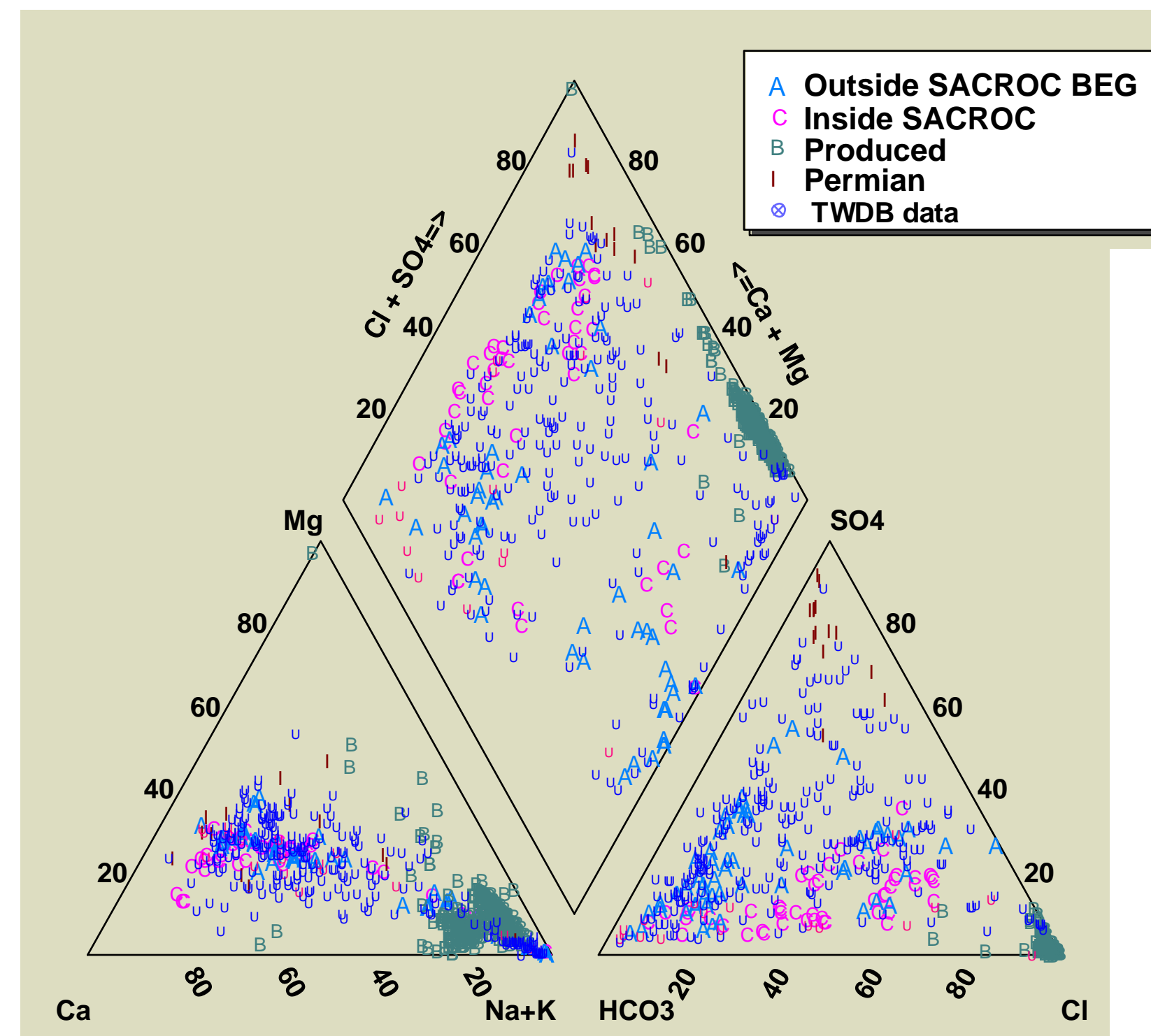


Fig. 4. Piper diagram of (1) Dockum chemistry outside and inside SACROC, (2) Permian groundwater, (3) produced brine, and (4) regional TWDB data.

- Distribution of anions shows that Dockum water outside SACROC trends toward Permian (CaSO<sub>4</sub>) 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

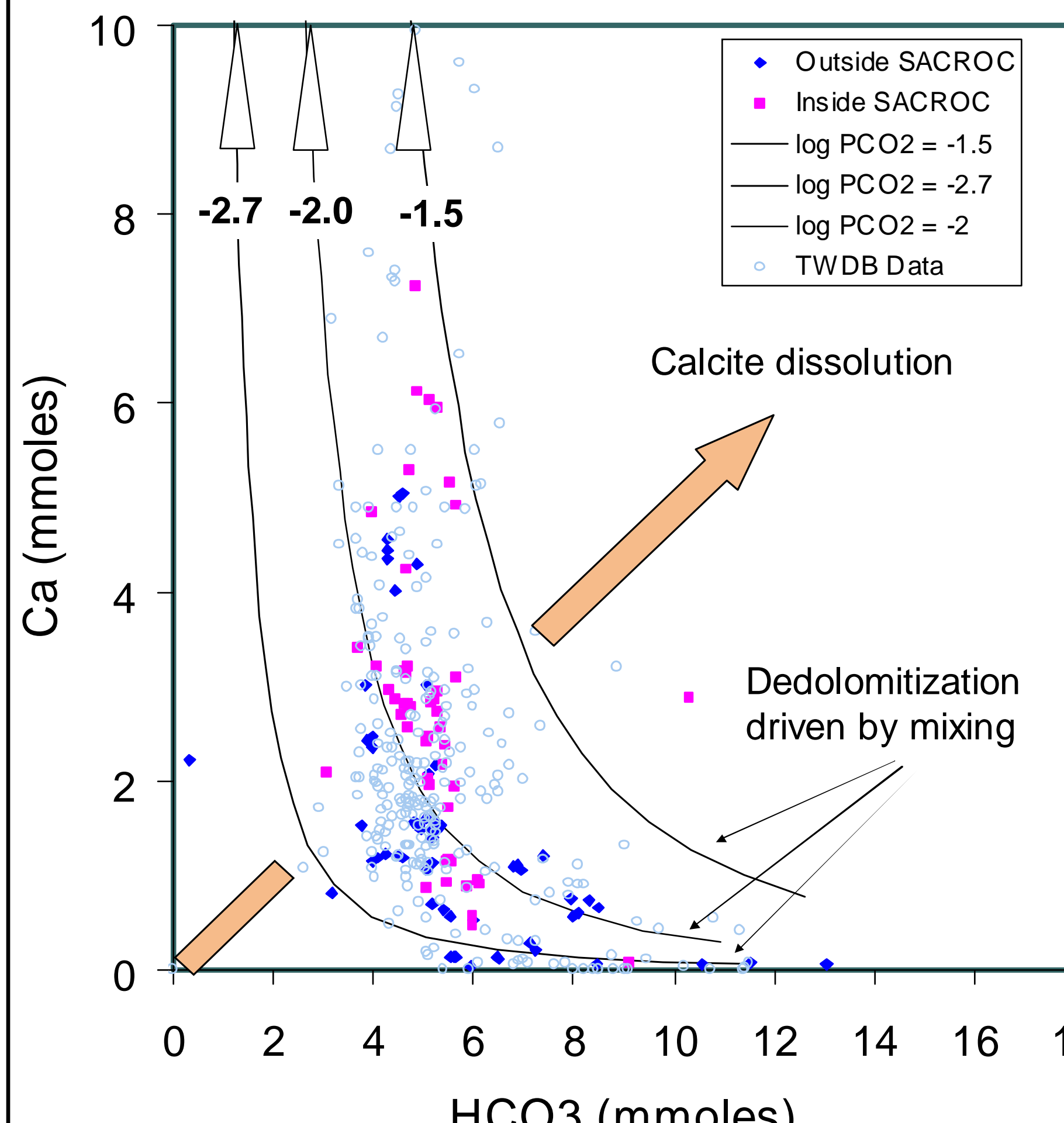


Fig. 5. Modeling of carbonate processes: calcite dissolution and dedolomitization.

- Dedolomitization [Ca<sup>2+</sup> + CaMg(CO<sub>3</sub>)<sub>2</sub> = Mg<sup>2+</sup> + 2CaCO<sub>3</sub>] of aquifer carbonate caused by mixing of Dockum water with Permian water dominates the system.
- Data fit modeled curves for dedolomitization (log pCO<sub>2</sub> = -1.5, -2.0, and -2.7 shown) but do not fit the modeled trend for calcite dissolution [CO<sub>2(aq)</sub> + H<sub>2</sub>O + CaCO<sub>3</sub> = Ca<sup>2+</sup> + 2HCO<sub>3</sub><sup>-</sup>], which is a common effect of CO<sub>2</sub> gas in freshwater aquifers (orange arrow in fig. 5).
- Modeled rock-water reaction progress is toward high Ca<sup>2+</sup> and low HCO<sub>3</sub><sup>-</sup>. Data trend from pCO<sub>2</sub> of about 10<sup>-2.7</sup> to 10<sup>-1.5</sup> with increased reaction, suggesting that CO<sub>2</sub> is being added to the system.
- Again, there is no distinction between samples collected inside versus outside SACROC.

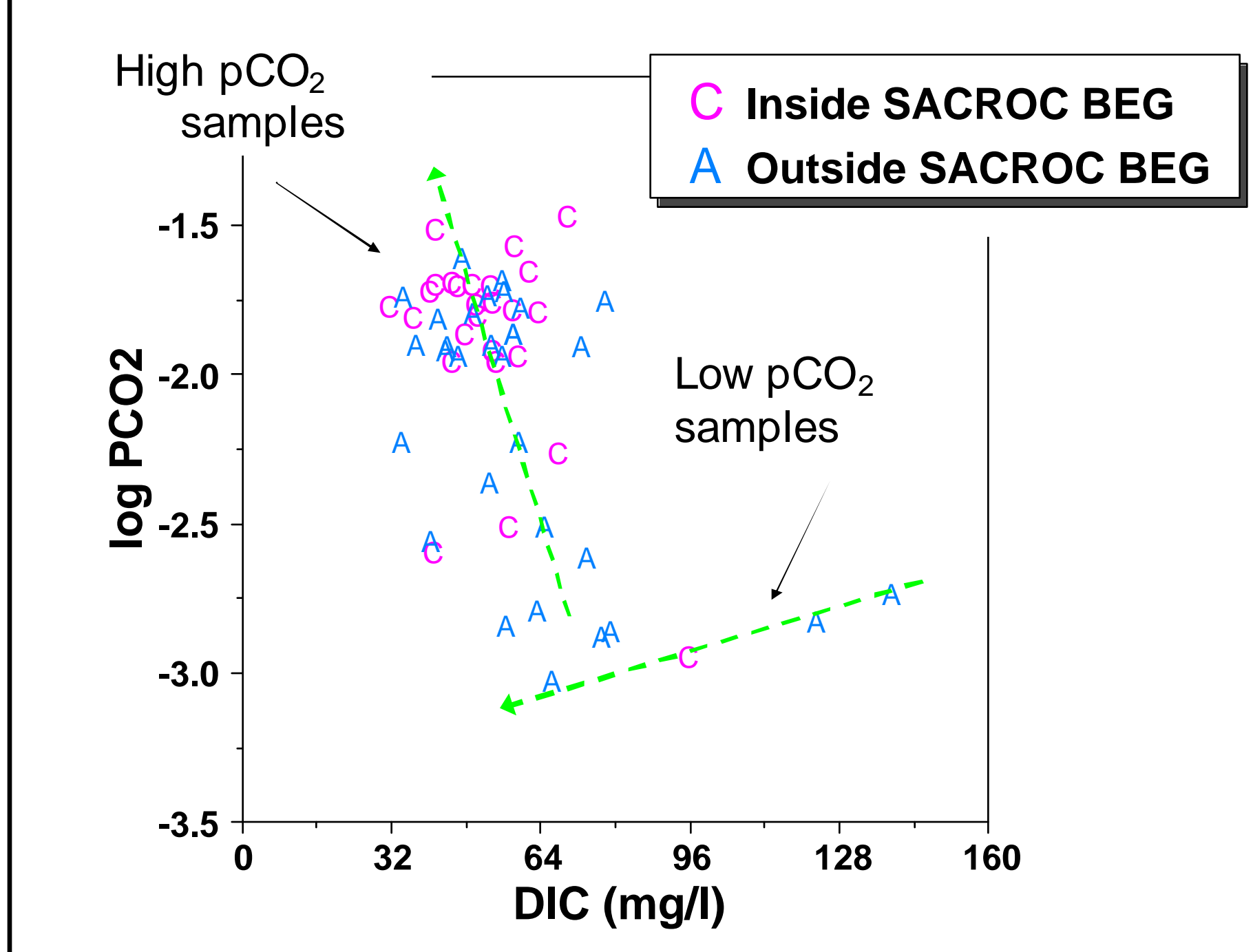


Fig. 6. Analyzed DIC vs. calculated log pCO<sub>2</sub> for selected GCCC samples.

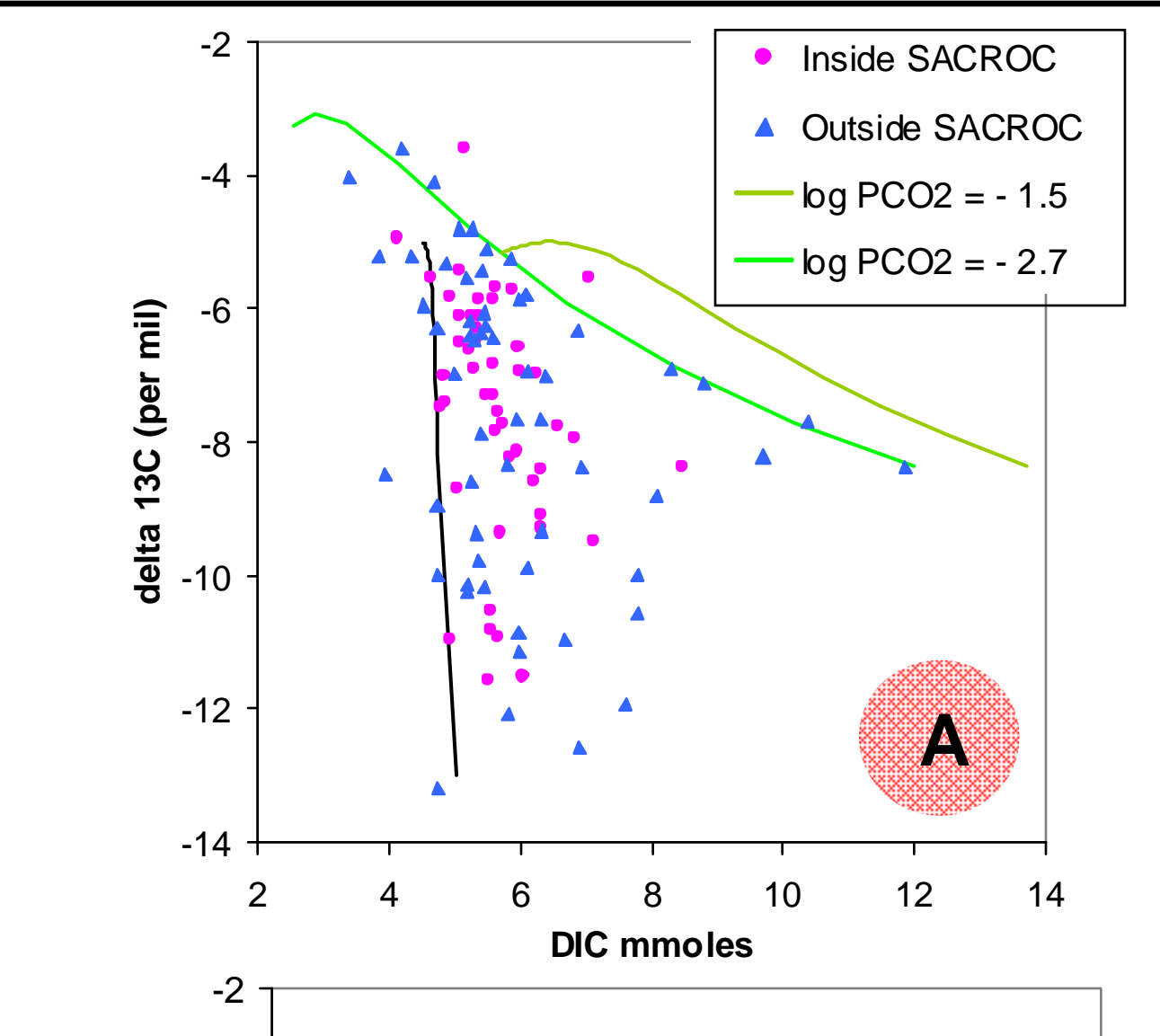
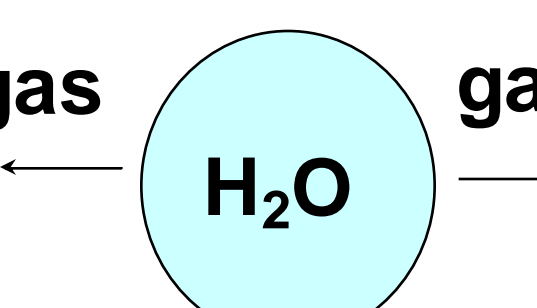
- A few samples with low pCO<sub>2</sub> (Ca<sup>2+</sup> < 0.3 mmoles; fig. 5) show decreasing dissolved inorganic carbon (DIC) with decreasing pCO<sub>2</sub> (fig. 6), as would be expected for degassing during dedolomitization in an open system where CO<sub>2</sub> is free to diffuse.
- Samples with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

## CO<sub>2</sub> Source Identification Modeling

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

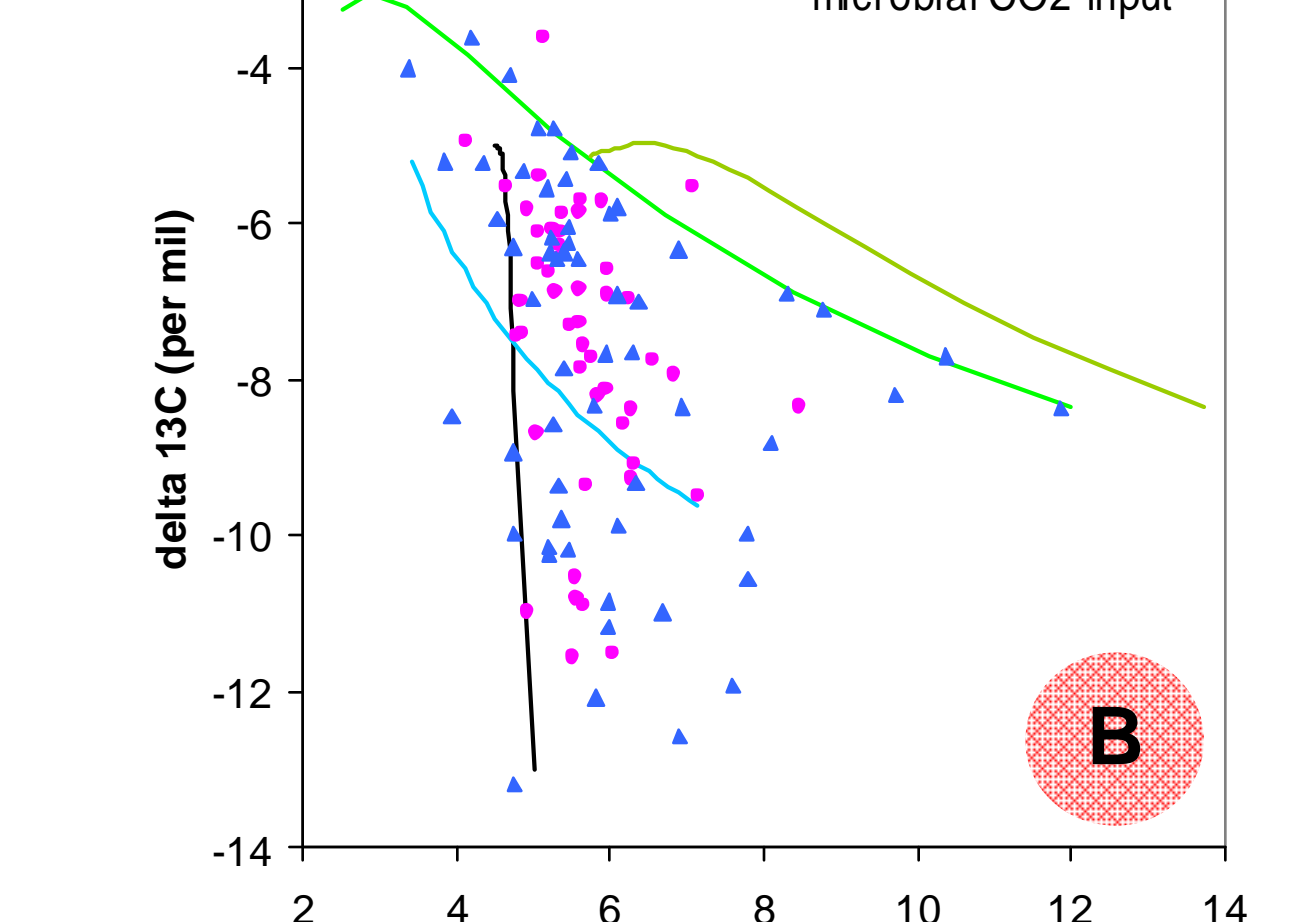
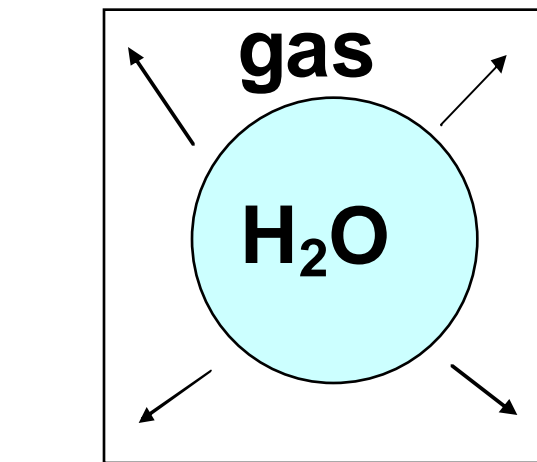
### A. Open-system degassing

- CO<sub>2</sub> source is degassing during dedolomitization.
- Green lines = model output for constant pCO<sub>2</sub>. Isotopic trends for low-pCO<sub>2</sub> samples (fig. 6) can be explained by this process in which rate of CO<sub>2</sub> production = rate of diffusion.
- Black line = model output for slightly increasing pCO<sub>2</sub>. Isotopic trends for degassing in which rate of CO<sub>2</sub> production < diffusion may explain the remainder of the data.



### B. Closed system

- Increasing pCO<sub>2</sub> where CO<sub>2</sub> production >> diffusion.
- CO<sub>2</sub> 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 CO<sub>2</sub> source

- pCO<sub>2</sub> increases owing to external source of CO<sub>2</sub>: injectate from EOR activities.
- CO<sub>2</sub> 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) shows potential impact.

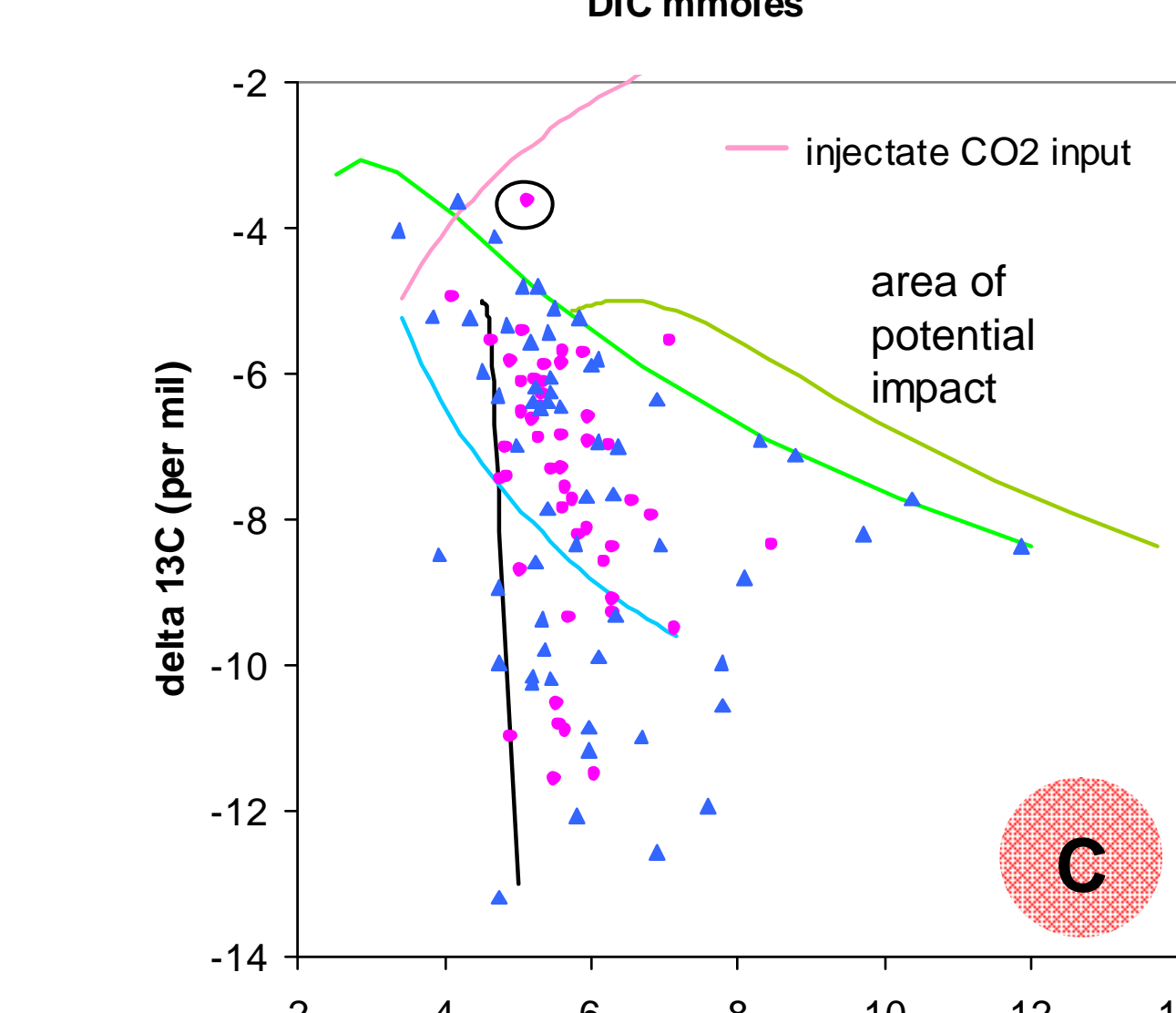
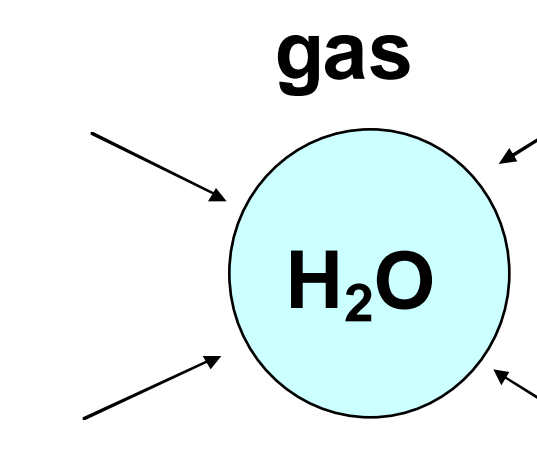


Fig. 7. pCO<sub>2</sub> systems and their related isotopic trends.

## Conclusions

- In a system where dedolomitization is dominant over calcite dissolution, carbon isotopes have limited use for identifying injectate CO<sub>2</sub> in shallow groundwater.
- The composition of most Dockum samples collected above the SACROC CO<sub>2</sub> 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 CO<sub>2</sub> injection practices at SACROC.
- One sample shows possible impact from injectate CO<sub>2</sub>, however, complex water mixing relationships may play a role.

**References:**  
Appelo, C.A.J., and Postma, D., 2005, *Geochemistry, Groundwater and Pollution*, Amsterdam, The Netherlands, AA Balkema.  
Back, W., Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., and Rubin, M., 1983, Process and rate of dedolomitization: mass transfer and 14C dating in a regional carbonate aquifer: *Geological Society of America Bulletin*, v. 94, p. 1415-1429.  
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Litynski, J.T., Klara, S.M., McIlvried, H.G., and Srivastava, R.D., 2006, *The United States Department of Energy's Regional Carbon Sequestration Partnerships program: a collaborative approach to carbon management*: *Environment International*, v. 32, p. 128-144.