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Role of dedolomitization in the detection of anthropogenic CO₂ in freshwater aquifers

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ABSTRACT: Our examination of groundwater geochemistry at a site where CO₂ has been injected for decades shows that understanding water-rock interaction is critical to correct interpretations regarding CO₂ storage evaluation. Whereas it is currently widely accepted that input of CO₂ into an aquifer system will result in calcite dissolution leading to increases in HCO₃⁻ and decreases in pH, we have found that these generalizations may not hold true in all hydrogeologic settings. For example, our geochemical models show that the process of dedolomitization will mimic the effects of calcite dissolution by increasing Ca²⁺ and decreasing pH, but this reaction is in response to input of calcium ions, not CO₂. The dedolomitization model also indicates that dissolved HCO₃⁻ is consumed in the initial phases of water-rock interaction; a trend very different from the progression that results from reaction of CO₂ with calcite. Under simulated circumstances of exogenous CO₂ input, water-rock interactions continue to be driven by Ca²⁺ rather than CO₂. If these geochemical trends are observed in the absence of an understanding of the hydrogeologic system, erroneous interpretations regarding CO₂ storage may result. Errors could be either at sites where CO₂ leakage has occurred but is not detected or at sites where non-injection-induced changes are mistakenly assumed to indicate leakage. The implication for monitoring geologic sequestration sites is that characterization of the fundamental geochemical processes is necessary for correctly assessing the consequences of CO₂ input.

1 INTRODUCTION

Monitoring groundwater resources above geologic carbon sequestration reservoirs is proposed as a method for ensuring that potable water supplies have been protected and that CO₂ is adequately sequestered with respect to the biosphere. Currently, the position of many researchers is that simple carbonate parameters can be used for monitoring. This hypothesis is based on the premise that a predictable consequence of CO₂ in a dilute aquifer is an increase in dissolved inorganic carbon (DIC) predominantly as bicarbonate ion (HCO₃⁻), a decrease in pH, and mobilization of ions such as calcium (Ca²⁺) and/or trace metals (Assayag et. al., 2009; Apps, et. al., 2009; Wang & Jaffe, 2004; Carroll et. al., 2009).

The results of a groundwater study at a site where CO₂ has been injected for decades (the SACROC oil field) give strong evidence against these conclusions. At SACROC, natural and man-induced processes have created a geochemical system that is more complex and reacts differently to CO₂ than the simple system put forth by previous researchers. The implications are that groundwater monitoring strategies at geologic sequestration sites may need to be site-specific to hydrogeologic setting and those that

use natural constituents will have limited use given the variability of these environments.

2 APPROACH

To test methodologies for CO₂ storage evaluation using shallow aquifers, we targeted a potable water source (Dockum aquifer) above a long-duration (>35 years) large-scale (~200 km²) engineered CO₂ injection in west Texas. The SACROC oil field in Scurry County, TX, currently operated by Kinder Morgan (KM) has injected CO₂ for enhanced oil recovery (EOR) since 1972 with approximately 50% recovery and recycling of injected CO₂. This site provides the opportunity to investigate if groundwater chemistry can be effectively used as a monitoring tool at sequestration sites.

To accomplish our objectives, we compared the groundwater geochemistry of samples collected in the area of CO₂ injection (inside SACROC) to that of groundwater samples collected from areas that have not experienced CO₂ injection (outside SACROC). Geochemical perturbations lying outside the normal range of groundwater variability could signal anthropogenic CO₂ input.

3 METHODS

Approximately 100 fresh to slightly saline groundwater samples from the Triassic-age Dockum Group and the Paleocene-Eocene Ogallala Formation and 8 samples from Permian-age evaporite-bearing sandstones were collected from 59 private water wells (50- to 500-ft-deep) and 1 spring during five water sampling trips, June 2006 - November 2008. Ten samples of brines co-produced by KM from the 6,000- to 7,000-ft injection/production zone were also analyzed. Additional geochemical data on co-produced brines were provided by KM and historical records for Dockum and Permian water geochemistry collected by the Texas Water Development Board between 1956 and 2008 from eight Texas counties were also added to the data set. Two samples of Dockum drill cuttings from depth intervals of 450-460 ft and 370-380 ft were examined for mineralogy using SEM with the aid of an energy dispersive X-ray system which can identify chemical composition of small areas.

4 RESULTS AND DISCUSSION

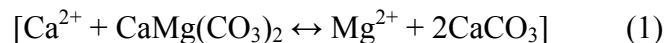
Background geochemical influences on Dockum geochemistry were identified using major element trends (figure 1) with consideration of regional

Dockum groundwater samples collected by the TWDB (from 1956-2007) in areas removed from CO₂-EOR operations (faint open diamonds). Geochemical variability in Dockum groundwater sampled from outside SACROC during the study is consistent with non-CO₂-related local and regional trends suggesting little or no impact from CO₂-EOR activities. Distribution of cations indicates Ca-Na-K cation exchange has influenced Dockum and Permian groundwater. Trends in anions point to mixing relationships between Dockum, Permian, and produced waters with a higher component of produced water influencing samples within the SACROC boundaries. Hydrogeochemical relationships suggest the higher component of produced water inside SACROC is due to leaching into the Dockum of historically-produced brine formerly stored in unlined surface pits. Mixing of Dockum with Ca-SO₄ Permian groundwater is thought to occur along a well-documented Permian dissolution zone located at the base of the Dockum (i.e., Dutton, 1989). Mixing models utilizing end members from all three water types also suggest that dedolomitization is a significant geochemical control.

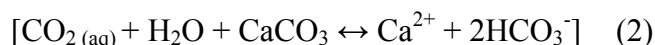
4.1 Effects of mixing and dedolomitization on carbonate geochemistry

Dissolution of dolomite and precipitation of calcite (dedolomitization) fueled by input of calcium ions is widely documented in many hydrologic systems (Back et. al., 1979, 1983; Plummer & Back 1980; Hanshaw & Back 1985; Back & Baedecker 1989). Dissolution of gypsum or anhydrite within a carbonate aquifer, mixing with Ca-SO₄ waters (López-Chicano et. al., 2001) or impact from gypsum-rich fertilizers (Pacheco & Szocs, 2006) is commonly the source for calcium ions fueling dedolomitization. In the SACROC area, input of Ca²⁺ ions is from two sources; mixing of Dockum waters with Permian Ca-SO₄ waters and infiltration of Na-Cl production brines which drives cation exchange with Ca²⁺ sorbed to aquifer clays.

The process of dedolomitization according to the following equation:



creates a significantly different carbonate environment than that of calcite dissolution:



A system undergoing dedolomitization is not driven by CO₂ but instead by input of calcium ions. This finding is significant with regard to monitoring sequestration sites because it is in contrast to the assumption that CO₂ input will drive any aquifer system containing carbonate minerals toward

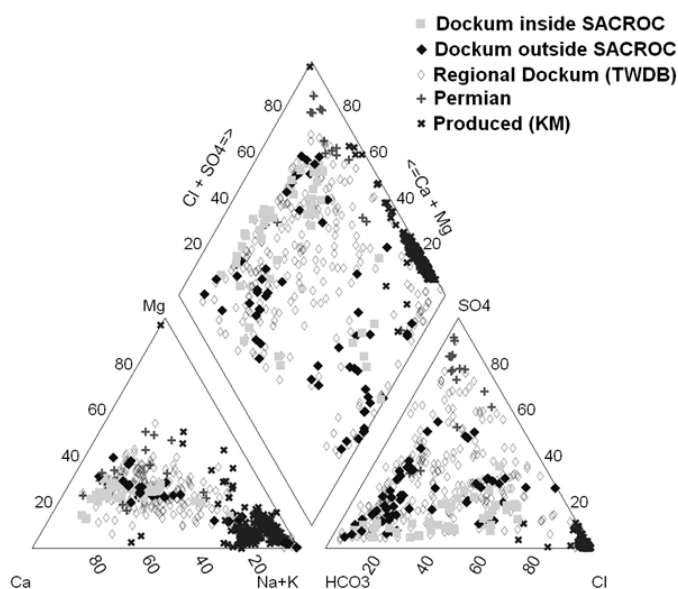


Figure 1. Piper diagram of (1) Dockum chemistry outside and inside SACROC, (2) Permian groundwater, (3) produced brine, and (4) regional TWDB data.

geology, stratigraphy, and past and present local EOR practices. Geochemical trends in Dockum groundwater sampled inside SACROC (grey squares) are compared to those of groundwater sampled outside SACROC (black diamonds) in figure 1. Also shown are Na-Cl brines coproduced with oil at SACROC (x's), Ca-SO₄ waters from underlying Permian strata (crosses), and historic regional

production of bicarbonate ions. With calcium ions identified as the geochemical driving force in the Dockum aquifer near SACROC, we used geochemical modeling to ascertain the effects of CO_2 in this type of a system

4.2 Modeling dedolomitization

The PHREEQC code was used to constrain and compare the roles of CO_2 in systems dominated by dedolomitization with those dominated by calcite dissolution. During calcite dissolution fueled by CO_2 (equation 2), 1 mole of Ca^{2+} and 2 moles of HCO_3^- are produced and data will trend along a line with a slope of 0.5 on a plot of Ca^{2+} versus HCO_3^- (thick shaded arrow in figure 2). Data from this study do not follow calcite dissolution trends but rather fall within the trends modeled in this study for addition of Ca^{2+} ions and dedolomitization.

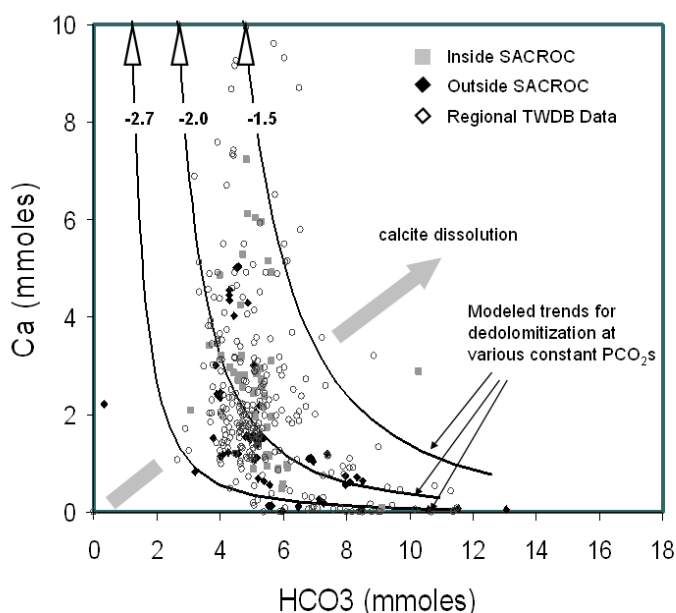


Figure 2. Modeling of carbonate processes calcite dissolution and dedolomitization. Modeled trends for different conditions of constant PCO_2 at $10^{-1.5}$, $10^{-2.0}$, and $10^{-2.7}$ are shown.

Modeled geochemical trends for dedolomitization under conditions of constant PCO_2 with cation exchange were constructed using the PHREEQC code by adding 30 mmol/L of CaSO_4 in 30 steps to a high HCO_3^- , low Ca^{2+} Dockum water in equilibrium with calcite and dolomite at various values of fixed PCO_2 . Modeled values for PCO_2 correspond to the range measured from headspace analyses (PCO_2 from $10^{-2.7}$ to $10^{-1.5}$) and are within normal ranges for aquifers (Clark & Fritz, 1997).

The results of numerical modeling show that dissolved HCO_3^- in the initial solution slows dolomite dissolution in the early stages of reaction by supplying some of the anion necessary for calcite precipitation. As calcite precipitates, dissolved HCO_3^- in the initial water is quickly consumed and HCO_3^- concentrations decrease rapidly. Ca^{2+} is also con-

sumed during calcite precipitation, but because it is being supplied to the system by mixing with CaSO_4 waters, its concentration slightly increases. After dissolved HCO_3^- in the initial water is consumed, dolomite dissolution becomes the main source of HCO_3^- for calcite precipitation. At this point, the kinetics of dedolomitization control the supply of dissolved HCO_3^- available to react with Ca^{2+} and calcium accumulates in the system. During this process, CO_2 degasses slightly and pH decreases.

Trends in pH and Ca^{2+} observed during dedolomitization, if taken out of hydrogeologic context, may falsely indicate CO_2 leakage into an aquifer. These trends are similar to those expected from reaction of calcite and CO_2 , but they are activated by calcium input rather than CO_2 . A trend of decreasing HCO_3^- with water-rock interaction is the opposite of what would be expected from reaction of calcite and CO_2 . Samples with relatively high bicarbonate concentrations may be assumed to have experienced interaction with anthropogenic CO_2 when in fact they represent the least geochemically evolved samples in the system.

4.3 Effects of CO_2 input during dedolomitization

According to the model, raising PCO_2 in a system undergoing dedolomitization under the normal aquifer conditions observed at the study site (PCO_2 between $10^{-1.0}$ and $10^{-3.0}$) increases the mass and rate of dolomite dissolution and decreases the mass of calcite precipitation. HCO_3^- consumption, system degassing, and pH all decrease at higher PCO_2 . Although the geochemical evolution of a water experiencing dedolomitization and simultaneous CO_2 increase will shift towards higher HCO_3^- concentrations, it will maintain the same overall evolutionary trajectories (modeled curves in fig. 2).

A well-defined hydrogeologic system, complete with modeled trends for various values of constant PCO_2 , gives the opportunity to visually detect an increase in CO_2 in the system. Data from the field study show an overall increase in PCO_2 with geochemical evolution as samples generally shift from clustering near modeled trend lines for low constant PCO_2 (about $10^{-2.7}$ to $10^{-2.0}$ in low Ca^{2+} samples) to modeled trend lines for higher constant PCO_2 (about -1.5 in high Ca^{2+} samples). This shift suggests that CO_2 is building in the system, most likely from degassing during dedolomitization rock-water interaction (Romanak & Smyth, 2008; Romanak et. al., 2009; Smyth et. al., 2009).

If values of PCO_2 in the aquifer were to increase above normal values due to input of exogenous CO_2 ($\text{PCO}_2 \gg 10^{-1}$), the model shows that water rock interaction would continue to be dominated by input of calcium ions rather than CO_2 . Under these conditions, dolomite dissolution and calcite precipitation

persist, but the amount of HCO_3^- in the water is controlled by dissolution of the exogenous CO_2 . As long as Ca^{2+} input continues and dolomite remains as a mineral phase, the system is thermodynamically unlikely to reflect the conditions of calcite dissolution that are suggested by some researchers.

5 CONCLUSION

The geochemical driving forces of the hydrogeologic system must be defined before the consequences of CO_2 input can be predicted. In the Dockum aquifer, as well as in many other aquifers, mixing of concentrated waters (in this case Na-Cl brines with cation exchange and/or Ca- SO_4 Permian evaporite waters) drives dedolomitization and creates a significantly different carbonate environment than that of simple calcite dissolution. Whereby calcite dissolution is driven by CO_2 , dedolomitization is driven by calcium ions which create undersaturation of the system with respect to dolomite and oversaturation with respect to calcite. Input of CO_2 into these very different systems has been modeled to produce very different outcomes. In the simple system, DIC increases with increases in $P\text{CO}_2$ as previous researchers have predicted. However, in the case of dedolomitization, the modeled evolution of groundwater under constant $P\text{CO}_2$ proceeds towards lower HCO_3^- concentrations. Increases in CO_2 simply shift but maintain the overall evolutionary trajectories which would yield inaccurate conclusions if taken out of hydrochemical context. Errors could be either at sites where CO_2 leakage has occurred but is not detected or at sites where non-injection induced changes are mistakenly assumed to indicate leakage.

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