

Geochemical and lithium isotope tracking of dissolved solid sources in Permian Basin carbonate reservoir and overlying aquifer waters at an enhanced oil recovery site, northwest Texas, USA

Samantha Pfister^a, Rosemary C. Capo^a, Brian W. Stewart^{a,*}, G.L. Macpherson^b, Thai T. Phan^{a,c}, James B. Gardiner^{a,c,d}, J. Rodney Diehl^c, Christina L. Lopano^c, J. Alexandra Hakala^c

^a Department of Geology and Environmental Science, University of Pittsburgh, Pittsburgh, PA 15260, USA

^b Department of Geology, 120 Lindley Hall, University of Kansas, Lawrence, KS 66045, USA

^c Department of Energy-National Energy Technology Laboratory, 626 Cochran Mill Rd., Pittsburgh, PA 15236, USA

^d AECOM, 626 Cochran Mill Rd., Pittsburgh, PA 15236, USA

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ABSTRACT

Geochemistry and lithium isotope compositions ($\delta^7\text{Li}$) of Permian Basin produced water and potable groundwater from overlying aquifers at an enhanced oil recovery (EOR) site in Gaines County, northwest Texas, are used to evaluate the effects of brine-groundwater-rock interactions, identify sources of dissolved solids, and characterize fluid flow and mixing processes. $\delta^7\text{Li}$ values (per mil deviations from the LSVEC standard $^7\text{Li}/^6\text{Li}$ ratio) for produced water from dolostones of the San Andres Formation ranged from +10.9 to +15.6‰ and fall within the range of formation waters from other sandstone/carbonate reservoir rocks in North America, Europe and the Middle East. These differ from produced waters from hydraulically fractured shales from the U.S. Appalachian Basin, including the Marcellus Shale, which tend to have lower $\delta^7\text{Li}$ values and higher Li/Cl, possibly indicating greater interaction with a terrigenous component. The San Andres produced water chemistry and Li isotope ratios are consistent with Neogene meteoric water interacting with marine and continentally-derived evaporites (e.g., portions of the Guadalupian Salado Formation), as well as other terrestrial sources along the flow path.

Groundwater from the Triassic Dockum Group-Santa Rosa aquifer ($\delta^7\text{Li}$ range of +20.6 to +23.5‰) is isotopically distinct from waters from the overlying Ogallala Formation (+10.6 to +16.5‰) and the deeper San Andres Formation, indicative of hydrologic isolation from both meteoric recharge and from deeper brines in the field area. 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.

1. Introduction

Waters co-produced with oil and gas extraction provide important information about downhole conditions in the reservoir, as well as the geologic and hydrologic history of the hydrocarbon-producing formation (e.g., Land and Prezbindowski, 1981; Walter et al., 1990; Chaudhuri et al., 1992; Hanor, 1994; Kharaka and Hanor, 2004; Engle et al., 2016). The Permian Basin in the western United States hosts a number of significant hydrocarbon reservoirs, and has been considered a potential site for high-level nuclear waste storage below low-permeability seals (Dutton, 1987), and more recently for long-term geologic carbon sequestration. High permeability rocks in the Permian Basin

have been identified as potential carbon storage formations because of the low geothermal gradient in the area and close proximity to CO₂ pipelines (DOE-NETL, 2010). Carbon sequestration field studies have been conducted at a number of enhanced oil recovery (EOR) sites in the Permian Basin, including the SACROC field, the Mean's San Andres field, and the Wasson Denver project (Magruder et al., 1990; Stevens et al., 2001). Major structures within its boundaries include the Central Basin Platform, Delaware Basin, Midland Basin, and Northwest and Eastern Shelf (Fig. 1a). The Central Basin Platform is of particular economic importance due to its shallower oil plays in comparison to surrounding basins.

The High Plains-Ogallala aquifer, one of the largest freshwater

* Corresponding author.

E-mail address: bstewart@pitt.edu (B.W. Stewart).

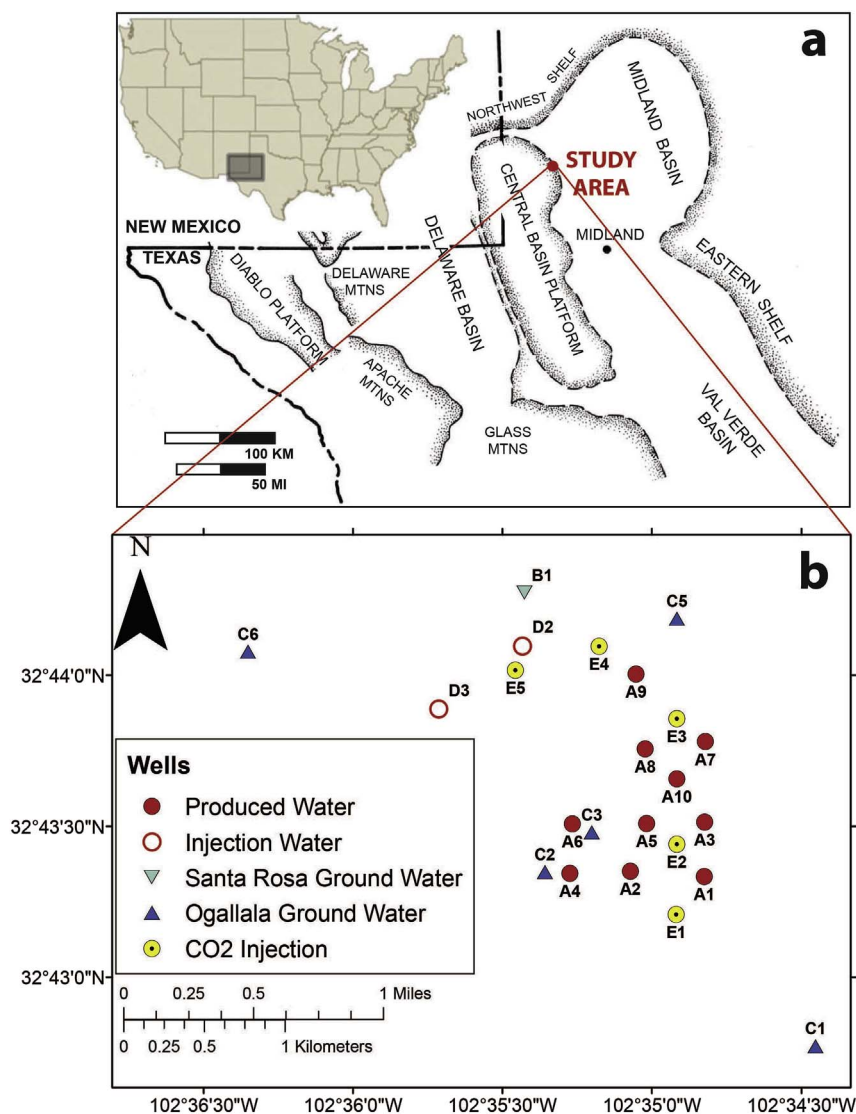


Fig. 1. a) Major Permian Basin structures in Texas and New Mexico. The produced waters for this study were sampled from oil wells located on the eastern flank of the Central Basin Platform and western edge of the Midland Basin (modified from Ward et al., 1986). b) Wells sampled for San Andres produced water (A), Santa Rosa groundwater (B), Ogallala groundwater (C), and injection water (D), as well as locations of CO₂ injection wells in the field area (E).

systems in the world and a critical water resource for much of the central and southwestern United States (e.g., Hornbeck and Keskin, 2014), overlies much of the Permian Basin hydrocarbon reservoir area. It is an important drinking water resource and the main source of agricultural water for a large part of the central U.S.A. 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). Oil extraction from underlying reservoirs and the potential of long-term CO₂ storage beneath the aquifer have raised concerns about effects on water quality (Smyth et al., 2009). Although a number of studies have focused on potential environmental and health impacts of CO₂ injection-related metal mobilization on the aquifer, there still remains a need for detailed geochemical analysis and characterization of shallow groundwater and subsurface saline formation waters in the region (Carroll et al., 2010; Romanak et al., 2012).

Variations in the chemical and isotopic composition of formation and groundwater can be used as natural signatures of fluid migration, for early detection of saline fluids into overlying units, and as sensitive monitors of water-rock interaction. Natural isotopic tracers can be more sensitive to water quality changes than traditional elemental concentration and ratio indicators (Stewart et al., 1998; Banner, 2004;

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 (annual to decadal) and long (10²–10⁸ yr) timescales. The lithium (Li) isotopic measurements 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; Phan et al., 2016). Lithium is an incompatible element that is generally removed from solids during water-mineral reactions, often accompanied by isotopic fractionation, and sometimes taken up by alteration minerals such as smectite (Tomascak et al., 2016) and the octahedral sites of illite (Williams and Hervig, 2005; Williams et al., 2012, 2015). Interpretations of Li concentration and isotope variability are attributed to diagenesis of silicate minerals (e.g., Millot et al., 2011) that dominate sedimentary basin lithology and undergo temperature-dependent reactions. Subsurface systems are usually rock-dominated with abundant reactive phases (Land and Macpherson, 1992), and the enrichment of Li concentrations over amounts predicted from source fluids repeatedly demonstrates this. The enrichment of Li in oilfield formation waters (Collins, 1975; Wilson and Long, 1993; Chan et al., 2002; Williams et al., 2015) suggests that it could be released from the source rock along with the hydrocarbons, and therefore Li isotopes may provide important information about catagenesis and the origin of

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