

**GEOCHEMICAL AND LITHIUM ISOTOPE CHARACTERIZATION OF OGALLALA  
AQUIFER AND PERMIAN BASIN CARBONATE RESERVOIR WATERS AT AN  
ENHANCED OIL RECOVERY SITE, NORTHWEST TEXAS, USA**

by

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Samantha Pfister, M.S.

University of Pittsburgh, 2015

Geochemical and lithium isotope compositions ( $\delta^7\text{Li}$ ) of Permian Basin produced waters and groundwater from overlying aquifers at an enhanced oil recovery (EOR) site in Gaines County, northwest Texas were determined to evaluate the effects of brine-groundwater-rock interactions, identify sources of dissolved solids, and characterize fluid migration and mixing processes.  $\delta^7\text{Li}$  values for produced waters from dolostones of the Permian Basin San Andres Formation ranged from +11 to +16 per mil (‰) and fall within the range of formation waters from Gulf of Mexico and Appalachian basin oil and gas reservoir rocks. The chemical composition and TDS content (800 to 2,200 mg L<sup>-1</sup>) of water from five Tertiary Ogallala Formation groundwater wells in the study area is comparable to other groundwaters from the Southern High Plains aquifer. Groundwaters from the Triassic Dockum Group Santa Rosa ( $\delta^7\text{Li}$  range of +21 to +23) are isotopically distinct from waters from the San Andres and Ogallala Formations. In addition to tracking groundwater-brine mixing and water-rock interaction, temporal changes in the  $\delta^7\text{Li}$  composition of deep groundwater in the study area has potential use in the early detection of upward or injection-induced brine migration, prior to its incursion into the sensitive overlying Ogallala aquifer.

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## Preface

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## **1.0 INTRODUCTION**

### **1.1 CARBON CAPTURE IN GEOLOGIC FORMATIONS**

One approach to the mitigation of the effects of anthropogenic greenhouse gas emissions on Earth's climate system involves the injection of carbon dioxide (CO<sub>2</sub>) extracted from the exhaust stream of fossil fuel combustion facilities, such as coal-fired power plants, into subsurface geologic units (Rubin et al., 2007). Potential geologic carbon storage sites include unmineable coal beds, fractured igneous and metamorphic rocks, and high porosity sedimentary rocks (Plasynski et al., 2009; Crawshaw and Boek, 2013). The International Panel on Climate Change (IPCC) specified that subsurface geologic units for carbon storage should have the ability to retain a minimum of 99% of the injected CO<sub>2</sub> for at least 1,000 years, and that assessment and storage must be based on measurable parameters (IPCC, 2006). Successful long-term storage of environmentally significant amounts of CO<sub>2</sub> into geologic formations is contingent on accurate determination of long-term storage capacity, and site-specific assessment, identification and mitigation of CO<sub>2</sub> injection-related risks (Birkholzer and Tsang, 2008, and references therein). Sensitive monitoring, verification and accounting (MVA) tools are also needed that can detect subsurface changes relevant to the accurate assessment of these parameters over both short (during injection) and long (centuries) time scales (DePaolo and Cole, 2013, and references therein).

## 1.2 APPLICATIONS OF GEOCHEMICAL AND ISOTOPIC TOOLS FOR CARBON STORAGE

Detailed characterization of fluid and rock components of geologic carbon storage systems provides key information for the development of predictive models, assessment of carbon storage, and long-term monitoring and verification. These methods include the analysis of waters from producing, monitoring, and groundwater wells, and baseline characterization of both formation waters and groundwater from overlying aquifers (Fessenden et al., 2010; Keating et al., 2014; Newell et al., 2014). Geochemical and isotopic composition of liquid and solid components of storage reservoirs, seal rocks, and sensitive aquifers, and temporal variations in these signatures can aid in the identification and rate determinations of water-CO<sub>2</sub>-rock interactions within the storage reservoir and overlying aquifers. These processes include mineral dissolution and precipitation, CO<sub>2</sub> trapping in stable minerals (e.g. magnesite, siderite, dawsonite), and the mobilization or retention of chemical species such as trace metals by sorption/desorption and cation exchange (DePaolo and Cole, 2013). As a window into subsurface processes, geochemical and isotopic signatures can also be useful MVA tools for the early identification of wellbore and changes that could compromise the retention of CO<sub>2</sub> in the target formation and indicate the migration of CO<sub>2</sub> or CO<sub>2</sub>-affected fluids or brines out of the storage unit and into overlying aquifers.

Natural geochemical and isotopic tracers can discriminate between different formation brines and other sources of dissolved solids and have been used to quantify mixing among fluids from multiple sources (Chapman et al., 2012; Warner et al., 2014). Variations in the chemical and isotopic composition of formation and groundwater can be used as natural signatures of fluid

or CO<sub>2</sub> migration, for early detection of leakage of CO<sub>2</sub> or saline fluids into overlying units, and as sensitive monitors of aquifer water quality changes, without the need for the injection of synthetic tracers (Hammack et al., 2013). Natural isotopic tracers can be more sensitive to water quality changes than traditional elemental concentration and ratio indicators (Kolesar Kohl et al., 2014). Temporal elemental and isotopic changes can be used for monitoring and source identification of fluid migration and water quality changes over both short (over the injection period) and long (centuries) timescales.

### **1.3 CARBON STORAGE AND ENHANCED OIL RECOVERY**

Geologic carbon storage in sedimentary rocks requires a high porosity stratigraphic zone and a regionally confining seal rock. The reservoir should be of sufficient depth ( $\geq 1000$  m) to maintain CO<sub>2</sub> in a supercritical state, and unsuitable as a drinking water aquifer (Merrill et al., 2015; US Environmental Protection Agency, 2010). The Department of Energy (DOE) National Carbon Sequestration Database and Geographic Information System (NATCARB) indicates that depleted oil and gas reservoir rocks and deep saline formations are among the most numerous high carbon storage capacity units within the United States (Figure 1). Oil and gas-bearing formations are also active or potential sites for the simultaneous recovery of oil-in-place, the majority of which (85 to 94%; Meyer, 2008) remains in the reservoir following the primary pumping phase (Melzer, 2012; USGS, 2013; Warwick et al., 2012; Brennan et al., 2015; Buursink, 2014; Buursink, 2015). Secondary phase enhanced oil recovery (EOR) methods such as waterflooding the field can release up to an additional 30%; and tertiary phase mechanisms

such as gas injection EOR can remove another 8 to 20% (Meyer, 2008). Within the United States, more than half of EOR production is via the injection of gases such as carbon dioxide (<http://energy.gov/fe/science-innovation/oil-gas-research/enhanced-oil-recovery>).

CO<sub>2</sub>-injection EOR has been used for decades; the first commercial project was developed in 1972 in the Scurry Area Canyon Reef Operators Committee (SACROC) Unit of the Kelly-Snyder Field in West Texas (Meyer, 2008). During this process, CO<sub>2</sub> that has been compressed into a supercritical fluid enters the reservoir rock via an injection well. As the CO<sub>2</sub> moves through the rock and dissolves into saline formation fluids or brines, oil is released and is subsequently pumped out of a producing well. Following recovery, the CO<sub>2</sub> is either recycled for re-injection or allowed to remain in the oil-bearing rock. Monitoring of CO<sub>2</sub>-injection EOR sites indicates that CO<sub>2</sub> left in the subsurface remains within the reservoir rock (Kharaka et al., 2006).



Figure 1. Maps of CO<sub>2</sub> storage potential in oil and gas reservoirs (top) and saline formations (bottom) in North America (from DOE NATCARB, 2012).

Detailed site-specific geologic, petrophysical and geochemical characterization of subsurface lithologies and associated pore fluids are essential for the accurate assessment of CO<sub>2</sub> injection-related changes in porosity and permeability in the storage formation, and the potential for the creation of fractures or seismicity. Research in this area has accelerated over the last decade, and includes experimental investigations and studies of natural analog, EOR, and test sites (Bickle et al. 2013, and references therein). As of March 2015, 9.9 metric tons of CO<sub>2</sub> have been injected in large-scale CO<sub>2</sub> injection field tests at sites including those of DOE's US Regional Carbon Sequestration Partnership (RCSP) in the Permian, Gulf Coast, Williston, Powder River and Illinois Basins (<http://energy.gov/fe/9932381-metric-tons-co2-injected-march-18-2015>). Multiple field experiments have been conducted to determine CO<sub>2</sub>-induced geochemical changes on groundwater aquifers (Kharaka et al., 2010; Trautz et al., 2013; Newell et al., 2014) as well as those effects on cap rock and wellbore integrity (Carey et al., 2007; Newell and Carey, 2013).

Active EOR sites also provide an opportunity to assess long-term changes in reservoir storativity, and to improve predictive models of the subsurface effects of large-scale CO<sub>2</sub> injection (e.g., Viswanathan et al., 2008; Class et al., 2009; Yang et al., 2014). These studies can complement experimental and field-based natural analog studies focused on CO<sub>2</sub>-brine-rock interactions that affect petrophysical properties of both storage and cap rock and can result in either porosity enhancement by fracturing or mineral dissolution, or porosity reduction due to cementation (e.g., Kaszuba et al. 2005; 2013). This requires an understanding of mineral dissolution-precipitation reactions and reaction kinetics. However, there is a lack of agreement between experimental and field-based rate determinations, and additional research is needed in this area (DePaolo and Cole, 2013).

EOR sites have undergone extensive mapping and other geologic characterization related to oil and gas exploration that can provide information regarding possible leakage pathways and other sequestration-related issues. EOR field studies can be used to identify the potential impacts of CO<sub>2</sub> migration into shallow aquifers (e.g., Keating et al., 2011; Fessenden, 2012; Trautz et al., 2013; and references therein), to test the effectiveness of MVA tools, and to assess and mitigate risk during the critical period immediately following the initiation of supercritical CO<sub>2</sub> injection. This includes improving well-bore integrity (Carey, 2013; Mason et al. 2013), assessing petrophysical effects of CO<sub>2</sub> brine interaction on caprock, and identifying factors (e.g., seismicity) that could create injection-related conduits resulting in CO<sub>2</sub> leakage out of the storage formation (Tsang et al., 2008; DePaolo and Cole, 2013).

Carbon sequestration field studies have been conducted at a number of EOR sites in the Permian Basin, including the SACROC field, the Man's San Andres field, and the Wason Denver project, one of the worlds' largest and longest CO<sub>2</sub>-floods (Stevens et al., 2001). High permeability rocks in the Permian Basin of the southwestern United States have been identified as potential carbon storage formations because of the low geothermal gradient in the area as well as close proximity to CO<sub>2</sub> pipelines (DOE NETL, 2010). Major structures within its boundaries include the Central Basin Platform, Delaware Basin, Midland Basin, and Northwest and Eastern Shelf, (Figure 2). The Central Basin Platform is of particular economic importance due to its shallower oil plays in comparison to surrounding basins.

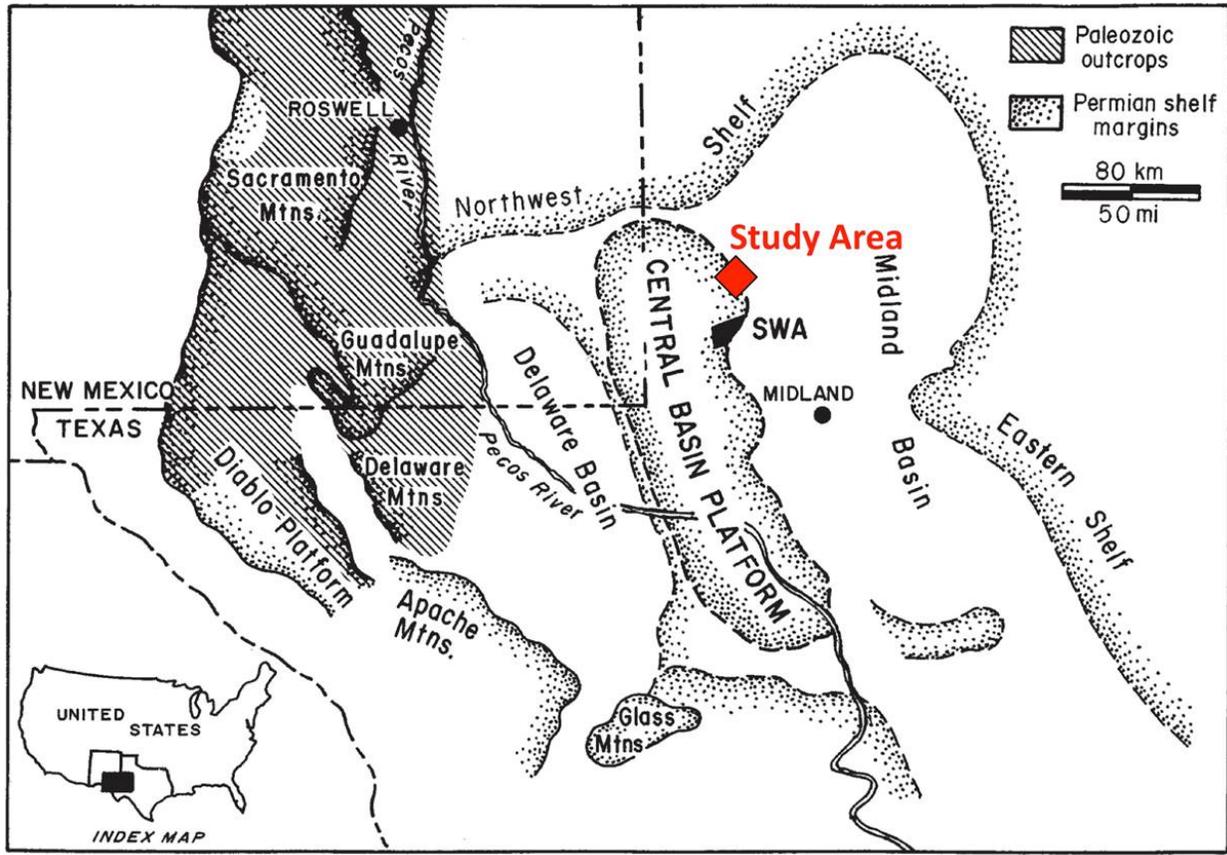


Figure 2. Major Permian Basin structures in Texas and New Mexico, with the study area location on the eastern flank of the Central Basin Platform (from Stueber et al., 1998).

Another important consideration affecting the location of geologic carbon storage sites in the United States is the High Plains-Ogallala aquifer, one of the largest freshwater systems in the world (Figure 3) and a critical water resource for much of the central and southwestern United States (Sophocleous, 2010). It is an important drinking water resource and the main source of agricultural water for a large part of the central US. Decreased recharge and increased agricultural use due to prolonged drought conditions, particularly in the southwest and including much of the Permian Basin, have accelerated depletion of this critical groundwater resource and affected water quality (Mehta et al., 2000; Gurdak et al., 2009; Scanlon et al., 2009;

Venkataraman and Uddameri, 2012). Although a number of studies have focused on potential environmental and health impacts of CO<sub>2</sub> injection-related metal mobilization on the aquifer, there still remains is a need for detailed geochemical analysis and characterization of shallow groundwater and subsurface saline formation waters in the region (Carroll et al., 2009; Siirila et al., 2012; Romanak et al., 2012).

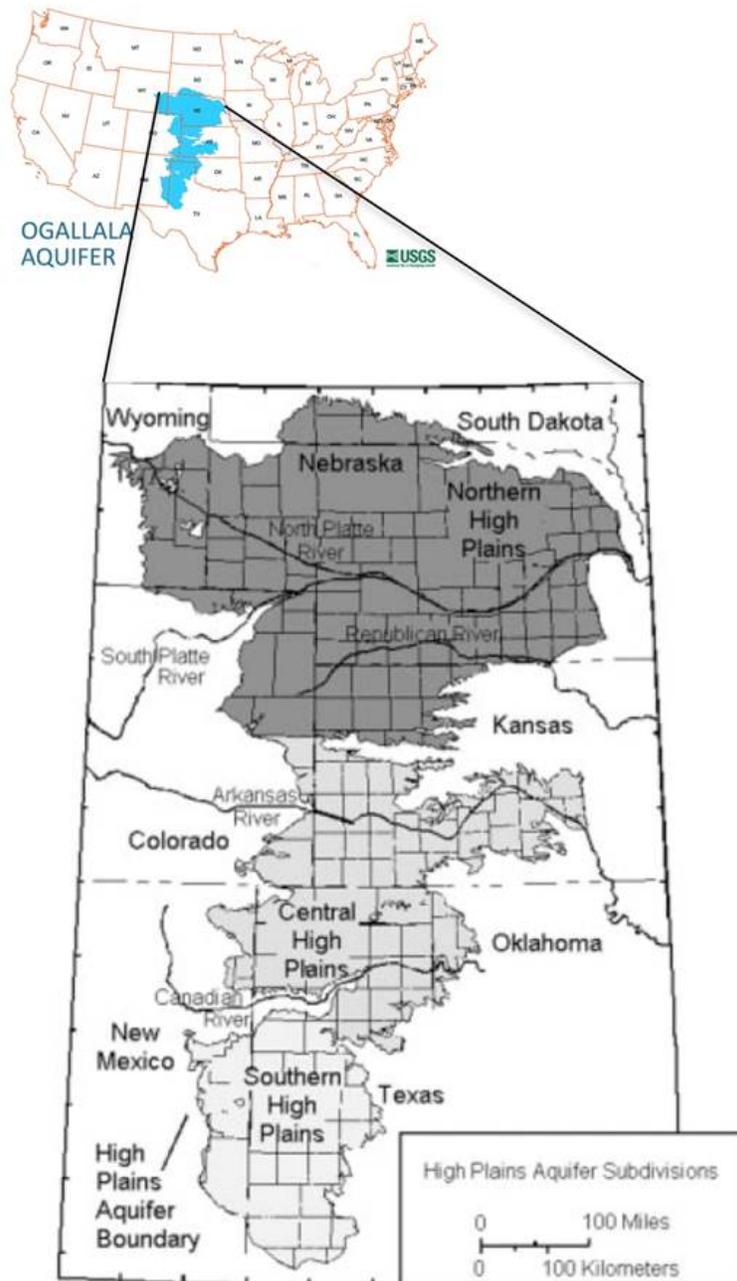


Figure 3. Map showing the extent and major subdivisions of the Ogallala/High Plains aquifer in the USA (from USGS and Rosenberg et al., 1999).

## 1.4 RESEARCH OBJECTIVES AND APPROACH

Geochemical and isotopic characterization of formation brines and groundwater can be used to identify subsurface mineral dissolution and precipitation reactions and cation exchange processes that provide insight into CO<sub>2</sub>-water-rock interactions. The lithium (Li) isotopic composition of produced water from oil and gas-bearing units have proven useful in determining the origin and evolution of basinal brines and identification of the effect of temperature on subsurface water-rock interactions (Chan et al., 2002; Millot et al., 2011; Macpherson et al., 2014). Lithium isotopic composition can also aid in tracking fluid migration paths and in source determination of dissolved constituents in formation and groundwaters. The use of natural geochemical and isotopic signatures requires site-specific baseline characterization of both fluid (brine, groundwater) and solid phases (reservoir rock, caprock, fracture fill and aquifers) followed by fluid sampling during and after injection.

This study was conducted at an EOR site in the Seminole oilfield within the San Andres Platform Carbonate play of the Permian Basin Central Basin Platform (Broadhead et al. 2004). Dolomitic rocks of the Upper Permian (Guadalupian) San Andres Formation comprise one of the most important oil reservoirs in the Permian Basin. Carbonate hydrocarbon reservoirs are often targets of secondary and tertiary hydrocarbon recovery methods in the Permian Basin and elsewhere (Manrique et al., 2004). However, although carbonate host rocks can facilitate mineral trapping (i.e., CO<sub>2</sub> sequestration by its incorporation into stable minerals such as magnesite), spatial heterogeneity can complicate models of fluid-rock interactions and the ability to extrapolate pore-scale models to characterize large field areas (Crawshaw and Boek, 2013; Ager and Geiger, 2015).

This study is an investigation of brine-groundwater-rock interactions and TDS sources. Geochemical and lithium isotope compositions of produced waters and groundwaters from an EOR site in northwest Texas were used to identify and quantify fluid-rock interactions over different temporal scales and investigate produced/formation water pathways. The presence of overlying aquifers, including the Tertiary Ogallala Formation of the Southern High Plains aquifer, provides an opportunity to establish detailed baseline geochemical and isotopic parameters, and identify sources of TDS in the Southern High Plains-Ogallala aquifer.

## **2.0 SITE DESCRIPTION AND GEOLOGICAL SETTING**

### **2.1 SITE DESCRIPTION AND GEOLOGIC SETTING**

Secondary and tertiary EOR at the site included waterflooding and CO<sub>2</sub> injection. The study area is an EOR site approximately 5.23 mi<sup>2</sup> (~13.6 km<sup>2</sup>), within the Seminole oilfield, in Gaines County, Texas (Figure 2). The oilfield is within the San Andres Platform Carbonate play of the Permian Basin Central Basin Platform (Broadhead et al. 2004). Oil wells reach depths of approximately 5,350 ft (1,627 m) below the surface, tapping carbonate rocks of the San Andres Formation that is approximately 1,500 ft (457 m) thick in the region. These dolostones are characterized by high primary permeability and porosity, and were affected by diagenetic dolomitization, sulfate mineralization and karst-modification (Bebout and Carlson, 1986; Ruppel and Cander, 1988; Dutton et al., 2005). The San Andres dolostones and overlying evaporitic Ochoan Series of the Central Basin Platform form part of the Permian Composite carbon storage assessment unit (SAU) identified by the US Geological Survey as potentially suitable for carbon sequestration (Merrill et al., 2015).

The overlying Santa Rosa Sandstone member of the Dockum Group (approximately 1,500 ft; 457 m depth) is a locally important aquifer that is primarily used by the oil and gas industry in the field area. The Ogallala Formation aquifer is approximately 35 to 55 meters beneath the surface and 45 to 60 meters thick in Gaines County (Rettman and Leggat, 1966).

Groundwater flow is to the southeast (Engle and Blondes, 2014). Stratigraphy and generalized lithologies are shown in Figure 4.

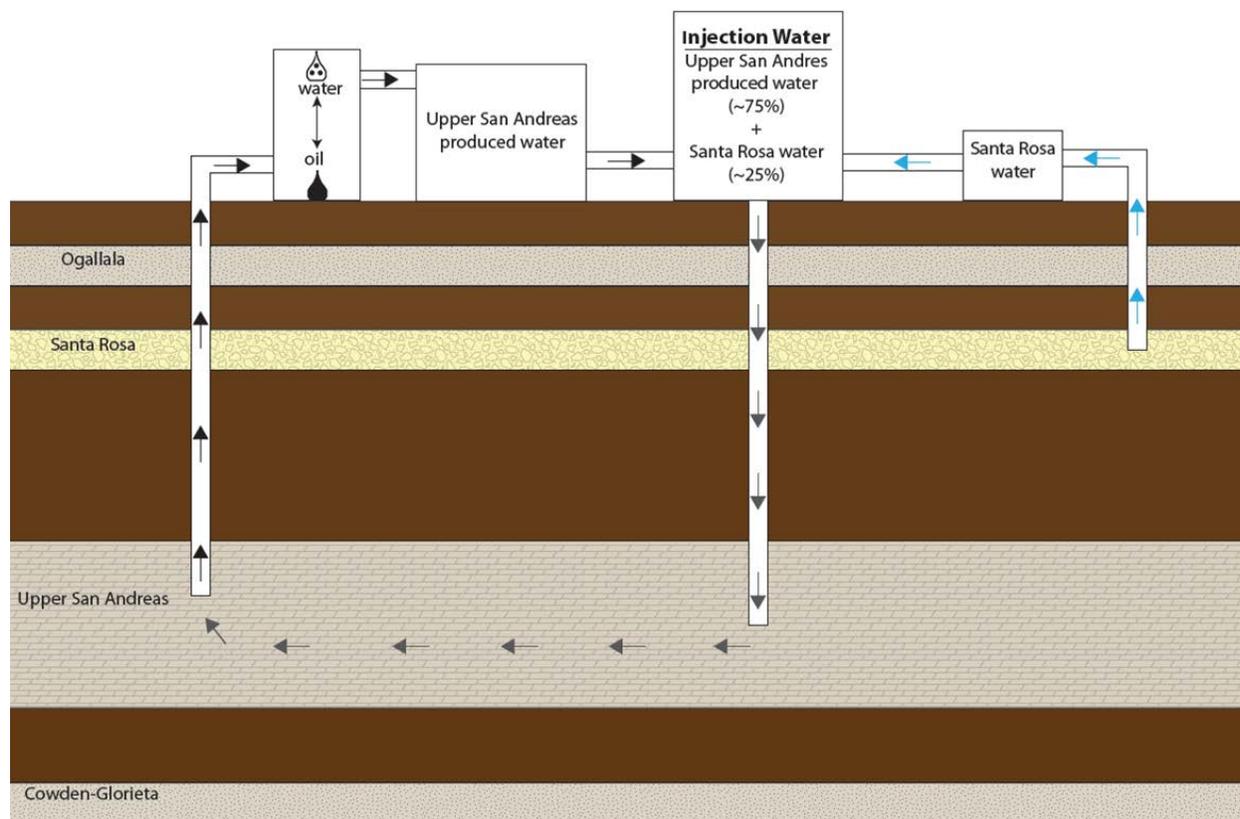
System	Series	Group/Formation	General Lithology
<i>Tertiary</i>		<b>Ogallala</b>	<i>fluvial and lacustrine clastics</i>
<i>Cretaceous</i>		<i>Fredericksburg</i>	<i>limestone sandstone</i>
		<i>Paluxy</i>	
<i>Triassic</i>		<b>Santa Rosa</b>	<i>fluvial-deltaic and lacustrine clastics</i>
<i>Permian</i>	<i>Ochoan</i>	<i>Dewey Lake</i>	<i>sandstone</i>
		<i>Rustler</i>	<i>salt, anhydrite</i>
		<i>Salado</i>	<i>salt</i>
	<i>Guadalupian</i>	<i>Tansill</i>	<i>anhydrite</i>
		<i>Yates</i>	<i>sandstone</i>
		<i>Seven Rivers</i>	<i>anhydrite</i>
		<i>Queen</i>	<i>sandstone</i>
		<b>San Andres</b>	<i>dolomite-sandstone</i>
	<i>Leonardian</i>	<i>Clear Fork</i>	<i>limestone-dolomite</i>
		<i>Wichita</i>	
	<i>Wolfcampian</i>	<b>Wolfcamp</b>	<i>shelf limestones, minor shale</i>
<i>Pennsylvanian</i>	<i>Cisco</i>		
	<i>Canyon</i>		
	<i>Strawn</i>		
	<i>Atokan</i>	<i>shale</i>	
	<i>Chester</i>		

Figure 4. Generalized stratigraphy of the study area (modified from Steuber, 1998).

The Southern High Plains portion of the Ogallala aquifer overlies the study area, and is an important source of irrigational and drinking water (Fahlquist, 2003). Compared to the northern part of the aquifer, Southern High Plains groundwater generally has higher TDS (median 800 mg L<sup>-1</sup> in shallow groundwater) and arsenic concentrations that can exceed the USEPA drinking water standard of 10 µg L<sup>-1</sup> (Mehta et al., 2000; Gurdak et al., 2009; Scanlon et al., 2009; Venkataraman and Uddameri, 2012).

## **2.2 SAMPLING STRATEGY AND LOCATIONS**

Waters were collected during three sampling periods from 18 wells in the study area: ten producing wells (Wells A1-A10); one Santa Rosa aquifer well drilled by the oil company (Well B1); and three residential (C2, C3 and C5) and two irrigation (C1 and C6) -purposed Ogallala aquifer wells. Waters were also collected from two injection wells (Wells D1 and D3); after the first sampling event, Well D3 was converted into a CO<sub>2</sub> injection well. Injection water consisted of groundwater from the Santa Rosa well (B1) mixed in a tank with recycled water from producing wells (Figure 5). Figure 6 shows sampling locations as well as the location of CO<sub>2</sub> injection wells (E1 through E5).



**Figure 5. Schematic of water injection and water mixing procedure at the East Seminole field; figure not to scale (from Gardiner, 2013).**

The East Seminole field has been periodically waterflooded and injected with CO<sub>2</sub> since the 1980s (Gray, 1989; USGS, 2012). The most recent phase of CO<sub>2</sub> injection at the study site began in October 2013 and continued through the remainder of the study period. Waterflooding of the field occurred prior to and concurrent with CO<sub>2</sub> injection as part of secondary recovery. The first set of samples was collected four months before CO<sub>2</sub> injection commenced (June 2013). The second and third sampling events occurred three months (January 2014) and seven months (May 2014) after the initiation of CO<sub>2</sub> injection. Because of logistical and operational issues,

water samples were not obtained for some wells for all three sampling events; collection dates are noted in the data tables.

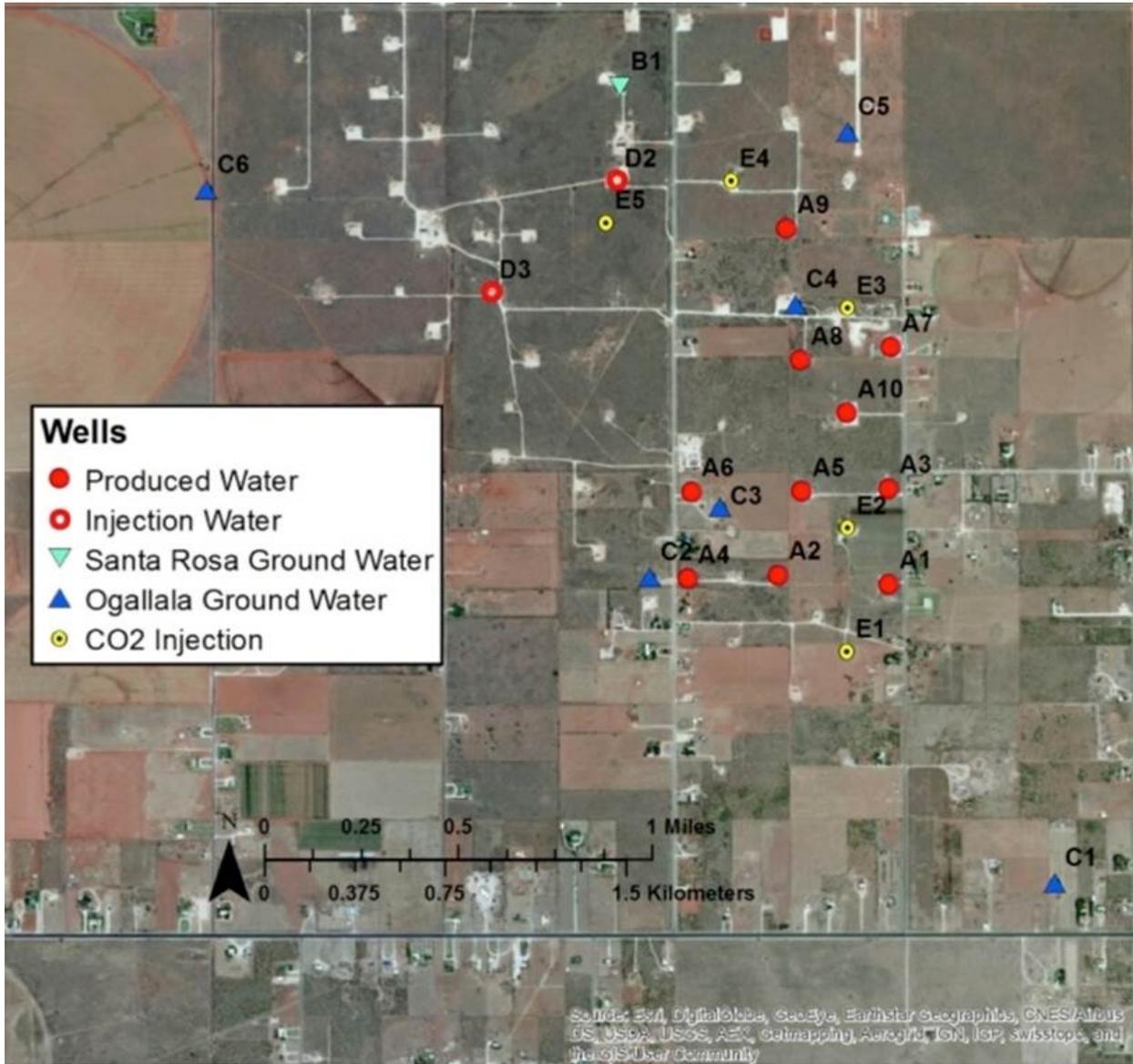


Figure 6. Well locations of produced water (A), Santa Rosa groundwater (B), Ogallala groundwater (C), and injection water (D) sampled in this study, as well as locations of CO<sub>2</sub> injection wells in the field area.

### **3.0 ANALYTICAL METHODS**

#### **3.1 FIELD METHODS AND SAMPLE COLLECTION**

Wells were sampled in June of 2013, January 2014, and May 2014. Waterflooding was ongoing at the site throughout the sampling period. CO<sub>2</sub> injection began in October 2013. At each site, pH, temperature, electrical conductivity, and reduction potential were measured using a multi-meter (YSI® Instruments) with analytical accuracy of  $\pm 0.2$ ,  $\pm 0.2^{\circ}\text{C}$ ,  $\pm 1\%$   $\mu\text{S cm}^{-1}$ , and  $\pm 20$  mV, respectively, and total dissolved solids (TDS) was analyzed using a refractometer (Atago MASTER-S28 Alpha Refractometer) with analytical accuracy of  $\pm 2,000$  mg L<sup>-1</sup>. All samples were collected at the wellhead into pre-rinsed carboys that were conditioned with sample water using new, pre-cleaned sample tubing for each sample. Waters were filtered with 0.45  $\mu\text{m}$  high capacity filters (EnviroTech GWE) into acid-washed Nalgene HDPE bottles. Produced water aliquots taken below the oil-water interface were passed through glass wool to remove large particulates and oil prior to filtration. Alkalinity was determined using Hach® titration methods, and calculated via the USGS Alkalinity Calculator (2012). Samples for major and trace cation analyses were preserved by acidification with ultrapure concentrated nitric acid to pH < 2. Samples for anion analysis were preserved by storage on ice followed by refrigeration at the lab.

### **3.2 GEOCHEMICAL (MAJOR, TRACE ELEMENT AND ANION) ANALYSIS**

Major and trace cations were analyzed using a Horiba Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; JY Ultima 2) and a VG Elemental Inductively Coupled Plasma-Mass Spectrometer (ICP-MS; PQII+XS) at the Kansas Geological Survey and University of Kansas, respectively. Anion concentrations were determined with a Dionex 4000i ion chromatograph (IC) equipped with an AS4a 4-mm analytical column and an AG4a guard column at the University of Kansas. Analytical accuracy and precision were determined by replicate analyses of samples, standards (ICP-OES: QCS-23; ICP-MS: Dionex 7 Anion Standard II (Br), QCS-23, and NIST1640a; IC: Dionex 7Anion Standard II) and matrix-matched solutions. Calibration curves were created using pure element solutions. Replicate samples were analyzed at least 25% of every run and analytical uncertainty is <10%.

### **3.3 LITHIUM ISOTOPE ANALYSIS**

Lithium concentrations and  $\delta^7\text{Li}$  determinations were conducted at the University of Pittsburgh. Lithium separation of samples, reference standards (Seawater: NASS-6 and CB-25), sample replicates and procedural blanks was conducted under clean lab conditions using a method modified from Choi et al. (2013). Li yields and procedural blanks were determined by ICP-MS.  $\delta^7\text{Li}$  compositions for samples with column yields  $\geq 99\%$  and blank  $< 0.06\%$  were determined on a Thermo Neptune Plus multicollector-ICP-MS (MC-ICP-MS) using a sample-bracketing technique and normalization to the L-SVEC standard. The measured  $\delta^7\text{Li}$  value for NASS-6 was

$29.60 \pm 2.22$  (n=6); CB-25 yielded  $\delta^7\text{Li}$  of  $9.56 \pm 0.49$  (n=8). Long-term reproducibility for  $\delta^7\text{Li}$  is estimated to be  $\leq 1\text{‰}$  ( $2\sigma$ ).

## 4.0 RESULTS

### 4.1 MAJOR AND TRACE ELEMENT GEOCHEMISTRY OF PRODUCED WATERS

Major element data for San Andres produced and injection waters are presented in Table 1; trace element data are given in Table 2. Produced waters are sodium-chloride type (Figure 7) and calcium is approximately 20 % of the total cation load; sulfate makes up approximately 25% of the anion load. Major element chemistry of the injection waters is indistinguishable from the San Andres produced waters (Figures 7, 8), reflecting long term pumping and reinjection of the same waters. Produced water from San Andres Formation wells are saline (TDS from 24,400 to 42,200 mg kg<sup>-1</sup>) with pH ranging from 6.2 to 7.4 (Figure 8). Sodium ranged from approximately 6,300 to 13,900 mg kg<sup>-1</sup> and chloride from approximately 10,400 to 20,600 mg kg<sup>-1</sup>. Detectable hydrogen sulfide at the wellhead is indicative of reducing conditions in the formation. Alkalinity for produced and injection waters ranged from 1,110 to 1,800 mg kg<sup>-1</sup>. Cerium (Ce), cobalt (Co), chromium (Cr), iron (Fe), lanthanum (La), lead (Pb), vanadium (V) and zinc (Zn) were below detection limits in all produced and injection water samples.

**Table 1. Major and minor geochemistry of produced water samples. All analytes measured by ICP-OES except Li and Br (ICP-MS), Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> (ion chromatograph), and HCO<sub>3</sub><sup>-</sup> (field titration).**

Site	Date sampled <sup>a</sup>	pH	Mg	Ca	Na	K	B	Si	Sr	Li	Br	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TDS <sup>b</sup>
			----- mmol kg <sup>-1</sup> -----										mg kg <sup>-1</sup>		
<i>San Andres produced water</i>															
A1	2013-06	6.5	11.5	31.7	310	4.14	0.320	0.188	0.305	0.255	0.076	324	49.4	24.6	26,600
	2014-01	7.2								0.265				26.7	
	2014-05	6.6								0.257				26.7	
A2	2013-06	6.5	11.1	29.9	318	4.27	0.317	0.214	0.298	0.261	0.090	293	39.1	22.1	24,500
	2014-01	7.3	20.0	37.2	318	9.59	0.376	0.325	0.325	0.278	0.146	354	47.4	24.7	28,300
	2014-05(A) <sup>c</sup>	6.5	11.7	30.7	283	3.12	0.312	0.208	0.296	0.248	0.095	305	40.2	25.5	24,400
	2014-05(B) <sup>c</sup>		11.7	31.2	274	3.61	0.316	0.224	0.298	0.250	0.103	310	40.5	25.5	24,500
A3	2013-06	6.3	13.7	36.2	492	5.40	0.384	0.434	0.366	0.298	0.106	511	47.3	26.2	37,600
	2014-01	6.8	14.5	37.2	457	8.34	0.336	– <sup>d</sup>	0.361	0.275	0.130	446	45.8	26.1	34,500
	2014-05	6.5	13.4	36.2	415	6.98	0.352	0.214	0.360	0.282	0.139	447	41.9	27.0	33,200
A4	2013-06	6.3	17.3	35.2	350	12.1	0.395	0.346	0.347	0.233	0.143	382	48.6	22.4	30,000
	2014-01	6.2	12.4	31.2	331	4.88	0.302	–	0.314	0.231	0.100	355	46.9	23.1	27,900
A5	2014-01	7.3	10.7	30.2	393	1.11	0.270	–	0.276	0.212	0.088	295	46.0	23.6	26,900
	2014-05(A) <sup>c</sup>	6.9								0.202				23.8	
A6	2013-06	6.4	10.3	33.2	320	3.94	0.322	0.197	0.304	0.236	0.078	302	50.8	18.2	25,800
	2014-01	6.5								0.235				20.6	
A7	2013-06	6.3	15.5	37.7	457	6.29	0.384	0.218	0.406	0.340	0.105	487	42.8	27.8	35,700
	2014-01	6.2	16.4	39.9	418	7.52	0.377	–	0.405	0.327	0.171	530	43.2	29.4	36,700
A8	2013-06	6.6	14.1	35.4	418	5.75	0.380	0.189	0.397	0.340	0.117	423	38.3	27.1	32,000
	2014-01	6.5								0.235				25.7	
	2014-05	6.7								0.320				26.7	
A9	2014-05(A) <sup>c</sup>	6.6	13.1	36.7	401	11.7	0.429	0.353	0.420	0.203	0.118	434	43.1	18.8	32,200
	2014-05(B) <sup>c</sup>		12.7	36.4	435	5.24	0.371	0.234	0.387	0.198	0.116	443	43.8	18.8	33,100
A10	2013-06	6.5	14.7	39.2	605	5.96	0.405	0.151	0.381	0.271	0.084	581	43.7	21.1	42,200
<i>Injection water</i>															
D2	2013-06	6.5	12.3	32.7	368	4.94	0.351	0.195	0.333	0.259	0.090	361	40.9	21.5	28,300
	2014-01	6.3	13.7	36.2	381	4.99	0.349	–	0.374	0.275	0.125	429	45.5	25.3	31,900
	2014-05	6.4	12.8	34.2	415	6.09	0.331	0.203	0.344	0.256	0.081	358	40.6	25.7	29,700
D3	2013-06	6.4	11.1	30.9	290	4.63	0.297	0.188	0.296	0.244	0.061	327	41.4	22.3	25,300

<sup>a</sup>Year and month

<sup>b</sup>Total dissolved solids calculated from the sum of the measured cations and anions.

<sup>c</sup>(A) and (B) refer to field duplicate samples.

<sup>d</sup>Hyphen (–) indicates below detection limit.

**Table 2. Trace metal concentrations (by ICP-MS) of produced water samples.**

Site	Sampling Date <sup>a</sup>	Al	Ba	Cu	Mn	Mo	Ni	Rb	U
umol kg <sup>-1</sup>									
<i>San Andres produced water</i>									
A1	2013-06	– <sup>c</sup>	0.307	–	0.275	–	–	2.01	–
	2014-01	–	0.241	–	–	–	3.29	2.26	0.00415
	2014-05	–	0.232	0.264	1.89	–	2.42	2.16	–
A2	2013-06	–	0.221	–	0.169	–	–	2.21	–
	2014-01	–	0.251	–	0.812	–	–	2.45	0.00890
	2014-05(A)	–	0.208	–	0.222	–	3.42	2.15	–
	2014-05(B)	1,156	0.213	0.258	0.228	–	3.58	2.19	–
A3	2013-06	15,047	0.392	–	0.406	–	–	2.49	–
	2014-01	–	0.301	–	0.353	–	1.50	2.38	0.00534
	2014-05	471	0.302	–	2.84	–	1.79	2.47	–
A4	2013-06	–	0.371	–	1.44	0.407	4.58	2.31	–
	2014-01	–	0.218	–	0.359	–	3.56	2.07	0.00343
A5	2014-01	–	0.214	–	11.80	–	3.87	1.56	0.00500
	2014-05(A)	–	0.265	–	5.77	–	2.62	1.50	–
	2014-05(B)	–	0.269	–	5.72	–	3.17	1.52	–
A6	2013-06	–	0.329	–	0.253	–	–	2.02	–
	2014-01	–	0.228	–	0.146	–	6.06	2.09	0.00301
A7	2013-06	2,754	0.349	–	0.570	–	–	3.19	–
	2014-01	–	0.273	–	–	–	1.39	3.23	0.00385
A8	2013-06	–	0.336	–	0.837	–	–	3.18	–
	2014-01	–	0.264	–	0.739	–	1.98	2.93	0.00462
	2014-05	–	0.261	–	0.242	–	1.61	2.96	–
A9	2014-05(A)	–	0.403	–	2.04	–	–	2.54	–
	2014-05(B)	–	0.405	–	1.93	–	1.93	2.49	–
A10	2013-06	–	0.417	–	0.835	–	–	2.09	–
<i>Injection water</i>									
D2	2013-06	–	0.355	–	1.53	–	–	2.36	–
	2014-01	–	0.264	–	0.661	–	1.36	2.68	0.00437
	2014-05	–	0.244	–	4.31	–	1.58	2.33	–
D3	2013-06	–	0.316	–	0.508	–	–	1.99	–

<sup>a</sup>Year and month. (A) and (B) refer to field duplicate samples.

<sup>c</sup>Hyphen (–) indicates below detection limit.

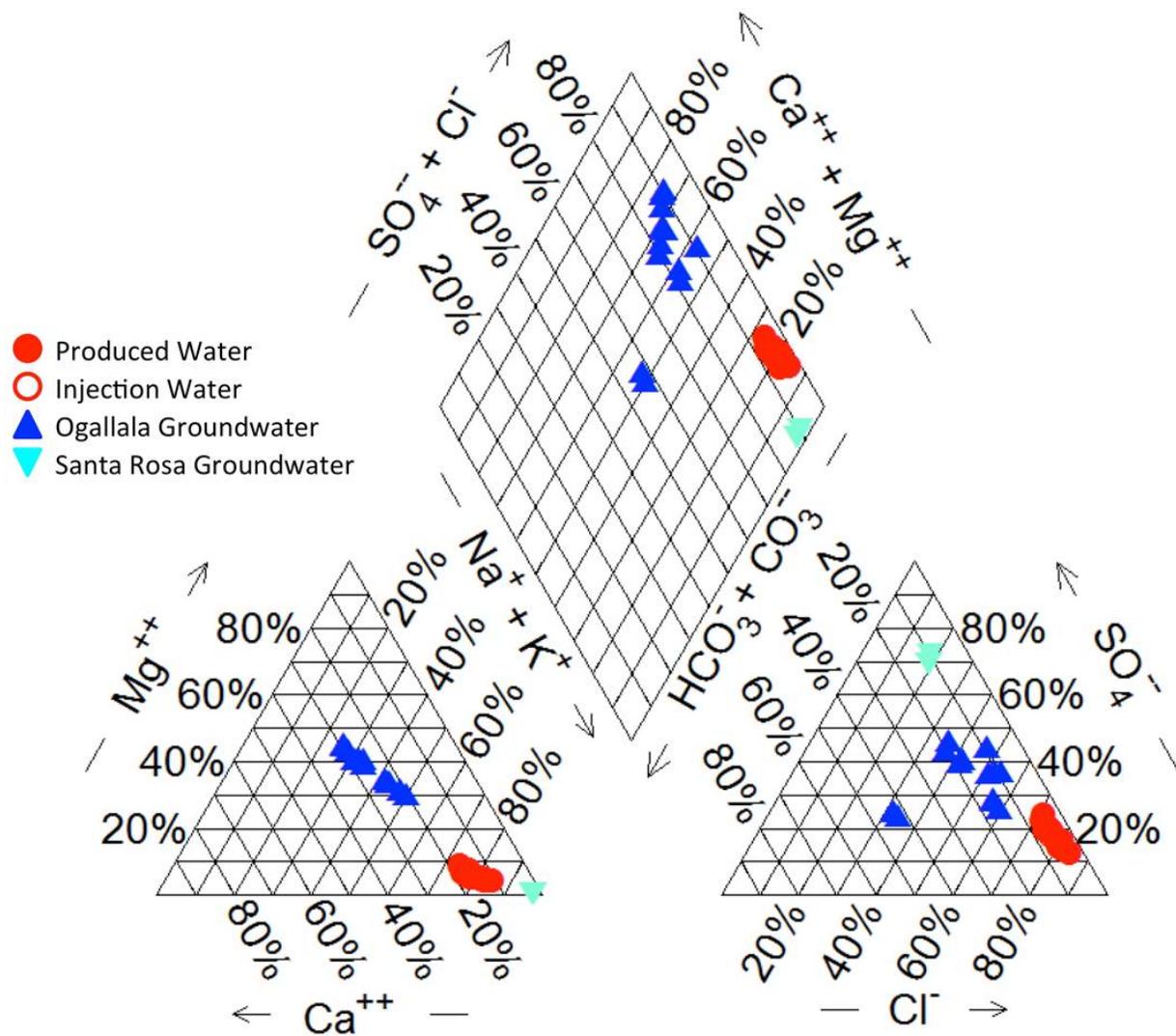


Figure 7. Piper plot of all samples analyzed in this study.

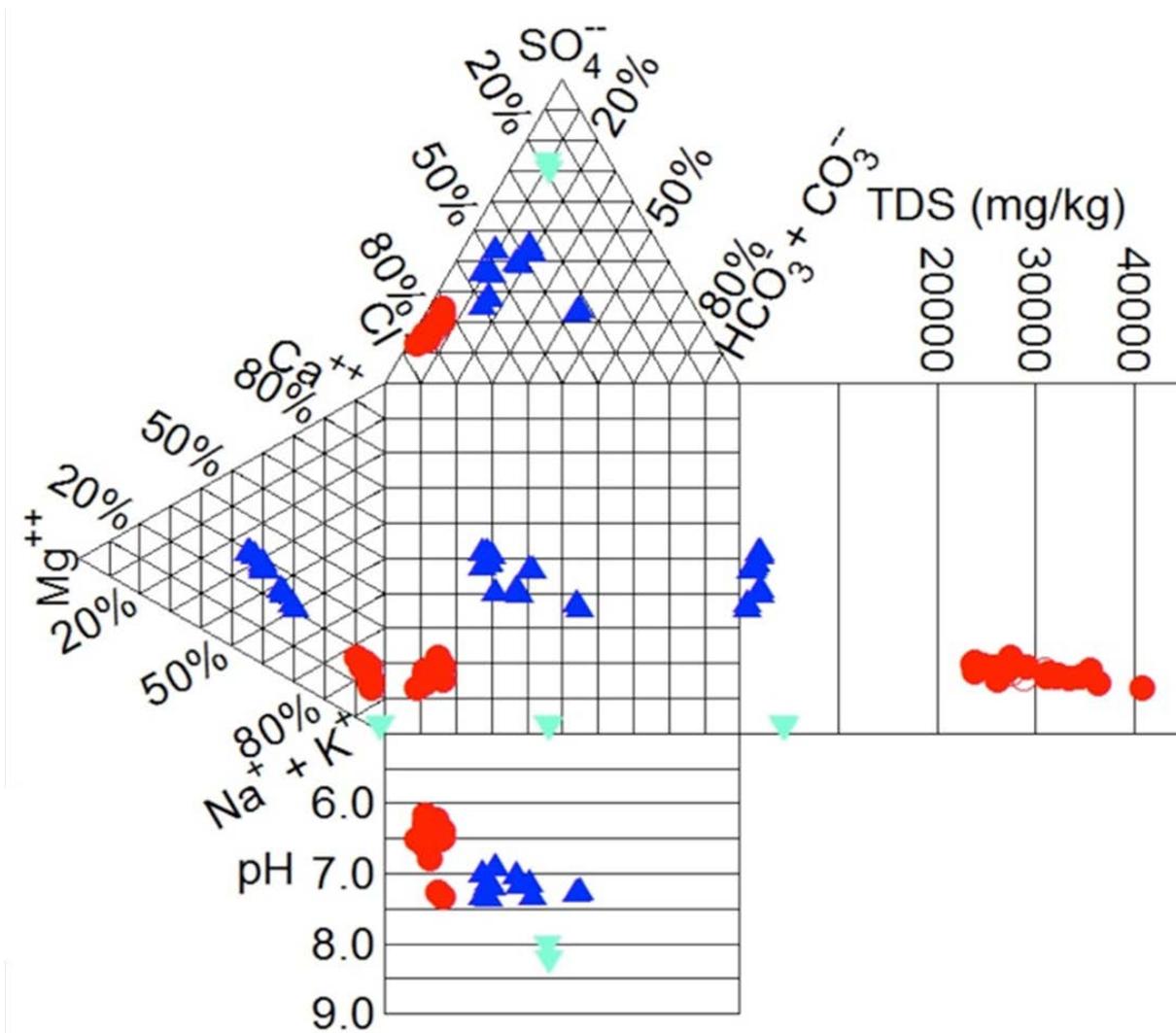


Figure 8. Durov plot of all samples analyzed in this study. Symbols the same as Figure 7.

## 4.2 OGALLALA & SANTA ROSA GROUNDWATER GEOCHEMISTRY

### 4.2.1 Groundwater major anions and cations

The major constituents of Ogallala and Santa Rosa groundwater samples are presented in Table

3. Ogallala aquifer groundwater pH was circumneutral, with values that ranged from 6.9 to 7.4,

and TDS in the range of 797 to 2,200 mg kg<sup>-1</sup> (Figure 8). Up to 50% of the cation load consisted of sodium (Na<sup>+</sup>), with nearly equal amounts of calcium (Ca<sup>2+</sup>) and magnesium (Mg<sup>2+</sup>) making up the remainder (Figure 7). The total anion load for most Ogallala samples contained less than 20% bicarbonate (HCO<sub>3</sub><sup>-</sup>), and slightly more chloride (Cl<sup>-</sup>) than sulfate (SO<sub>4</sub><sup>2-</sup>) (Figure 7).

The salinity of groundwater from the Santa Rosa aquifer in the area precludes its use for drinking water or agricultural purposes. Total dissolved solid values for the Santa Rosa well, B1, locally used by the oil and gas industry, ranged from 4,520 to 4,650 mg kg<sup>-1</sup>, and pH values ranged from 8.0 to 9.1 (Figure 8). The dominant cation was Na<sup>+</sup> making up greater than 90%. SO<sub>4</sub><sup>2-</sup> made up approximately 70% of the total anion load (Figure 7).

**Table 3. Major and minor geochemistry of groundwater samples. All analytes measured by ICP-OES except Li and Br (ICP-MS), Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> (ion chromatograph), and HCO<sub>3</sub><sup>-</sup> (field titration).**

Site	Well type <sup>a</sup>	Depth (m)	Date sampled <sup>b</sup>	pH	Mg	Ca	Na	K	B	Si	Sr	Li	Br	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	TDS <sup>c</sup>	
					----- mmol kg <sup>-1</sup> -----												mg kg <sup>-1</sup>	
<i>Santa Rosa aquifer groundwater</i>																		
B1	I	460	2013-06	8.0	0.469	0.616	61.3	0.181	0.120	0.184	0.0096	0.0340	0.0112	11.4	23.7	6.09	4520	
			2014-01(A) <sup>d</sup>	9.1									0.0369				7.10	
			2014-05(A) <sup>d</sup>	8.2	0.444	0.474	60.0	0.141	0.124	0.152	0.0093	0.0339	0.0213	12.5	23.7	7.52	4600	
			2014-05(B) <sup>d</sup>		0.448	0.477	61.3	0.139	0.124	0.154	0.0094	0.0328	0.0213	12.5	23.8		4650	
<i>Ogallala aquifer groundwater</i>																		
C1	A	53	2013-06	6.9	5.31	3.77	13.9	0.234	0.0906	1.26	0.0466	0.0391	0.0254	14.0	6.36	2.80	1930	
			2014-01	7.2	5.27	3.74	14.0	0.227	0.0895	1.22	0.0466	0.0392	0.0233	13.9	6.51	6.31	2160	
			2014-05	7.1	5.47	3.87	13.5	0.236	0.0925	1.27	0.0483	0.0405	0.0205	14.8	6.76	6.08	2190	
C2	R	47	2013-06	7.3	1.72	1.23	5.83	0.111	0.0323	0.865	0.0157	0.0189	0.0062	3.55	1.29	4.76	797	
			2014-05	7.3	1.81	1.30	5.61	0.115	0.0318	0.876	0.0164	0.0182	0.0054	4.20	1.37	5.26	859	
C3	R	55	2013-06	7.0	4.65	3.24	7.48	0.250	0.0334	1.15	0.0394	0.0361	0.0224	14.1	2.96	3.62	1470	
			2014-01	7.4	5.27	3.82	8.09	0.251	0.0390	1.27	0.0435	0.0386	0.0272	16.0	3.87	4.51	1730	
			2014-05	7.1	5.31	3.79	8.44	0.255	0.0389	1.27	0.0441	0.0360	0.0205	15.8	3.91	4.42	1730	
C5	R	55	2013-06	7.3	7.24	4.77	8.31	0.322	0.0568	1.12	0.0652	0.0369	0.0318	18.9	6.29	3.33	2090	
			2014-01(A) <sup>d</sup>	7.2	7.12	4.84	8.31	0.350	0.0562	1.21	0.0668	0.0380	0.0332	19.0	6.35	3.85	2130	
			2014-05	7.2	7.08	4.87	9.09	0.348	0.0558	1.09	0.0663	0.0357	0.0259	18.9	6.45	4.69	2200	
C6	A	46	2013-06	7.2	3.92	2.64	6.52	0.212	0.0302	0.936	0.0363	0.0288	0.0156	6.77	4.19	3.47	1250	
			2014-05	7.4	3.99	2.79	6.96	0.218	0.0309	0.908	0.0371	0.0261	0.0154	7.90	4.49	4.46	1390	

<sup>a</sup>Industrial (I), residential (R) or agricultural (A)

<sup>b</sup>Year and month

<sup>c</sup>Total dissolved solids calculated from the sum of the measured cations and anions. TDS for sample B1-2014-05(B) based on alkalinity from field duplicate.

<sup>d</sup>(A) and (B) refer to field duplicate samples.

#### 4.2.2 Trace element geochemistry of groundwaters

Trace element data for groundwater samples from Ogallala and Santa Rosa wells are presented in Table 4. Ce, La, and Zn were below the detection limit in all Ogallala water samples. Aluminum (Al), rubidium (Rb), Ce, Co, Cr, Fe, La, Pb, V, and Zn were below detection limits in the Santa Rosa groundwater samples.

Vanadium concentrations in Ogallala aquifer groundwaters ranged from 49 to 99  $\mu\text{g kg}^{-1}$ . Although the US Environmental Protection Agency (EPA) has not established a drinking water maximum contaminant level (MCL) for V, several states have set a health risk limit of 50  $\mu\text{g L}^{-1}$  for drinking water (CA and MN Health Depts.). The Superfund removal action limit established by the EPA is 250  $\mu\text{g L}^{-1}$ . Although elevated, V concentrations of Ogallala groundwater in the study area falls within the range of 9.4 to 190  $\mu\text{g L}^{-1}$  (median 37  $\mu\text{g L}^{-1}$ ) found in 47 domestic water wells in the Southern High Plains Aquifer (Fahlquist, 2003). In a study of groundwater in the western Texas Panhandle region, Hopkins (1993) detected V in 91% of Ogallala aquifer groundwater wells, with concentrations ranging from 20 to 532  $\mu\text{g L}^{-1}$ .

Elevated V in groundwater can originate from natural and anthropogenic sources. Vanadium is a redox sensitive transition element that can occur in high concentrations (>10 ppm) in some shales. Elevated  $\text{V}^{5+}$  concentration in surficial aquifers suggests soil leaching and is typically associated with oxic and alkaline groundwater as  $\text{H}_2\text{VO}_4^-$ . Solubility is controlled by sorption-desorption reactions on aquifer oxides and amorphous phases (Wright et al., 2014). In

1999, V from an industrial leak contaminated some wells in Hockley County to the north but locally, V is associated with alteration of Cenozoic volcanic material (Potratz 1980).

**Table 4. Trace metal concentrations (by ICP-MS) of groundwater samples.**

Site	Sampling Date <sup>a</sup>	Al	Ba	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Rb	U	V
$\mu\text{mol kg}^{-1}$														
<i>Santa Rosa aquifer groundwater</i>														
B1	2013-06	– <sup>c</sup>	0.0472	–	–	–	–	1.15	0.393	10.6	–	–	0.00164	–
	2014-01(A) <sup>b</sup>	–	0.0344	–	–	–	–	0.775	0.379	21.8	–	–	0.00123	–
	2014-01(B) <sup>b</sup>	–	0.0537	–	–	0.100	–	2.48	0.389	20.8	–	–	0.00136	–
	2014-05(A) <sup>b</sup>	–	0.0499	–	–	–	–	1.86	0.395	14.8	–	–	0.00099	–
	2014-05(B) <sup>b</sup>	–	0.0475	–	–	–	–	1.82	0.481	13.7	–	–	0.00109	–
<i>Ogallala aquifer groundwater</i>														
C1	2013-06	0.243	0.283	–	–	–	–	0.297	0.273	0.419	–	–	0.07142	1.18
	2014-01	–	0.274	–	–	–	–	0.364	0.0848	0.504	–	–	0.05966	0.98
	2014-05	–	0.275	–	0.523	–	–	0.464	–	0.329	–	–	0.06512	1.34
C2	2013-06	0.0749	0.407	–	–	0.154	–	0.0121	0.0718	–	0.00309	–	0.02790	1.59
	2014-05	–	0.468	–	–	0.0343	–	0.0115	0.0821	–	–	–	0.02672	1.50
C3	2013-06	0.0318	0.455	–	0.612	0.0614	–	–	0.0422	–	0.00096	0.00290	0.03416	1.36
	2014-01	–	0.469	–	0.927	0.0946	–	0.0099	0.0381	–	–	0.00172	0.03403	1.08
	2014-05	–	0.548	–	0.696	0.3446	–	–	0.0470	–	0.00204	–	0.03407	1.08
C5	2013-06	0.0867	0.610	–	0.681	0.1621	3.74	0.167	0.0634	0.148	0.00299	0.00768	0.04327	1.72
	2014-01(A) <sup>b</sup>	27.2	0.640	0.0044	0.848	0.1684	9.60	0.141	0.0635	–	0.00070	0.02036	0.04201	1.94
	2014-05	–	0.591	–	0.727	0.0330	0.0092	0.255	0.0724	0.199	–	0.00656	0.04176	1.64
C6	2013-06	0.0938	0.334	–	–	0.0653	–	0.0839	0.0885	0.154	0.00087	–	0.04079	1.80
	2014-05	–	0.395	–	–	0.0716	–	0.0366	0.0974	0.164	–	–	0.04243	1.60

<sup>a</sup>Year and month

<sup>b</sup>(A) and (B) refer to field duplicate samples

<sup>c</sup>Hyphen (–) indicates below detection limit.

### 4.3 LITHIUM ISOTOPE COMPOSITION

Lithium isotope data for the San Andres produced water, injection water, Ogallala groundwater, and Santa Rosa Formation groundwater are presented in Table 5. The total range of  $\delta^7\text{Li}$  in the San Andres produced waters is +10.9 to +15.6, which is very comparable to the range in the Ogallala aquifer samples (+10.6 to +16.5). In contrast, the Santa Rosa groundwater samples yield  $\delta^7\text{Li}$  values in the range of +20.6 to +23.5, significantly higher than the Ogallala or San Andres values. San Andres waters have higher Li concentrations (1.4-2.4 mg kg<sup>-1</sup>) than Santa Rosa or Ogallala waters (Figure 9), both of which fall within the range of 0.13-0.28 mg kg<sup>-1</sup>.

**Table 5. Lithium isotope data for all samples.**

Site	Date sampled <sup>a</sup>	Li, mmol kg <sup>-1</sup>	$\delta^7\text{Li}^b$
<i>San Andres produced water</i>			
A1	2014-05	0.257	14.30 14.00
A2	2013-06	0.261	14.83
	2014-01	0.278	15.65 15.39
	2014-05(A)	0.248	15.27
	2014-05(B)	0.250	14.20
	2013-06	0.298	12.79 12.81
A3	2014-01	0.275	14.03
	2014-05	0.282	13.78 13.37
	2013-06	0.233	13.60 12.84 12.75
A4	2014-01	0.231	13.98
	2014-01	0.212	15.32
	2014-05(A)	0.202	13.85
A5	2014-05(B)	0.209	14.94 14.78
	2013-06	0.236	15.65
A6	2014-01	0.235	14.78 14.27
	2013-06	0.340	15.28
A7	2014-01	0.327	13.43
	2013-06	0.340	13.05
A8	2014-01	0.305	13.55
	2014-05	0.320	12.34 12.53
	2014-05(A)	0.203	11.37 10.90
A9	2014-05(B)	0.198	12.33
	2013-06	0.271	14.76
A10			
<i>Injection water</i>			
D2	2013-06	0.259	11.87 12.53
	2014-01	0.275	11.53
	2014-05	0.256	11.94
D3	2013-06	0.244	14.48 14.09
<i>Santa Rosa aquifer groundwater</i>			
B1	2013-06	0.0340	20.70 20.59
	2014-01(A)	0.0369	23.47
	2014-01(B)	0.0383	22.85 22.73
	2014-05(A)	0.0339	22.28 21.10
	2014-05(B)	0.0328	21.67 21.47
<i>Ogallala aquifer groundwater</i>			
C1	2013-06	0.0391	15.70
	2014-01	0.0392	16.46
C2	2013-06	0.0189	11.56
	2014-05	0.0182	11.36 11.59 11.06
	2013-06	0.0361	13.28
C3	2014-01	0.0386	14.57 14.23 14.01
	2014-05	0.0360	14.70
	2013-06	0.0369	14.84
C5	2014-01	0.0380	14.70
	2014-05	0.0357	14.95 14.96
	2013-06	0.0288	11.64 12.52 11.47
C6	2014-05	0.0261	10.62

<sup>a</sup>Year and month

<sup>b</sup>Column duplicates where indicated. (A) and (B) are field duplicates.

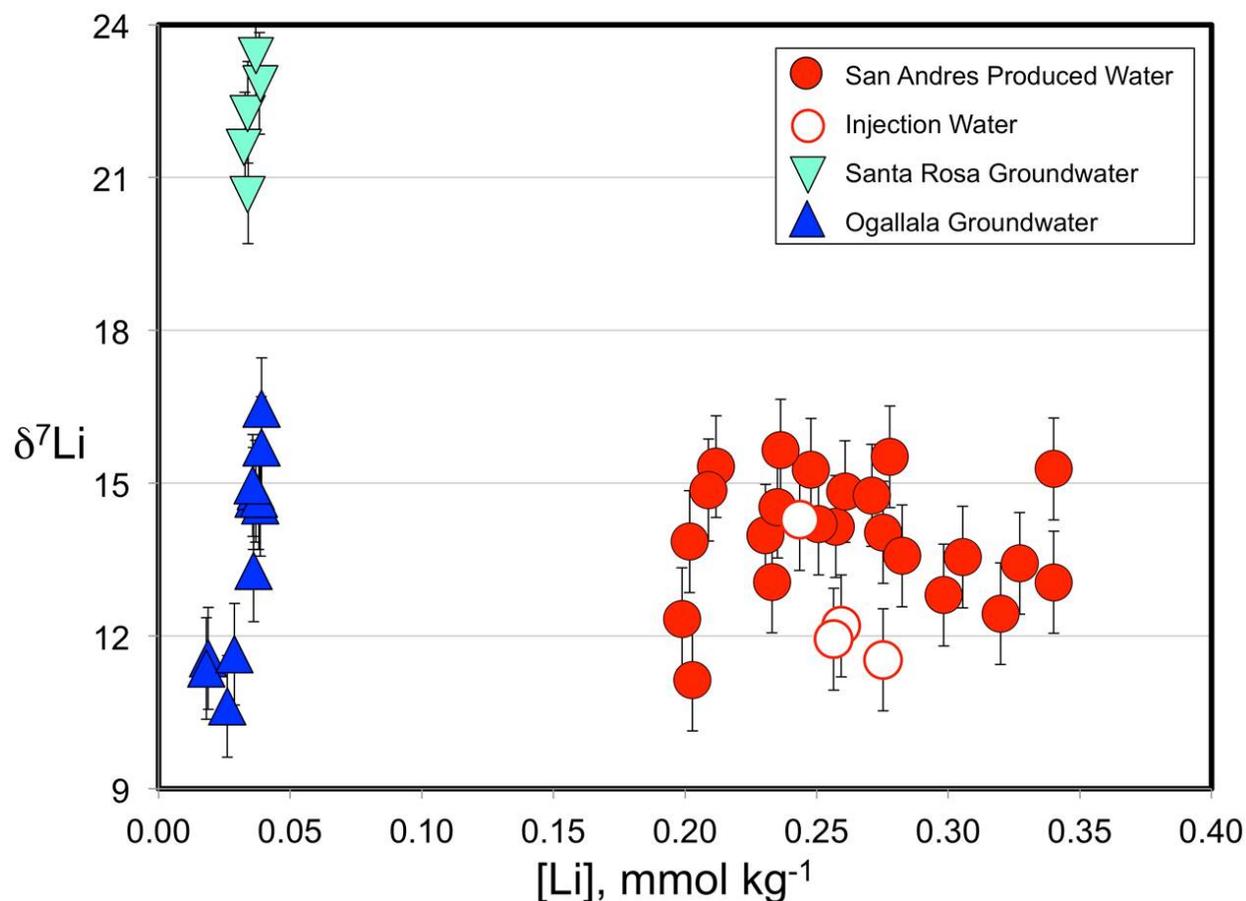


Figure 9. Lithium isotopes ( $\delta^7\text{Li}$ ) plotted against lithium concentrations  $[\text{Li}]$  for all samples analyzed in this study. Error bars represent the estimated long-term external reproducibility ( $\pm 1\%$ ).

Undiluted San Andres formation waters from the eastern flank of the Central Basin Platform (Stueber et al., 1998) have higher concentrations of Li (up to  $7.3 \text{ mg L}^{-1}$ , average  $3.9 \text{ mg L}^{-1}$ ) than the produced waters from the East Seminole site. This is likely the result of dilution resulting from waterflooding related to EOR at the latter site. Injection water is composed of a mixture of recycled San Andres produced water and Santa Rosa groundwater, which have significantly different Li isotope compositions (Figure 9). This difference in  $\delta^7\text{Li}$  could conceivably shift the isotopic composition of waters produced from the San Andres Formation.

However, mixing calculations indicate that in order to generate a measurable shift the  $\delta^7\text{Li}$ , Santa Rosa groundwater would have to be added at amounts  $\geq \sim 70\%$  (Figure 10), which appears to be the maximum addition. Therefore, we assume that the  $\delta^7\text{Li}$  values of San Andres produced water are negligibly different than those of the original formation water.

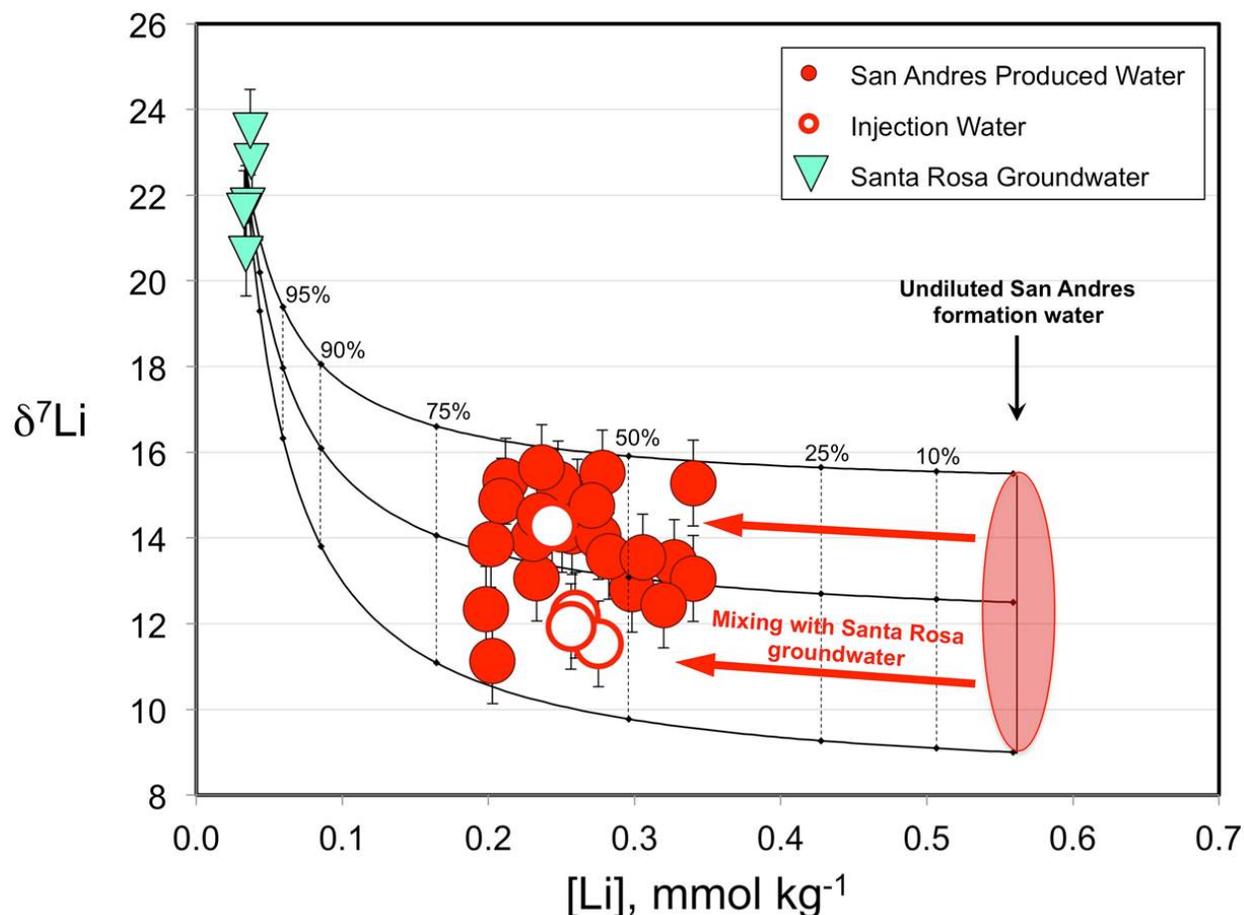


Figure 10. Mixing curve between Santa Rosa groundwater values from this study and approximate lithium concentrations of undiluted San Andres Formation water (Stueber et al., 1998); percentages represent the fraction of added Santa Rosa groundwater.

The range of  $\delta^7\text{Li}$  values measured in San Andres produced waters is comparable to oil and gas field formation waters in the Appalachian Basin (Macpherson et al., 2014; Warner et al., 2014) and Gulf Coast Sedimentary Basin (Macpherson et al., 2014); above the range observed in the Paris Basin (Milot et al., 2011), and below that in the Heletz-Kokhav oil field, Israel (Chan et al., 2002) (Figure 11). Lithium concentrations are generally lower than most of these oilfield brines (Figure 12), again most likely due to waterflooding at the East Seminole site.

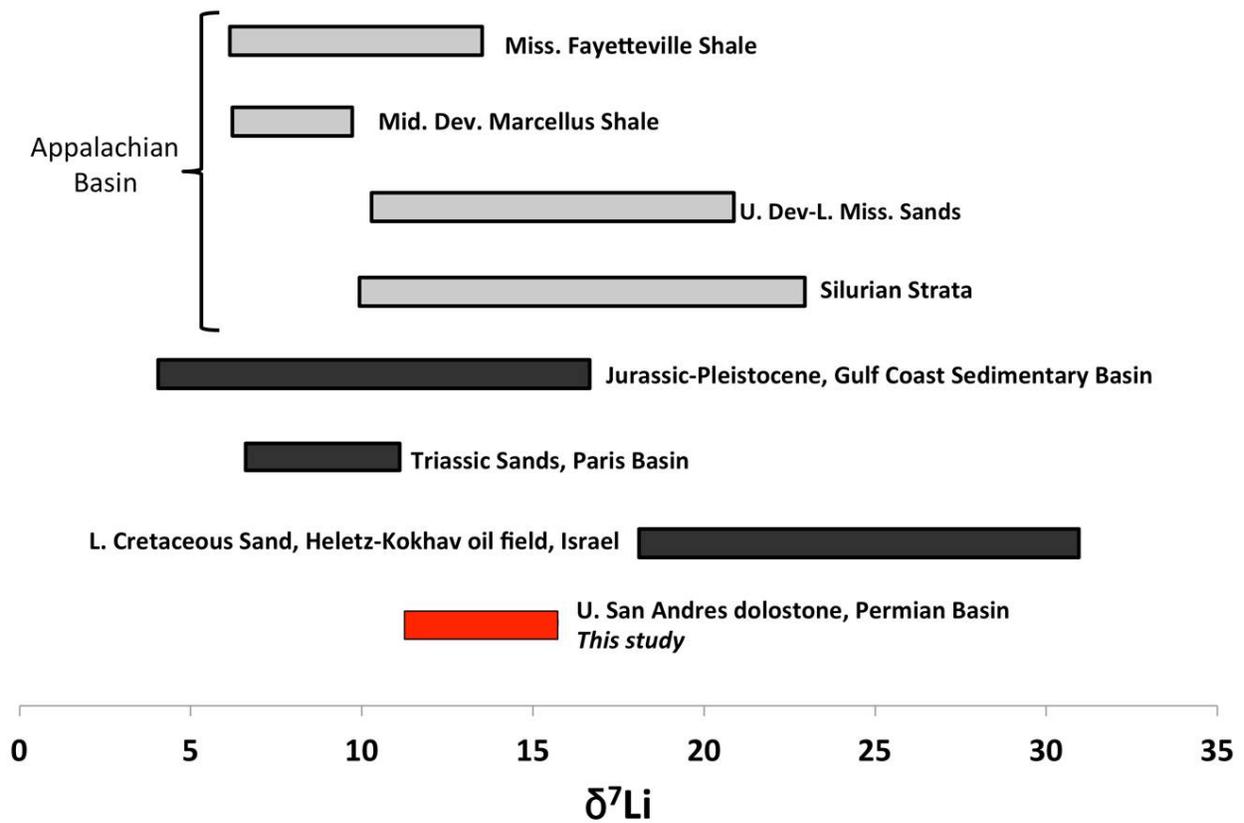


Figure 11.  $\delta^7\text{Li}$  values from this study compared to published formation waters from other hydrocarbon producing basins (Chan et al., 2002; Millot et al., 2011; Macpherson et al., 2014; Warner et al., 2014).

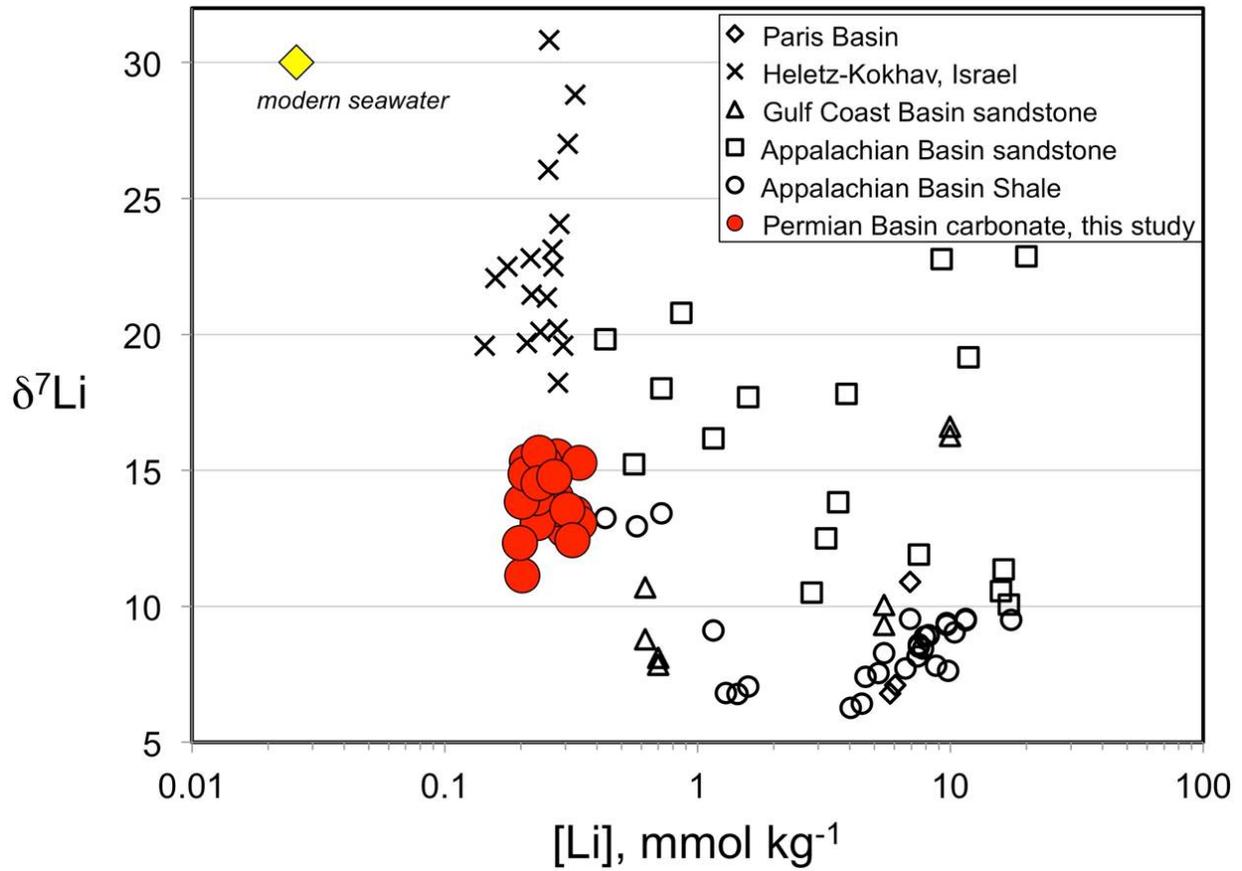


Figure 12.  $\delta^7Li$  values vs.  $[Li]$  for samples analyzed in this study (solid red circles) and published formation waters (data from Chan et al., 2002; Millot et al., 2011; Macpherson et al., 2014; Warner et al., 2014). Modern seawater (yellow diamond) is shown for comparison.

## 5.0 DISCUSSION

### 5.1 EVOLUTION OF PRODUCED WATERS

#### 5.1.1 Sources of dissolved constituents in San Andres produced waters

Permian Basin formation water chemistry can reflect a complex history of seawater evaporation, ion exchange, halite dissolution, dolomitization, and precipitation of gypsum (Dutton, 1987; Engle and Blondes, 2014). Based on the predictable variation of Na/Br and Cl/Br in response to seawater evaporation and halite dissolution (Walter et al., 1990), Stueber et al. (1998) suggested that the San Andres formation waters on the eastern flank of the Central Basin Platform are primarily meteoric in origin with subsequent halite (and minor K-rich salt) dissolution responsible for salinity, in contrast to deeper brines that have a significant evaporated seawater component. We compared San Andres produced waters from East Seminole in the central part of the platform to the data of Stueber et al. (1998) (Figure 13). The East Seminole waters also fall along the halite evaporation trend, extending to significantly higher Na/Br and Cl/Br values than those measured by Stueber et al. (1998). This could be due to (1) additional halite dissolution induced by injection of more dilute waters during waterflooding, or (2) a greater extent of halite dissolution by meteoric water in the central part of the platform. The effects of dilution by Santa Rosa Formation groundwaters during waterflooding can clearly be seen in a

plot of Na vs. Cl (Figure 14), with the East Seminole waters falling along a mixing trend between the eastern Platform formation waters and more dilute Santa Rosa groundwater.

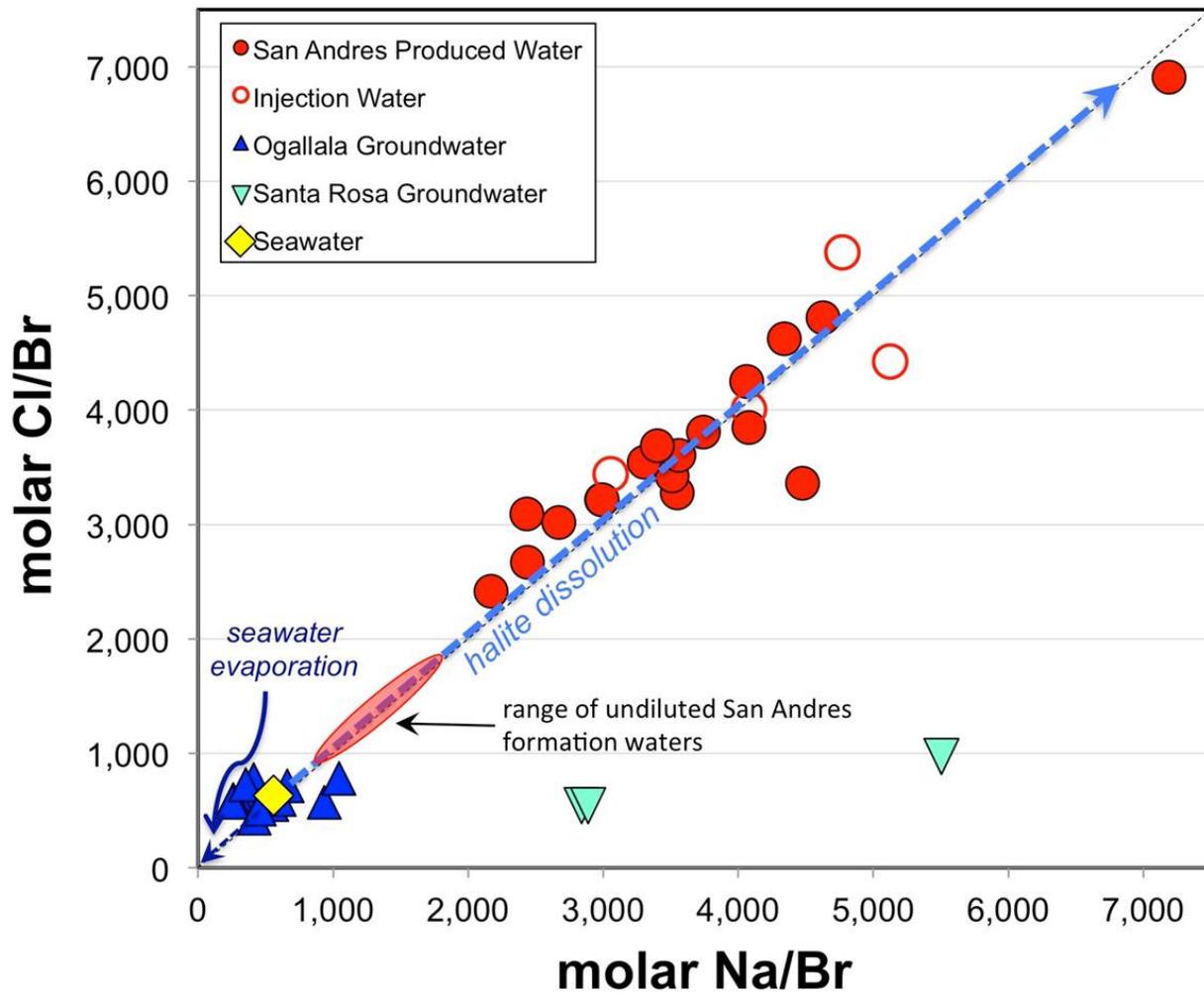


Figure 13. Molar Cl/Br vs. molar Na/Br ratios for samples in this study compared to the range of undiluted San Andres formation waters reported by Stueber et al. (1998). The halite dissolution trend (blue dashed line) extends from modern seawater along a 1:1 line (Walter et al., 1990).

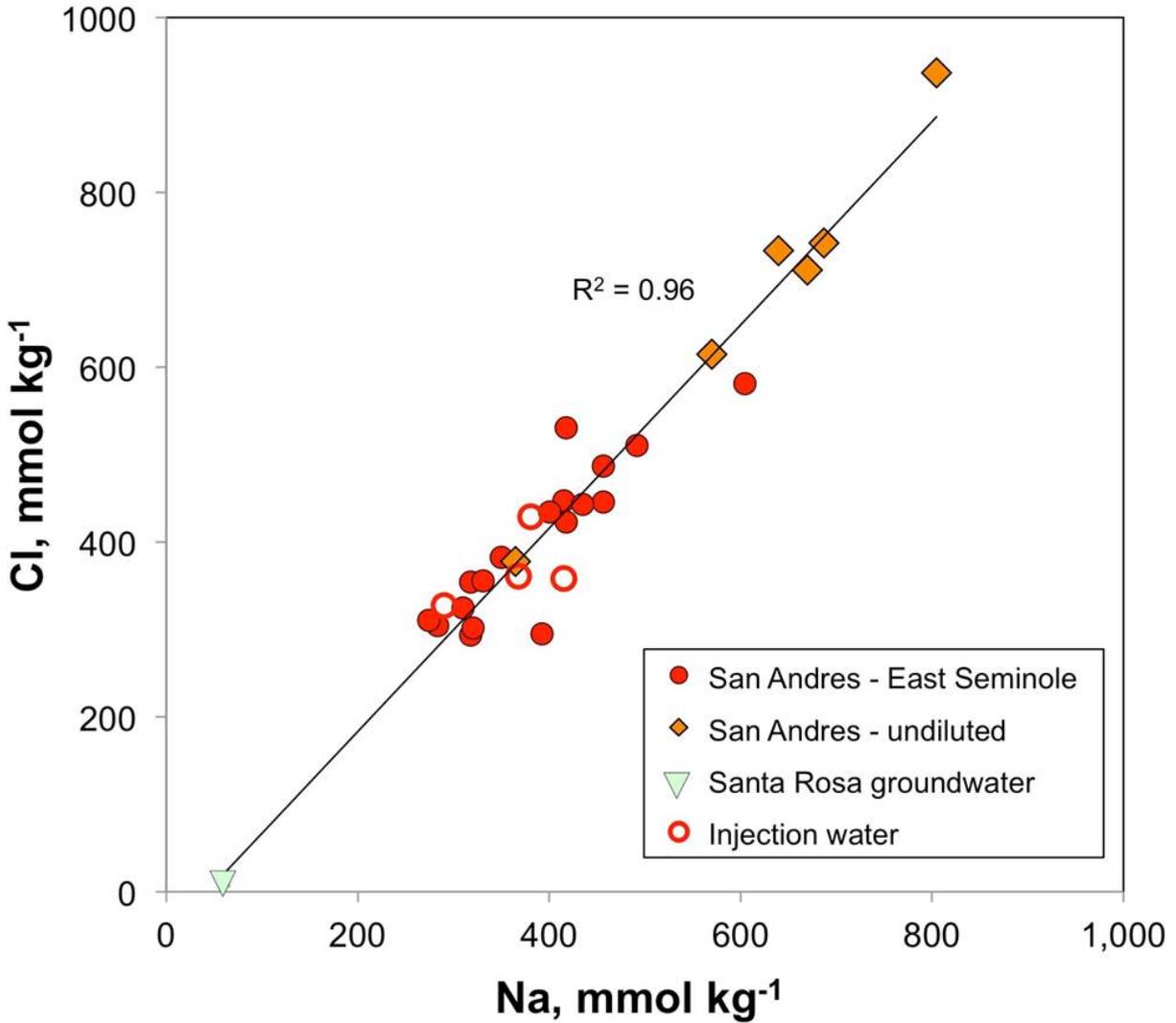


Figure 14. Cl vs. Na for San Andres produced water, injection water, and Santa Rosa formation water from this study, and undiluted San Andres produced water from Stueber et al. (1998).

Because the San Andres is a dolomitic reservoir, it is expected that the dolomite host rock itself will exert some control on water chemistry. Molar concentrations of Ca are in excess of Mg for all produced water samples, but Ca and Mg vary with a slope very close to unity when combined with the eastern Platform data (Figure 15). We suggest that this covariation reflects

dissolution of dolomite host rock, with the “excess” Ca (the intercept at Mg = 0 on Figure 15) being inherited from interaction of meteoric waters with anhydrite evaporite units.

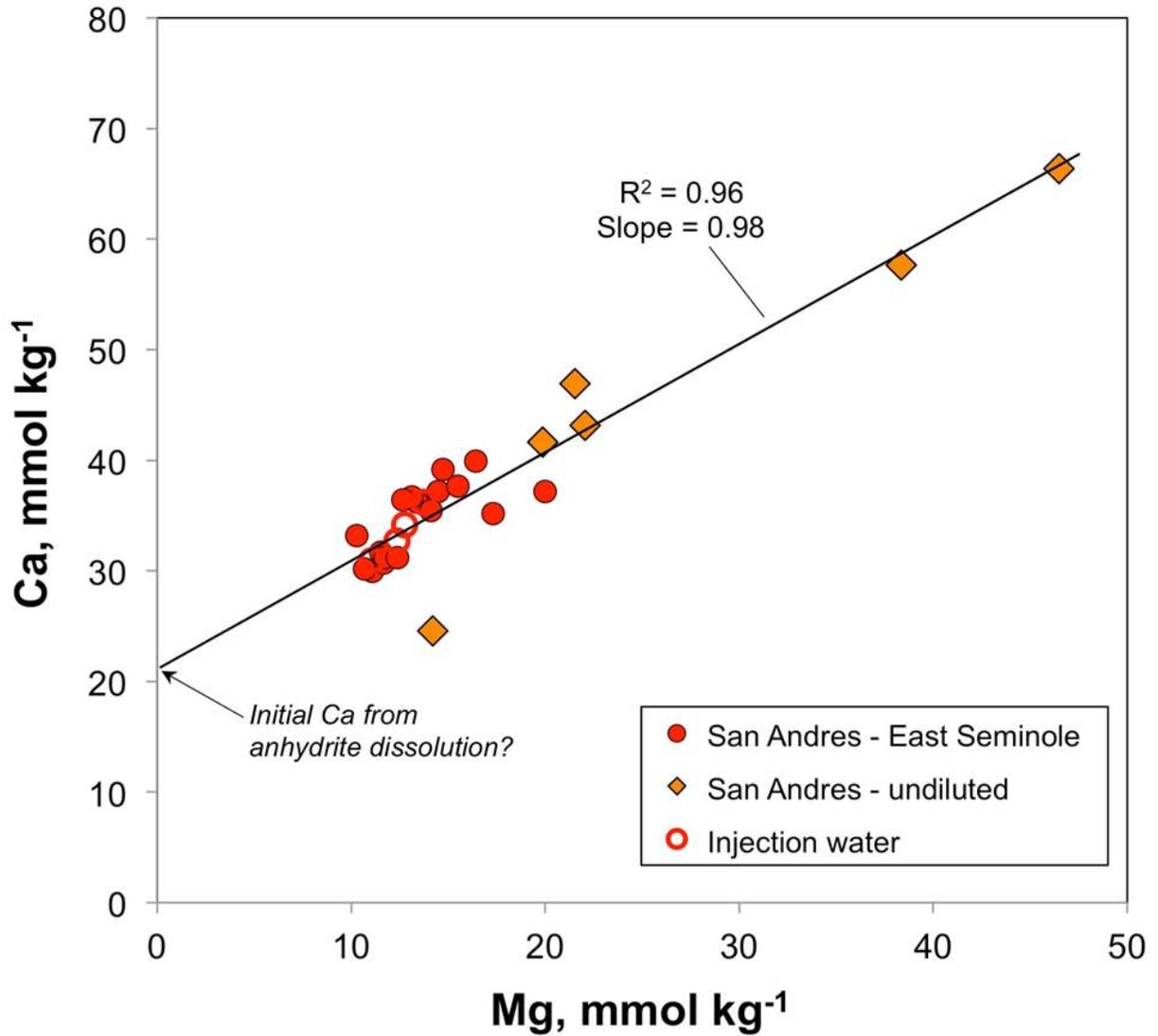


Figure 15. Ca vs. Mg for San Andres produced and injection water from this study, and undiluted San Andres produced water from Stueber et al. (1998).

### 5.1.2 Lithium isotopes in San Andres produced water

Major element data discussed in Section 5.1.1 and stable isotope data from Stueber et al. (1998) strongly suggest that San Andres waters are primarily meteoric in origin, with the recharge originating in southeastern New Mexico (Stueber et al., 1998; Barnaby et al., 2004). The bulk of the TDS appears to have originated from dissolution of evaporite deposits in the flowpath; hence this is the likely origin of the Li in San Andres waters. Evaporites would inherit  $\delta^7\text{Li}$  values similar to those of the water from which they precipitate, but the Li isotope composition of Permian seawater is not currently known. Misra and Froelich (2012) extended the marine  $\delta^7\text{Li}$  record back to about 70 Ma using carbonate from a deep sea core, and found secular variations with  $\delta^7\text{Li}$  values as low as  $\sim+20$  at 60 Ma. Given this level of variation, it is not unreasonable to surmise values as low as  $+10$  to  $+15$  during the Permian. If this were the case, then the  $\delta^7\text{Li}$  values in San Andres produced waters would represent Permian seawater/evaporites, modified by later interaction with reservoir minerals. In general, exchange with and alteration of silicate minerals is likely to raise the  $\delta^7\text{Li}$  of the interacting waters.

The spread in  $\delta^7\text{Li}$  values of the produced water suggests that the original formation waters are affected by more than one component of Li. Because these waters are hosted in a carbonate reservoir, the calcitic/dolomitic host rocks are one possible endmember. Marine carbonate typically incorporates Li that is 2-4 ‰ lighter (lower  $\delta^7\text{Li}$ ) than the water from which it precipitates (Marriott et al., 2004; Pogge von Strandmann et al., 2013). The concentration of Li in marine carbonate is low (typically 0.5-1.5 ppm; Marriott et al., 2004). Assuming a difference in  $\delta^7\text{Li}$  of 15 ‰ (likely a maximum difference), even the dilute San Andres produced waters would need to dissolve more than one third of their mass in carbonate to shift  $\delta^7\text{Li}$  by 5-

‰, the total range observed in this study. This would push the water chemistry to much higher Ca concentrations than are actually observed (Figure 7). Interaction with clays and other silicate minerals, either in the present host formation or during migration of the formation waters, is a more likely scenario for creating the spread of  $\delta^7\text{Li}$  values. A modest positive correlation of Li with  $\text{HCO}_3^-$  (Figure 16) indicates possible hydrolysis reactions with a Li-bearing silicate mineral such as K-feldspar could help create a spread of  $\delta^7\text{Li}$  values.

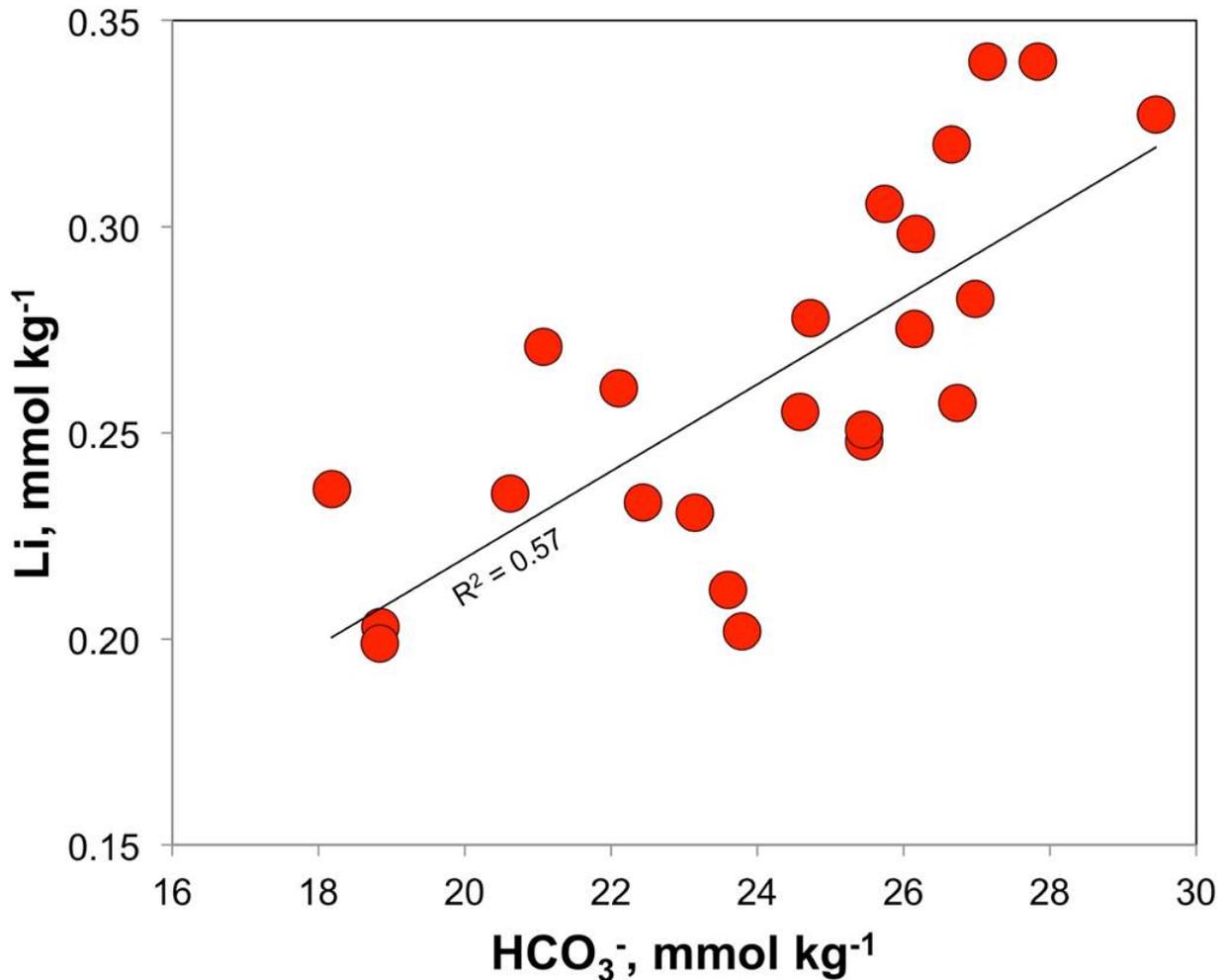


Figure 16. Correlation of Li with  $\text{HCO}_3^-$  for San Andres produced water from this study.

## **5.2 FACTORS CONTROLLING GROUNDWATER CHEMISTRY IN POST-PERMIAN UNITS**

### **5.2.1 TDS sources in Ogallala groundwater**

The major cation and anion trends from Ogallala groundwater samples in this study are comparable to other data from the southern High Plains aquifer, generally falling on the low-Ca and low-carbonate end of the spectrum (Figure 17). Chaudhuri and Ale (2014) attributed increased salinization and contamination of Ogallala aquifer groundwater in Texas between 1960 and 2010 to agricultural and hydrocarbon exploration activities, and to natural processes such as percolation of recharge through surface playas and mixing with high TDS water from underlying units. The upward migration of these saline waters has been exacerbated in some areas by high-capacity wells used for irrigation (Gurdak et al., 2009).

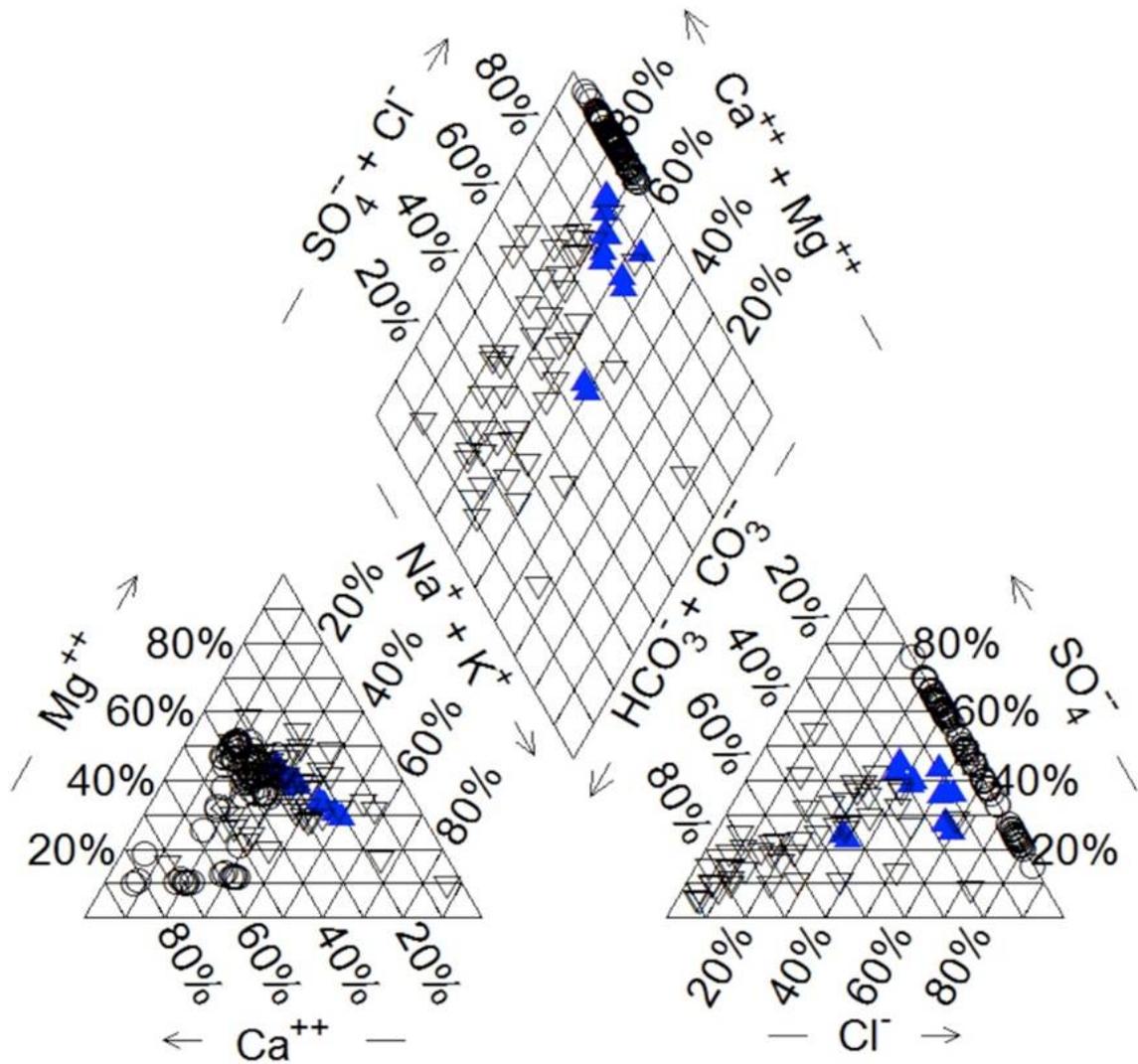


Figure 17. Piper plot comparing the geochemistry of the Ogallala formation samples collected in this study (solid blue triangles) with previously reported Southern High Plains data (inverted hollow triangles, Fahlquist et al., 2003; hollow circles, Fryar et al., 2001; hollow squares, Scanlon et al., 2009; hollow diamond, Mehta et al., 2000).

Given that these samples were collected from an active oil extraction and EOR site, contamination from deeper groundwaters (i.e., from the Santa Rosa Formation) and formation waters (San Andres produced waters) must be considered a possibility. In particular, a

correlation of [Li] with  $\delta^7\text{Li}$  (Figure 18a) and the overlap in  $\delta^7\text{Li}$  values between Ogallala and San Andres waters are suggestive of possible contamination. A plot of  $\delta^7\text{Li}$  vs.  $1/[\text{Li}]$  (a mixing diagram, Figure 19) shows that likely Ogallala mixing trajectories using two possible [Li]- $\delta^7\text{Li}$  trends do not point either toward the San Andres formation waters or toward the Santa Rosa groundwater values. Thus, neither upward migration of formation waters nor downward percolation of released oilfield produced water into the Ogallala aquifer appears to have taken place at this location. A modest correlation of  $\delta^7\text{Li}$  with Si (Figure 18b) could represent a weathering reaction with a Li-bearing mineral such as K-feldspar in the soil zone during infiltration.

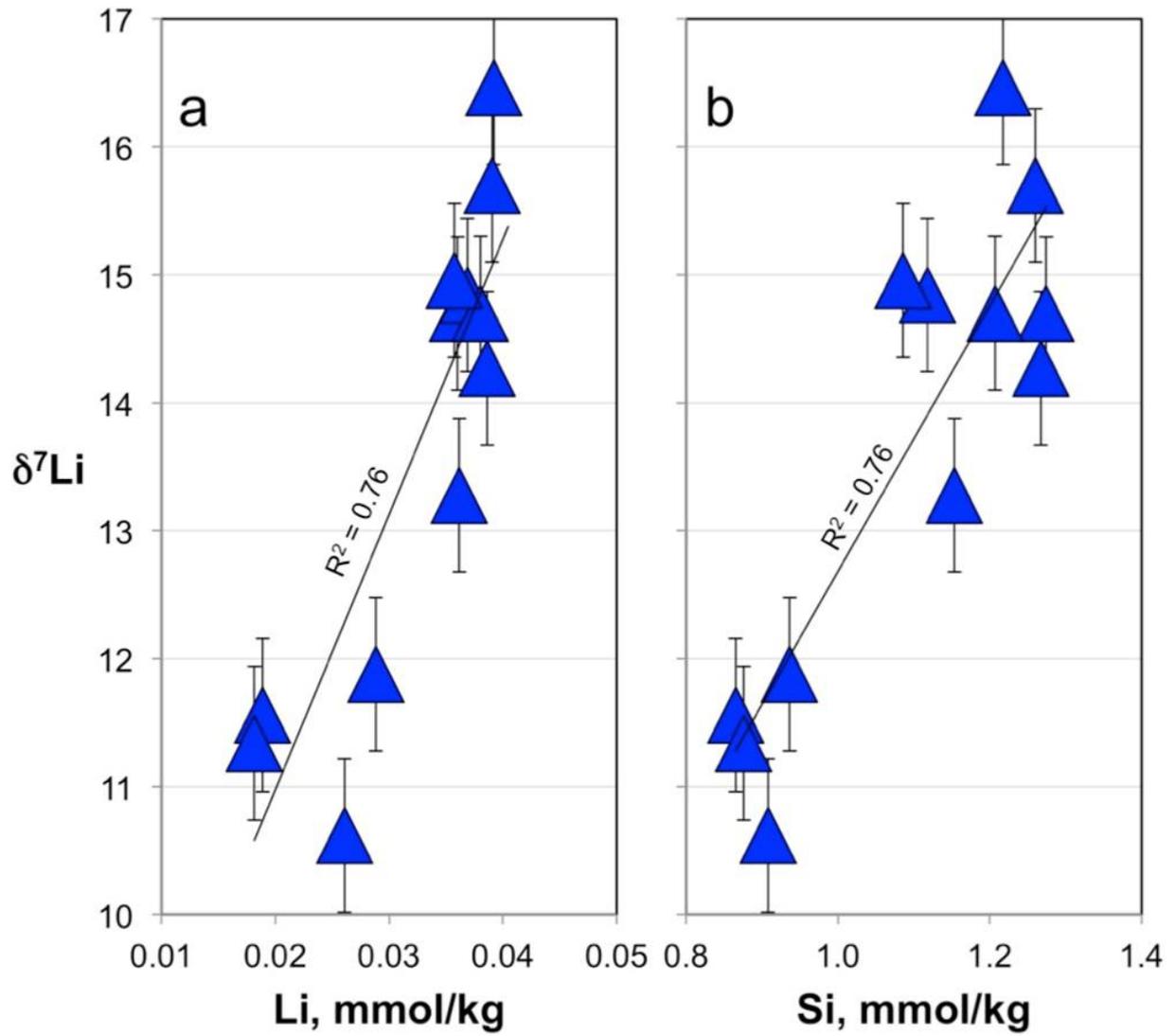
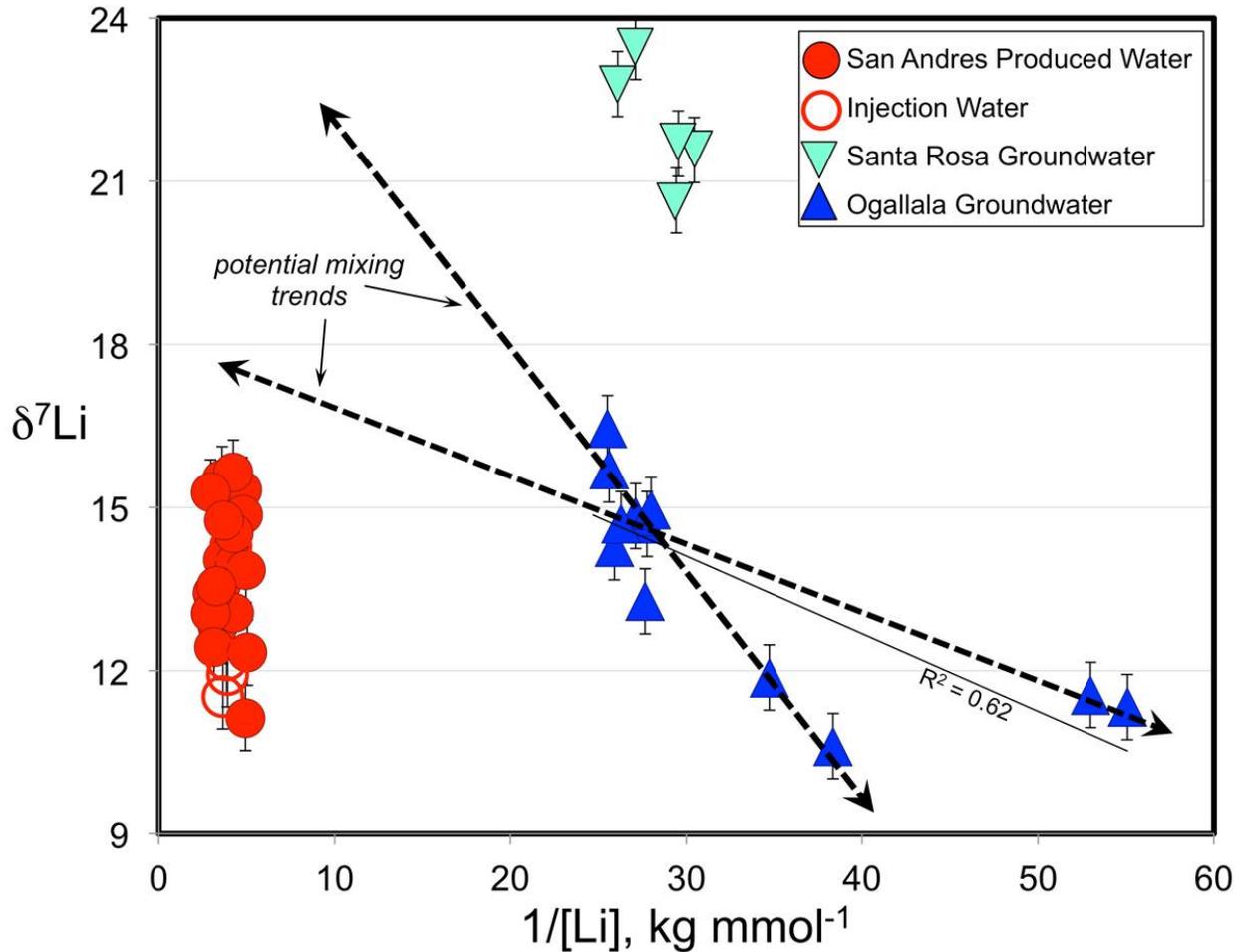


Figure 18.  $\delta^7\text{Li}$  values of Ogallala samples analyzed in this study plotted against a) [Li] and, b) [Si].



**Figure 19. Mixing diagram ( $\delta^7\text{Li}$  vs.  $1/[\text{Li}]$ ) depicting two possible trajectories for formation water mixing to explain  $[\text{Li}]$  vs.  $\delta^7\text{Li}$  trends. In both cases, the high- $[\text{Li}]$  endmember does not correspond to either Santa Rosa groundwater or San Andres produced water.**

The overlap in  $\delta^7\text{Li}$  values between San Andres formation waters and Ogallala aquifer waters provides the possibility that these disparate groundwater systems share a common source of Li. For the San Andres waters, evaporite salts from units such as the overlying Salado Formation (Ochoan Group) are a likely source (Stueber et al., 1998; Barnaby et al., 2004). While Permian salts are stratigraphically below the Tertiary Ogallala aquifer, Neogene uplift (Senger et al., 1987) provided deep groundwater recharge to the west, and may have allowed

westward erosion of Permian evaporites into the Ogallala recharge area, providing a source for the extensive playa deposits. Percolation of water through playa lake bottoms during wet periods would result in dissolution of soluble salts and transport into the Ogallala aquifer (Nativ, 1992). During this process, Li ultimately derived from Permian seawater would be delivered to the shallow aquifer system, giving it a signature similar to that of the San Andres produced waters. A playa/evaporite source of Li is likely to be in the form of chloride or sulfate minerals.  $\delta^7\text{Li}$  values of Ogallala waters show modest correlations with sulfate (Figure 20a) and chloride (Figure 20b) but no correlation with bicarbonate (Figure 20c). The latter would be affected by the combined contributions from carbonate minerals, which would contribute very little Li, and silicate weathering reactions, which could contribute (or sequester) variable amounts of Li.

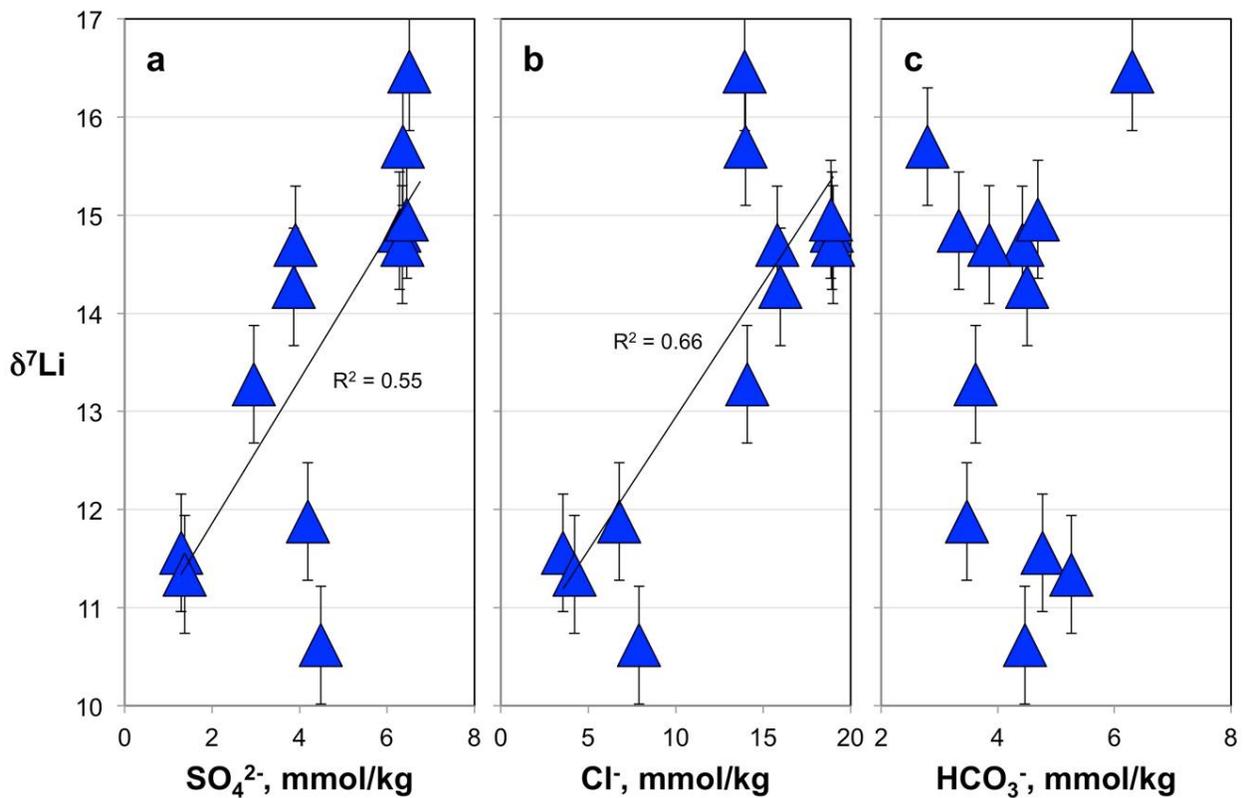


Figure 20.  $\delta^7\text{Li}$  values of Ogallala samples analyzed in this study plotted against a)  $\text{SO}_4^{2-}$ , b)  $\text{Cl}^-$ , and c)  $\text{HCO}_3^-$ .

The Ogallala well water samples show a possible correlation of  $\delta^7\text{Li}$  with depth (Figure 21), with deeper wells. This points to a variable contribution from water-silicate interaction, with either discontinuities within the aquifer (i.e., isolated lenses) or water chemistry gradients. The trend of heavier  $\delta^7\text{Li}$  with depth is consistent with a greater amount of fluid-silicate interaction (possibly a longer residence time) deeper in the reservoir (Liu et al., 2015).

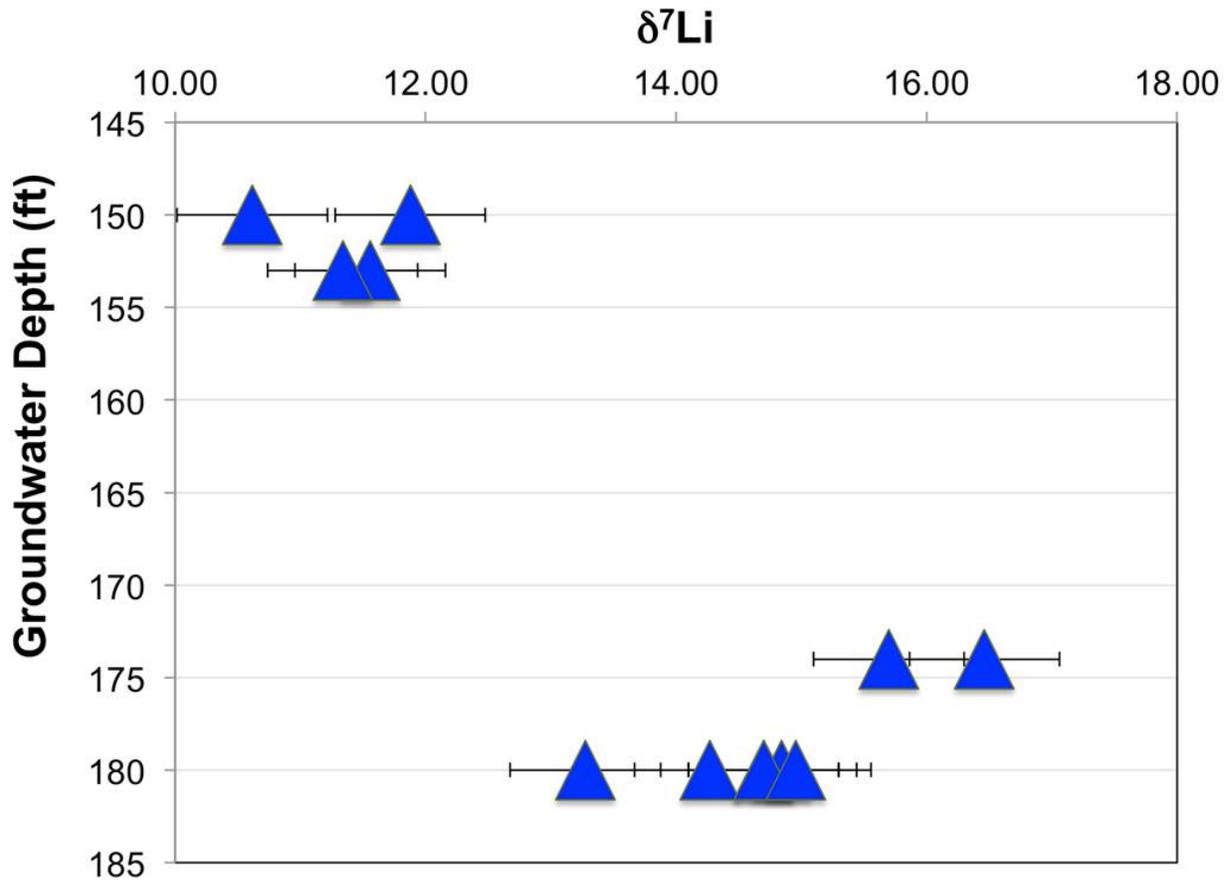


Figure 21.  $\delta^7\text{Li}$  values of Ogallala samples analyzed in this study plotted as a function of well depths.

### **5.2.2 Santa Rosa groundwater**

The Santa Rosa Formation lies between the San Andres Formation and the Ogallala aquifer, yet it contains Li with a very different isotopic composition than either (Figure 9). Because it overlies the main Permian evaporite units, it most likely escaped the downward flowing meteoric waters that interacted with the evaporites. In addition, it is isolated from regional surface recharge that may have interacted with playa lakes containing a Permian salt component. Thus, the  $\delta^7\text{Li}$  of Santa Rosa waters is more likely to reflect interaction of meteoric waters with the clastic component of the unit itself. The relatively high  $\delta^7\text{Li}$  values of waters from this unit could have been imparted by long term fluid-rock interaction, which tends to enrich the fluid in isotopically heavy Li (Chan et al., 1992; Liu et al., 2015). While we only have Santa Rosa samples from a single well, we note that the chemistry of these waters differs significantly from both the Ogallala aquifer and the San Andres produced waters (Figure 7), falling well off the halite dissolution/seawater evaporation trend (Figure 13).

## **5.3 DEEP BRINE MIGRATION AND GROUNDWATER MIXING**

Enhanced oil recovery and CO<sub>2</sub> injection for geologic carbon sequestration both carry risks of forcing deep brines to shallower levels through faults or previous wellbores. Thus, it is important to develop geochemical tools that can sensitively detect upward movement of brines in time to prevent significant contamination. At the East Seminole site, the intermediate Santa Rosa groundwater provides a monitoring point for possible upward movement of San Andres

brines during EOR. While the Ogallala and San Andres waters have essentially identical  $\delta^7\text{Li}$  values, the large difference in  $\delta^7\text{Li}$  between Santa Rosa and San Andres waters makes Li isotopes a sensitive monitor for incursion of the deeper brines. Based on measured  $\delta^7\text{Li}$  and  $[\text{Li}]$  values, only a few percent of San Andres water would need to mix with Santa Rosa waters to produce a significant shift in  $\delta^7\text{Li}$  (Figure 22). Thus, monitoring of the Santa Rosa Formation waters could provide an early warning before brines reach the more sensitive overlying Ogallala aquifer. The extent to which  $\delta^7\text{Li}$  can serve as a monitor for brine migration or leakage in any given situation depends on regional geologic and hydrologic conditions (cf. Warner et al., 2014), and requires collection and analysis of baseline values for all possible end members.

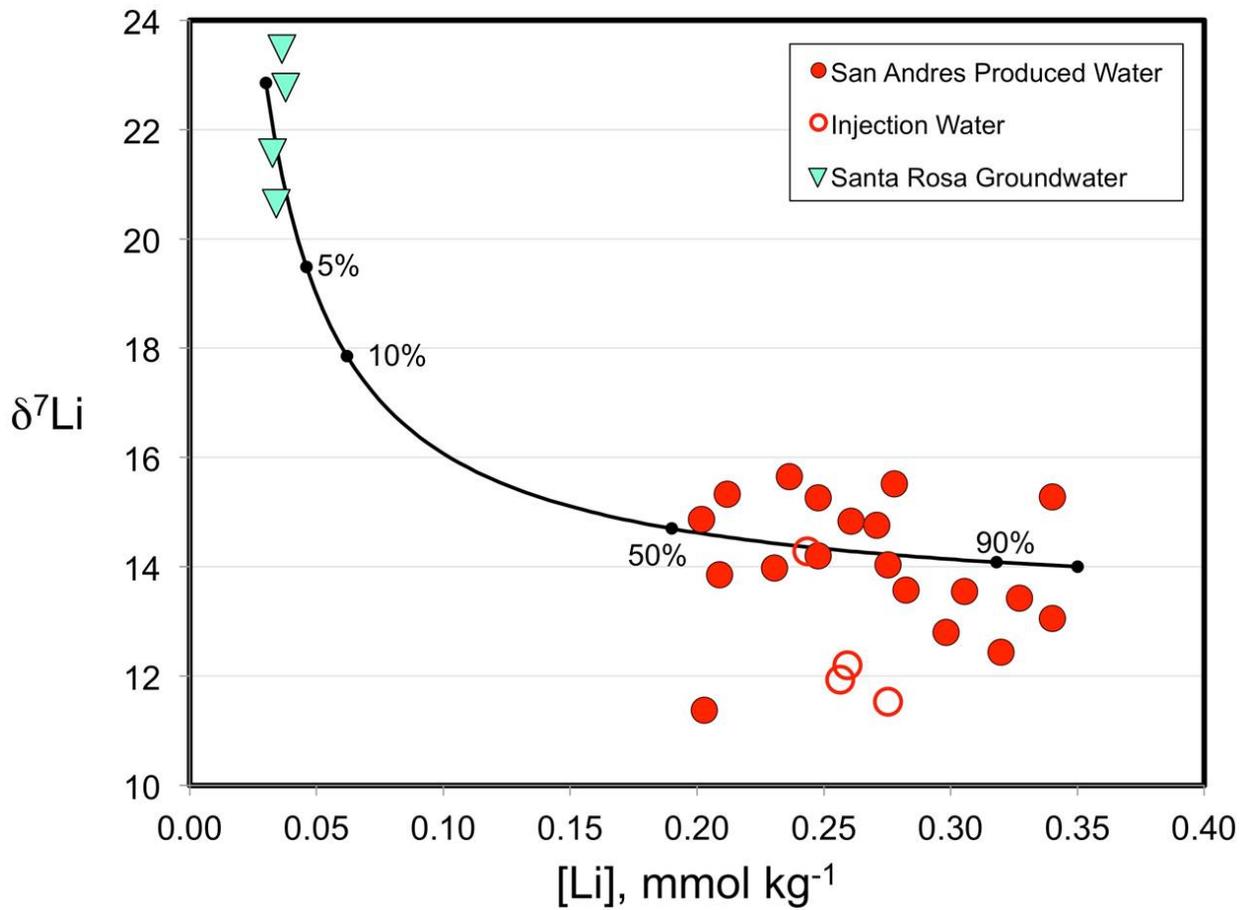


Figure 22. Mixing model for San Andres formation water mixing with Santa Rosa groundwater. Numbers on the curve represent percentages of San Andres formation water added.

## 6.0 CONCLUSIONS

- Produced water from the San Andres carbonate reservoir records its chemical history despite previous waterflooding and CO<sub>2</sub> injection in the East Seminole field.
- $\delta^7\text{Li}$  values for produced waters from the San Andres Formation carbonate reservoir (+10.9 to +15.7) fall within the range of formation waters from Gulf of Mexico and Appalachian shale and sandstone reservoirs
- San Andres produced waters inherited their  $\delta^7\text{Li}$  values primarily from evaporite units that were dissolved by infiltrating meteoric water in the Neogene. This suggests a Permian seawater  $\delta^7\text{Li}$  value about 20‰ lower than present-day seawater.
- Ogallala aquifer groundwater chemistry in the study area is comparable to that of other Southern High Plains aquifer waters.
- $\delta^7\text{Li}$  values of the Ogallala aquifer may be inherited from playa lakes in their recharge area. The salts in these lakes are derived in part from eroded Permian evaporites, and thus impart a Li isotopic signature on the Ogallala waters that overlaps significantly with San Andres produced waters.
- The trend of increasing TDS content, higher  $\delta^7\text{Li}$ , and lower Li concentrations observed in shallow vs. deeper Ogallala and Santa Rosa aquifer groundwater is consistent with increased residence time in the aquifer.

- The intermediate depth Santa Rosa groundwater aquifer lies above Permian evaporites and is shielded from infiltrating waters by the Ogallala aquifer (and underlying aquitard). Therefore, the elevated Santa Rosa groundwater Li isotope composition reflects prolonged interaction with clay and other silicate minerals in the aquifer.
- A major consideration for the selection of stratigraphic zones for CO<sub>2</sub> injection is the potential migration of CO<sub>2</sub> or displaced saline formation waters into shallow aquifers that could result in the degradation of groundwater quality via salinization and the mobilization of metals and other chemical species. In addition to its use as a natural tracer of groundwater-brine mixing and water-rock interactions, the  $\delta^7\text{Li}$  composition of deep groundwater has potential as a monitoring tool to identify CO<sub>2</sub> injection-induced fluid migration into overlying permeable units prior to its intrusion into sensitive shallow aquifers. Although  $\delta^7\text{Li}$  values of San Andres oilfield waters overlap with those of groundwaters from the Ogallala aquifer,  $\delta^7\text{Li}$  of waters from both units are distinct from Santa Rosa groundwater that lies between the two. Thus, a shift in the  $\delta^7\text{Li}$  of groundwater from wells tapping the Santa Rosa aquifer could be used to detect upward fluid migration.
- Chemical and isotopic spatial heterogeneity over short (km-scale) distances reinforce the need to integrate detailed geologic and geochemical characterization into interpretations of subsurface processes and predictive models of water-rock interactions.

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