Elemental and isotope geochemistry of Smackover Formation brine in southwest Alabama

By

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Abstract

This study investigates the geochemical evolution of brines within the Smackover Formation in southwest Alabama through elemental and isotopic analyses, coupled with geochemical modeling techniques. Major ion and trace element analysis displays Na-Cl-Ca dominated hydrochemical facies and a distinct lack of carbonates (HCO_3^- or CO_3^{2-}) in the Alabama brine samples in this study. Lower sulfate concentrations, coupled with high H_2S levels in some brines, suggest sulfate removal mechanisms such as bacterial sulfate reduction or precipitation of sulfate minerals. Analysis of Cl/Br, Na/Br, and K/Br ratios indicates the acquisition of salinity through the mixing of meteoric water with evaporated seawater reaching halite saturation, rather than halite dissolution. Isotopic trends of $\delta^{18}O$ and $\delta^{2}H$ also suggest a mixture of meteoric water with remnant evaporated seawater reaching gypsum and halite saturation. The strontium isotopic ratios of the brine range from 0.707403-0.710026, higher than that of Jurassic seawater (0.7071). The varying extent of water-rock interaction can be understood by the relationship between $^{87}Sr/^{86}Sr$ and alkali elements (K and Li). Multiple fluid pathways may be taken through the siliciclastic basement rock as water is forced into the Smackover Formation. Geochemical modeling predicts a Cl-Mg facies after halite saturation, contrasting with the observed Na-Cl-Ca dominance in the Smackover Formation brines. This suggests the influence of water-rock interaction such as dolomitization.

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Introduction

The Gulf of Mexico holds a wealth of oil, gas, and mineral resources that although extensively studied, provide opportunities for further research and expansion of current knowledge. The unique stratigraphy and structure of the subsurface contribute heavily to the occurrence of the Smackover Formation brine waters (Figure 1). Strategically important elements present in the brine, such as lithium (Li) and bromide (Br) are vital to industry. According to available data from the United States Geologic Survey (USGS) National Produced Water Database (Siefert et. al, 2022), lithium concentrations in the Smackover Formation range from 13.3 to 90.0 mg/L. Lithium is significant in the United States and worldwide as the reliability of the critical mineral industry shifts. The production of lithium-ion batteries for electric vehicles is one of the fastest-growing uses of lithium (Tarascon, 2010). The global lithium market is projected to be worth over six billion dollars by 2028 (Fortune Business Insight, 2022). Lithium extraction from oil-field brines produced from already established oil and gas wells could present economic growth opportunities. Technologies used for the extraction of lithium include gravity separation, electrodialysis, ion exchange resins, solvent extraction, nanofiltration, and electrochemical ion pumping (Zhan and Pan, 2022; Nie, 2017; Meng, 2022; Zhou, 2017; Li, 2019; Calvo, 2021; Liu, 2021; Vera, 2023).

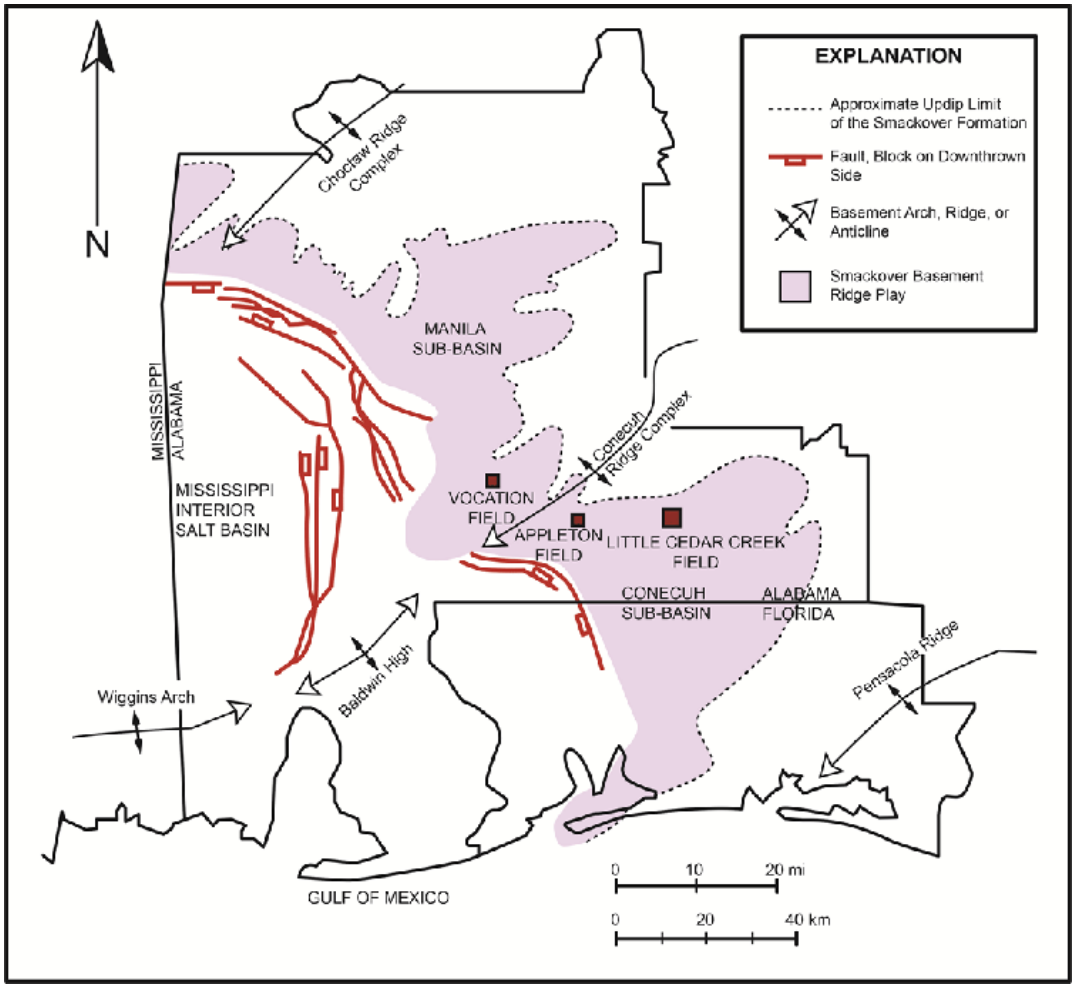
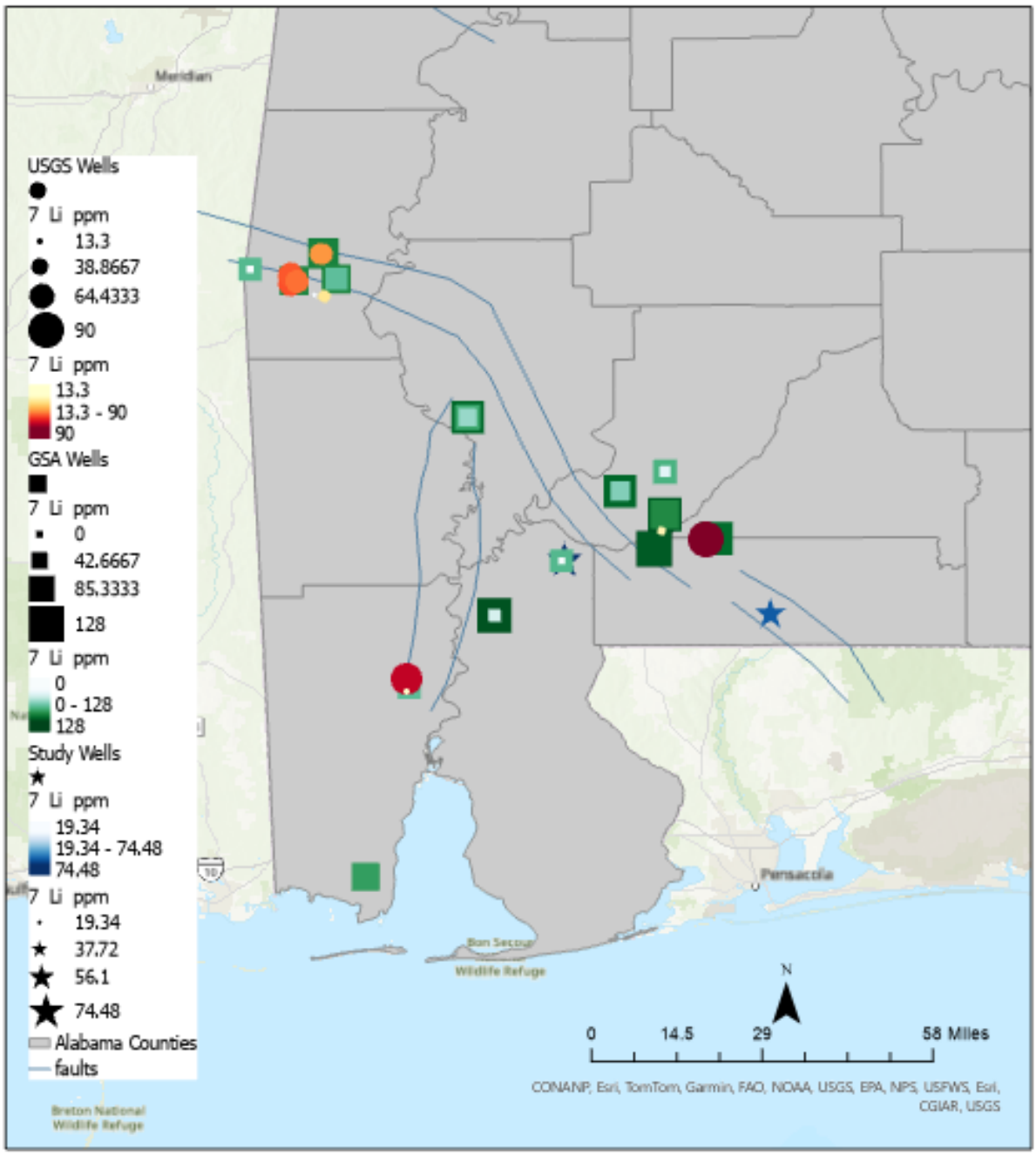


Figure 1: Map of study area in southwest Alabama including fault system and embayments (Tonietto and Pope 2013)

Proper disposal of brine through saltwater injection wells is regulated by government agencies, such as the EPA, to protect the integrity of surrounding drinking water resources. Each well and its stratigraphic unit harbors brine with varying concentrations of major ions and trace elements. The geochemical properties of the Smackover brine vary spatially throughout the northern Gulf region (Moldovanyi et al., 1992, 1993). Smackover Formation brines are associated with several oil-production fields (Guthrie et. al, 2023) surrounded by complex structures including fault blocks and basement arches and ridges in southwest Alabama (Fig. 1).

The origin and geochemical evolution of brines in sedimentary basins remain poorly understood. Preliminary data indicated that the concentrations of trace elements in our study area may be potentially high enough to be considered for further exploration (Guthrie et al, 2023). Bromide and lithium concentrations increase substantially as seawater evaporates and bitterns form (Collins, 1976). These trace elements may be sourced from the Louann Salt or acquired via water-rock interaction (Moldovanyi et al., 1992, 1993). Available data from the Alabama Geologic Survey and the USGS Produced Waters Database (Siefert et al. 2022) indicate high level of variation of concentrations of these elements bromide (2-2,190 mg/L) and lithium (13-90 mg/L) (Figs. 2 and 3) in the study area.



Sources: USGS, GSA, Alabama Geographic Information Office
by: Kelly Kreitzer

Figure 2: Map of lithium concentrations in mg/L (Alabama Geographic Information Office 2016; Siefert et. al, 2022; Guthrie 2020)

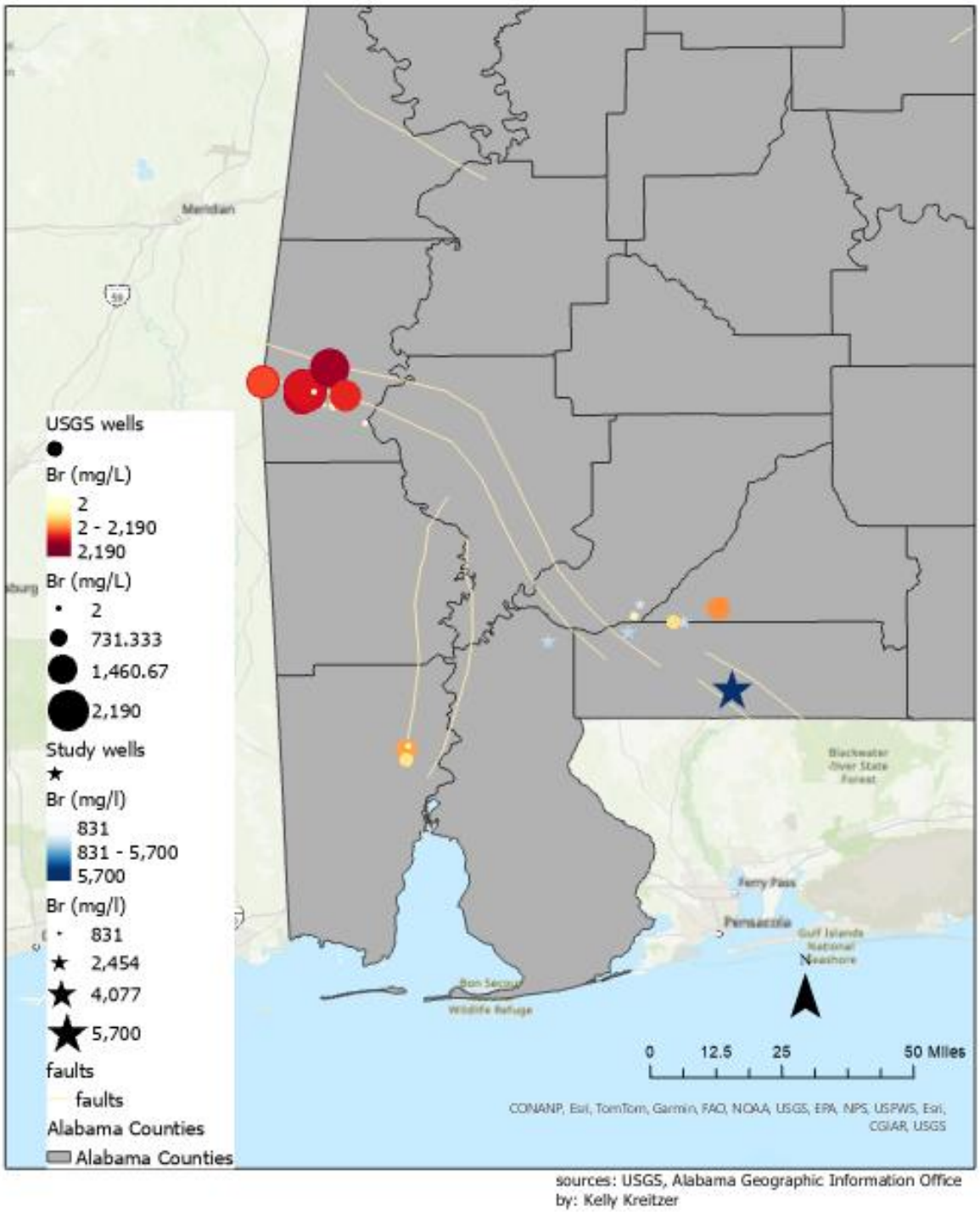


Figure 3: Map of bromide concentrations in mg/L (King, 2005; Alabama Geographic Information Office 2016; Siefert et. al, 2022)

Previous studies (e.g., Stueber and Walter, 1991; Penny et. al, 2003) have used Cl/Br ratios, stable isotope relationships, radiogenic isotopes, and noble gases to determine the sources of salinity influenced by evaporated seawater or dissolution of halite associated with evaporite. Cl/Br ratios demonstrate how saline water is compared to seawater and evaporated seawater (Stueber and Walter, 1991). Chloride concentrations change as evaporation and halite mineralization occurs while the bromide is largely unaffected by halite precipitation and other water-rock interaction processes such as bacterial sulfate reduction and dolomitization (Collins, 1976). The composition of stable isotopes (oxygen and hydrogen) and radiogenic isotopes (strontium) may reveal the extent of mixing between meteoric, seawater, and brine water due to their distinct isotopic signatures. The concentrations of atmospheric noble gases such as Kr, Ar, Ne and He may also act as geochemical tracers as brine originating from seawater is characteristically depleted in noble gas concentrations due to increasing salinity and decreasing solubility (Gerber, 2017). Yet questions remain about the fluid mixing and water-rock interaction mechanisms that control the geochemical evolution of brines. Because the Smackover Formation consists mainly of limestone and dolomite, there may still be reservoir-quality porosity and permeability at a depth of approximately 2400-4900 meters (Benson, 1984; Heydari, 2000). This and surrounding fault zones provide potential migration pathways for the brine to travel upward into the Smackover Formation as overpressure or thermohaline convection forces the water from the underlying strata. The underlying strata and formation water could be the sources of trace elements and major ions.

As groundwater of different origins moves through the subsurface and interacts with each other, they can react with rock to release or introduce ions such as lithium, bromide, or strontium. The geochemical composition of trace elements and isotopes may be used to test hypotheses made

for the source of salinity and trace elements. Previous studies indicate that the geochemical evolution of brines is likely controlled by water-rock interactions, mixing with evaporite brines, and biogeochemical processes (Moldvanyi et al., 1993). Characterizing brines and elucidating controls on their chemical composition thus becomes a factor in predicting the feasibility of economically extracting useful elements and potential contamination of subsurface disposal.

To address critical gaps in our understanding of the origin and geochemical evolution of Smackover Formation brines in the study area, the proposed study will center on the following two questions:

- Research Question 1: What is the source of salinity in the Smackover Formation brine?

Hypothesis 1 – The salinity might be produced from a combination of processes involving the dissolution of Jurassic-age marine salts, mixing with highly evaporated marine waters, or water-rock interactions.

Method 1.1- Oxygen and hydrogen isotopic composition of brines and meteoric water will be analyzed to identify potential "endmembers" of deep circulation fluids and the nature of mixing. Elevated $\delta^{18}O$ values relative to $\delta^{2}H$ may indicate inputs from isotopically heavier silicate or carbonate minerals via water-rock interaction.

Method 1.2- Strontium isotope composition of brines will be analyzed to identify potential more radiogenic sources that contain silicate minerals (e.g., biotite, feldspar, pyroxene); these minerals are known to have elevated $^{87}Sr/^{86}Sr$ ratios relative to Jurassic seawater (0.7071) and Jurassic marine carbonate/evaporite (0.7068 to 0.7072).

- Research Question 2: What water-rock interaction and fluid mixing processes may control the Smackover Formation's brine Br composition?

Hypothesis 2 – Bromide concentration is less affected by evaporation with respect to chloride.

Method 2 – Cl, Na, and Br composition will be analyzed to determine their ratios relative to seawater and evaporated seawater. Brines saturated with halite tend to exhibit lower Cl/Br and Na/Br ratios than those in seawater or moderately evaporated seawater since Cl and Na are removed by halite precipitation while Br will remain the remnant evaporated solution.

Geology

This study will focus on the Smackover Formation, an Upper Jurassic unit that can be found along the Gulf Coast of the United States. The Smackover can generally be broken into two to three distinct members. The lower Smackover is a silty limestone and dolomite that grades up into a dense limestone in the center before it becomes an oolitic limestone in the upper Smackover (Dickenson, 1968; Collins, 1976). This sequence is indicative of a subtidal and intertidal depositional environment (Claypool and Macini, 1989). The Gulf of Mexico is one of the most productive hydrocarbon-generating basins, producing ~3% of the world's Jurassic-age petroleum reserves (Heydari, 1997). The upper sequences act as reservoir rocks as they have higher porosities and mitigate the storage and migration of the hydrocarbons (Tew, 1993). The Smackover is underlain by the Norphlet Formation and the Louann Salt. The Norphlet Formation is primarily sandstone and conglomerate (Heydari, 1997). The Louann Salt is an evaporite formation that may serve as a trap for the local accumulation of migrating hydrocarbon in the surrounding domed-up sedimentary rocks. Overlaying the Smackover is the Buckner Anhydrite which acts as a low permeability seal rock for hydrocarbons that move through the Smackover (Kopaska-Merkel et.al, 1993). The depth of the Smackover in southwest Alabama ranges approximately from 11,000 to 12,000 feet.

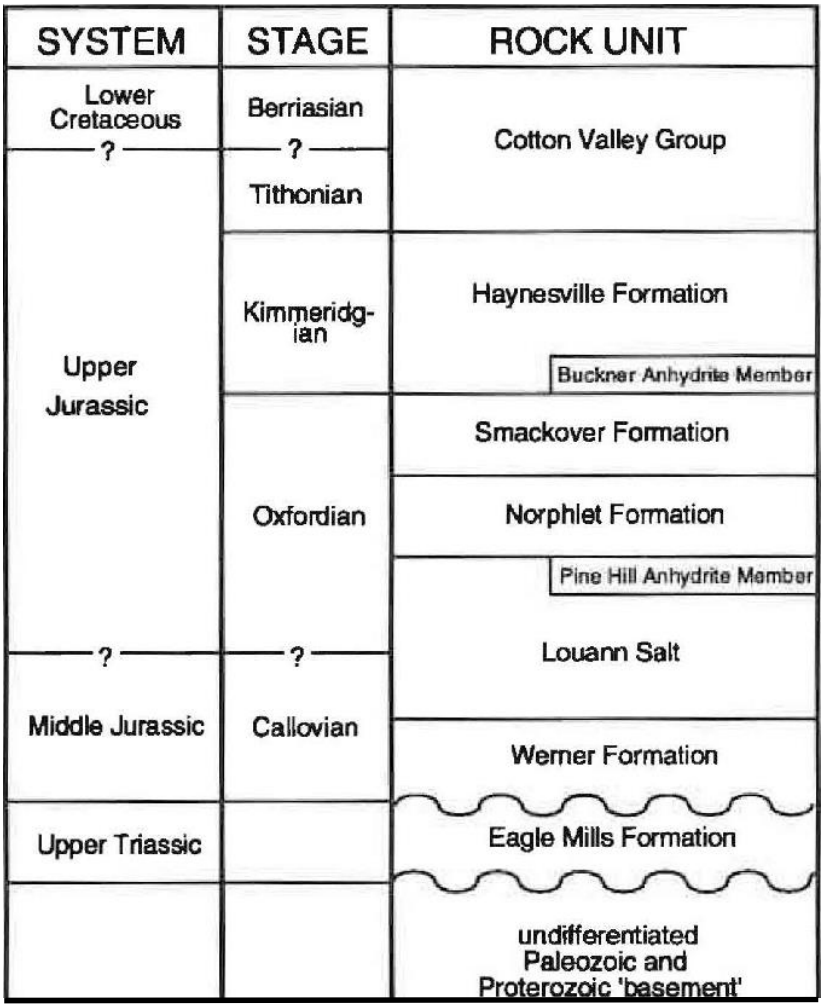


Figure 4: Stratigraphic column of Southwest Alabama (Kopaska-Merkel, 2020)

Pre-Triassic tectonics associated with the formation of the Gulf of Mexico is responsible for creating potential water transport pathways through the basin's stratigraphy and structure. Granitic pegmatites are considered one of the highest-producing sources of lithium and could be responsible for the high lithium concentrations present in the brine as Permian age granitic basement rocks containing minerals such as biotite, feldspars, and muscovite that lays at a depth beneath the Smackover Formation (Jancsek, 2023). Crustal extension formed the horst graben structures in the Pre-Triassic (Permian) basement. As the Louann Salt was deposited in the basin,

it filled in the voids of the horst-graben structures. Jurassic sediments overlaid the Louann Salt as the basin continued to spread apart (Hudec, 2013). There are regional fault systems associated with Gulf of Mexico tectonics. In our study area, the northern boundary of the basin bounds the Smackover Formation and the peripheral fault system bounds the up-dip limit of the Louann Salt (Figure 1). The peripheral fault system includes the Pickens-Gilbertown, West Bend, and Pollard-Foshee fault systems. These fault systems are likely the result of the Cretaceous age movement from the Louann Salt (Macini, 1987). The two main embayments in our study area, the Manila and Conecuh, opened beyond this fault system.

Geochemical and Hydrologic Processes

Several geochemical processes have been identified in influencing the geochemistry of the Smackover Formation brine. Available brine geochemistry data from the USGS Produced Waters Database (Siefert et. al, 2022) suggest that brine samples from the Smackover Formation contain significantly higher proportions of chloride, sodium, and calcium (Figures 5-6). The bulk geochemistry of the Smackover Formation brines shows notable deviation from that of seawater or seawater evaporation trajectory (Figure 5). Water rock interaction, mixing of different types of waters, and sulfate reduction have been considered as the primary processes influencing water chemistry beyond evaporation. The Smackover Formation has characteristically high concentrations of H_2S and low concentrations of metals (Kharaka, 1984). Sulfate likely derived from evaporated seawater or anhydrite-, gypsum-, and epsomite-rich evaporites, which could be used in the sulfate reduction process (as an electron acceptor) to produce high concentrations of H_2S seen in some areas of the Smackover Formation (Moldovanyi et. al, 1993; Heydari, 1997). The original seawater or evaporated seawater bearing high magnesium concentrations in the form of magnesium chloride (Figure 5) may react with the limestone to drive dolomitization. The

calcium released during dolomitization may produce the Na-Cl-Ca dominant hydrochemical facies (Figure 5), or undergo cation exchange with the lithium or sodium in the clay minerals of the Triassic granitic basement rock (Collins, 1976). Other alkali elements present in high concentrations include rubidium, potassium, and cesium. Interestingly, H_2S-rich waters tend to have higher concentrations of alkali elements in comparison to H_2S-poor waters in the Smackover Formation (Moldovanyi et. al., 1993).

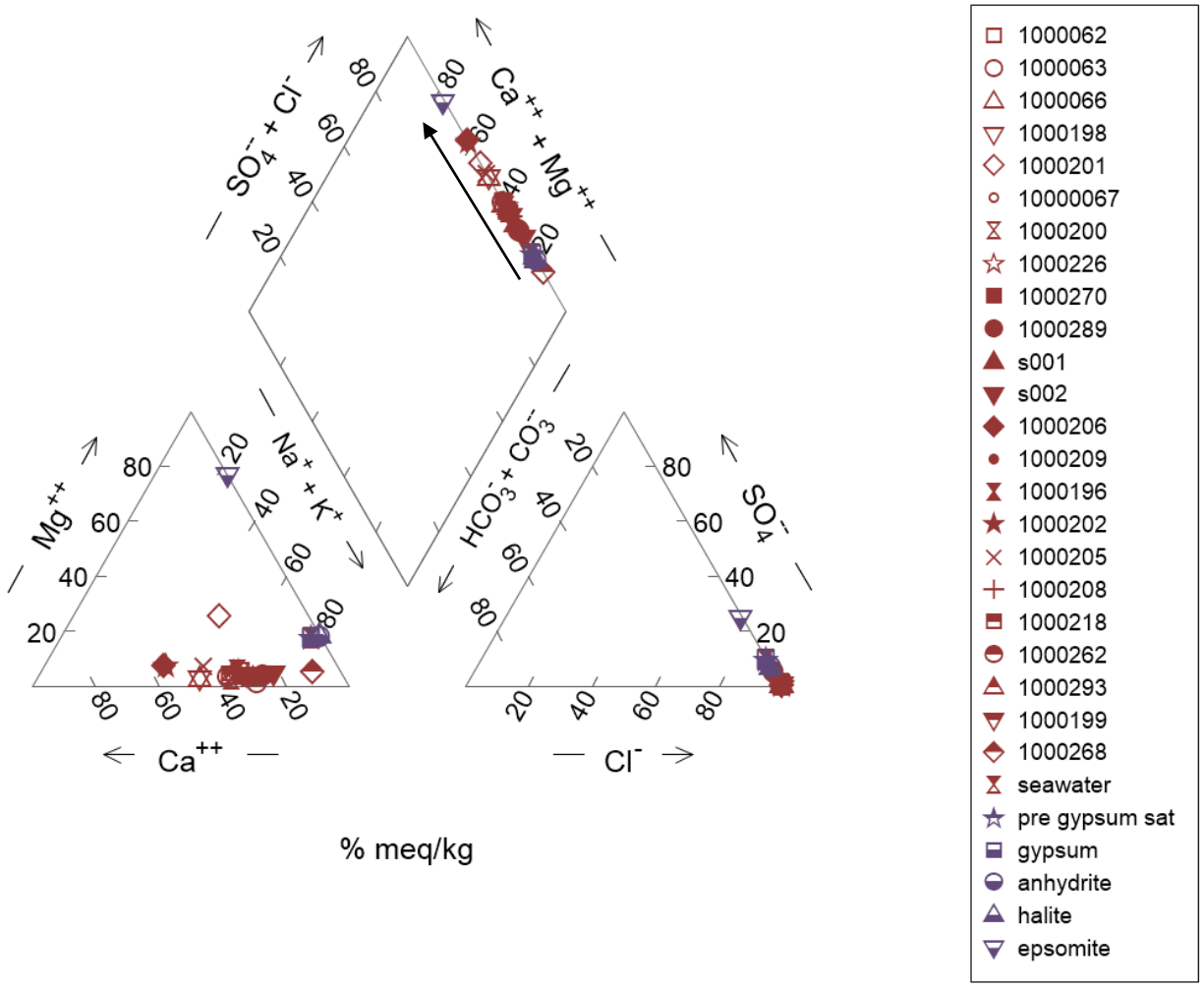
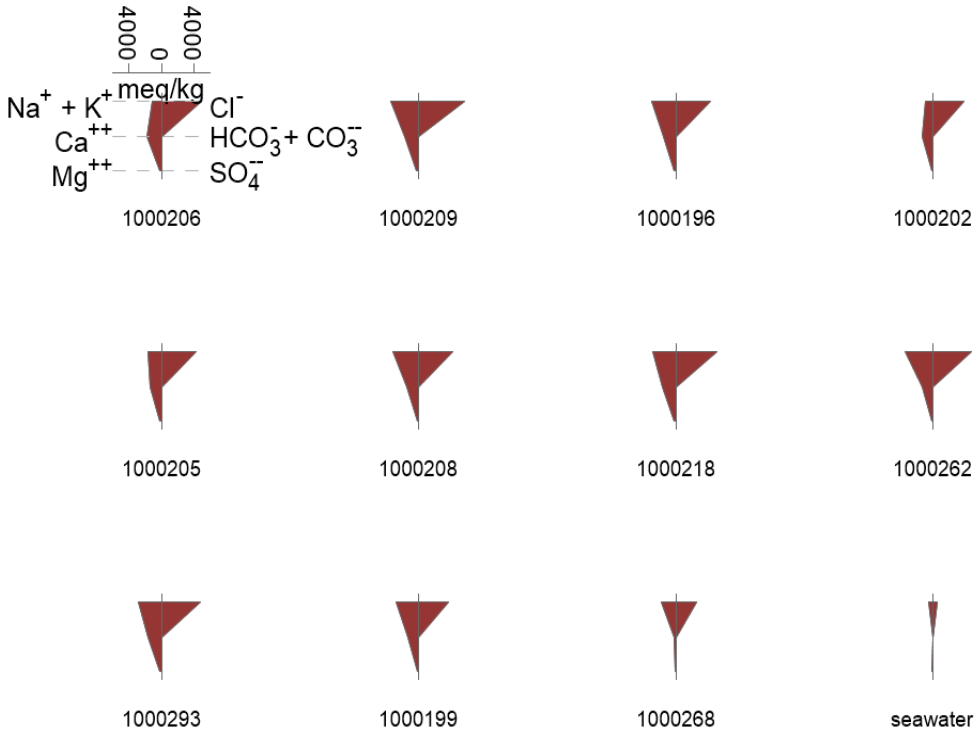


Figure 5: Piper diagram of sampled USGS wells (with sample IDs), seawater, and evaporated seawater reaching saturation with respect to gypsum, anhydrite, halite, and epsomite ($MgSO_4 \cdot 7H_2O$). The arrow indicates the theoretical evaporation geochemical trajectory calculated by the Geochemist's Workbench.



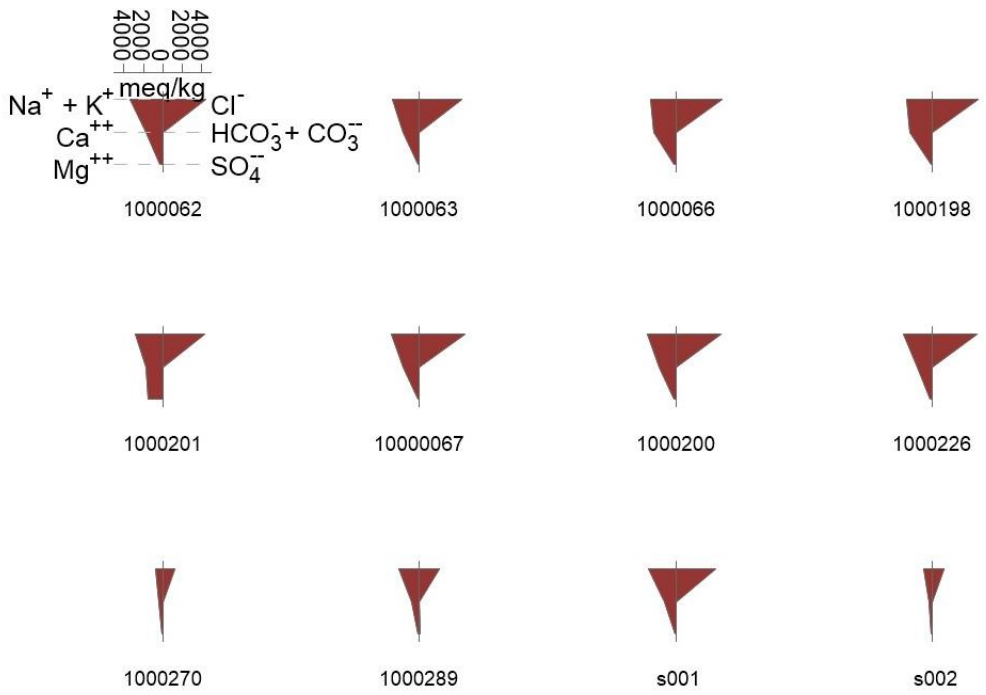


Figure 6: Stiff diagrams of sampled USGS wells with sample IDs

Tectonics and faulting associated with dome-up movement of Louann Salt might provide a possible pathway for brine migration and transport of trace elements. The widespread presence of overpressure in the deep Gulf of Mexico basin sediments may drive brines toward shallow sediment under hydrostatic conditions (Harrison and Summa, 1991). These present-day overpressure conditions arose from periods of increasing sediment accumulation basinward where the overpressured zones expanded with the influx of sediments deposited in the basin and eventually restricted basinward meteoric water movement to the area (Harrison and Summa, 1991). Hansom and Lee (2005) conducted numerical simulations to investigate various mechanisms responsible for overpressure development and maintenance in various hydrogeologic environments. The distribution of overpressure is an important consideration because it can influence the flow paths of hydrocarbon and basin brines (Hansom and Lee,

2005). Numerical modeling (e.g., Evans and Nunn, 1989; Evans et al., 1991; Canova et al., 2018) also indicated possible thermohaline convection of brine near salt domes that facilitates upward advection of deep basin fluids along the salt flank and associated structure.

Brines from the Arkansas Smackover Formation had a range of 3.9 to 6.9 ‰ for $\delta^{18}O$ and -22 to -6‰ $\delta^{2}H$ relative to SMOW (Moldovanyi et. al, 1993). This range indicates some sort of mixing, but the extent of mixing and the source of salinity remain poorly understood. Strontium isotopic ratios of 0.7071 to 0.7101 have been reported for brines in the upper Smackover Formation in southern Arkansas (Stueber, 1984). This is indicative of the mixing of basin fluid that has interacted with silicate minerals and differs from the ratio range for Jurassic seawater (0.7068-0.7072) (Steuber, 1984). Lithium isotopic ratios can also be used as a tracer of brine origin. Waters draining from igneous rock sources tend to have higher $\delta^{6}Li$ ratios (-5.5 to -11.8 ‰) than from marine evaporites (-20 to -22‰), carbonates (-26 to -32‰), silicates (-6 to -28 ‰), and from the mean seawater value (-32.3‰) (Huh et. Al, 1998). Repetitive seawater evaporation, the dissolution of evaporites, or the mixing of different types of waters will each have their own unique isotopic signatures. Sampling in the embayments just past the up-dip limit of the Louann Salt in the study area would be an indicator that the brine geochemical composition is impacted by migration pathways made by the fault system.

Objectives

The main objectives of this project are to 1) characterize the major ion, trace element, and isotopic (O, H, Sr) compositions of brines, 2) determine the potential sources of salinity in brines, and 3) identify potential water-rock interaction and fluid mixing that may influence brine geochemistry. These objectives will help fill the knowledge gaps in the study area and address societal concerns about the potential environmental pollution of produced water and the

economic recovery of lithium and bromide. Oxygen, strontium, and hydrogen isotope analysis will give insight into the hydrogeological processes that produced the source of salinity and the potential water-rock interaction and nature of mixing of the deep-circulating water.

Materials and Methods

Sampling Sites and Brine Collection Processes

Brine samples were sampled from 8 Smackover production wells in Southwest Alabama (Figure 7). The sampling target eight wells with a range of levels of alkali elements (Li, Na, K, etc.) and Br. Kharaka et.al (1987) and Lico et.al (1982) provided methods for the collection and preservation of brine for geochemical analysis. It is essential that field samples are prepared in a way that prevents contamination. Ideally, samples should be taken close to the wellhead to avoid corrosion inhibitors and the potential precipitation of metal oxyhydroxides and carbonates in or downline the separator. PVC tubing connects the wellhead to a carboy or similar container with a spigot at the bottom. Tubing is attached to the wellhead and flushed before connection to the carboy. According to the EPA (Vail, 2013), adequate purging of the well should be carried out by pumping two to three times the volume of the well. For this study, samples were collected from storage tank facilities, instead of wellhead at well sites, thus redox- and temperature-sensitive water quality parameters such as oxidation-reduction potential (ORP) and dissolved oxygen cannot be not measured in the field. Any container filled with samples were rinsed twice or more times with the sample. Samples completely filled their containers and were kept in a dry refrigerated environment to prevent evaporation. Water quality parameters such as H_2S, alkalinity, and pH were measured in Geoscience laboratories at Auburn University. Due to oxidation during the storage stage in tanks at well sites, the H_2S measured values in the lab only represent the minimum levels in the Smackover Formation. Total dissolved solids (TDS) and

specific gravity were measured at the USGS BRInE Laboratory. The samples for trace element analysis were filtered 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 dry from positive-filtered airflow (Lico, 1982; Ball, 1980). Filtration through a 0.45 µm filter may also be run to ensure oil and like particles are removed from the sample (Lico, 1982).

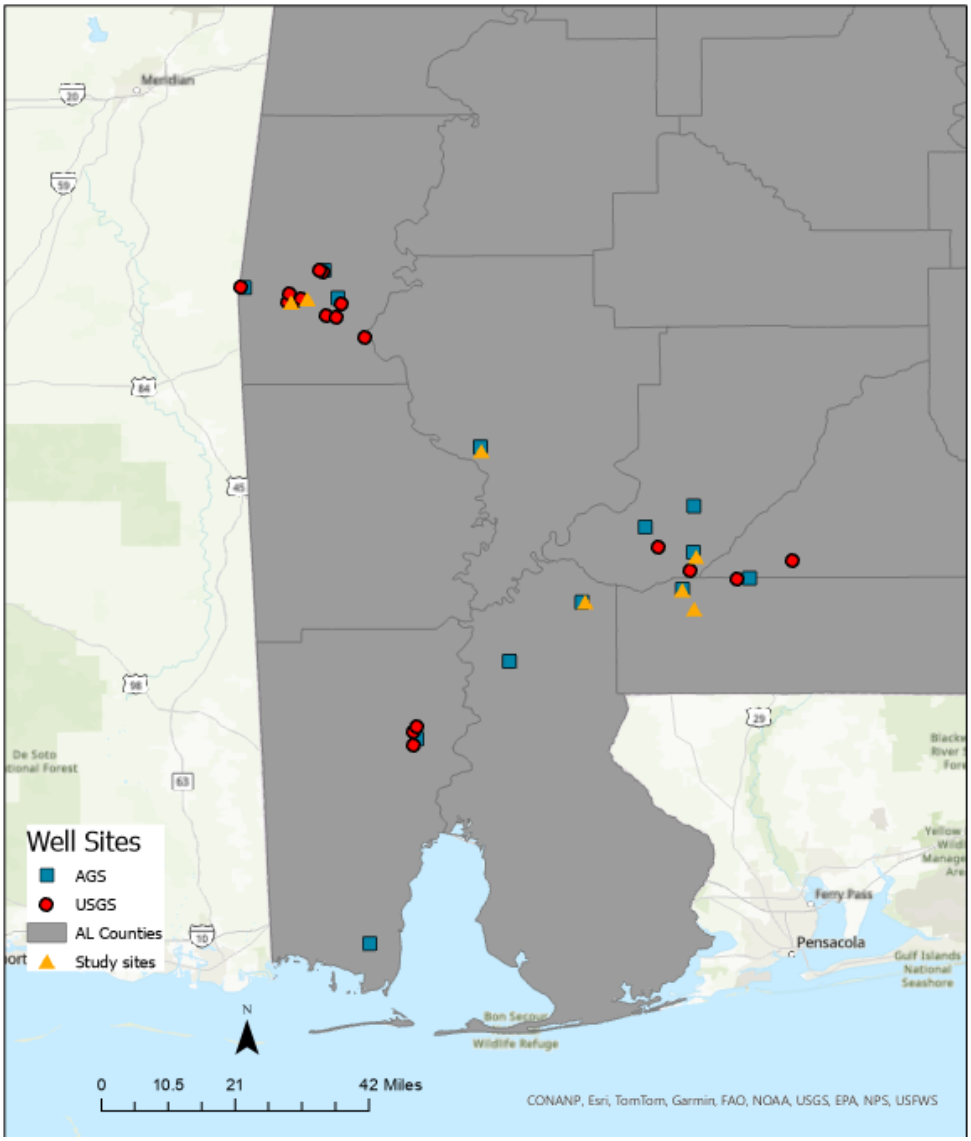


Figure 7: Well site locations for sampling Smackover brines (Alabama Geographic Information Office 2016; Siefert et. al, 2022; Guthrie, 2020)

Oxygen and Hydrogen Stable Isotope Analysis

Stable isotope ratios of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) of eight brines and twenty rainwater samples were measured using a standard CO_2 and H_2-water equilibrium method (Hilkert et al. 2001; Dubr et al. 2001) at the National High Magnetic Field Laboratory at Florida State University. Rainwater samples were collected seasonally from February to December in Auburn, Alabama, using a rain gauge. These samples were stored and refrigerated in 60 mL Nalgene bottles until analysis. 0.5 mL of water samples and standards are injected into small glass vials that hold 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 (Finnigan GasBench II) into a Finnigan MAT Delta Plus XP stable isotope ratio mass spectrometer (IRMS) for hydrogen isotope analysis. For oxygen analysis, 0.3% CO_2 in He was used as the equilibration gas (Horita, 1988). Oxygen isotope measurements were carried out after an equilibration time of 24 hours at 25°C. Isotopic composition is expressed as per mil deviation from the Vienna Standard Mean Ocean Water (VSMOW) standard (Kendall and McDonell, 1998):

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

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

Alkalinity and Hydrogen Sulfide Analysis

The HACH digital titrator test kit was used to measure the alkalinity using the titration method (USEPA Method 8203). 4500-S2-D Methylene Blue Method (*Standard Methods For the Examination of Water and Wastewater*) was used to measure hydrogen sulfide concentrations with the HACH 1900 Series portable photo spectrometer. The instrument was calibrated using solutions of varying concentrations between 0-100 mg/L. R^2 of the five-point calibration curve was 0.9916. To preserve the total sulfide concentration of samples in the field, 1 mL of 1M zinc acetate was added to the sample vessels prior to sampling. In the field, 25mL of sample was added to the vessel. Using drops of 1M KOH, the pH was adjusted to approximately 9. In the laboratory, the liquid above the precipitate was removed and replaced with DI water. 5 mL of dimethyl-p-phenylenediamine reagent and 1 mL of ferric chloride were added quickly in succession. After thirty minutes, the samples were taken to the photo spectrometer. At a wavelength of 670nm, the instrument measured at least 10 mL of each sample.

Cation and Trace Element Analysis

Cation and trace element concentrations of brine samples were measured using an Agilent 7900 quadrupole inductively coupled plasma mass spectrometry (ICP-MS) at Auburn University and an inductively coupled plasma optical emission spectrometry (ICP-OES) at the USGS BRInE Laboratory following the same sample preparation procedure. Brine samples were first filtered with vacuum assistance through 1.0 µm and 0.45 µm filters. 120 µL of 70% HNO_3 was added to 60 mL of the filtered sample for acidification to 2%. Samples must be acidified in order to preserve trace metals for ICP analysis (Papas, R.S., 2012).

Microwave digestion (EPA method 3015a) was conducted before ICP-MS analysis to remove any oil or other related impurities present in the samples. One set of vessels contained 10 mL of unacidified unfiltered sample, 35 mL DI water, and 5 mL 70% HNO_3 (diluted 5x). The

other set contained 10 mL of filtered and 2% acidified sample, 35 mL DI water, and 5 mL 70% HNO_3 (diluted 5x). 2 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 50x to ensure they would be within the calibration range of ICP-MS and minimize atomic interference.

Lithium and strontium have ICP-MS detection limits of 0.189 µg/L and 0.004 µg/L, respectively (PerkinElmer Inc., 2017). Calibration standards for ICP-MS analysis included the environmental calibration standard, Indium as an internal verification standard mixed with a T connector, and an added standard for lithium. Atomic interference issues can occur while analyzing bromine because its mass/charge ratio can be produced by isotopes of other elements or polyatomic ions. ICP-OES is an alternative method largely free of atomic interference that may more accurately measure trace elements in the sample without much dilution. The detection limit of ICP-OES (in the range of mg/L) is lower than that of ICP-MS (in the range of nano-µg/L).

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. The main challenge surrounding the use of TIMS to analyze oilfield brine is the high oil content (~10% in the Smackover samples analyzed). To remove the oil, the brine can either A. be centrifuged, B. be chemically removed, or C. be burned off at a high temperature.

Sr contents in crude oils usually range from 9 ppb to 33 ppb (Yasnygina et al., 2015) whereas Sr contents in brines from this study are more than 1040 ppm (Table 1 and Table 2). In this case, typical hydrocarbons do not contain a significant amount of strontium, relative to the samples, and thus the oil does not have to be removed for Sr isotope analysis. 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% 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 HNO_3. Eichrom Sr-Spec resins were used for separation of Sr by liquid chromatography in micro-columns. Purified Sr separates were loaded to degassed tungsten filaments. Sr isotopic ratios were measured by a dynamic multi-collector mode. Sr isotopic compositions were normalized to $^{86}Sr/^{88}Sr=0.1194$. Measured $^{87}Sr/^{86}Sr$ values are 0.710251±11 for Sr standard NBS 987 and 0.705003±9 for rock standard BCR-2. More analytical details have been documented in Ozdamar et al. (2024).

Anion Analysis

Anions (chloride, bromide, sulfate) of brine samples were measured at the USGS BRInE Laboratory using a Horiba Ultima Expert ICP-OES. A batch of 35mL of each unacidified sample was created for anion analysis by filtering with vacuum assistance through 0.45 µm and 1.0 µm filters. For anion chromatography, a small sample volume is passed through the positively charged resin in the column where the anions are separated and measured (Ptaf, 1996).

Geochemical Modeling

Geochemist's Workbench (Bethke, 2008) was used to 1) construct the hydrochemical facies, 2) calculate the saturation index of key evaporite and sulfate minerals in the Alabama Smackover Formation brines analyzed in this study, as well as those available from the USGS Produced Waters Database (Siefert et. al, 2022). Hydrochemical facies reflect fluid mixing, the consequence of water-rock interaction within the lithologic framework, and spatial variations in brine geochemistry. The saturation state of minerals would reveal the dominant solid phases in the brines and identify potential water-rock interaction and fluid mixing that influences the geochemistry of the brine. A simulation of seawater evaporation was also 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 is compared to those of Smackover Formation brines. The Pitzer equations and activity model available in GWB was used to calculate activity coefficients in concentrated brines with high ionic strength.

Results and Discussion

Major Ion and Trace Element Composition

Table 1 shows pH, concentrations of hydrogen sulfide, total dissolved solids (TDS), and specific gravity of brines measured in the laboratory. The brines sampled have acidic to slightly acidic pH values (5.44-6.20). Hydrogen sulfide concentration in these brines ranges from nearly 0 to more than 100 mg/L. TDS of brines ranges from 162,000 to 308,000 mg/L and specific gravity varies between 1.108 to 1.218. Zero Phenolphthalein and Bromcresol Green-Methyl alkalinity values mean there are no carbonates (CO_3^{2-} or HCO_3^-) present in Cl-dominated brines with elevated salinity.

Well Name	Sample #	pH	Sulfide concentration (mg/L)	δD, ‰	$\delta^{18}O$, ‰	87Sr/86Sr	TDS (mg/L)	Specific Gravity
Jimmerson #4-6	1	5.49	>100	4.5	3.3	0.707403	298000	1.212
Bollinger 25-9 #1	2	6.14	5.16	-7.2	0.1	0.708251	222000	1.145
Tims 8-2 #1	3	6.2	45.6	-10.3	-1.0	0.708349	162000	1.109
International Paper Company 20-9 #1	4	5.44	0	1.7	2.1	0.708210	308000	1.218
Blackstone Callon 9-9 #2	5	5.37	1.05	3.7	0.9	0.708603	271000	1.206
Coffin 14-10 #1	6	5.66	54.51	-7.6	0.0	0.708438	240000	1.16

Grissett 36-16 #1	7	5.63	5.16	-4.6	-1.0	0.710026	281000	1.164
Cox 5-10 #1	8	5.77	0.498	-7.6	1.6	0.708483	229000	1.182

Table 1: Brine water quality measurements and O, H, and Sr isotope compositions. Measured alkalinity values are zero for all samples analyzed.

The results of IC analysis of anions and ICP-MS and ICP-OES analysis of cations are shown in Tables 2 and 3. The Piper diagram (Figure 8) shows that the brines analyzed are mainly a Na-Cl-Ca type water with elevated concentrations of Cl^- (94,600-190,000 mg/L), Na^+ (32,200-73,300 mg/L), and Ca^{2+} (14,000- 48,200 mg/L) significantly higher than those in seawater (Cl^- = 19,000 mg/L; Na^+ = 10,600 mg/L, Ca^{2+} = 400 mg/L.) These hydrochemical facies are similar to those from the USGS Produced Waters Database (Figure 5). Water-rock interaction such as dolomitization could add Ca^{2+} to the solution. That Ca^{2+} may be used in the precipitation of gypsum that removes both Ca^{2+} and SO_4^{2-} from the solution. Brines are also enriched in Br (831-5,700+ mg/L), Sr (1,045-2,381 mg/L), Li (19.34-70.65 mg/L), and Ba (1.77-147.84 mg/L). The level of regulated trace elements (e.g., As, Cr, Cd are low in the brines analyzed (Table 2).

Well Name	Sample #	Li (mg/L)	Na (mg/L)	Mg (mg/L)	K (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)	Zn (mg/L)	Sr (mg/L)	Ba (mg/L)	Cr (µg/L)	Cu (µg/L)	Cd (mg/L)	Co (µg/L)	As (µg/L)
Jimmerson #4-6	11	44.76	72572	4076	3687	33708	4.11	1.00	0.06	1868	1.77	15.43	6.39	0.00	0.10	0.54
Bollinger 25-9 #1	12	31.58	45726	2230	4540	22693	55.55	22.60	10.21	1438	18.10	5.24	26.73	0.05	_	0.22
Tims 8-2 #1	13	19.34	39187	1431	3105	13990	31.65	28.30	5.27	1046	20.25	4.82	14.95	0.02	0.15	1.21
International Paper Company 20-9 #1	14	74.48	73980	1956	6745	33758	64.86	48.70	36.07	2286	147.84	8.36	46.28	0.24	0.23	0.56
Blackstone Callon 9-9 #2	15	70.65	71136	1897	6707	31966	173.70	189.09	38.02	2382	134.46	8.11	28.06	0.20	0.35	9.11
Coffin 14-10 #1	16	55.44	55682	1533	5362	25619	118.35	89.67	33.85	1851	82.02	42.35	15.68	0.18	1.51	1.00
Grissett 36-16 #1	17	43.39	31035	2866	2296	44464	151.00	28.28	12.21	2114	119.27	14.32	11.61	0.17	0.33	0.46
Cox 5-10 #1	18	65.41	66110	1815	6115	29771	155.80	100.41	26.69	2193	97.07	7.39	23.09	0.13	_	0.85

Table 2: ICP-MS analysis of cation and trace element concentrations in brines.

Well Name	Sample #	Br mg/L	Cl mg/L	SO4 mg/L	B mg/L	Ba mg/L	Ca mg/L	Fe mg/L	K mg/L	Li mg/L	Mg mg/L	Mn mg/L	Na mg/L	Si mg/L	Sr mg/L
Jimmerson #4-6	1	1900	190000	184	210	<157	32800	<157	3370	47.3	3940	<15.6	73100	<17.5	1740
Bollinger 25-9 #1	2	1220	125000	85.1	149	<126	24300	<126	4530	34.5	2290	55.8	47100	<14	1460
Tims 8-2 #1	3	831	94600	46.7	89.5	<84.1	14000	<84.3	3000	18.8	1350	30.7	39300	<9.37	1040
International Paper Company 20-9 #1	4	2180	190000	<36	273	<157	31000	<157	6350	72.2	1780	59.7	73300	<17.5	2150
Blackstone Callon 9-9 #2	5	2250	181000	70.8	251	<140	31200	172	6340	67.2	1770	166	70000	<15.6	2300
Coffin 14-10 #1	6	1710	138000	59.3	207	<126	24700	<126	5270	54	1420	111	55500	<14	1770
Grissett 36-16 #1	7	1970	159000	54	227	<157	26800	<157	5640	59.7	1560	140	63700	<17.5	2030
Cox 5-10 #1	8	>5700	137000	<28	102	<126	48200	<126	2090	49.3	2970	162	32200	<14	2230

Table 3: IC analysis of anion and ICP-OES analysis of cation and trace element concentrations of brine samples.

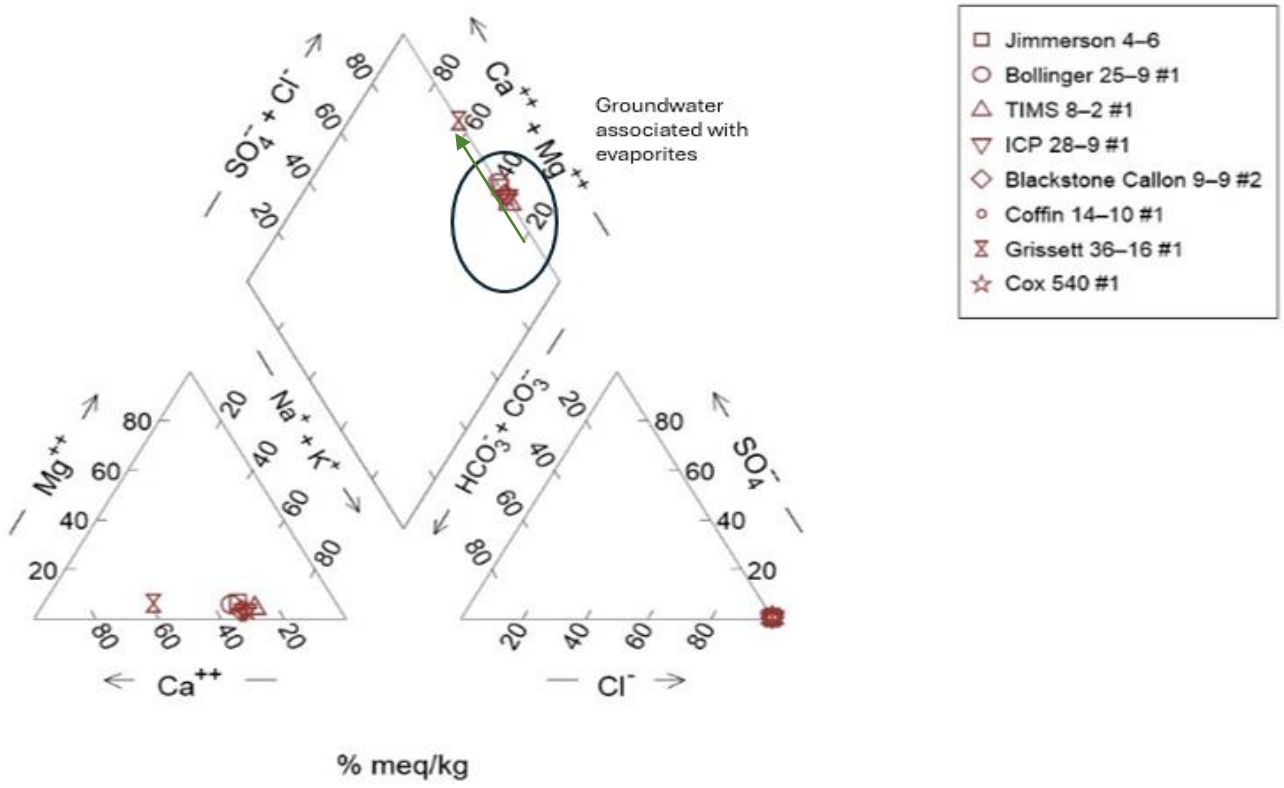


Figure 8: Piper plot of sampled brines

A Gibbs diagram (Figure 9) was also constructed to further understand how fluid mixing and water-rock interaction may affect the geochemical evolution of the brines. Brine data falls in the area of the plot with higher TDS and lower Na/(Na+Ca) values than seawater. Evaporation and water-rock interactions are the primary evolution processes that create this distinction between the chemistry of the brines, seawater, and surface water in this plot. Evaporation or mixing groundwater with higher salinities would cause the shift of surface water or freshwater groundwater towards the upper right corner of the Gibbs Diagram. The shift from precipitation to seawater to brine could be due to the mixing of meteoric water with Jurassic seawater,

evaporated seawater,or by the dissolution of evaporite minerals in meteoric water (Marandi and Shand, 2018). Different extent of interaction of brines with carbonate minerals may explain the wide range and relatively lower ratios of Na/(Na+Ca) relative to seawater. For example, the dolomitization process would lead to higher Ca concentration in brines:

$$2\ CaCO_3 + Mg^{2+} \Leftrightarrow CaMg(CO_3)_2 + Ca^{2+} \quad (2)$$

The Gibbs diagram was originally intended for surface-water interactions, so interpretations of this diagram for groundwater processes need to be sufficiently supported with other chemical elements (K^+, SO_4^{2-}, etc.).

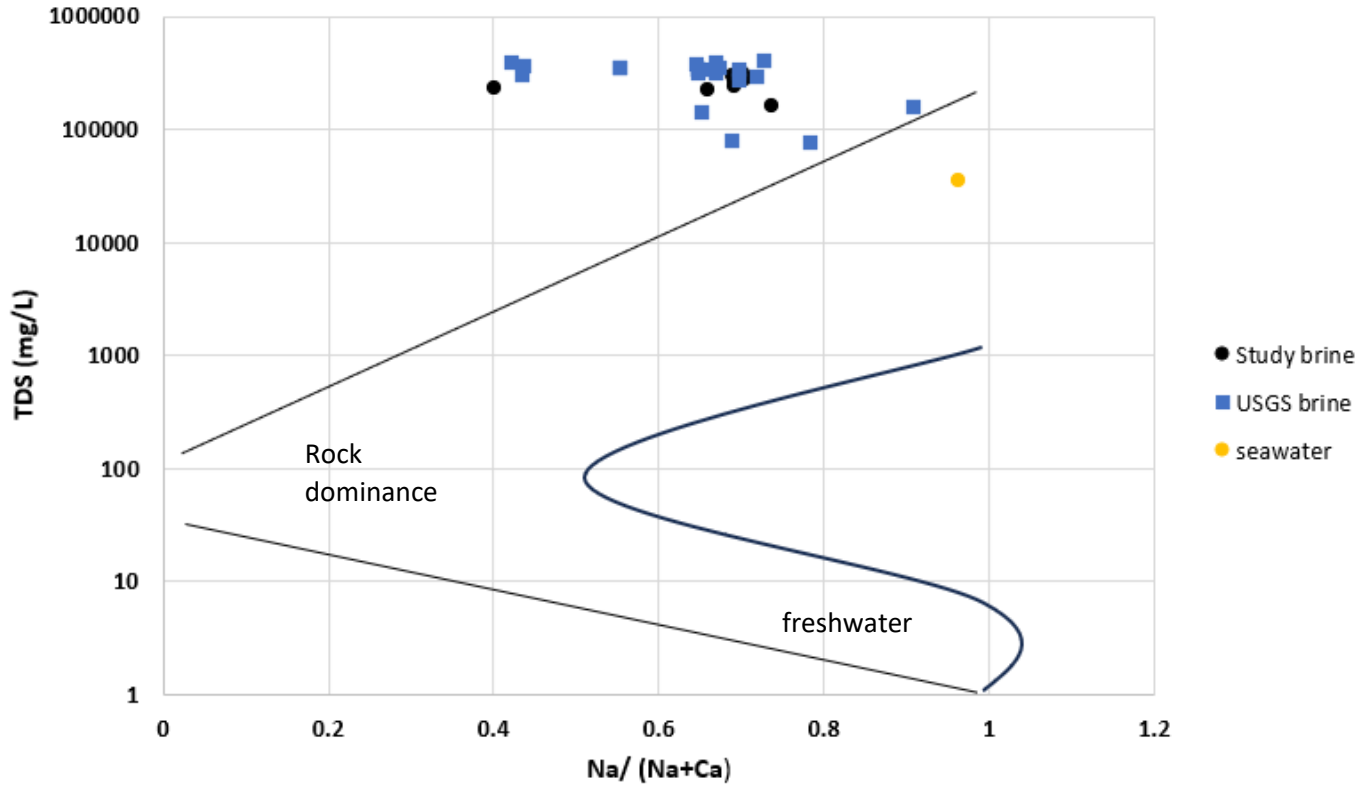


Figure 9: Gibbs (1970) diagram of Smackover Formation brines and seawater.

Cl/Br and Cation/Br ratios

Since various natural waters exhibit different cation-Br ratios (Stueber and Walter, 1991; Davis et al., 1998; Penny et. al, 2003), significant shifts of the ratios from the seawater evaporation trend would indicate the source of salinity in Na-Cl-dominated brines (Figures 10-12). The seawater evaporation trend (Carpenter, 1978) reveals that the Cl/Br ratios remain constant during seawater evaporation. The ratio of Cl to Br decreases in the solution after halite precipitation (Figure 10). Cl is removed, while Br is not removed in the precipitation of halite in this system, leading to the decreasing Cl/Br ratios in the remaining solution. Samples with higher Cl/Br ratios would plot to the left of the curve and would be indicative of halite dissolution because Cl would be readded back into the solution. The Smackover Formation brine samples analyzed in this study have lower Cl/Br ratios (ranging from 24.04- 113.84) and Na/ Br ratios (ranging from 5.65-47.29) than those of seawater and plot to the right of the seawater evaporation trajectory (Figure 10-11), indicating that brines acquired salinity from mixing with evaporated seawater reaching halite precipitation, instead of dissolution of halite. Therefore, it is unlikely that the source of salinity would be derived from the dissolution of halite associated with Louann Salt. The K/Br ratios also plot to the right of the seawater evaporation trajectory (Figure 12), indicating significant loss of K via water-rock interaction. Loss of K in evaporated seawater or brines may be attributed to the diagenetic precipitation of K-rich clays (e.g., illite) from kaolinite or the formation of K-feldspar from Na-rich albite or plagioclase feldspar (Carpenter, 1978; Land, 1987; Egeberg and Aagaard, 1989; Stueber and Walter, 1991). Moreover, the oxygen and hydrogen isotopic signatures (see section below) indicate different degrees of mixing of this evaporated seawater endmember (mostly likely reaching halite saturation) with infiltrating meteoric water under some influence of water-rock interaction.

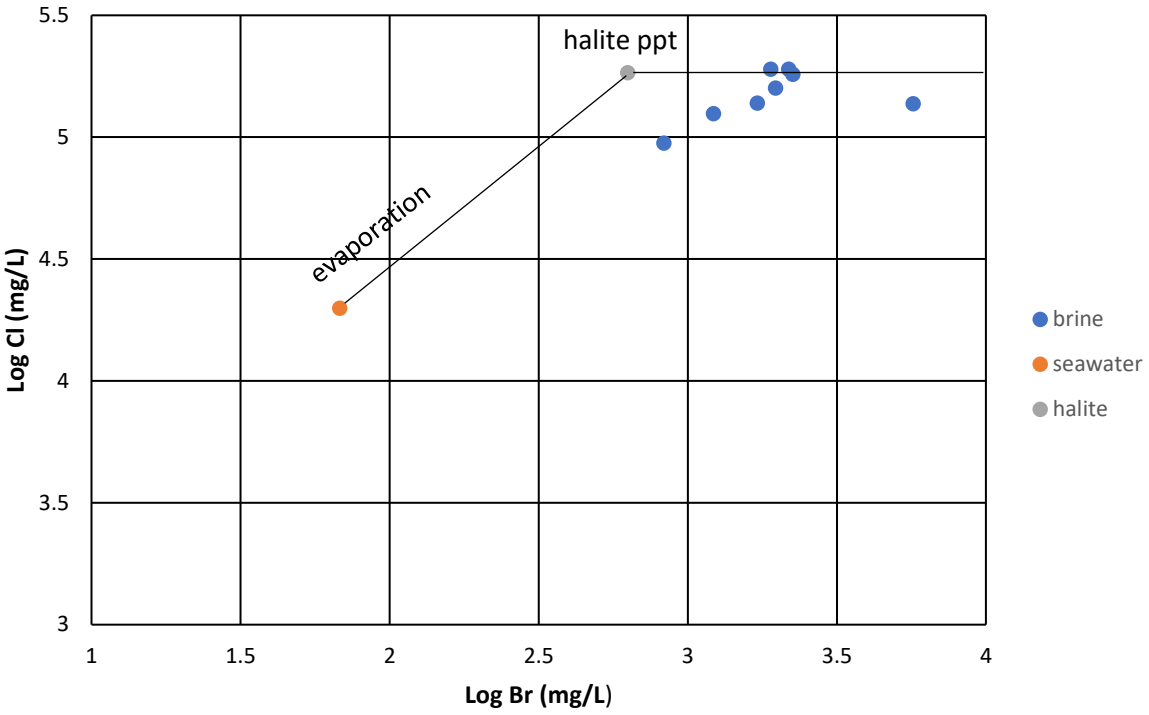


Figure 10: Cl-Br relation for sampled brines. All shown are concentrations for seawater, evaporation trajectory, and halite saturation (Carpenter, 1978), (Stueber et. al, 1984)

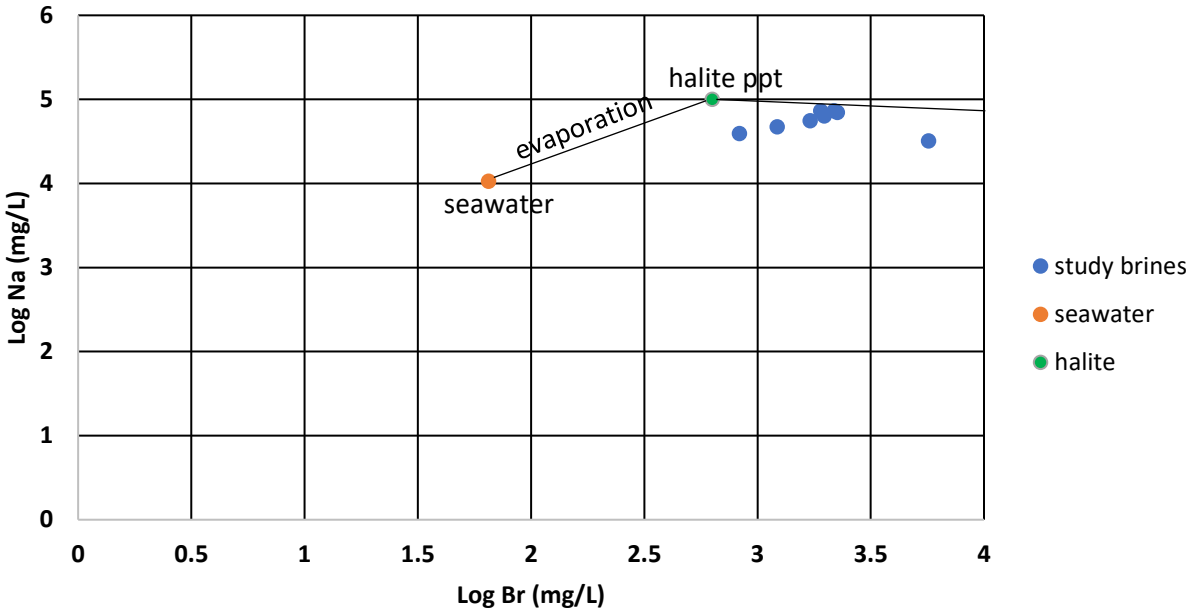


Figure 11: Na/ Br relation for sampled brines. All shown are concentrations for seawater, evaporation trajectory, and halite saturation (Carpenter, 1978), (Stueber et. al, 1984)

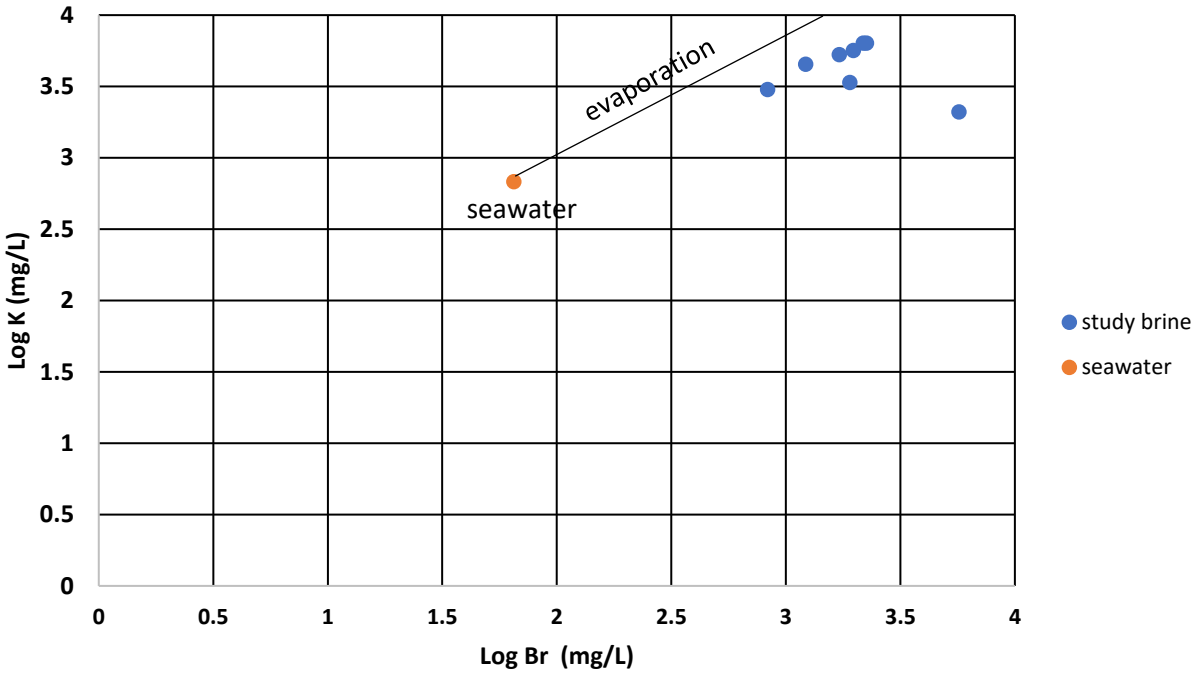


Figure 12: K/Br relation for sampled brines. All shown are concentrations for seawater, evaporation trajectory, and halite saturation (Carpenter, 1978), (Stueber et. al, 1984)

Oxygen and Hydrogen Isotope Ratios

Meteoric Water

Ratios of stable isotopes represent useful indicators of water sources (e.g., meteoric water, seawater, evaporated seawater) and water-rock interaction. The comparison of isotopic signatures of the brines with those of meteoric water, seawater, and evaporated seawater will provide insight into the source of salinity and influence of water-rock interaction. Variations in $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios vary in natural waters due to isotopic fractionation during hydrologic evaporation and condensation (Lambert and Aharon, 2008). Lighter isotopes (i.e., ^{16}O and ^{1}H)

are preferentially held in the vapor phase because they tend to evaporate more readily. This leaves higher proportions of ^{18}O and ^{2}H in the seawater while the vapor becomes more enriched in ^{16}O and ^{1}H. After vapor condensation, the rainwater formed will have heavier isotopic composition than the vapor, but lighter than those of original seawater. Both $\delta\ ^{18}O$ and $\delta^{2}H$ values also change with the seasons (Kopec et. al, 2018), this temperature effect on isotopic fractionation is well demonstrated in our samples as seen in Figures 13 and 14. Our data show that oxygen and hydrogen isotope compositions are less depleted in the summer months (July, August, September) than other seasons, which is consistent with the theory that isotopic fractionation decreases with increasing temperatures. According to Hoefs (2009), the fractionation parameter α is inversely proportional to the square of temperature.

Precipitation Date	**$\delta^{2}H$,‰**	**$\delta^{18}O$, ‰**	**Precipitation amount (in)**
12-Feb-23	-68.6	-10.6	-
17-Feb-23	0.7	-2.3	0.08
10-Mar-23	-17.9	-3.6	0.48
18-Mar-23	-42.7	-7.7	1.08
26-Mar-23	-18.8	-3.6	0.16
8-Apr-23	-28.9	-5.2	0.02
27-Apr-23	-14.5	-3.9	0.04
29-Apr-23	-78.3	-11.6	0.08
18-May-23	-34.8	-6.2	0.09
4-Jun-23	-27.0	-4.5	0.22
14-Jun-23	-24.6	-5.5	1.19

19-Jun-23	-15.7	-3.9	0.18
2-Jul-23	1.6	-1.8	0.03
4-Jul-23	-0.1	-2.0	0.57
21-Jul-23	3.0	-1.2	0.54
3-Aug-23	-9.6	-1.9	-
10-Aug-23	-2.8	-1.7	0.02
11-Oct-23	-71.4	-11.4	-
21-Nov-23	-22.7	-4.9	0.87
9-Dec-23	-32.9	-7.1	-

Table 4: O and H isotope composition of rainwater collected in Auburn, AL, during 2023; analytical precision was ±0.1‰ (1σ) for $\delta^{18}O$ and ±1‰ (1σ) for $\delta^{2}H$. Also shown are corresponding rainfall amount associated with each precipitation event (data from https://www.climate.gov/maps-data/dataset/past-weather-zip-code-data-table)

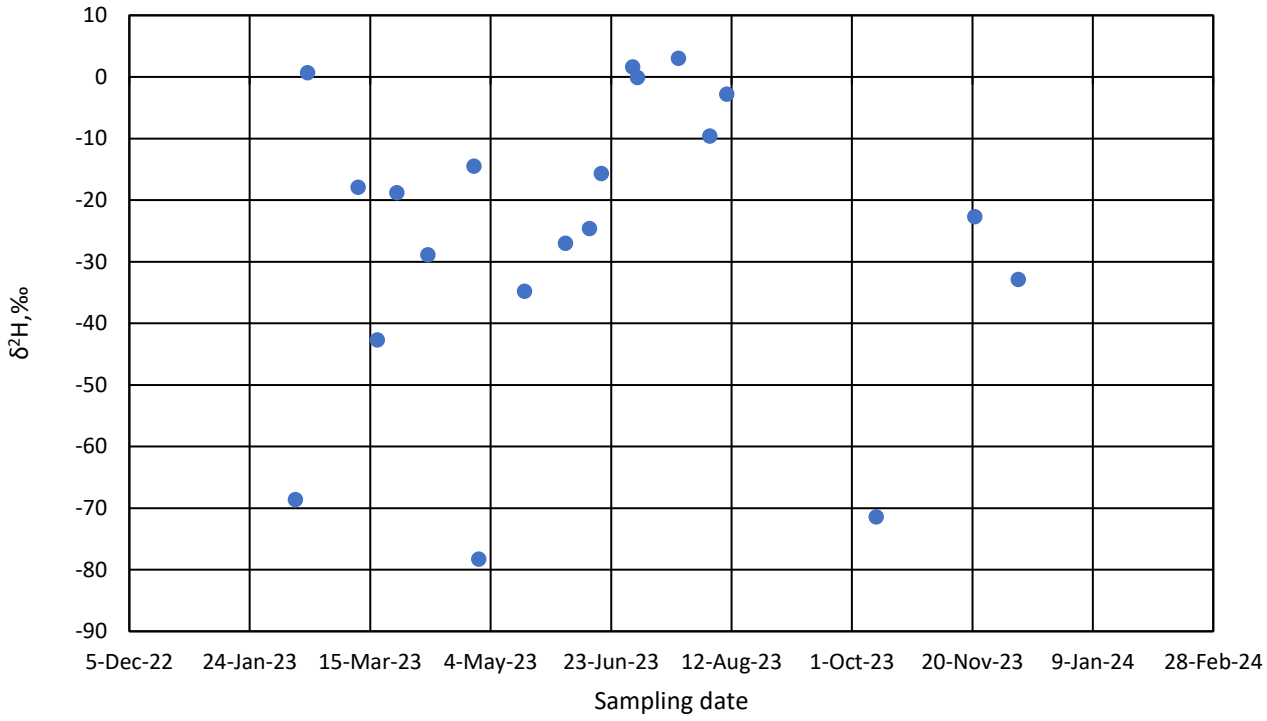


Figure 13: Variation of δ^2H over time during 2023 sampling period. The analytical precision was ± 1 ‰.

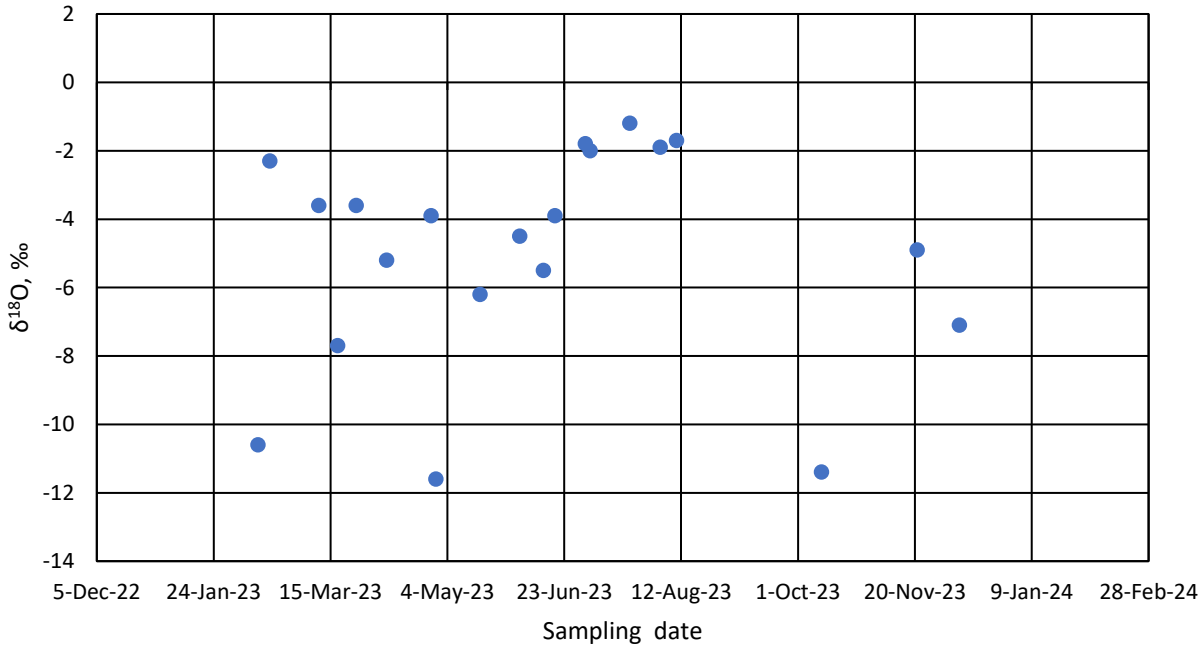


Figure 14: Variation of δ ^{18}O over time during the 2023 sampling period. The analytical precision was ± 0.1 ‰.

The oxygen and hydrogen isotopic composition of rainwater collected in Auburn, AL (Table 3) and those collected in Tuscaloosa, AL (Lambert and Aharanm 2010) were used to construct a local meteoric water line. Figures 15 and 16 show the relationship between oxygen and hydrogen isotope composition of rainwater and the amount of precipitation. Although heavy rainfall associated with major storms tends to have more depletion in heavy isotopes (Lambert and Aharon, 2008), our data show no clear correlations between the rainfall amount and oxygen and hydrogen isotopic composition.

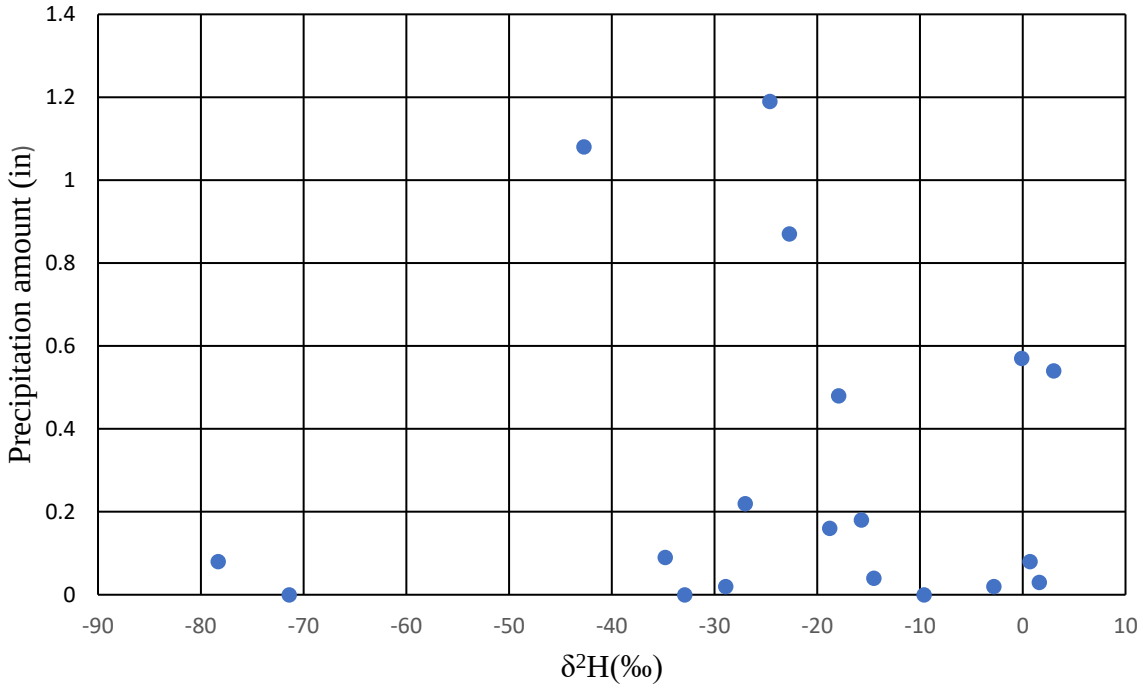


Figure 15: Amount of precipitation vs. δ^2H of rainwater

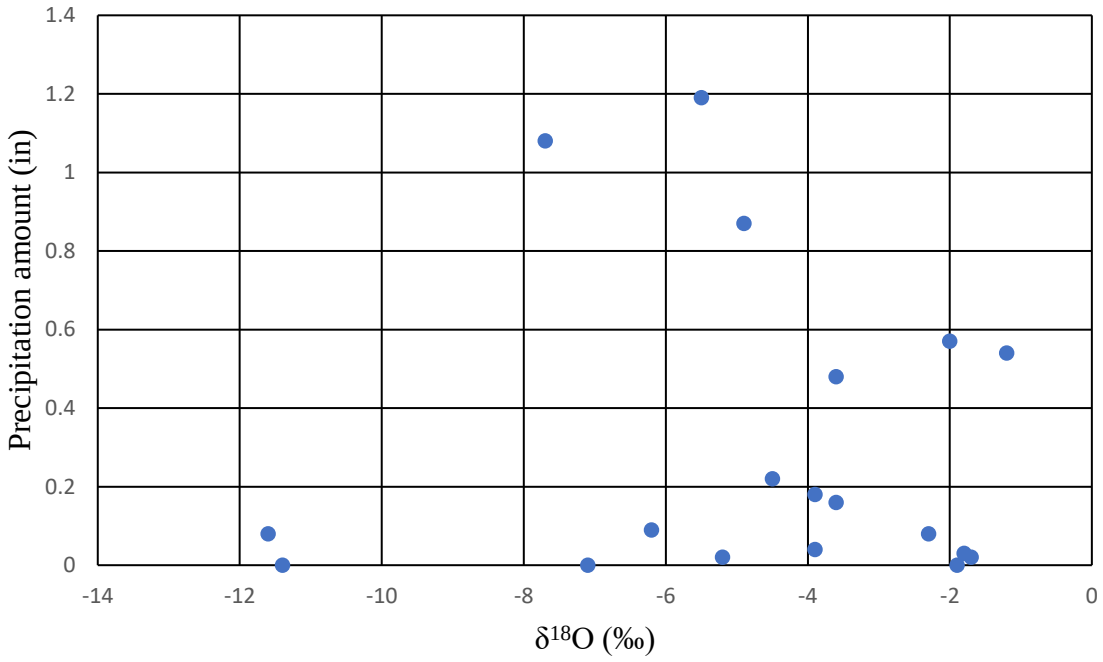


Figure 16: Amount of precipitation vs. $\delta^{18}O$ of rainwater

Brine Water

Ratios of oxygen and hydrogen isotopes of the Alabama Smackover Formation brine (Table 4) relative to seawater (SMOW), the seawater evaporation trajectory line (Holser, 1979), and local meteoric water lines are shown in Figure 17. The average global meteoric water line can be represented by the equation $\delta^2H = 8\ \delta^{18}O + 10$. Most local meteoric water lines have a slope within +/- 0.5 of 8, but slopes between 5-9 are common ("Resources on Isotopes," 2004). The local meteoric water line, calculated as a linear regression on the rainwater data collected in Auburn (this study) and Tuscaloosa, can be expressed by the equation $\delta^2H = 6.2098\ \delta^{18}O + 5.2041$. The "hooked" seawater evaporation curve displays the relationship between oxygen and hydrogen isotopic ratios in seawater as it evaporates to the points of gypsum and halite saturation. The dashed line in Figure 17 represents possible mixing trends between meteoric water and evaporated seawater past the point between gypsum to halite saturation. The isotopic

composition of brines mostly falls along these mixing trends with different proportions of mixing of evaporated seawater and meteoric water. Interaction of brines with isotopically heavy silicate or carbonate minerals may lead to enrichment of $\delta^{18}O$ with little or no changes in $\delta^{2}H$. Thus, the isotopic signatures of the Smackover brine observed may also partly result from water-rock interaction. Previous studies (e.g., Moldovanyi et. al,1993; Kaharka et. al, 1987) also showed that the isotopic composition of the Smackover Formation brines in Arkansas tend to be enriched in $\delta^{18}O$ and depleted in $\delta^{2}H$ relative to seawater, where the brines with little to no H_2S have less enriched $\delta^{18}O$ and more depleted $\delta^{2}H$ values as compared to hydrogen sulfide-rich brines (Moldovanyi et. al, 1993). Overall, the $\delta^{18}O$ and $\delta^{2}H$ relationship and Cl-Br, Na-Br, and K-Br trends clearly indicate the mixing of the remnants of evaporated seawater (reaching halite saturation) with meteoric water, likely under the influence of geochemical interaction between fluids and isotopically heavy minerals.

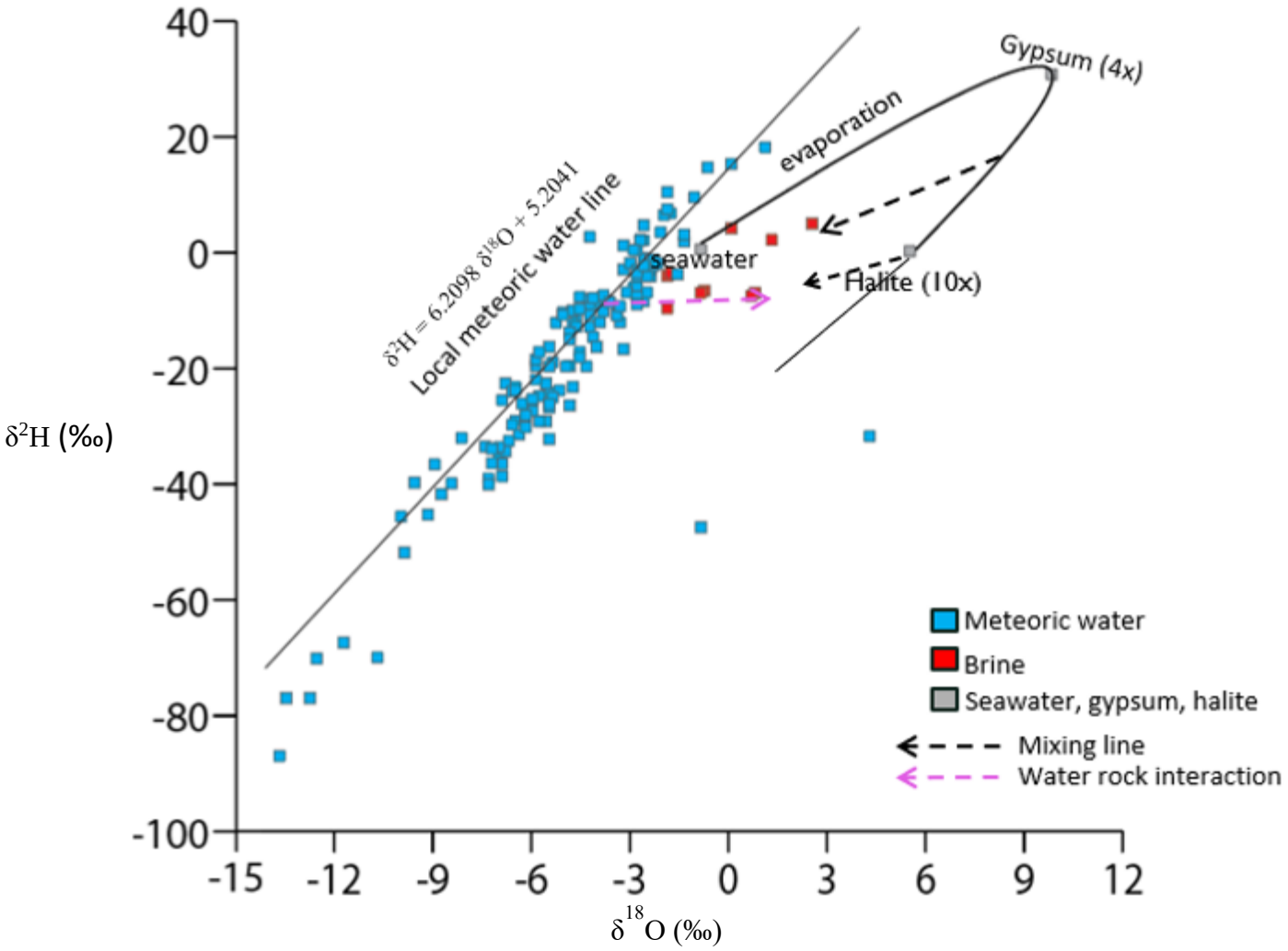


Figure 17: Hydrogen and oxygen isotopic composition of brines, plotted along seawater evaporation trajectory and meteoric water line (R^2 = 0.7626). Also shown are isotopic composition of seawater and evaporated seawater reaching gypsum and halite saturation (Holser, 1979). Dashed lines show potential mixing trends of evaporated seawater and meteoric water and water-rock interaction.

Strontium Isotope Ratios

The strontium isotopic ratios ($^{87}Sr/^{86}Sr$) of the brine range from 0.707403-0.710026 (Table 2). Sample 1 has a relatively low isotopic ratio that is comparable to that of Jurassic

seawater (0.7070) (Stueber et. al, 1984). All other samples are more radiogenic than the Jurassic seawater, indicating water-rock interaction that involves siliciclastic or igneous rock sources.

All the samples from this study, with the exception of sample 1, were relatively low in H_2S (<100 mg/L) compared to H_2S-rich Smackover Formation brines reported in Arkansas (Moldovanyi, et al, 1993). The H_2S concentrations reported here only represent the minimum level since the brines were sampled from storage tanks instead of directly from the wellhead. In Figure 18, six of the eight brines in this study (in a box) have $^{87}Sr/^{86}Sr$ ratio values within a range of 0.708210-0.708603, but their H_2S concentrations vary widely from 0-60 mg/L. The brines inside the box show weak to no correlation between those two variables. Whereas for Smackover Formation brines in Arkansas, the overall trend is that as H_2S concentrations increase, $^{87}Sr/^{86}Sr$ ratios increase and become more radiogenic (Figure 19). Low H_2S concentration wells are less radiogenic than high H_2S wells. For the limited number of samples analyzed in the Alabama study area, no clear trends are observed between $^{87}Sr/^{86}Sr$ ratios and the level of H_2S in part because H_2S reported here in brines from storage tanks represents the minimum level.

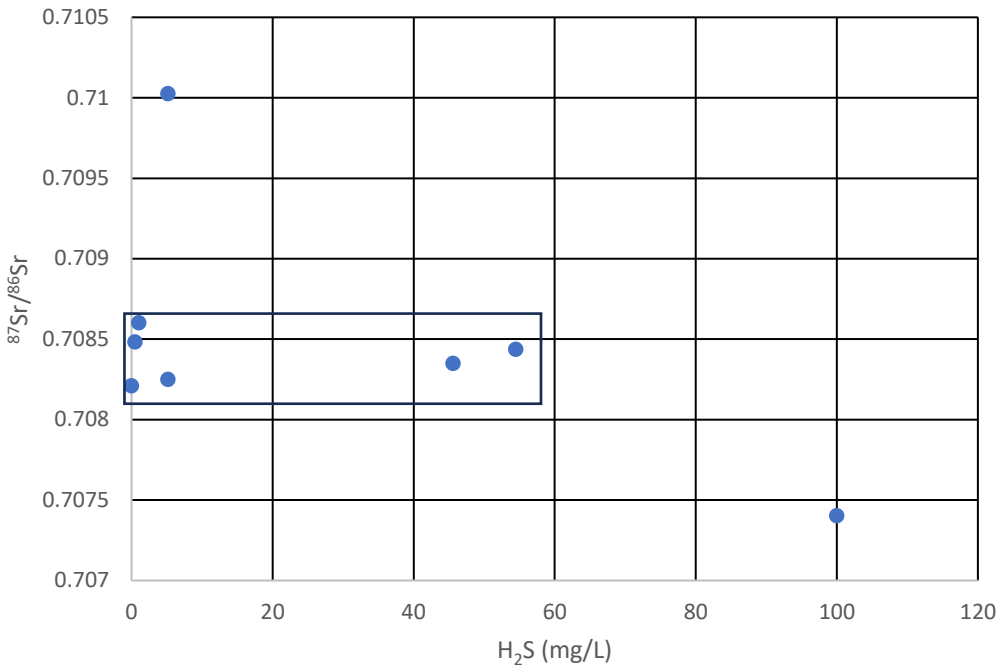


Figure 18: $^{87}Sr/^{86}Sr$ isotope ratios vs H_2S concentration of Alabama Smackover Formation brines, brines within box represent $^{87}Sr/^{86}Sr$ ratio values within a range of 0.708210-0.708603

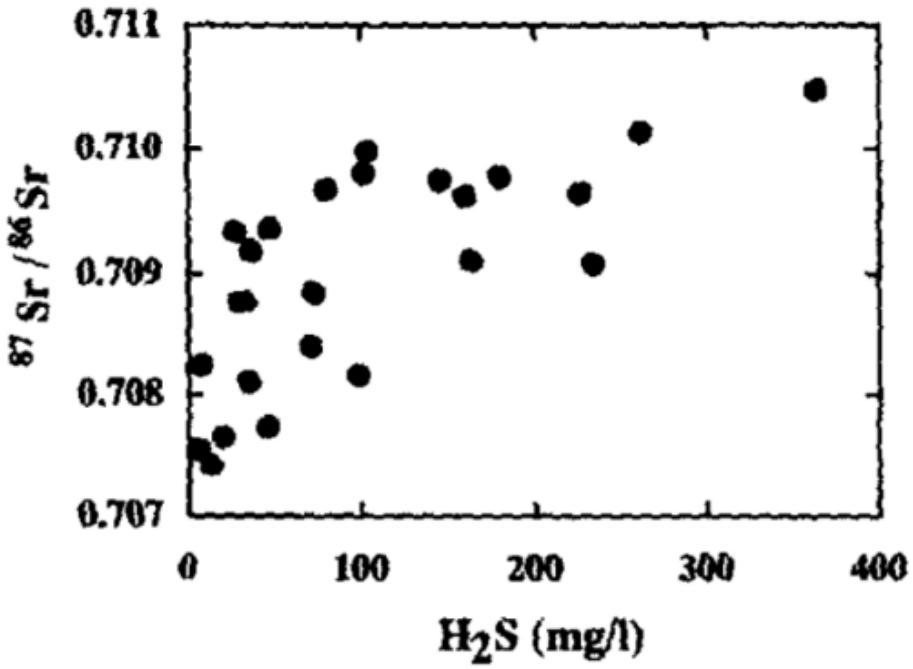


Figure 19: $^{87}Sr/^{86}Sr$ isotope ratios vs H_2S concentration of Arkansas Smackover brines (Moldovanyi et. al, 1993)

Figure 20 displays no relationship between the $^{87}Sr/^{86}Sr$ ratios vs. 1000/Sr concentration (mg/L). The lack of a straight line does not support a two-component mixing model. Instead, the data require 3-component mixing or subsequent alterations after two component-mixing. Alteration of brines by water-rock interaction and input of Sr would create the non-linear relationship as shown in Figure 20. Two components mixing with no alteration from water-rock interaction would exhibit a linear relationship because there would be only two unique isotopic signatures combining (Moldovanyi et. al, 1993). The Louann Salt has an $^{87}Sr/^{86}Sr$ ratio of 0.70838 (Stueber et. al, 1984). Fluids originating in the Louann Salt or deeper strata with greater radiogenic ratios were possibly forced upward into the Smackover Formation by overpressure and mixed with the less radiogenic Jurassic-age seawater to achieve the more radioactive $^{87}Sr/^{86}Sr$ ratios of these brines. The observed Sr concentrations, ranging from 1,045-2,381 mg/L, are significantly higher than those in seawater (7.2-8.2 mg/L) or evaporated seawater (Angino et al., 1966); this suggests an input of Sr derived from Sr-rich mineral sources such as carbonate (calcite and dolomite), sulfate (e.g., barite), and evaporite (e.g., gypsum and anhydrite) (Moldovanyi, et al, 1993). Alternatively, the brines might acquire Sr from the deep basin fluids migrating through the local fault system into the Smackover Formation. The siliciclastic igneous basement rock containing clay minerals and K-feldspars could be the source of Sr and other alkaline elements such as K and Li (Moldovanyi et. al,1990). Moldovanyi et. al (1990) found that Arkansas Smackover Formation H_2S-rich brines have a strong relationship between $^{87}Sr/^{86}Sr$ ratios and K and Li concentrations. Brines with little to no H_2S do not show a strong correlation between $^{87}Sr/^{86}Sr$ ratios and K and Li concentrations. With a limited number of analyses, our

data do not show such correlations (Figures 21 and 22). The varying Sr, Li, and K concentrations could be dependent on varying pathways as fluids are moving from the basement rocks into the Smackover Formation. The siliciclastic basement rock and carbonate rocks along the fluid pathway could also be responsible for introducing the more radiogenic Sr isotopes and a portion of the Li and other alkali elements such as K. Moreover, Sr can substitute Ca in mineral structure (e.g., calcite) and actively involve in water-rock interaction. The level of Li may be influenced by geochemical reactions with minerals in this system.

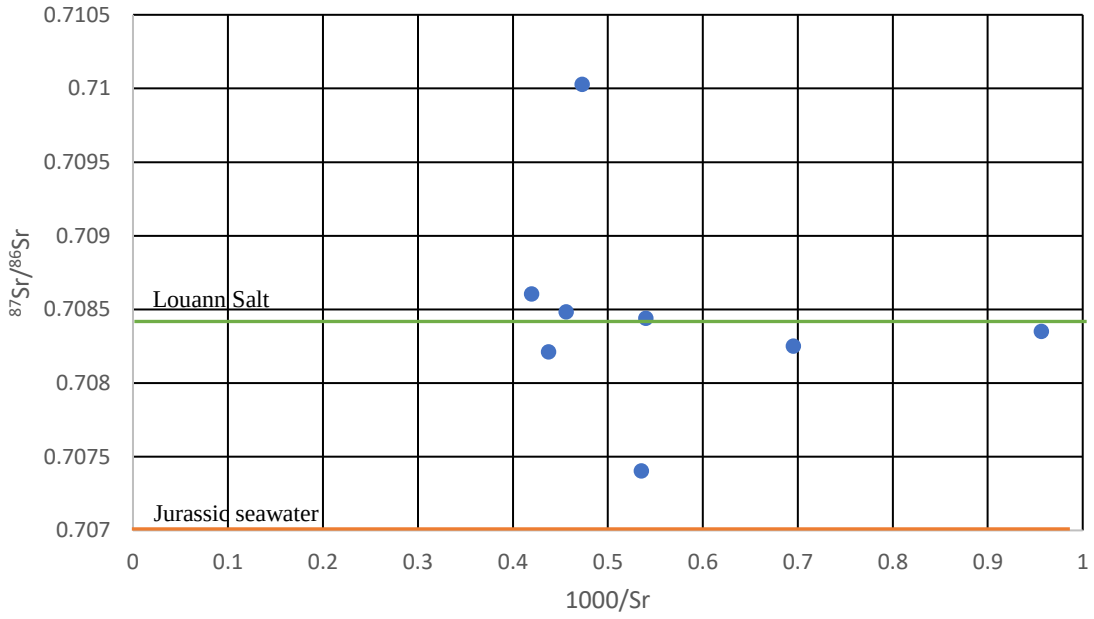


Figure 20: Brine $^{87}Sr/^{86}Sr$ ratios vs. 1000/Sr concentration (mg/L). Orange line represents Jurassic seawater (y= 0.707), green line represents Louann Salt (y= 0.70838) (Stueber et. al, 1984).

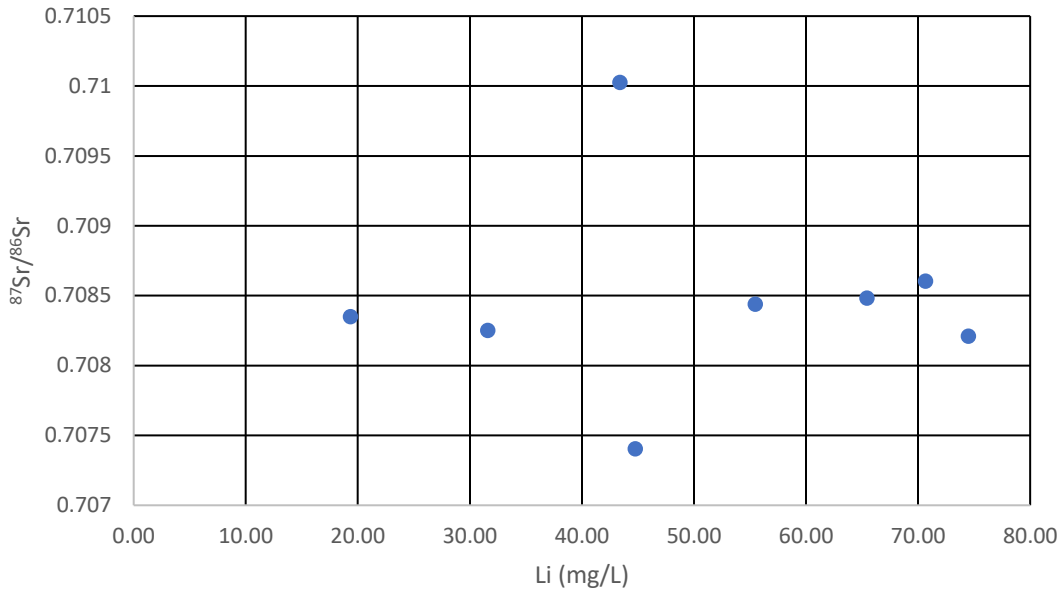


Figure 21: Sr isotope ratios vs. Li concentrations in Alabama Smackover brines.

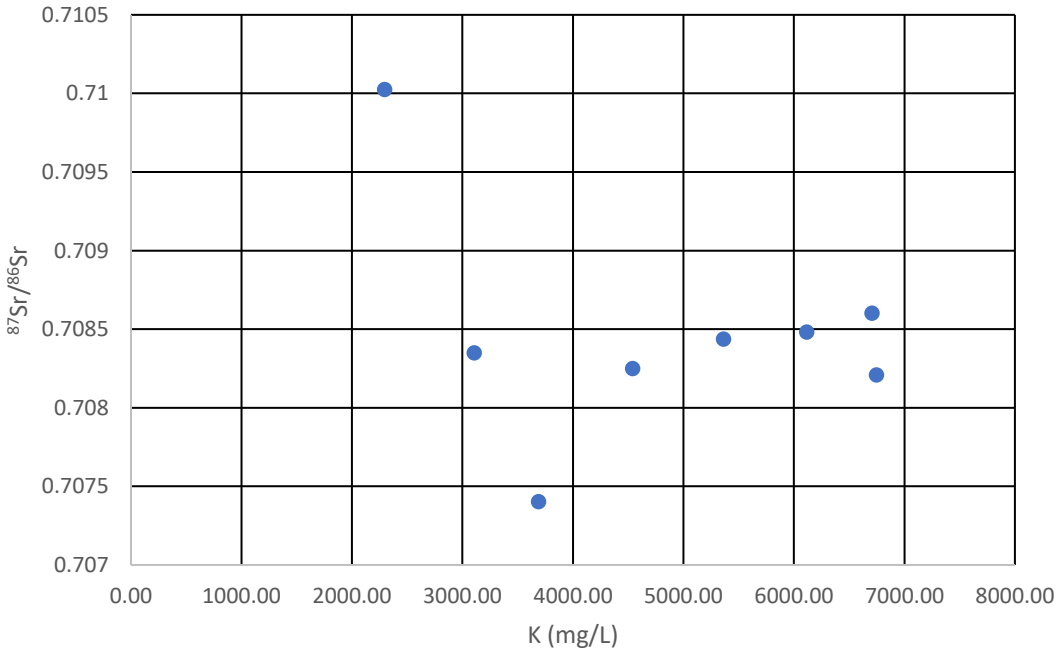


Figure 22: Sr isotope ratios vs K concentrations in Alabama Smackover brines.

Geochemical Modeling

Table 5 shows the calculated saturation index (SI) of evaporite and sulfate minerals in brines. Barite ($BaSO_4$) is the only saturated mineral (SI ranging from +1.19 to +1.85) in the brines analyzed. Barite is known to form in oilfield brines and its scale formation near wellheads may reduce permeability and cause permanent formation damage. Barite is economically valuable for the energy industry because it is an important mineral constituent of the mud (20-60 wt %) used to drill oil and gas wells. The solubility of barite is so low that it rarely adds any dissolved sulfate into the solution and this could account for the low sulfate concentrations in the brine (Bahadori et. al, 2012). Other minerals present with a log Q/K >-3 include halite (NaCl), gypsum ($CaSO_4 \cdot H_2O$), anhydrite ($CaSO_4$), celestite ($SrSO_4$), sylvanite (KCl), and bassanite ($2CaSO_4 \cdot H_2O$). Because these evaporite minerals are undersaturated, a mixing of evaporated seawater with less concentrated fluids is likely to have occurred. The introduction or mixing of a meteoric type of water would reduce the saturation index of evaporite minerals in the brine. Meteoric water would dilute the concentrations of ions necessary for the formation of these minerals or dissolve those minerals back into solution. The saturation index of carbonate minerals could not be calculated due to the lack of measurable alkalinity (HCO_3^- or CO_3^{2-}) in brines for that species.

	Jimmerson #4-6	**Bollinger 25-9 #1**	**Tims 8-2 #1**	**Blackstone Callon 9-9 #2**	**Coffin 14-10 #1**	**Cox 5-10 #1**
Barite ($BaSO_4$)	1.8523	1.5323	1.1924	1.4130	1.3588	1.3795

Halite (NaCl)	-0.7246	-1.0988	-1.3265	-0.7675	-0.9787	-0.8615
Gypsum ($CaSO_4*H_2O$)	-1.3460	-1.6163	-1.9421	-1.7469	-1.8060	-1.8722
Anhydrite ($CaSO_4$)	-1.4313	-1.7017	-2.0465	-1.8323	-1.8914	-1.9576
Sylvite (KCl)	-1.7126	-1.7681	-2.0940	-1.4623	-1.6535	-1.5664
Bassanite ($2CaSO_4*H_2O$)	-2.0834	-2.3537	-2.6938	-2.4844	-2.5435	-2.6097
Celestite ($SrSO_4$)	-0.2590	-0.6113	-0.9512	-0.5353	-0.6888	-0.6885

Table 5: Mineral saturation indices for Alabama Smackover Formation brine samples calculated by GWB using the uppermost limit for input basis values.

The Harvie-Moller-Weare activity model (Harvie et. al, 1984) was used to predict mineral precipitation and the evolution of fluid geochemistry of seawater as it evaporates (Bethke, 2008). Figure 26 shows the sequence of minerals that precipitate as more than 99% of water is removed from 1 kg of seawater. Dolomite and gypsum are the first minerals to precipitate in the evaporation of seawater. The model also predicts that HCO_3^- will be removed by the precipitation of carbonate minerals including dolomite and magnesite. This prediction of very low concentration HCO_3^- is consistent with near zero alkalinity observed in the Smackover Formation brines (Table 4). 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.

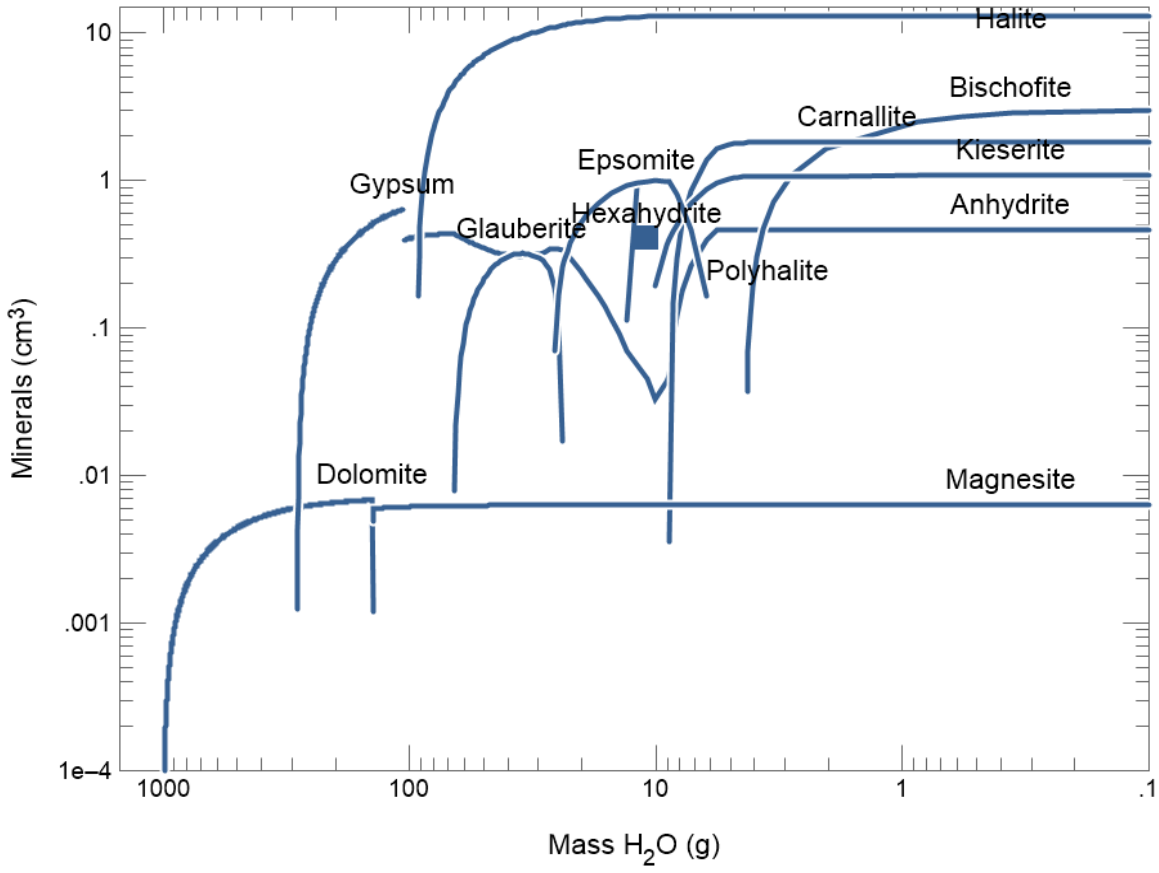


Figure 26: Volumes of minerals precipitated during seawater evaporation

Because the Na concentration is much less in the original seawater than Cl, when halite forms, it depletes Na more rapidly in the solution with respect to Cl (Figure 27). With further evaporation, the precipitation of glauberite ($Na_2Ca(SO_4)_2$) may remove both Na^+ and SO_4^{2-} from the brine:

$$CaSO_4 + 2\ Na^+ + SO_4^{2-} \Leftrightarrow Na_2Ca(SO_4)_2$$

(2)

As the volume of halite increases and water volume decreases, the fluid shifts from Na-Cl-dominated facies to Mg-Cl-dominated facies (Figure 27). Then glauberite will react with anhydrite, K^+, Mg^{2+}, and SO_4^{2-} to form polyhalite ($K_2MgCa_2(SO_4)_4.2H_2O$). The polyhalite will remove SO_4^{2-} and K^+ from the solution. Only three minerals, including halite (NaCl), bischofite ($MgCl_2.6H_2O$), carnallite ($KMgCl_3.6H_2O$), that form in the simulation have Cl in their composition. Those three minerals cannot precipitate until a certain concentration of Cl ions is reached in the solution. As halite precipitation equalizes, the rate at which Cl is removed from the solution slows down, and water continues to evaporate at the same rate, thus the concentration of Cl ions increases in the solution once again. At this point, Cl-bearing bischofite and carnallite can precipitate because the concentration of Cl is high enough to approach their saturation.

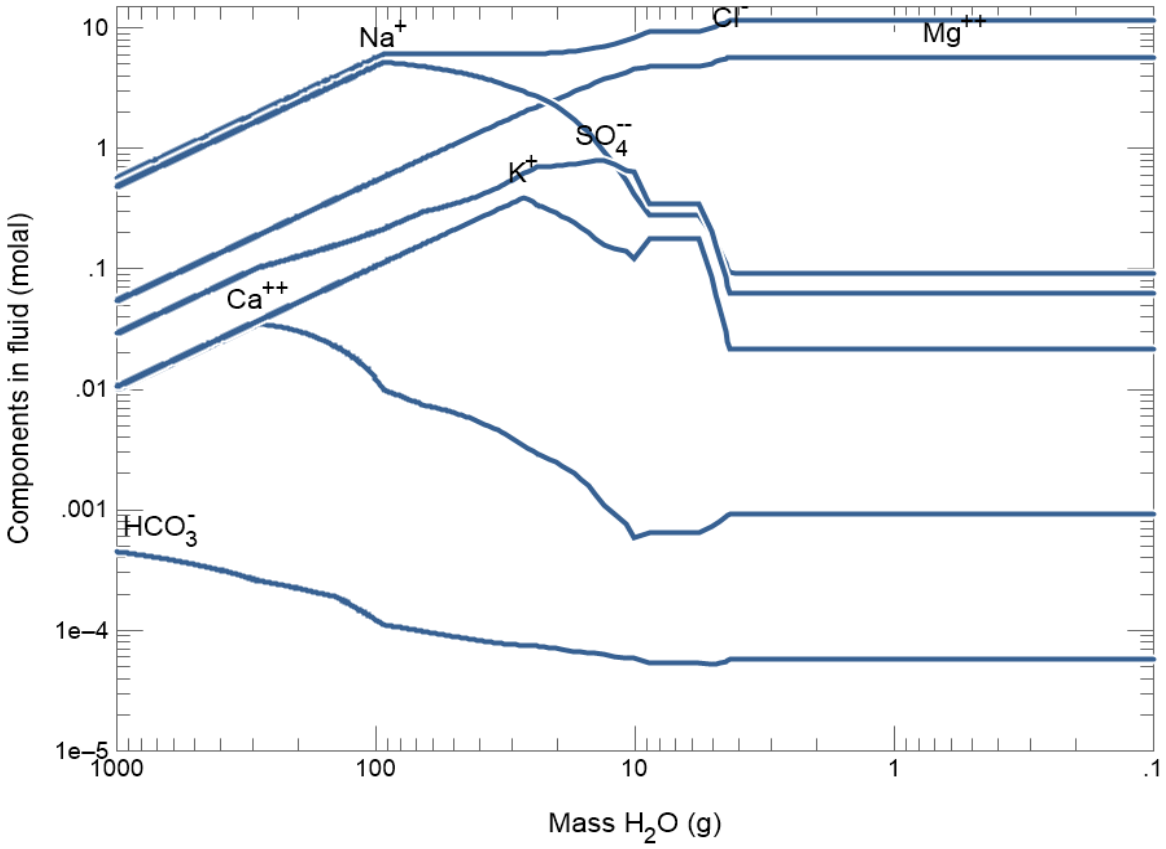


Figure 27: fluid chemistry of seawater evaporation

The predicted sequence of mineral precipitation explains the geochemical evolution of brine reaching different stage of evaporation (Figure 26). The predicted Cl-Mg hydrochemical facies dominated after the precipitation of halite is different from the observed Na-Cl-Ca facies of Smackover Formation brines (Figure 8), 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 of Cl-Mg to Cl-Ca facies in evaporated seawater. Ca released by dolomitization may exchange with lithium or sodium in the clay minerals associated with the Triassic granitic basement rocks or other basin strata.

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 oilfield brines in southwest Alabama. The main hydrochemical facies were identified as a Na-Cl-Ca type brine with elevated concentrations of Cl (94,600-190,000 mg/L), Na (32,200-73,300 mg/L), and Ca (14,000- 48,200 mg/L) that are significantly higher than those in seawater. Brines are also enriched in Br (831-5,700+ mg/L), Sr (1,045-2,381 mg/L), Li (19.34-70.65 mg/L), and Ba (1.77-147.84 mg/L). Sulfate concentrations (< 184 mg/L) are significantly lower than those in seawater (2,710 mg/L), this and high H_2S level of some brines indicate non-conservative sulfate removal by bacterial sulfate reduction or precipitation of sulfate minerals (e.g., barite and evaporite minerals). Low Cl/Br ratios (24.04-113.84) and Na/Br ratios (31.11-47.29) indicate that the brines acquired salinity from mixing with evaporated seawater reaching halite precipitation, instead of dissolution of halite. The $\delta^{18}O$ and $\delta^{2}H$ trends also indicate the mixing of meteoric water with remnant evaporated seawater that reaches gypsum and halite saturation. Some brines exhibit enrichment in $\delta^{18}O$ and slight depletion in $\delta^{2}H$ relative to seawater, suggesting an exchange of heavier $\delta^{18}O$ isotopes with silicate or carbonate rocks via water-rock interaction.

The $^{87}Sr/^{86}Sr$ ratios of most brines analyzed (ranging from 0.707403-0.710026) are higher than that of Jurassic seawater (0.7070), indicating significant exchange of radiogenic Sr with siliciclastic or igneous rock sources. Geochemical modeling of seawater evaporation predicted a dominated Cl-Mg hydrochemical facies after the precipitation of halite. This predicted Cl-Mg facies is different from the observed Smackover Formation brines dominated by Na-Ca-Cl. Water-rock interaction such as dolomitization would lead to a shift of the Mg-Cl facies of evaporated seawater to Ca-Cl dominated brines. The observed enrichments in Ca and radiogenic

Sr and the depletion of sulfate indicate that seawater evaporation alone cannot account for the chemical evolution of brines. This study uncovered evaporated seawater (that reached halite precipitation) as the source of salinity, possible mixing trends between meteoric water and evaporated seawater, and geochemical influence from water-rock interaction. Li, Sr, and Br enrichments near fault zones indicate that water-rock interaction stemming from the movement of basin fluids along the peripheral fault system that bounds the up-dip limit of the Louann Salt likely introduced the more radiogenic strontium isotopes and high concentrations of alkali elements (Li, K) derived from the siliciclastic or igneous basement rocks.

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