

Elemental and isotope geochemistry of Smackover Formation brines in Alabama and Arkansas: Implications for fluid mixing and water-rock interaction

Kelly Kreitzer^a, Ming-Kuo Lee^{a,*}, Haibo Zou^a, Yang Wang^b, Andrew L. Masterson^c, Ann Sullivan Ojeda^a, Zeki M. Billor^a, Natalia Malina^d, Gregory M. Guthrie^e, Bonnie McDevitt^c, Ann Arnold^e, Demi Durham^a

^a Department of Geosciences, Auburn University, Auburn, AL, 36849, USA

^b Department of Earth, Ocean and Atmospheric Science and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, 32306-4520, USA

^c U.S. Geological Survey, Geology Energy & Minerals Science Center, Reston, VA, 20192, USA

^d Department of Chemistry and Biochemistry, Florida Atlantic University, Boca Raton, FL, 33431, USA

^e Groundwater Assessment Program, Geological Survey of Alabama, Tuscaloosa, AL, 35486-6999, USA

ARTICLE INFO

Editorial handling by Elisa Sacchi

Keywords:

Brine geochemistry
Brine migration
Strontium isotopic ratios
Stable oxygen and hydrogen isotopes
Smackover formation
Geochemical modeling
Lithium
Bromide

ABSTRACT

This study investigates the geochemical characteristics of brines within the Upper Jurassic Smackover Formation in Alabama and Arkansas through elemental and isotopic analyses and geochemical modeling to reveal the extent and nature of fluid mixing and water-rock interactions. Smackover Formation brines exhibit Na-Cl-Ca hydro-geochemical facies and sulfate depletion relative to seawater. Lower sulfate concentrations, coupled with high H₂S concentrations in some brines (0–364 mg/L) at temperatures >80°C, suggest that thermochemical sulfate reduction occurred. Cl/Br and Na/Br ratios indicate that salinity was controlled by the mixing of meteoric water with evaporated seawater that had reached halite saturation, rather than by halite dissolution. The δ¹⁸O and δ²H values of the brines also suggest mixing between meteoric water and evaporated seawater that had reached gypsum and halite saturation. Geochemical modeling of seawater evaporation predicts a Cl-Na or Cl-Mg facies after halite saturation, contrasting with the observed Cl-Ca dominance of the Smackover Formation brines. The Ca-enriched brines may have evolved from Cl-Mg-dominated evaporated seawater through dolomitization of limestone. The ⁸⁷Sr/⁸⁶Sr ratios range from 0.70740 to 0.71048, higher than the average of Jurassic seawater (0.707). The non-linear relationship between ⁸⁷Sr/⁸⁶Sr and 1000/Sr suggests alteration of brine geochemistry by fluid mixing or by inputs from Sr and ⁸⁷Sr-enriched rock sources. Lithium concentrations are positively correlated with ⁸⁷Sr/⁸⁶Sr ratios and TDS in brines enriched in these constituents. These correlations suggest deeper-seated geogenic sources and have implications for Li exploration in the northern Gulf Coast basin. Normal faults associated with the pre-Jurassic topography may have provided potential pathways for brine migration into the Smackover Formation under the influence of overpressure or thermohaline convection in the Gulf Coast.

1. Introduction

Smackover Formation brines in the northern Gulf Coast region potentially contain economic quantities of lithium, bromine, barium, and other elements that are strategically important (Knierim et al., 2024). Lithium plays a significant role in green energy transition (Ghorbani et al., 2024) and the production of rechargeable batteries is one of the fastest-growing uses of lithium (Tarascon, 2010).

Understanding the origin, geochemical evolution, and long-range migration of brines in sedimentary basins is important for assessing the role of brines in forming some of the world-class ore deposits. High levels of lithium (up to 600+ mg/L) were reported in the Smackover Formation brines in Texas and Arkansas (Collins, 1976; Moldovanyi et al., 1993; Knierim et al., 2024). In southwest Alabama, Smackover Formation brines are associated with several oil-production fields (Guthrie et al., 2023) developed on fault blocks that formed pre-Jurassic

* Corresponding author.

E-mail address: leeming@auburn.edu (M.-K. Lee).

<https://doi.org/10.1016/j.apgeochem.2026.107086>

Received 4 June 2026; Received in revised form 2 September 2026; Accepted 9 September 2026

Available online 11 September 2026

0883-2927/© 2026 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

basement arches and ridges. Available data from the Geological Survey of Alabama (Guthrie et al., 2023) and the U.S. Geological Survey (USGS) Produced Waters Geochemical Database (Blondes et al., 2023) indicate substantial variation in the concentrations of lithium (13–90 mg/L) and bromide (2–2190 mg/L) of Smackover Formation brines in southwest Alabama. Although lithium and bromine concentrations increase as seawater evaporates (Collins, 1976; McCaffrey et al., 1987), evaporation alone is unlikely to produce lithium concentrations on the order of hundreds of mg/L. It is not clear how various geogenic sources (e.g., Li-rich igneous basement rocks or shales) or water-rock interaction (e.g., isomorphic substitution of Li in clay minerals by ions of similar size) may introduce varying amounts of Li into brines beyond seawater evaporation.

Previous geochemical and isotopic analyses of basin fluids suggested that brines could have originated either as ancient seawater (White, 1965; Ferguson et al., 2018), evaporated seawater (Carpenter, 1978), geothermal fluids (Subasinghe et al., 2025), or meteoric water (Clayton et al., 1966). The process of membrane infiltration through shale has been proposed as a mechanism to effectively retain dissolved ions to form concentrated brines (Graf et al., 1966; Kharaka et al., 1973). Stueber and Walter (1991) and Penny et al. (2003) combined stable and radiogenic isotopic signatures and Cl/Br ratios to determine the sources of salinity influenced by evaporated seawater or dissolution of halite. Knauth (1988) and Hanor (1994) demonstrated that brines could transform geochemically over time through water-rock interaction and fluid mixing. Land and Prezbindowski (1982) proposed that Cl-Na-Ca brines in the Gulf Coast region acquired their salinity by dissolution of evaporites (halite) and then became enriched in Ca through albitization of feldspars. Hydrodynamic mechanisms that drive the long-range migration of dense and heavy brines across sedimentary basins also draw many investigations. Several numerical models (e.g., Tóth, 1962, 1980; Bethke and Marshak, 1990; Stanislavsky and Gvirtzman, 1999) explored the mechanisms of brine migration that could set the stage for

water-rock interaction and facilitate fluid mixing along the pathway. Many questions remain about the nature and extent of fluid mixing as well as water-rock interaction processes that control the geochemical evolution of brines in sedimentary basins.

Lithium sources have been found in produced waters and oil and gas field brines globally (Darvari et al., 2024; Marza et al., 2024; Balaram et al., 2024; Munk et al., 2025). The primary objective of our study is to characterize the major ion, trace element, and isotopic ($^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$) compositions of new brine samples collected from the Smackover Formation in Alabama and compare these data with existing data from Smackover Formation brines in Arkansas (Moldovanyi and Walter, 1992, 1993; Blondes et al., 2023; Knierim et al., 2024) and Alabama (Blondes et al., 2023). We conduct geochemical modeling to determine and compare the main hydrogeochemical facies of Smackover Formation brines and evaporated seawater. Our research centers on addressing two questions: (1) What is the source of salinity in Smackover Formation brines? and (2) What water-rock interaction and fluid mixing process(es) may control the Smackover Formation brine composition? To this end, this study characterizes brines using major element chemistry and isotopic tracers in order to elucidate the controls on their chemical composition, which represents a key factor in predicting the location and potential feasibility of economically extracting lithium (McDevitt et al., 2024).

2. Geology

This study focuses on the Smackover Formation, a Late Jurassic (Oxfordian) unit that can be found along the northern Gulf Coast of the United States (Fig. 1). Triassic crustal extension formed the horst-and-graben structures in the Paleozoic basement, with grabens later filled by Jurassic sediments as the basin continued to expand (Hudec et al., 2013). The Jurassic Smackover Formation, deposited in a shallow marine environment, can generally be divided into two to three distinct

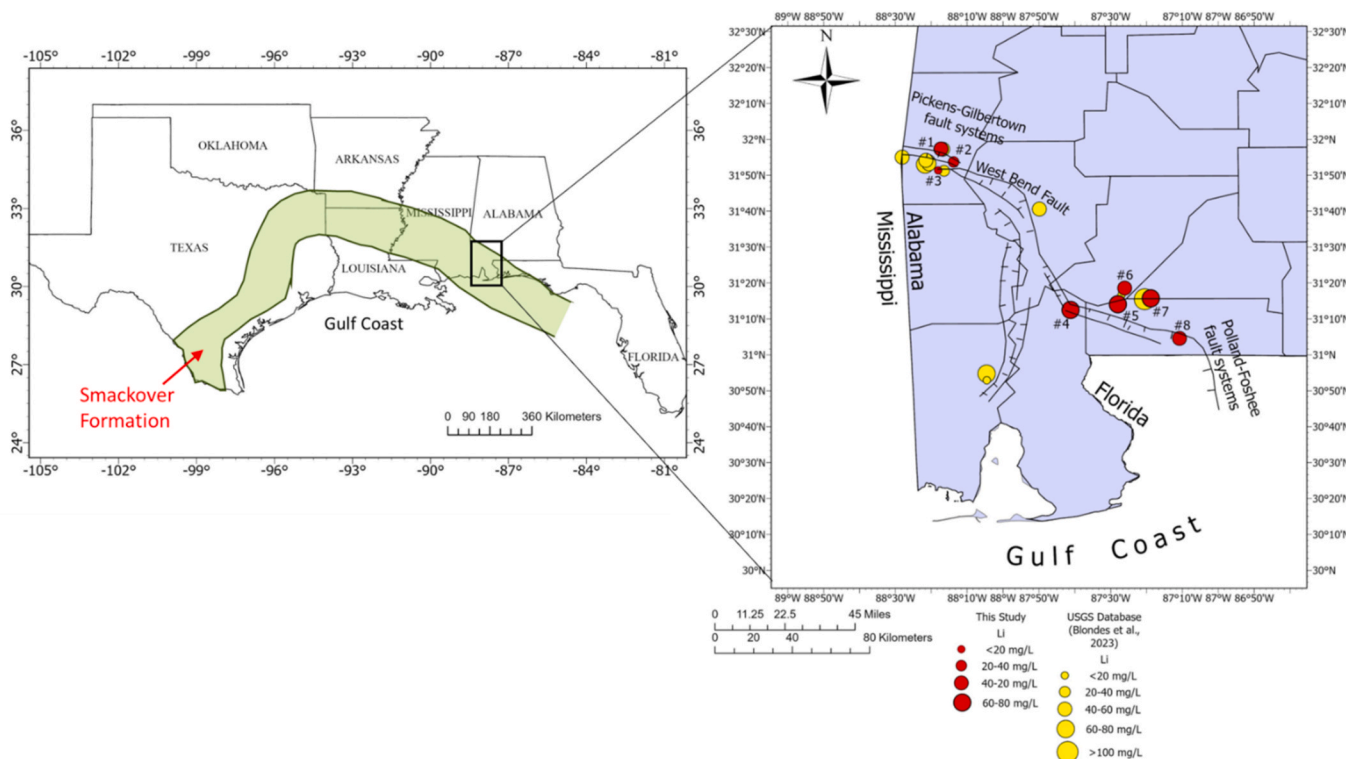


Fig. 1. Location map of Smackover Formation oil and gas producing wells for brine sampling near three peripheral fault systems including the Pickens-Gilbertown, West Bend, and Pollard-Foshee fault systems in Alabama study area (after Mancini et al., 1987; Tonietto and Pope, 2013). The right panel also shows lithium concentrations in brines. The left panel shows the areal, subsurface distribution of the Upper Jurassic Smackover Formation in the investigated area of the northern Gulf Coast (modified after Collins, 1976; Moldovanyi et al., 1993).

members. The lower Smackover Formation consists of silty limestone and dolomite that grade upward into a middle member consisting of dense limestone. The upper member is composed mainly of oolitic limestone (Dickinson, 1968; Collins, 1976). This sequence is indicative of a subtidal and intertidal depositional environment (Claypool and Mancini, 1989). The Gulf Coast is recognized as a premier, highly productive oil and gas basin, producing ~3% of the world's Jurassic petroleum reserves (Heydari et al., 1997; Whidden et al., 2023). The upper Smackover Formation sequence commonly acts as a hydrocarbon reservoir because of its high porosity and ability to host the storage and promote the migration of hydrocarbons (Tew et al., 1993). The Smackover Formation is underlain by the Norphlet Formation and the Louann Salt (Fig. 2). The Norphlet Formation consists primarily of sandstone and conglomerate (Heydari et al., 1997). The Louann Salt is an evaporite formation composed of massive halite with intercalated anhydrite and silty and sandy intervals (Fredrich et al., 2007). The Louann Salt may serve as a trap for the local accumulation of migrating hydrocarbon in the surrounding domed-up sedimentary rocks as a result of its post-depositional upward movement and piercing through overlying rocks (salt diapirism). The thickness of the Louann Salt varies across the region, reaching more than 6000 ft (~1820 m) in the Alabama study area (Mancini et al., 1990). Overlying the Smackover Formation is the Haynesville Formation consisting of interbedded evaporite strata, sandstones, and carbonates. The Buckner Anhydrite Member at the base of the Haynesville Formation acts as a low permeability seal rock for hydrocarbons and other fluids that move through the Smackover Formation (Kopaska-Merkel et al., 1993). The depth of the Smackover Formation in southwest Alabama ranges approximately from 11,000 to 12,000 ft (~3350 to 3650 m). A basinward thickening wedge of clastic, terrigenous sediments accumulated in the basin from the Upper Cretaceous through the Tertiary and continues to accumulate today. Jurassic

strata in the study area unconformably overlie an assemblage of igneous rocks (Guthrie and Raymond, 1992). Primary diabase and potassium feldspar-rich granophyre mineralogies have been locally replaced along mylonitic zones and fractures by sub-to lower-greenschist facies mineral assemblages. Metaluminous granophyre in the suite follows a calc-alkaline trend together with pyroxenite. Trace element ratios of Ta/Yb and Rb/(Yb + Ta) indicate a volcanic or syn-collisional arc environment for emplacement. Biotite separates from granodiorite yield a $^{40}\text{Ar}/^{39}\text{Ar}$ cooling age (~300°C) of approximately 329 Ma (Guthrie et al., 1994).

Structural, tectonic, stratigraphic, and hydrologic features of the Gulf were described in detail by Harrison and Summa (1991). A peripheral fault system, which includes the Pickens-Gilbertown, West Bend, and Pollard-Foshee fault systems, forms the northern limit of Upper Jurassic sedimentary units in our Alabama study area (Fig. 1). Movement along the peripheral fault system was concomitant with movement along the earlier system and was likely the result of the diapiric movement of the Louann Salt (Mancini et al., 1987, 2019). Two embayments, the Manila and Conecuh embayments, were formed by faulting along the earlier system (Tonietto and Pope, 2013). This complex structural system, associated with the development of the Gulf basin, may have served as potential pathways for fluid migration through the basin's stratigraphy.

Recharge of meteoric water around the northern Gulf occurred during the Jurassic to the early Tertiary in response to topographic relief and associated hydraulic gradient (Harrison and Summa, 1991). The widespread presence of overpressure in the deep Gulf basin shale units throughout much of the Tertiary may have driven brines toward the surrounding sediments or the basin's margin, where a meteoric regime under hydrostatic conditions prevailed (Harrison and Summa, 1991). Overpressure generated by rapid accumulation of low-permeability shale in the basin's depocenters restricted basinward infiltration of meteoric water (Harrison and Summa, 1991). Other processes such as hydrocarbon generation and clay (smectite) dehydration in deep basin strata may also contribute to overpressure development and maintenance (e.g., Neuzil, 1995; Hansom and Lee, 2005). Numerical modeling (e.g., Evans and Nunn, 1989; Evans et al., 1991; Canova et al., 2018) has also indicated that thermohaline convection of brine may occur along the flanks of salt domes, facilitating the upward advection of deep basin fluids.

3. Methods

3.1. Sampling sites and brine collection processes

Brine samples were collected from eight oil and gas wells producing from the more porous limestone interval in upper Smackover Formation in southwestern Alabama (Fig. 1). The sampling targeted eight wells with a range of concentrations of major and minor elements (e.g., Na, Ca, Li) and anions (Cl and Br) (Moldovanyi et al., 1992; Blondes et al., 2023; Guthrie et al., 2023; Knierim et al., 2024). The collection and analysis of brine samples for geochemical characterization closely followed the methods described by Lico et al. (1982), Kharaka et al. (1987), and Cantlay et al. (2020). For this study, samples were collected from separator tanks near the wellhead, instead of directly from the wellhead. Redox- and temperature-sensitive water quality parameters such as oxidation-reduction potential (ORP) and dissolved oxygen were not measured in the field because the collection method perturbed these parameters. All sampling containers were rinsed two or more times with the brine waters. Sampling containers were filled with minimal headspace and were kept in a dry refrigerated environment to prevent evaporation. Samples pH values were measured by an Orion Star A211 benchtop pH meter and H₂S concentrations were determined via the modified Cline assay (Cline, 1969) in Geosciences Laboratories of Auburn University. Due to oxidation during the storage stage in tanks at the well sites, the measured H₂S values in the laboratory underestimate

System	Stage	Geologic Unit
Lower Cretaceous?	Berriasian	Cotton Valley Group
	Tithonian	
Upper Jurassic	Kimmeridgian	Haynesville Formation
		Buckner Anhydrite Member
	Oxfordian	Smackover Formation
		Norphlet Formation
		Pine Hill Anhydrite Member
Middle Jurassic?	Callovian	Louann Salt
		Werner Formation
Upper Jurassic		Eagle Mills Formation
		Undifferentiated Paleozoic Sedimentary Rocks and Proterozoic Basement

Fig. 2. Simplified stratigraphic column of the southwest Alabama study area (modified after Kopaska-Merkel, 1998). A more comprehensive stratigraphic column of the northern Gulf, spanning from the Jurassic to the Quaternary, was presented by Wu et al. (1990) and Harrison and Summa (1991).

the actual concentrations in the Smackover Formation brines. Total dissolved solids (TDS) and specific gravity were measured at the USGS BRInE Laboratory in Reston, VA. The samples for trace element and cation analysis were filtered immediately upon return to the laboratory through a 0.1 μm filter into polyethylene bottles prepped by cleaning with ten percent nitric acid followed by deionized-distilled water and a final drying by positive-filtered airflow (Lico et al., 1982).

3.2. Oxygen and hydrogen stable isotope analysis

Stable isotope ratios of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) of eight brines and twenty rainwater samples were measured using a standard CO_2 and H_2 -water equilibrium method (Horita, 1988; Hilkert and Avak, 2001; Duhr and Hilkert, 2001) at the National High Magnetic Field Laboratory at Florida State University. Previous stable isotope studies have suggested that meteoric water can potentially circulate to depths of about 5 km, particularly in areas with greater topographic relief (McIntosh and Ferguson, 2021) and along high-permeability fault zones (Lee and Bethke, 1996; Ingebritsen and Manning, 1999). Rainwater samples were collected monthly during major precipitation events from February to December in 2023 in Auburn, Alabama, using a rain gauge. These samples were stored and refrigerated in 60 mL Nalgene™ bottles until analysis. Briefly, 0.5 mL of water samples and standards were injected into small glass vials that held platinum catalyst rods. The vials were flushed with 2% H_2 in He and then allowed to equilibrate isotopically overnight at 25°C. Headspace gas was introduced via an on-line, continuous-flow system (Thermo Finnigan GasBench II) into a Finnigan MAT Delta Plus XP stable isotope ratio mass spectrometer (IRMS) for hydrogen isotope analysis. For oxygen isotope analysis, 0.3% CO_2 in He was used as the equilibration gas. Oxygen isotope measurements were carried out after an equilibration time of 24 h at 25°C. Oxygen and hydrogen isotopic compositions are expressed as per mil deviation from the Vienna Standard Mean Ocean Water (VSMOW) standard (Kendall and Caldwell, 1998):

$$\delta (\text{‰}) = (R_{\text{sample}} / R_{\text{standard}} - 1) \cdot 1000 \quad (1)$$

Where R is the ratio of the heavy to light isotope (i.e., $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$) in the sample or the standard. The analytical precision was $\pm 0.1\text{‰}$ (1σ) for $\delta^{18}\text{O}$ values and $\pm 1\text{‰}$ (1σ) for $\delta^2\text{H}$ values. The analytical precision was determined based on repeated analyses of laboratory standards (YW-ST-1, SLC-tap, and QD) analyzed along with the samples.

3.3. Hydrogen sulfide analysis

The 4500-S2-D Methylene Blue Method (Eaton et al., 2005) was used to measure dissolved sulfide concentrations with a HACH 1900 Series portable photo spectrometer. To preserve the total sulfide concentration of samples in the field, 1 mL of 1 M zinc acetate was added to the sample vessels (50 mL centrifuge tubes) prior to sampling. In the field, 25 mL of sample was added to the vessel using a pipette. The pH was adjusted to approximately 9 as measured by pH paper strips using drops of 1 M KOH. The liquid above the precipitate was removed and replaced with ultra-pure water in the laboratory. 5 mL of 0.2% w/w N, N-dimethyl-p-phenylenediamine sulfate in 20% sulfuric acid and 1 mL of 10% ferric chloride in 2% sulfuric acid were added to the sample container quickly in succession. After 30 min, 10 mL of the sample was transferred in cuvettes and the absorption at 670 nm was measured. The instrument measured at least 10 mL of each sample at a wavelength of 670 nm. The instrument was calibrated using solutions of varying concentrations between 0 and 100 mg/L prepared from a 1000 mg/L Na_2S stock solution. R^2 of the five-point calibration curve was 0.9916.

3.4. Cation and trace element analysis

Cation concentrations of brine samples were measured using an

inductively coupled plasma optical emission spectrometry spectrometer (ICP-OES) at the USGS BRInE Laboratory and trace elements were analyzed using an Agilent 7900 quadrupole inductively coupled plasma mass spectrometer (ICP-MS) at Auburn University following the sample preparation protocol described by Jubb et al. (2020). Brine samples with high loads of suspended particles and oils were first filtered with vacuum assistance through 1.0 μm and 0.45 μm filters to minimize potential atomic interference and deposition of salt crystals on equipment. Then 120 μL of 70% HNO_3 was added to 60 mL of the filtered sample for acidification to 2%. Samples were acidified in order to preserve trace metals for ICP analysis (Pappas, 2012).

Microwave digestion (U.S. Environmental Protection Agency. Method 3051A, 2007) was conducted before ICP-MS analysis to remove any oil or other related impurities present in the unfiltered samples. One set of vessels contained 10 mL of unacidified, unfiltered sample, which was diluted five-fold by mixing with 35 mL of DI water and 5 mL of 70% HNO_3 . The other set contained 10 mL of filtered, acidified sample, 35 mL of DI water, and 5 mL of 70% HNO_3 . Two blanks containing 45 mL of DI water and 5 mL of 70% HNO_3 were added. After microwave digestion, each set of samples was diluted 50 $\times$ to minimize atomic interference by bringing analyte concentrations within the calibration range and reducing matrix effects.

Calibration solutions for ICP-MS analysis were prepared by diluting Agilent Environmental Calibration Standards (catalog numbers 5183-4688 and 5183-4682) and Indium certified reference material (Inorganic Ventures MSIN-10PPM-125ML). A lithium standard (Inorganic Ventures, MSLI-10PPM-125ML) was added to the calibration solutions. Atomic interference issues can occur when mass/charge ratio of certain elements is identical to that produced by polyatomic ions. ICP-OES provides more accurate measurements of brine samples because it is largely unaffected by atomic interferences and requires less sample dilution than ICP-MS. The detection limit of ICP-OES (in the range of mg/L) is higher than that of ICP-MS (in the range of ng/L to low $\mu\text{g/L}$). ICP-OES is thus more suitable for brines samples with very high level of total dissolved solids (TDS) while ICP-MS provides better resolution for trace elements at levels of a few $\mu\text{g/L}$ or lower.

3.5. Strontium isotope analysis

Strontium isotope analyses were conducted on brine samples using a multi-collector thermal ionization mass spectrometer (TIMS-Finnigan MAT 262) at Auburn University. Small amounts (1–2 mL) of brine that had been filtered through 1.0 μm and 0.45 μm filters and acidified to 2% using 70% distilled HNO_3 were transferred to 14-mL clean Teflon beakers and were dried on a hot plate. The dried samples were re-dissolved in 2 M distilled HNO_3 . Eichrom Sr-Spec resins (50–100 μ) were used for separation of Sr by liquid chromatography in micro-columns. Purified Sr separates were loaded to degassed pure tungsten filaments. Sr isotopic ratios were measured by a dynamic multi-collector mode. Sr isotopic compositions were normalized to a $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.1194. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ values are 0.710251 ± 0.000011 for Sr carbonate standard NIST SRM 987 and 0.705003 ± 0.000009 for USGS geochemical reference material standard BCR-2 (Columbia River Basalt).

3.6. Anion analysis

Anion (Cl , Br , SO_4) concentrations of brines were measured via ion chromatography on a Dionex ICS-2100. A batch of 35 mL of each unacidified sample was created for anion analysis by filtering with vacuum assistance through 0.45 μm and 1.0 μm filters. Analytical precision (2σ) on IC anion analyses is about $\pm 5\%$.

3.7. Geochemical modeling

Geochemist's Workbench (GWB) (Bethke, 2021) was used to construct the hydrochemical facies and predict mineral precipitation

and the evolution of fluid geochemistry of seawater as it evaporates. Hydrogeochemical facies reflect the source composition of water, processes of water-rock interaction within the lithologic framework, and possible fluid mixing. A simulation of seawater evaporation (Bethke, 2021) was conducted to investigate the geochemical evolution of remnant brines and the sequence of minerals that precipitate during seawater evaporation. The bulk calculated geochemistry of evaporated remnant brines was compared to those of Smackover Formation brines. The Pitzer equations and Harvie-Moller-Weare activity model (Harvie et al., 1984) available in GWB were used to calculate activity coefficients in concentrated brines with high ionic strength.

3.8. Historical samples

To assess the origin and geochemical variations of Smackover Formation brines, we compare the concentrations and relationships of multiple chemical parameters available in the USGS Produced Waters Geochemical Database (Blondes et al., 2023) and new data from Arkansas (Knierim et al., 2024) and Alabama (this study).

4. Results and discussion

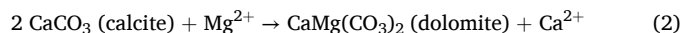
4.1. Major ion and trace element composition

Table 1 shows pH, concentrations of H₂S, TDS, and specific gravity of brines measured in the laboratory. The brines sampled have acidic to slightly acidic pH values (5.44–6.20). H₂S concentrations in these brines range from nearly 0 to more than 100 mg/L (greater than the calibration used in the analysis). TDS content of brines ranges from 162,000 to 308,000 mg/L and specific gravity varies between 1.108 and 1.218.

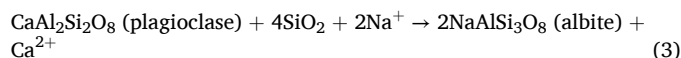
Elemental compositions analyzed by ICP-OES and IC are reported in Tables 2 and 3. Major cation concentrations from the ICP-OES analysis (Table 2) are consistent with those from ICP-MS analysis (Table S1). The Smackover Formation brines in the study area are mainly a Cl-Na-Ca type water (Fig. 3) with elevated concentrations of Cl[−] (94,600–190,000 mg/L), Na⁺ (32,200–73,300 mg/L), and Ca²⁺ (14,000–48,200 mg/L), which are greatly enriched relative to modern seawater (Cl[−] = 19,000 mg/L; Na⁺ = 10,600 mg/L, Ca²⁺ = 400 mg/L) (McCaffrey et al., 1987). Sulfate concentration in brines (50–670 mg/L) is notably lower than that in modern seawater (~2650 mg/L) (McCaffrey et al., 1987). Brines are also enriched in Br (83–5700 mg/L), Sr (1045–2381 mg/L), Li (19.34–70.65 mg/L), B (90–273 mg/L), and Ba (1.77–147.84 mg/L) compared to modern seawater. The Cl-Ca hydrochemical facies in the Alabama study area (Fig. 3) are similar to those reported in existing datasets of Arkansas and Alabama (Blondes et al., 2023; Knierim et al., 2024).

The Gibbs diagram (Fig. 4) further demonstrated substantially higher TDS and lower Na/(Na + Ca) of brines, relative to seawater. About 88% (449/509) of the Arkansas samples in the historical database (Blondes et al., 2023) have TDS > 200,000 mg/L (Fig. 4). The remaining 12% of samples, with TDS < 200,000 mg/L, may reflect freshwater dilution, although it is unclear whether this resulted from natural processes or

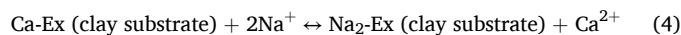
well operations. The broad range in TDS likely reflects variations in fluid sources and mixing processes. Water-rock interaction may explain the departure from seawater evaporation domain, as well as the broad range and relatively low Na/(Na + Ca) ratios compared with evaporated seawater. For example, dolomitization could add Ca²⁺ to the solution:



Dolomitization would lead to a 1:1 M ratio between Ca enrichment (ΔCa) and Mg depletion (ΔMg). Relative to evaporated seawater at halite saturation (Ca²⁺ = 307 mg/L; Mg²⁺ = 19,600 mg/L) (Carpenter, 1978), Ca enrichment and Mg depletion in Smackover Formation brines in Arkansas and Alabama are $+817 \pm 270$ mM/L and -654 ± 99 mM/L, respectively. The $\Delta\text{Ca}/\Delta\text{Mg}$ ratios (-1.250 ± 0.590) show greater Ca enrichment with respect to Mg depletion. The log Ca/Mg molar ratios of brines analyzed range from -1.18 to $+1.79$ (mean = 0.74 ± 0.23). This wide variation is likely attributable to calcite-dolomite disequilibrium or other water-rock interactions. Because thermodynamic equilibrium data for dolomite at relatively low temperatures are limited, using Ca/Mg ratios to evaluate calcite-dolomite equilibrium or the potential for dolomitization in sedimentary environments remains challenging (Hyeong and Capuano, 2001). Land and Prezbindowski (1982) suggested that albitization of plagioclase may remove Na⁺ and add Ca²⁺ to brines:



The deep Jurassic Eagle Mills Formation formed in the southern Arkansas rift zone frequently hosts plagioclase-rich igneous or wacke rock intervals (Mills and Li, 2021). Fig. 5 shows that Na is depleted relative to Cl beyond what would be expected from conservative seawater evaporation. Alternatively, clay minerals may retain Na⁺ and release Ca²⁺ into solution via cation exchange (Appelo, 1994; Penny et al., 2003):



Here, Ca-Ex represents exchangeable Ca on clay surfaces. The northern Gulf basin is a mud-dominated basin (Harrison and Summa, 1991). Many Mesozoic (e.g., Haynesville & Bossier formations) and Cenozoic units contain thick sequence of marine clays and shales. Thus, the enrichment in Ca and depletions in Na and Mg in brines may be a result of various water-rock interactions such as dolomitization, albitization, and cation exchange with clay minerals.

4.2. Cl/Br and Na/Br ratios

Various natural waters exhibit different Cl/Br and Na/Br ratios, and significant shifts of these ratios from the seawater evaporation trend can indicate the source of salinity in brines (Stueber and Walter, 1991; Davis et al., 2005; Penny et al., 2003). The seawater evaporation trend (Carpenter, 1978; Carpenter and Trout, 1978) reveals that the Cl/Br ratios in solution remain constant during seawater evaporation up to the

Table 1

Brine water quality measurements and $\delta^{18}\text{O}$, $\delta^2\text{H}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic compositions. Reported errors for $^{87}\text{Sr}/^{86}\text{Sr}$ values are 2 sigma (2σ). The replicate $^{87}\text{Sr}/^{86}\text{Sr}$ value for Sample #1 is 0.707412 ± 18 (2σ), consistent with the value of 0.707403 ± 9 (2σ) in this table.

Sample #	pH	H ₂ S (mg/L)	$\delta^2\text{H}$ (v. VSMOW) (‰)	$\delta^{18}\text{O}$ (v. VSMOW) (‰)	$^{87}\text{Sr}/^{86}\text{Sr} \pm 2\sigma$	Total Dissolved Solids (TDS) (mg/L)	Specific Gravity
1	5.49	>100	4.5	3.3	0.707403 ± 0.000009	298,000	1.212
2	6.14	5.2	−7.2	0.1	0.708251 ± 0.000019	222,000	1.145
3	6.20	45.6	−10.3	−1.0	0.708349 ± 0.000017	162,000	1.109
4	5.44	BDL ^a	1.7	2.1	0.708210 ± 0.000030	308,000	1.218
5	5.37	1.2	3.7	0.9	0.708603 ± 0.000014	271,000	1.206
6	5.66	54.5	−7.6	0.0	0.708438 ± 0.000022	240,000	1.160
7	5.63	5.2	−4.6	−1.0	0.710026 ± 0.000021	281,000	1.164
8	5.77	0.5	−7.6	1.6	0.708483 ± 0.000035	229,000	1.182

^a Below Detection Limit.

Table 2

Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of cation concentrations (in mg/L) of brine samples. Table S1 shows results of cation and trace element concentrations from Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis.

Sample ID	B	Ba	Ca	Fe	K	Li	Mg	Mn	Na	Si	Sr
1	210	<157	32,800	<157	3370	47	3940	<16	73,100	<18	1740
2	149	<126	24,300	<126	4530	35	2290	56	47,100	<14	1460
3	90	<84	14,000	<84	3000	19	1350	31	39,300	<9	1040
4	273	<157	31,000	<157	6350	72	1780	60	73,300	<18	2150
5	251	<140	31,200	172	6340	67	1770	166	70,000	<16	2300
6	207	<126	24,700	<126	5270	54	1420	111	55,500	<14	1770
7	102	<126	48,200	<126	2090	49	2970	162	32,200	<14	2230
8	227	<157	26,800	<157	5640	60	1560	140	63,700	<18	2030

Table 3

Ion Chromatography (IC) analysis of anion concentrations in brine samples.

Sample ID	Br mg/L	Cl mg/L	SO ₄ mg/L
1	1900	190,000	184
2	1220	125,000	85
3	831	94,600	47
4	2180	190,000	<36
5	2250	181,000	71
6	1710	138,000	59
7	>5700	137,000	<28
8	1970	159,000	54

Br concentrations with respect to those from Alabama, suggesting a higher range of seawater evaporation beyond halite saturation and perhaps lower degree of dilution from meteoric water. Statistical analysis of brine geochemistry reveals bimodal or multimodal distributions for Cl and Br (Huang et al., 2026), suggesting possible variations in fluid sources, hydrochemical processes, or the temperatures of water-rock interaction (Yardley et al., 2003). Among all data analyzed, only a few samples from the historical Alabama database (Blondes et al., 2023) plot along the seawater evaporation line, indicating their origin from evaporated seawater before reaching halite saturation. The linear Cl/Br trends at lower Cl concentrations can be explained by mixing between meteoric water and halite-saturated brines (dashed lines; Fig. 6). Linear trends among brines with higher Cl concentrations can be explained by mixing between halite-saturated brines and seawater, or evaporated seawater below halite saturation. The overall Cl/Br and Na/Br trends imply that the brines acquired salinity from evaporated seawater reaching halite precipitation, instead of halite dissolution. Therefore, it is unlikely that the source of salinity would be the dissolution of Louann Salt. The majority of Smackover Formation brines also have lower K/Br ratios (Fig. S2) relative to evaporated seawater, indicating significant loss of K through water-rock interaction, such as the diagenetic formation of K-rich clays (e.g., illite) from smectite or kaolinite, or the precipitation of K-rich feldspar from albite or plagioclase feldspar (e.g., Carpenter and Trout, 1978; Egeberg and Aagaard, 1989; Stueber and Walter, 1991).

4.3. Oxygen and hydrogen isotope ratios of rainwater and brines

The comparison of the isotopic signatures of the brines with those of meteoric water, seawater, and evaporated seawater provides insight into the source of salinity and the influence of water-rock interaction. Fig. 7 shows the oxygen and hydrogen isotopic composition of the Smackover Formation brines in Alabama and Arkansas (Table 1) relative to VSMOW, the seawater evaporation trajectory (Holser, 1979), and the local meteoric water line established from the rainwater samples collected in Alabama. The oxygen and hydrogen isotopic compositions of seawater and meteoric water have changed through geologic time (Galili et al., 2019; Johnson and Wing, 2020). Two “hooked” seawater evaporation curves in Fig. 7 display the relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of seawater as it evaporates to the points of gypsum and halite saturation. These two curves bracket the range of plausible seawater isotopic compositions from the Jurassic ($\delta^{18}\text{O} \approx -3\text{‰}$) to the Neogene ($\delta^{18}\text{O} \approx 0\text{‰}$) (Galili et al., 2019; Johnson and Wing, 2020). The dashed lines in Fig. 7 represent possible mixing trends between meteoric water and evaporated seawater and between gypsum to halite saturation. With modern seawater ($\delta^{18}\text{O} \approx 0\text{‰}$), the isotopic compositions of brines mostly fall along these mixing trends, reflecting different proportions of mixing of evaporated seawater and meteoric water. Assuming a postulated Jurassic seawater ($\delta^{18}\text{O} \approx -3\text{‰}$), the brines in Alabama (this study) could be interpreted as evaporated seawater below gypsum saturation, mixtures of evaporated seawater and seawater, or meteoric water altered by water-rock interaction. Interaction between water and carbonate or silicate minerals at elevated temperatures may lead to

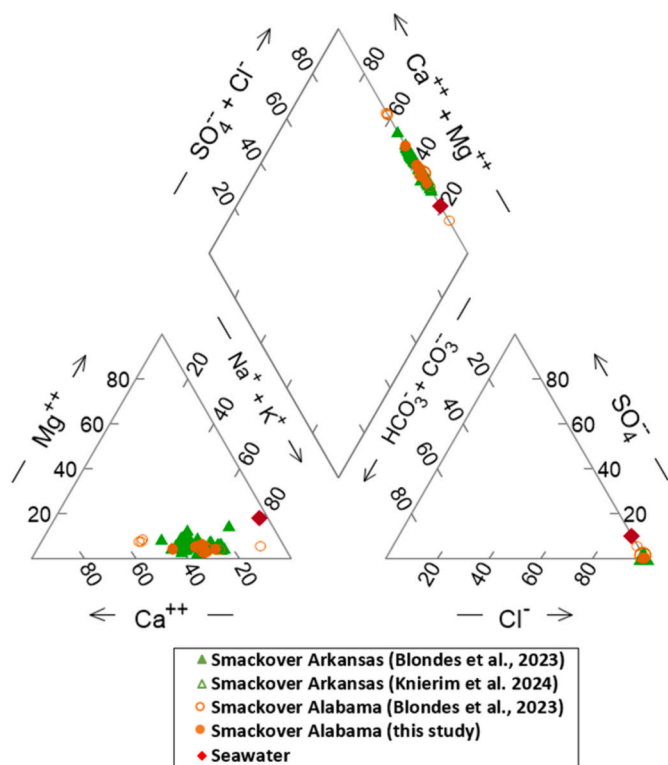


Fig. 3. Piper diagram showing the major hydrogeochemical facies of seawater and brines from the Smackover Formation in Arkansas (Blondes et al., 2023; Knierim et al., 2024) and Alabama (Blondes et al., 2023; this study).

halite saturation point. The Cl/Br (Fig. 6) and Na/Br (Fig. S1) ratios decrease in the solution after halite precipitation, because halite excludes bromine during precipitation. Samples with higher Cl/Br and Na/Br ratios plot to the left of the curve and are indicative of halite dissolution, which adds Cl and Na back into the solution. The vast majority of Smackover Formation brines have lower Cl/Br and Na/Br ratios than those of seawater and plot to the right of the seawater evaporation trajectory (Fig. 6 and Fig. S1). Brines from Arkansas clearly have higher

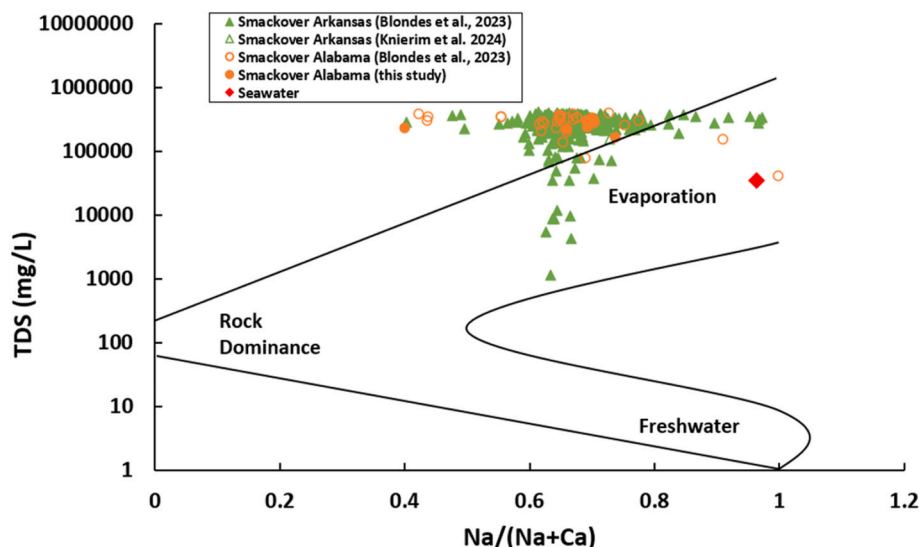


Fig. 4. Gibbs diagram of seawater and brines from the Smackover Formation in Arkansas (Blondes et al., 2023; Knierim et al., 2024) and Alabama (Blondes et al., 2023; this study). Lines define boundaries between three distinct domains of rock, freshwater, and evaporation (Marandi and Shand, 2018).

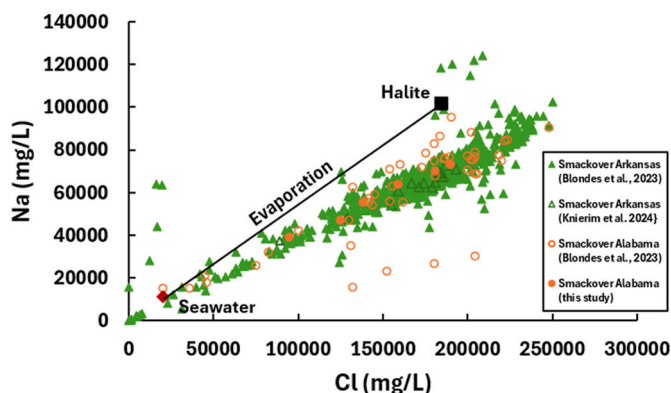


Fig. 5. Na-Cl relation for Smackover Formation brines in Arkansas and Alabama. Also shown are concentrations for seawater, evaporation trajectory, and halite saturation point at 25°C. (Carpenter, 1978).

enrichment of ^{18}O in brines, while the $\delta^2\text{H}$ values of brines can be buffered through interaction with hydrogen-bearing minerals (Warr et al., 2021). Brines in geothermal areas also display a similar positive

oxygen isotope shift, with little or no change in hydrogen isotope ratios, relative to their source waters, because rocks contain considerably less hydrogen than oxygen (Craig, 1966; Clark and Fritz, 1997). Temperatures of Smackover Formation brines in Alabama range from 73 to 80°C (Blondes et al., 2023). In contrast, Smackover brines in southern Arkansas have higher temperatures (123–219°C), perhaps due to higher heat flow (e.g., Jones, 1970; Ewing, 2009; Blackwell et al., 2011), which may explain their greater positive oxygen isotope shift relative to Alabama brines (Fig. 7). Thus, the isotopic signatures of the Smackover Formation brine observed may also partly result from water-rock interaction or input from geothermal fluids. Overall, the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ relationship and the Cl-Br and Na-Br trends clearly indicate mixing of remnants of evaporated seawater (reaching halite saturation) with meteoric water, likely under the influence of geochemical interactions between fluids and isotopically heavy minerals.

4.4. Strontium isotope ratios

Strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of the brines, ranging from 0.707403 to 0.710026 (Table 1), are higher than those of Jurassic seawater (0.7068–0.7072) (Stueber et al., 1984; Jones et al., 1994), indicating inputs of more radiogenic sources from siliciclastic rocks that

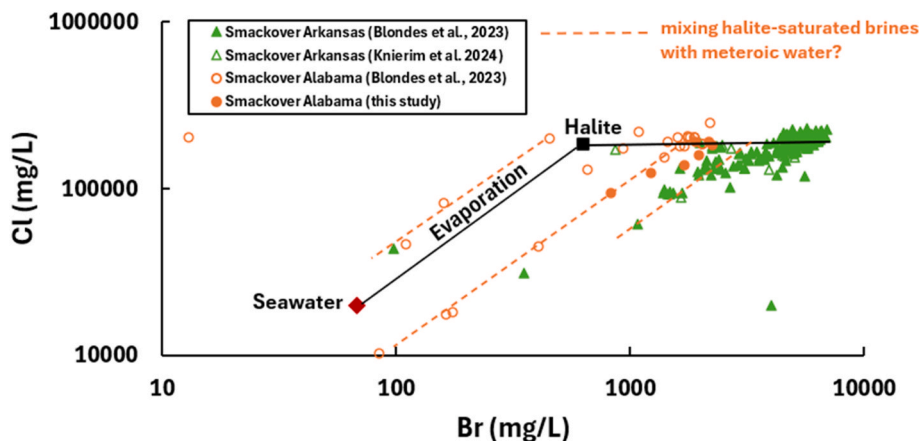


Fig. 6. Cl-Br relationships for Smackover Formation brines. Also shown are the concentrations for seawater, the evaporation trajectory, and halite saturation (Carpenter, 1978; Stueber et al., 1984). The orange dashed lines demonstrate potential mixing trends between halite-saturated brines and meteoric water under constant-ratio dilution. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

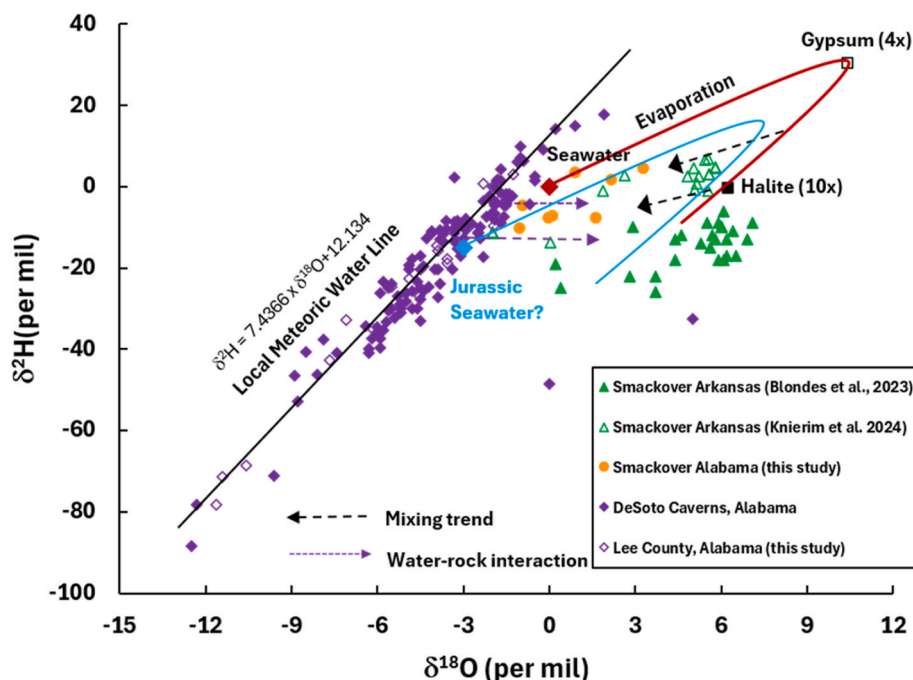


Fig. 7. Hydrogen and oxygen isotopic composition of the brines, plotted together with the meteoric water line ($R^2 = 0.7626$) and two evaporation curves corresponding to modern seawater (red; $\delta^{18}\text{O}$ of $\sim 0\text{‰}$) and postulated Jurassic seawater (blue; $\delta^{18}\text{O} \approx -3\text{‰}$ and $\delta^2\text{H} \approx -15\text{‰}$, assuming $\delta^2\text{H} = 5 \delta^{18}\text{O}$) (Galili et al., 2019). Also shown are isotopic composition of rainwater collected in DeSoto, AL (Lambert and Aharon, 2010), and seawater and evaporated seawater reaching gypsum and halite saturation (Holser, 1979). Dashed lines show potential mixing trends of evaporated seawater and meteoric water and water-rock interaction. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

are rich in K-feldspar, mica, and clay minerals (Faure and Mensing, 2005). Fig. 8 displays the relationship between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. 1000/Sr concentration (mg/L^{-1}). The lack of a linear correlation does not support a two-component mixing model. Instead, the data require multicomponent mixing or substantial water-rock interaction after two component-mixing. A non-linear relationship could result from water-rock interaction and Sr inputs from different sources. Fluids originating from deeper strata with greater radiogenic source material possibly migrated into the Smackover Formation by overpressure or thermohaline convection and mixed with less radiogenic Jurassic-age seawater to achieve the more elevated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these brines. The observed Sr concentrations, ranging from 1045 to 2381 mg/L, are significantly higher than those in modern seawater (7.2–8.2 mg/L) (Angino et al., 1966), suggesting inputs of Sr derived from Sr-rich minerals such as carbonate (calcite and dolomite), sulfate (e.g.,

barite), evaporite (e.g., gypsum, anhydrite, and celestite), and silicate minerals (e.g., feldspar and biotite) (Moldovanyi et al., 1993).

Correlations exist between radiogenic Sr and Li, for Arkansas Smackover Formation brines enriched in these elements (Fig. 9), indicating deeper-seated geogenic sources. Weak but positive correlations exist between radiogenic Sr and H_2S (Fig. 10), and between Li and TDS (Fig. S3), implying spatial variations in lithology and mineralogy of their sources, as well as in the geochemical processes that affect the brines. Siliciclastic or igneous rocks, such as granophyre in the underlying igneous complex, could be sources of Sr and other alkaline elements such as Li and K (Moldovanyi et al., 1993). Elevated H_2S could be produced by bacterial or thermochemical sulfate reduction occurring at different temperatures. Microbial sulfate reduction typically occurs at lower temperatures (40–80°C; Cheng et al., 2014) and is therefore less likely to control sulfate concentration in deep brines. However, bacteria may be adaptable to harsh environments, and bacterial-mediated sulfate reduction has been reported in deep-sea hydrothermal environments where temperatures reach up to 110°C (Jørgensen et al., 1992).

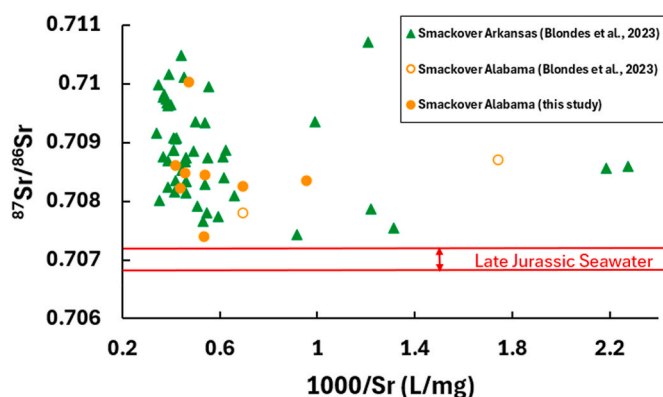


Fig. 8. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. 1000/Sr concentration (mg/L) in Smackover Formation brines. Also shown is the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Jurassic seawater with a mean composition of 0.707 (Stueber et al., 1984).

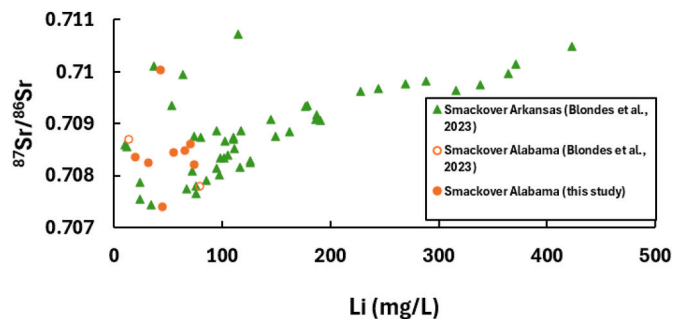


Fig. 9. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios vs. Li concentrations in the Smackover Formation brines.

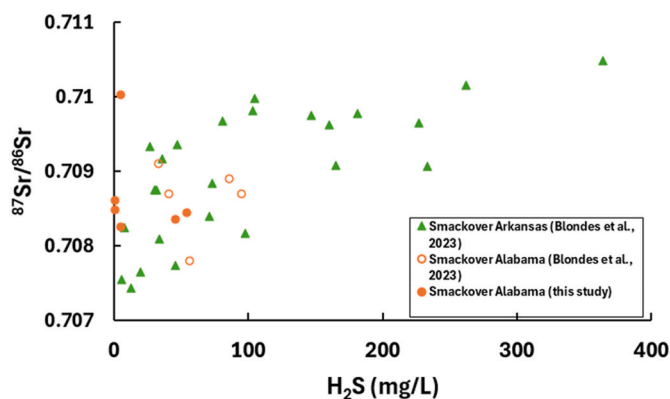


Fig. 10. $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios vs. H_2S concentrations in the Smackover Formation brines.

4.5. Potential geogenic sources of Li

The variations in Li and Sr concentrations in brines across the northern Gulf Coast from Texas to Alabama may reflect differences in geogenic sources and hydrologic pathways (U.S. Geological Survey, 2019), as fluids migrated from deep basin strata into the Smackover Formation. Proterozoic (1800 to 1600 Ma) granites underlying the northern Gulf, known as the Sabine Block, exhibit high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7103–0.7124 (Clift et al., 2018). In contrast, younger granitic intrusive bodies (nepheline syenites) in Arkansas have lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7049–0.7052 (Benton and Zou, 2026). Granophyres in the igneous complex in southern Alabama have a crystallization age of 329 Ma (Guthrie et al., 1994). Jancsek et al. (2023) found that the Li content of granite decreases by two to three-orders of magnitude in samples heavily altered by hydrothermal chloritization, which may be responsible for Li mobilization in groundwater. Chloritized minerals in the Alabama igneous complex are associated with structural fabric elements, and clasts of these materials are present in the Eagle Mills Formation, indicating that chloritization predates Upper Triassic deposition

(Guthrie et al., 1994). The peripheral fault system that developed during the Mesozoic may have provided pathways for the migration of Li-bearing fluids generated during chloritization. Experiments by James et al. (2003) showed simultaneous release of both Li and Sr via hydrothermal alteration of oceanic crust and terrigenous sediments at relatively high temperatures ($>150^\circ\text{C}$). James et al. (1999) reported the association of Li (and other alkali elements), B, and S in rising hydrothermal fluids that formed massive sulfide deposits in overlying clastic sediments. Moreover, clay minerals are known to retain Li because isomorphic substitution of Mg^{2+} for Al^{3+} (or Al^{3+} for Si^{4+}) can accommodate Li^+ adsorption or occupation of vacant sites within the crystalline structure. Hüpers and Kopf (2012) showed that Li can be leached from the clay-rich sediments through smectite dehydration. These studies suggest various geogenic origins and mechanisms responsible for Li enrichment at different geologic settings, which mainly involve the leaching of Li from source rocks (e.g., granites, basalts, evaporites) and clay-rich (e.g., smectite) sediments, as well as the influx of Li (and other alkali elements) from ascending hydrothermal fluids. The relatively low Cl/Br and Na/Br ratios of brines do not support a geogenic source through evaporite (halite) dissolution (Fig. 6).

5. Geochemical modeling

Geochemist's Workbench (Bethke, 2021) can be used to predict mineral precipitation and the evolution of fluid geochemistry of seawater as it evaporates. Fig. 11 shows the sequence of minerals that precipitate as more than 99% of water is removed from 1 kg of seawater. Precipitation of dolomite and gypsum at the early stage would remove Ca^{2+} , Mg^{2+} , CO_3^{2-} and SO_4^{2-} from the solution. As evaporation proceeds, gypsum will be converted to anhydrite. When the mass of water decreases by an order of magnitude (decreasing from 1 kg to less than 0.1 kg), halite starts to form and eventually becomes the dominant mineral with the highest volume.

Na concentration (~ 0.49 mol/kg H_2O) is lower than Cl (~ 0.56 mol/kg H_2O) in the original seawater. When halite forms, it depletes both Na and Cl in the solution. With further evaporation, the conversion of

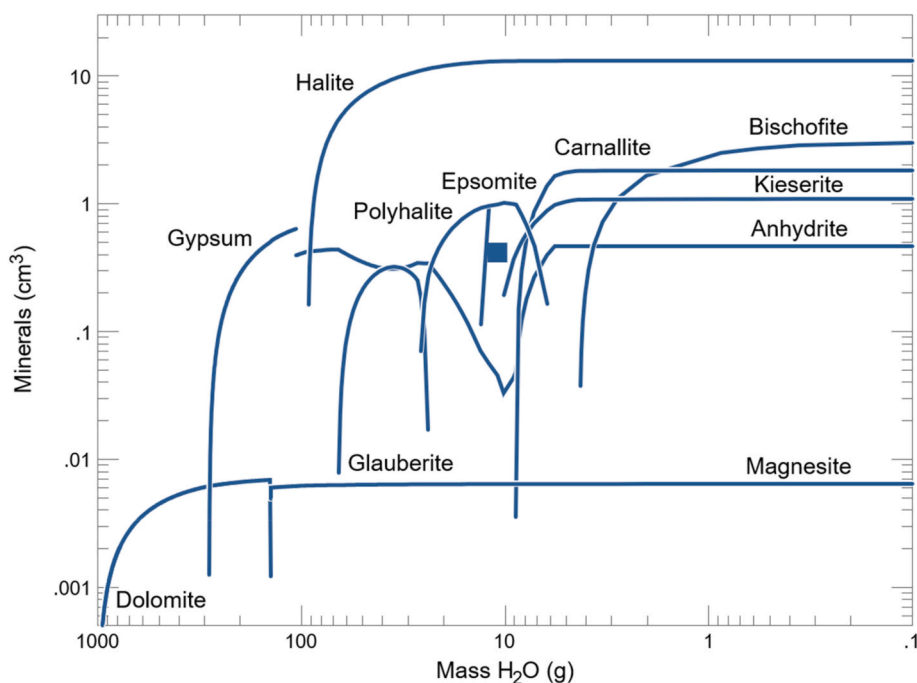


Fig. 11. Sequence and volumes of minerals precipitated during seawater evaporation derived from the geochemical modeling using the Geochemist's Workbench. Blue square shows the evaporation point where hexahydrate precipitates. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

anhydrite to glauberite ($\text{Na}_2\text{Ca}(\text{SO}_4)_2$) would remove both Na^+ and SO_4^{2-} from the brine:



The predicted drop in Na concentrations after halite precipitation (Fig. 12) is consistent with laboratory measurement of major ion concentrations of evaporated seawater at different stages (Carpenter, 1978; also refer to Fig. S1). As the volume of halite increases and evaporation continues, the fluid shifts from Cl-Na dominated facies to Cl-Mg dominated facies (Fig. 12).

The predicted Cl-Na hydrochemical facies formed during the early stage of evaporation or Cl-Mg facies dominated after the precipitation of halite is different from the observed Cl-Ca facies of Smackover Formation brines (Fig. 3), indicating seawater evaporation alone cannot account for the chemical evolution of brines. Water-rock interaction such as dolomitization (Equation (2)) would lead to a shift from Cl-Mg to Cl-Ca facies in evaporated seawater.

6. Summary

This research integrates elemental and isotopic (O, H, Sr) analyses and geochemical modeling techniques to investigate fluid mixing and water-rock interaction that might control the geochemical evolution of the Smackover Formation brines along the northern Gulf Coast. The main hydrogeochemical facies was identified as a Cl-Na-Ca-type brine, with concentrations of Cl (94,600–190,000 mg/L), Na (32,200–73,300 mg/L), and Ca (14,000–48,200 mg/L) significantly higher than those in modern seawater. The brines are also enriched in Br (831–5700+ mg/L), Sr (1045–2381 mg/L), Li (19.34–70.65 mg/L), and Ba (1.77–147.84 mg/L). Sulfate concentrations (<184 mg/L) in these brines are significantly lower than those in seawater (2710 mg/L). This depletion, along with the high H_2S levels observed in some brines, indicates non-conservative sulfate removal by thermochemical reduction. Microbial sulfate reduction typically occurs at lower temperatures between 40 and 80°C (Cheng et al., 2014) and is less likely to regulate sulfate concentration in deep brines. Low Cl/Br ratios (24.04–113.84) and Na/Br ratios (31.11–47.29) imply that the brines acquired salinity through mixing with evaporated seawater reaching halite precipitation,

rather than through halite dissolution. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ trends also indicate the mixing of meteoric water with remnant evaporated seawater that had reached gypsum and halite saturation. Some brines exhibit enrichment in ^{18}O and slight depletion in ^2H relative to seawater, suggesting the addition of ^{18}O from silicate or carbonate rocks via water-rock interaction.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of most brines analyzed (ranging from 0.70740 to 0.71048) are higher than that of Jurassic seawater (0.7070), indicating significant influx of radiogenic Sr from siliciclastic or igneous rock sources. Geochemical modeling of seawater evaporation predicted a predominantly Cl-Na or a Cl-Mg hydrogeochemical facies after halite precipitation. This predicted Cl-Mg facies differs from the Cl-Ca dominated Smackover Formation brines observed in this study. Water-rock interactions, such as dolomitization, could shift the composition of evaporated seawater from a Cl-Mg facies to Cl-Ca dominated facies. The observed enrichments in Ca and radiogenic Sr, together with sulfate depletion, indicate that seawater evaporation alone cannot account for the chemical evolution of Smackover brines. This study identified evaporated seawater that reached halite precipitation as the source of salinity, possible mixing between meteoric water and evaporated seawater, and geochemical influence from water-rock interactions, in agreement with previous studies in Arkansas (Moldovanyi et al., 1992, 1993). Enrichments of radiogenic Sr, Li, and H_2S could be derived from deep sources associated with the siliciclastic (e.g., Eagle Mills Formation) or igneous rocks. Although the proposed geogenic sources and related geochemical processes may explain the close association of these elements in Smackover Formation brines, the individual contribution of these different geogenic sources remain poorly understood and have not been quantified. The widespread occurrence of overpressure in the Gulf Coast, together with potential thermohaline convection near salt domes may facilitate the upward advection of deep basin brines along salt flanks and associated fault structure and their mixing with meteoric water along basin margins. Further geochemical, isotopic, and modeling studies could help to assess the potential geogenic sources, geochemical conditions, and hydrologic pathways contributing to Li enrichment in Smackover Formation brines.

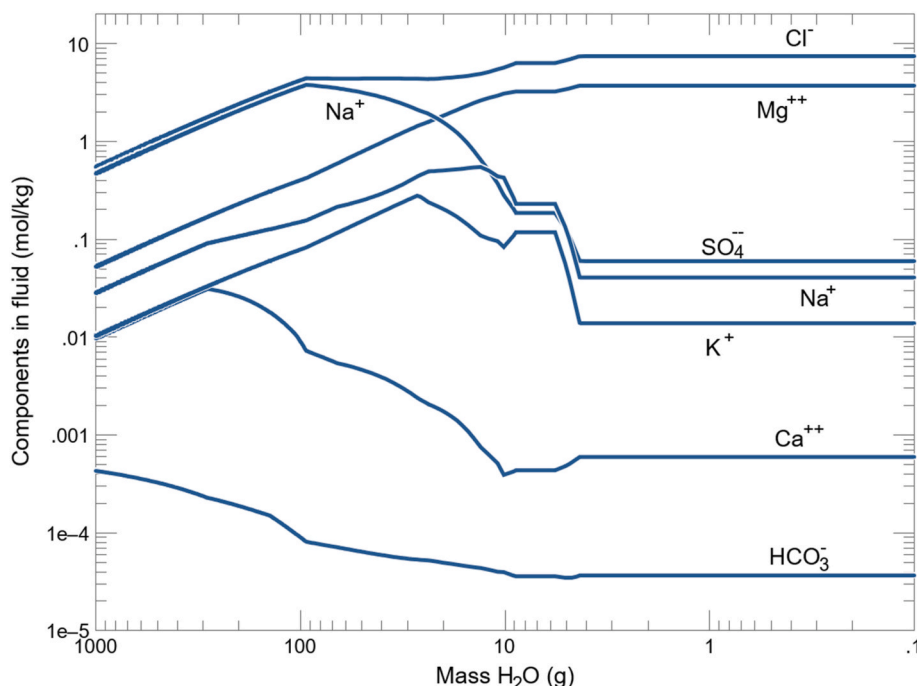


Fig. 12. Change in fluid composition during seawater evaporation derived from modeling using the Geochemist's Workbench.

CRediT authorship contribution statement

Kelly Kreitzer: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Ming-Kuo Lee:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. **Haibo Zou:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation. **Andrew L. Masterson:** Writing – review & editing, Visualization, Validation, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Ann Sullivan Ojeda:** Writing – review & editing, Resources, Methodology, Formal analysis, Data curation. **Zeki M. Billor:** Resources, Methodology, Formal analysis, Data curation. **Natalia Malina:** Writing – review & editing, Resources, Methodology, Formal analysis, Data curation. **Gregory M. Guthrie:** Writing – review & editing, Resources, Investigation, Conceptualization. **Bonnie McDevitt:** Writing – review & editing, Resources, Formal analysis, Conceptualization. **Ann Arnold:** Writing – review & editing, Resources, Investigation, Conceptualization. **Demi Durham:** Visualization, Data curation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ming-Kuo Lee reports was provided by US Geological Survey. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was supported with funding from the USGS Energy Resources Program and BRInE lab sample analysis was completed by Jessica Chenault and Amanda Herzberg. Institutions (Auburn University and USGS) participated in the program executed the contract via existing resources and benefited from sharing resource and analytical facilities (e.g., ICP-MS, ICP-OES, IC) at the partner institute. Stable hydrogen and oxygen isotope analyses were performed at the National High Magnetic Field Laboratory, which is supported by National Science Foundation Cooperative Agreement No. DMR-1644779 and the state of Florida. This research benefited greatly from field assistance from our colleagues in the Geological Survey of Alabama and State Oil and Gas Board in sampling brines from oil and gas production wells operating in southwest Alabama.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2026.107086>.

Data availability

Data will be made available on request.

References

- Angino, E.E., et al., 1966. Observed variations in the strontium concentration of sea water. *Chem. Geol.* 1, 145–153. [https://doi.org/10.1016/0009-2541\(66\)90013-1](https://doi.org/10.1016/0009-2541(66)90013-1).
- Appelo, C.A.J., 1994. Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer. *Water Resour. Res.* 30, 2793–2805. <https://doi.org/10.1029/94WR01048>.
- Balaram, V., et al., 2024. Lithium: a review of applications, occurrence, exploration, extraction, recycling, analysis, and environmental impact. *Geosci. Front.* 15. <https://doi.org/10.1016/j.gsf.2024.101868>.
- Benton, M., Zou, H., 2026. Geochronology, geochemistry, and petrogenesis of nepheline syenites from Granite Mountain, Arkansas alkaline province, USA. *Minerals* 16. <https://doi.org/10.3390/min16060587>.
- Bethke, C.M., 2021. *Geochemical and Biogeochemical Reaction Modeling*, third ed. Cambridge University Press.
- Bethke, C.M., Marshak, S., 1990. Brine migrations across North America - the plate tectonics of groundwater. *Annu. Rev. Earth Planet Sci.* 18, 287–315. <https://doi.org/10.1146/annurev.earth.18.1.287>.
- Blackwell, D.D., et al., 2011. SMU Geothermal Laboratory Heat Flow Pap of the Conterminous United States. Southern Methodist University Geothermal Laboratory, Dallas, Texas. <http://www.smu.edu/geothermal>.
- Blondes, M.S., et al., 2023. U.S. Geological Survey National Produced Waters Geochemical Database. <https://data.usgs.gov/datacatalog/data/USGS:64fa1e71d34ed30c2054ea11>.
- Canova, D.P., et al., 2018. Advective heat transport and the salt chimney effect: a numerical analysis. *Geofluids* 2018. <https://doi.org/10.1155/2018/2378710>.
- Cantlay, T., et al., 2020. Determining conventional and unconventional oil and gas well brines in natural sample II: cation analyses with ICP-MS and ICP-OES. *J. Environ. Sci. Health Part A* 55, 11–23. <https://doi.org/10.1080/10934529.2019.1666561>.
- Carpenter, A.B., 1978. Origin and chemical evolution of brines in sedimentary basins. *Okla. Geol. Surv. Circ.* 79, 60–77. <https://doi.org/10.2118/7504-MS>.
- Carpenter, A.B., Trout, M., 1978. Geochemistry of bromide-rich brines of the dead sea and Southern Arkansas. *Okla. Geol. Surv. Circ.* 79, 78–88.
- Cheng, T.-W., et al., 2014. Temperature-dependent variations in sulfate-reducing communities associated with a terrestrial hydrocarbon seep. *Microb. Environ.* 29, 377–387. <https://doi.org/10.1264/jsm2.ME14086>.
- Clark, I., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. CRC Press, New York, p. 328.
- Claypool, G.E., Mancini, E.A., 1989. Geochemical relationships of petroleum in Mesozoic reservoirs to carbonate source rocks of Jurassic Smackover Formation, southwestern Alabama. *AAPG Bulletin* 73, 904–924.
- Clayton, R.N., et al., 1966. The origin of saline formation waters: 1. Isotopic composition. *J. Geophys. Res.* 71, 3869–3882. <https://doi.org/10.1029/JZ071i016p03869>.
- Clift, P.D., et al., 2018. The Sabine Block, Gulf of Mexico: Promontory on the North American Margin? *Geology* 46, 15–18.
- Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454–458. <https://doi.org/10.4319/lo.1969.14.3.0454>.
- Collins, A.G., 1976. Lithium Abundances in Oilfield Waters, vol.1005. U. S. Geological Survey Professional Paper, pp. 116–123. <http://pubs.usgs.gov/pp/1005/report.pdf>.
- Craig, H., 1966. Isotopic composition and origin of the Red Sea and Salton Sea geothermal brine. *Science* 154, 1544–1548. <https://www.science.org/doi/10.1126/science.154.3756.1544>.
- Darvari, R., et al., 2024. Controls on lithium content of oilfield waters in Texas and neighboring states (USA). *J. Geochem. Explor.* 257. <https://doi.org/10.1016/j.gexplo.2023.107363>.
- Davis, S.N., et al., 2005. Uses of chloride/bromide ratios in studies of potable water. *Groundwater* 36, 338–350. <https://doi.org/10.1111/j.1745-6584.1998.tb01099.x>.
- Dickinson, K.A., 1968. Petrology of the Buckner Formation in adjacent part of Texas, Louisiana, and Arkansas. *J. Sediment. Petrol.* 38, 555–567.
- Duhr, A., Hilkert, A., 2001. Finnigan GasBench II: Automated H₂/H₂O equilibration for δ D determination on aqueous samples. *Thermo Electron Corp. Application Note*, 30049.
- Eaton, A.D., et al., 2005. 4500-S2-D methylene blue method. In: *Standard Methods for the Examination of Water and Wastewater*, Centennial Edition, twenty-first ed. American Public Health Association, Washington, D.C., USA.
- Egeberg, P.K., Aagaard, P., 1989. Origin and evolution of formation waters from oil fields on the Norwegian shelf. *Appl. Geochem.* 4, 131–142. [https://doi.org/10.1016/0883-2927\(89\)90044-9](https://doi.org/10.1016/0883-2927(89)90044-9).
- Evans, D.G., et al., 1991. Mechanisms driving groundwater flow near salt domes. *Geophys. Res. Lett.* 18, 927–930.
- Evans, D.G., Nunn, J.A., 1989. Free thermohaline convection in sediments surrounding a salt column. *Geophys. Res. Lett.* 84, 12413–12422.
- Ewing, T., 2009. The ups and downs of the Sabine uplift and the Northern Gulf of Mexico basin: Jurassic basement blocks, Cretaceous thermal uplifts, and Cenozoic flexure. *GCAGS Transactions*.
- Faure, G., Mensing, T.M., 2005. *Isotopes: Principles and Applications*. Wiley, p. 897.
- Ferguson, G., et al., 2018. The persistence of brines in sedimentary basins. *Geophys. Res. Lett.* 45, 4851–4858. <https://agupubs.onlinelibrary.wiley.com/doi/10.1029/2018GL078409>.
- Fredrich, et al., 2007. Mineralogy of deepwater Gulf of Mexico salt formations and implications for constitutive behavior. *J. Petrol. Sci. Eng.* 57. <https://doi.org/10.1016/j.petrol.2006.11.006>.
- Gallii, N., et al., 2019. The geologic history of seawater oxygen isotopes from marine iron oxides. *Science* 365, 469–473. <https://doi.org/10.1126/science.aaw9247>.
- Ghorbani, Y., et al., 2024. The strategic role of lithium in the green energy transition: towards an OPEC-style framework for green energy-mineral exporting countries (GEMEC). *Resour. Policy* 90. <https://www.sciencedirect.com/science/article/pii/S0301420724001041?via%3Dihub>.
- Graf, D.L., et al., 1966. The origin of saline formation waters, III: calcium chloride waters. *Illinois State Geological Survey Circular*. No. 397. <https://hdl.handle.net/2142/42919>.
- Guthrie, G.M., et al., 1994. Age and tectonic setting of subsurface plutonic rocks in south Alabama: implications for igneous activity along the Alleghanian suture. *Geol. Soc. America Abstracts with Programs* 26, 17.

- Guthrie, G.M., et al., 2023. The Smackover Formation in Alabama: an unconventional potential source for critical minerals, vol.2022. Geological Society of America Connects.
- Guthrie, G.M., Raymond, D.E., 1992. Pre-Middle Jurassic rocks beneath the Alabama coastal plain. *Alabama Geol. Survey Bull.* 150, 155.
- Hanor, J., 1994. Origin of Saline Fluids in Sedimentary Basins, vol. 78. Geological Society, London, Special Publications, pp. 151–174. <https://doi.org/10.1144/GSL.SP.1994.078.01.13>.
- Hansom, J., Lee, M.-K., 2005. Effects of hydrocarbon generation, basal heat flow and sediment compaction on overpressure development: a numerical study. *Pet. Geosci.* 11, 353–360. <https://doi.org/10.1144/1354-079304-651>.
- Harrison, W.J., Summa, L.L., 1991. Paleohydrology of the Gulf of Mexico Basin. *Am. J. Sci.* 291, 109–176. <https://doi.org/10.2475/ajls.291.2.109>.
- Harvie, et al., 1984. The prediction of mineral solubilities in natural water, the Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochem. Cosmochim. Acta* 48, 723–751.
- Heydari, E., et al., 1997. Depositional environments, organic carbon accumulation, and solar-forcing cyclicity in smackover formation lime mudstones, Northern Gulf Coast. *AAPG Bulletin* 81, 760–774. <https://doi.org/10.1306/522B4839-1727-11D7-8645000102C1865D>.
- Hilkert, A., Avak, H., 2001. Finnigan GasBench II: 18O-equilibration on water, fruit juice, and wine. Thermo Electron Corp, Application Note, 30048.
- Holser, W.T., 1979. Chapter 9. Trace elements and isotopes in evaporites. In: Burns, R.G. (Ed.), *Marine Minerals, Reviews in Mineralogy*, vol. 6. De Gruyter, Berlin, Boston, pp. 295–346. <https://doi.org/10.1515/9781501508646-013>.
- Horita, J., 1988. Hydrogen isotope analysis of natural waters using an H₂-Water equilibration method: a special implication to brines. *Chemical Geology: Isotope Geoscience Section* 72, 89–94. [https://doi.org/10.1016/0168-9622\(88\)90040-1](https://doi.org/10.1016/0168-9622(88)90040-1).
- Huang, X., et al., 2026. Critical review of lithium recovery from geothermal brines with implications for Smackover Formation, USA. *Energy Convers. Manag.* X 30. <https://doi.org/10.1016/j.ecmx.2026.101671>.
- Hudec, M., et al., 2013. Influence of deep Louann structure on the evolution of the Northern Gulf of Mexico. *AAPG Bulletin* 97, 1711–1735. <https://doi.org/10.1306/04011312074>.
- Hüpers, A., Kopf, A.J., 2012. Effect of smectite dehydration on pore water geochemistry in the shallow subduction zone: an experimental approach. *G-cubed* 13. <https://doi.org/10.1029/2012GC004212>.
- Hyeong, K., Capuano, R.M., 2001. Ca/Mg of brines in Miocene/Oligocene clastic sediments of the Texas Gulf Coast: buffering by calcite/disordered dolomite equilibria. *Geochem. Cosmochim. Acta* 65. <https://www.sciencedirect.com/science/article/pii/S0016703701006597>.
- Ingebritsen, S.E., Manning, C.E., 1999. Geological implications of a permeability-depth curve for the Continental crust. *Geology* 27 (2), 1107–1110. [https://doi.org/10.1130/0091-7613\(1999\)027<1107:GIOAPO>2.3.CO](https://doi.org/10.1130/0091-7613(1999)027<1107:GIOAPO>2.3.CO).
- James, R.H., et al., 1999. The alkali element and boron geochemistry of the Escanaba trough sediment hosted hydrothermal system. *Earth Planet Sci. Lett.* 171, 157–169. [https://doi.org/10.1016/S0012-821X\(99\)00140-5](https://doi.org/10.1016/S0012-821X(99)00140-5).
- James, R.H., et al., 2003. An experimental study of alteration of oceanic crust and terrigenous sediments at moderate temperatures (51 to 350°C): insights as to chemical processes in near-shore ridge-flank hydrothermal systems. *Geochem. Cosmochim. Acta* 67, 681–691. [https://doi.org/10.1016/S0016-7037\(02\)01113-4](https://doi.org/10.1016/S0016-7037(02)01113-4).
- Jancsek, K., et al., 2023. Granite alteration as the origin of high lithium content of groundwater in Southeast Hungary. *Appl. Geochem.* 149. <https://doi.org/10.1016/j.apgeochem.2023.105570>.
- Johnson, B.W., Wing, B.A., 2020. Limited Archaean Continental emergence reflected in an early Archaean ¹⁸O-Enriched Ocean. *Nat. Geosci.* <https://doi.org/10.1038/s41561-020-0538-9>.
- Jones, C.E., et al., 1994. Strontium isotopic variations in Jurassic and Cretaceous seawater. *Geochem. Cosmochim. Acta* 58, 3061–3074. [https://doi.org/10.1016/0016-7037\(94\)90179-1](https://doi.org/10.1016/0016-7037(94)90179-1). https://ui.adsabs.harvard.edu/link_gateway/1994GeCoA..58.3061J/.
- Jones, P.H., 1970. Geothermal resources of the northern Gulf of Mexico Basin. *Geothermics* 2, 14–26.
- Jørgensen, B.B., et al., 1992. Bacterial sulfate reduction above 100°C in deep-sea hydrothermal vent sediments. *Science* 258, 1756–1757. <https://doi.org/10.1126/science.258.5089.1756>.
- Jubb, A.M., et al., 2020. Direct trace element determination in oil and gas produced waters with inductively coupled plasma-optical emission spectrometry: advantages of high-salinity tolerance. *Geostandard and Geoanalytical Research* 44, 385–397. <https://doi.org/10.1111/ggr.12316>.
- Kendall, C., Caldwell, E.A., 1998. Chapter 2 - Fundamentals of isotope geochemistry. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*, pp. 51–86. <https://doi.org/10.1016/B978-0-444-81546-0.50009-4>.
- Kharaka, Y.K., et al., 1973. Isotopic composition of oil-field brines from Kettleman North Dome, California, and their geologic implications. *Geochem. Cosmochim. Acta* 37, 1899–1908. [https://doi.org/10.1016/0016-7037\(73\)90148-8](https://doi.org/10.1016/0016-7037(73)90148-8).
- Kharaka, Y.K., et al., 1987. Geochemistry of metal-rich brines from central Mississippi Salt Dome Basin, U.S.A. *Appl. Geochem.* 2, 543–561. [https://doi.org/10.1016/0883-2927\(87\)90008-4](https://doi.org/10.1016/0883-2927(87)90008-4).
- Knauth, L.P., 1988. Origin and mixing history of Brines, Palo Duro Basin, Texas, U.S.A. *Appl. Geochem.* 3, 455–474. [https://doi.org/10.1016/0883-2927\(88\)90019-4](https://doi.org/10.1016/0883-2927(88)90019-4).
- Knierim, K.J., et al., 2024. Lithium resource in the Smackover Formation brines of Southern Arkansas, vols. 2024–3052. US Geological Survey Fact Sheet. <https://doi.org/10.3133/fs20243052>.
- Kopaska-Merkel, D.C., et al., 1993. Reservoir characterization of the Smackover Formation in southwest Alabama. Geological Survey of Alabama. <https://doi.org/10.2172/6878244>. UNT Digital Library, DOE/BC/14425-7.
- Kopaska-Merkel, D.C., 1998. Jurassic Reefs of the Smackover Formation in South Alabama, vol. 195. Geological Survey of Alabama Circular, pp. 24–27.
- Lambert, J.W., Aharon, P., 2010. Oxygen and hydrogen isotopes of rainfall and dripwater at DeSoto Caverns (Alabama, USA): key to understanding past variability of moisture transport from the Gulf of Mexico. *Geochem. Cosmochim. Acta* 74, 846–861. <https://doi.org/10.1016/j.gca.2009.10.043>.
- Land, L.S., Prezbindowski, D.R., 1982. The origin and evolution of saline formation water, Lower Cretaceous carbonates, south-central Texas, U.S.A. *Dev. Water Sci.* 16, 51–74. [https://doi.org/10.1016/S0167-5648\(08\)70595-1](https://doi.org/10.1016/S0167-5648(08)70595-1).
- Lee, M.-K., Bethke, C.M., 1996. A model of isotope fractionation in reacting geochemical systems. *Am. J. Sci.* 296, 965–988.
- Lico, M.S., et al., 1982. Methods for collection and analysis of geopressed geothermal and oil field waters. US Geol. Survey Water Supply Paper 2194. <https://doi.org/10.3133/wsp2194>.
- Mancini, E.A., et al., 1987. Environments of deposition and petroleum geology of Tuscaloosa Group (upper Cretaceous), South Carlton and pollard fields, Southwestern Alabama. *AAPG Bulletin* 71, 1128–1142. <https://doi.org/10.1306/703C802E-1707-11D7-8645000102C1865D>.
- Mancini, E.A., et al., 1990. Jurassic sequence stratigraphy in the Mississippi interior salt Basin of Alabama. *Gulf Coast Assoc. Geol. Soc. Transac.* 40, 521–530.
- Mancini, E.A., et al., 2019. Depositional model for lithofacies of the Upper Jurassic Smackover Formation in the Conecuh embayment, onshore northeastern Gulf of Mexico: implications for petroleum exploration. *Gulf Coast Assoc. Geol. Soc.* 8, 89–103.
- Marandi, A., Shand, P., 2018. Groundwater chemistry and the Gibbs diagram. *Appl. Geochem.* 97, 209–212. <https://doi.org/10.1016/j.apgeochem.2018.07.009>.
- Marza, M., et al., 2024. Geological controls on lithium production from basinal brines across North America. *J. Geochem. Explor.* 257. <https://doi.org/10.1016/j.gexplo.2023.107383>.
- McCaffrey, M.A., et al., 1987. The evaporation path of seawater and the coprecipitation of Br⁻ and K⁺ with Halite. *J. Sediment. Petrol.* 57, 928–938. <https://doi.org/10.1306/212f8cab-2b24-11d7-8648000102c1865d>.
- McDevitt, B., et al., 2024. Utica/point pleasant brine isotopic compositions (⁶⁷Li, ⁸¹B, ⁸³Ba) Elucidate Mechanisms of Lithium Enrichment in the Appalachian basin. *Sci. Total Environ.* 947. <https://www.sciencedirect.com/science/article/pii/S0048969724047375>.
- McIntosh, J.C., Ferguson, G., 2021. Deep meteoric water circulation in Earth's crust. *Geophys. Res. Lett.* <https://doi.org/10.1029/2020GL090461>.
- Mills, C., Li, P., 2021. XRD analysis and petroleum potential of the Eagle Mills Formation and Paleozoic rocks in the subsurface, south Arkansas. *Kansas Geological Survey Information Circular* 45. <https://geology.arkansas.gov/docs/pdf/publication/information-circulars/IC-45%20Final%20Draft.pdf>.
- Moldovanyi, E.P., et al., 1992. New constraints on carbonate diagenesis from integrated Sr and S isotopic and rare Earth element data, Jurassic Smackover Formation, U.S. Gulf Coast: a reply. *Appl. Geochem.* 7, 93–97. [https://doi.org/10.1016/0883-2927\(92\)90018-X](https://doi.org/10.1016/0883-2927(92)90018-X).
- Moldovanyi, E.P., et al., 1993. Strontium, boron, oxygen, and hydrogen isotope geochemistry of brines from basal strata of the Gulf Coast sedimentary basin, USA. *Geochem. Cosmochim. Acta* 57, 2083–2099. [https://doi.org/10.1016/0016-7037\(93\)90095-E](https://doi.org/10.1016/0016-7037(93)90095-E).
- Moldovanyi, E.P., Walter, L.M., 1992. Regional trends in water chemistry, Smackover Formation, southwest Arkansas: geochemical and physical Controls I. *AAPG Bulletin* 76, 864–894. <https://doi.org/10.1306/BDF890C-1718-11D7-8645000102C1865D>.
- Munk, L., et al., 2025. Lithium brines: origin, characteristics, and global distribution. *Econ. Geol.* 120, 575–597. <https://doi.org/10.5382/econgeo.5134>.
- Neuzil, C.E., 1995. Abnormal pressures as hydrodynamic phenomena. *Am. J. Sci.* 295, 742–786.
- Pappas, R.S., 2012. Sample preparation problem solving for inductively coupled plasma-mass spectrometry with liquid introduction systems I. Solubility, chelation, and memory effects. *Spectroscopy* 27, 20–31.
- Penny, E., et al., 2003. Groundwater and microbial processes of Alabama coastal plain aquifers. *Water Resour. Res.* 39. <https://doi.org/10.1029/2003WR001963>.
- Stanislavsky, E., Gvirtzman, H., 1999. Basin-scale migration of continental-rift brines: paleohydrologic modeling of the dead sea basin. *Geology* 27, 791–794. [https://doi.org/10.1130/0091-7613\(1999\)027<0791:BSMOCR>2.3.CO;2](https://doi.org/10.1130/0091-7613(1999)027<0791:BSMOCR>2.3.CO;2).
- Stueber, A.M., et al., 1984. A strontium isotopic study of Smackover brines and associated solids, southern Arkansas. *Geochem. Cosmochim. Acta* 48, 1637–1649. [https://doi.org/10.1016/0016-7037\(84\)90333-8](https://doi.org/10.1016/0016-7037(84)90333-8).
- Stueber, A.M., Lynn, M.W., 1991. Origin and chemical evolution of formation waters from Silurian-Devonian strata in the Illinois basin, USA. *Geochem. Cosmochim. Acta* 55, 309–325. [https://doi.org/10.1016/0016-7037\(91\)90420-A](https://doi.org/10.1016/0016-7037(91)90420-A).
- Subasinghe, H.C.S., et al., 2025. Critical minerals extraction from geothermal brines. *JOULE* 5. <https://doi.org/10.1016/j.joule.2025.102171>.
- Tarascon, J.-M., 2010. Is Lithium the new gold? *Nat. Chem.* 2, 510. <https://doi.org/10.1038/nchem.680>.
- Tew, B.H., et al., 1993. Geologic framework of the Jurassic (Oxfordian) Smackover Formation the Alabama coastal waters area. *AAPG Bulletin* 77. <https://www.osti.gov/biblio/6963481>.
- Tonietto, S., Pope, M., 2013. Diagenetic evolution and its influence on petrophysical properties of the Jurassic Smackover Formation thrombolite and grainstone units of little cedar creek field, Alabama. *Gulf Coast Assoc. Geol. Soc.* 2, 68–84.

- Tóth, J., 1962. A theory of groundwater motion in small drainage basins in central Alberta, Canada. *J. Geophys. Res.* 67, 4375–4388. <https://doi.org/10.1029/JZ067i011p04375>.
- Tóth, J., 1980. Cross-formational gravity-flow of groundwater: A mechanism of the transport and accumulation of petroleum (the generalized hydraulic theory of petroleum migration). In: Roberts III, W.H., Cordell, R.J. (Eds.), *Problems of Petroleum Migration*. <https://doi.org/10.1306/St10411C8>.
- U.S. Environmental Protection Agency. Method 3015A (SW-846), 2007. *Microwave Assisted Acid Digestion of Sediments, Sludges, and Oils*. Washington, DC.
- U.S. Geological Survey, 2019. Lithium from source to sink: Genesis and evolution of Li brines and clays. <https://www.usgs.gov/centers/gmeg/science/lithium-source-sink-genesis-and-evolution-li-brines-and-clays>.
- Warr, O., et al., 2021. The role of low-temperature ^{18}O exchange in the isotopic evolution of deep subsurface fluids. *Chem. Geol.* 561. <https://doi.org/10.1016/j.chemgeo.2020.120027>.
- Whidden, K.J., et al., 2023. Assessment of Undiscovered, Technically Recoverable Conventional Oil and Gas Resources in the Upper Jurassic Smackover Formation, U. S. Gulf Coast." *U.S. Geological Survey Fact Sheet* 2023–3046.
- White, D.E., 1965. Saline waters of sedimentary rocks. In: Young, A., Galley, J.E. (Eds.), *Fluids in Subsurface Environments*. American Association of Petroleum Geologists. <https://doi.org/10.1306/M4360C14> vol. 4.
- Wu, S., et al., 1990. Allochthonous salt, structure and stratigraphy of the North-Eastern Gulf of Mexico. Part I: stratigraphy. *Mar. Petrol. Geol.* 7, 318–324. [https://doi.org/10.1016/0264-8172\(90\)90013-7](https://doi.org/10.1016/0264-8172(90)90013-7).
- Yardley, B., et al., 2003. Controls on the chemical composition of crustal brines. *J. Geochem. Explor.* 78, 133–135.