Strontium, boron, oxygen, and hydrogen isotope geochemistry of brines from basal strata of the Gulf Coast sedimentary basin, USA

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Abstract—Significant spatial heterogeneities exist in the stable isotopic composition of saline formation waters from reservoirs of the Smackover Formation (Upper Jurassic). We focused on the southwest Arkansas shelf, a structurally simple portion of one of the interior basins of the northern Gulf Coast sedimentary basin. Here, faulting and facies changes juxtapose dominantly oolitic carbonate strata against basal evaporites, red beds, and siliciclastics, as well as metamorphosed basement rocks. Brines from this area have exceptionally high Br and alkali element concentrations and have spatially heterogeneous hydrogen sulfide concentrations. Strontium, boron, oxygen, and hydrogen isotope compositions exhibit coherent relations with other aspects of brine geochemistry. Sr isotope compositions range from those expected for carbonates and evaporites deposited from Jurassic seawater (0.707) to radiogenic ratios as high as 0.7107. Generally, most radiogenic Sr isotope values are associated with H2S-rich waters which also have elevated alkali element (Li, B, K, Rb) concentrations. These alkali element-rich waters are also associated with portions of the South Arkansas fault system which reach basement.

Boron isotope compositions are similarly heterogeneous, ranging from values of +26 to +50‰. Brines with highest B contents are most depleted in 11B, consistent with boron input from brines generated from high-temperature siliciclastic diagenetic reactions. Normalizing B contents to Br in the brines reveals a reasonable mixing trend between a Dead Sea-type composition and Texas Gulf Coast-type shale/sand reservoir waters.

Oxygen and hydrogen isotope data exhibit regional variations which are controlled by meteoric water invasion along the northern limb of the southwest Arkansas Fault, which has surface expression. Although oxygen isotope compositions are often near equilibrium with respect to reservoir carbonate, it is more difficult to ascribe trends in δD values to local water-rock interaction. The stable isotope trends can be explained either in terms of an evolved marine evaporite brine or a water evolved via water-rock interaction, and mixing with meteoric water in the vicinity of the southwest Arkansas Fault. Spatial heterogeneity in isotopic composition of formation waters from this relatively restricted study area suggests that assumptions of a homogeneous Sr reservoir in dating regional mineralization events require careful assessment in ancient systems.

INTRODUCTION

ALTHOUGH THE IMPORTANCE of subsurface brines in processes such as hydrocarbon migration and MVT-mineralization is widely recognized (e.g., SVERJENSKY, 1984; OLIVER, 1986; GE and GARVEN, 1989; BETHKE and MARSHAK, 1990), in most instances, the origins of water and solutes remain controversial. Salinity of brines has historically been attributed to halite dissolution (LAND and PREZBINDOWSKI, 1981; HANOR, 1987), retention or reflux of evaporatively concentrated seawater (RITTENHOUSE, 1967; CARPENTER, 1978), shale membrane filtration (GRAF, 1982), and/or evaporation of non-marine fluids (HARDIE, 1990). However, major element trends used to characterize the evolution of saline formation waters can rarely be explained by a single process. The data are often equivocal, thereby necessitating integration of elemental data with various isotope systematics to constrain the origin of fluids and to constrain the relative importance of diagenetic processes in different lithologic associations and basinal settings.

Fluid inclusions in sediment-hosted ore deposits and in late-stage diagenetic minerals in petroleum reservoir host rocks are commonly highly saline (up to 120 g/L Cl, 55 g/L Na and 20 g/L Ca) and are generally interpreted to have been emplaced at moderate temperatures (100–150°C) and pressures (<500 bars; SVERJENSKY, 1984). The geochemical properties of fluid inclusions generally fall within the range of compositions measured in deep subsurface formation waters in the U.S. Gulf Coast sedimentary basin, especially those associated with Mesozoic strata (e.g., CARPENTER et al., 1974; CARPENTER and TROUT, 1978; KHARAKA et al., 1987). Because of the geochemical similarities, these basal Gulf Coast formation waters are considered to be akin to mineralizing fluids, for which they often serve as proxies in ore-forming geochemical models (SVERJENSKY, 1984).

The Gulf Coast sedimentary basin, active since Upper Triassic/Jurassic time, is particularly pertinent to the study of brine elemental and isotopic evolution. Here, stratigraphic associations of carbonate reservoirs with siliciclastics and evaporites are very similar to those in many sediment-hosted ore deposits. In particular, Jurassic carbonate sediments (Smackover Formation) are associated with basal siliciclastics (Eagle Mills Formation), evaporites (Werner, Louann and Buckner formations), and metamorphosed basement.
Smackover Formation waters are highly saline, and locally sulfide-rich. Furthermore, unlike waters in intracratonic settings, they have not been expelled from the basin and likely represent prograde geochemical evolution within the basin. Finally, unlike the "relict" hydrogeochemical system recorded in sediment-hosted ore deposits, we can observe directly spatial variability in isotopic composition in the fluids themselves. Regional, as well as temporal, variability in fluid geochemistry must be considered in dating mineralization events and in delimiting fluid migration pathways.

The elemental chemistry of Smackover Formation waters in southwest Arkansas has been reported by Collins (1974), Trout, (1974), Carpenter and Trout (1978), and Moldovanyi and Walter (1992). Importantly, the brines are characterized by complex geochemical heterogeneities occurring on a relatively small spatial scale. These heterogeneities are regionally systematic and have been modeled in terms of four major processes: evaporative concentration of seawater, meteoric recharge, thermochemical sulfate reduction, and water-rock interactions in carbonate and siliciclastic strata (Trout, 1974; Carpenter and Trout, 1978; Moldovanyi and Walter, 1992). Yet, questions regarding the extent of halite recrystallization and dissolution and the extent of mixing with deeper-circulating fluids, or the role of thermochemical sulfate reduction, remained unanswered because of the equivocal trends in major element geochemistry. In this paper, strontium, boron, oxygen, and hydrogen isotopic compositions are integrated with data on major, minor, and trace element chemistry of brines and with the geochemistry of diagenetic phases to identify the mechanisms of brine evolution, to address the origin of water and solutes, and to better constrain fluid mixing endmembers.

The strontium isotopic composition of subsurface waters identifies sources of Sr, constrains water-rock interactions, and may be used to trace the evolution and migration paths of fluids (Chaudhuri, 1978; Starinsky et al., 1983; Stueber et al., 1984, 1987; McNutt et al., 1984; Chaudhuri et al., 1987; Russell et al., 1988; McNutt et al., 1987; Mack, 1990; Stueber and Walter, 1991). Sr isotope systematics have been applied to metal sulfides, gangue minerals, and host rocks in MVT ore deposits to determine sources of fluids and timing of mineralization (Kesler et al., 1981; Lange et al., 1983; Medford et al., 1983; Kesler et al., 1988; Nakai et al., 1990; Brannon et al., 1991).

Oxygen and hydrogen isotopic data may also constrain fluid evolution by providing information regarding the source of water molecules and effects of water-rock interactions. In a classic study, Clayton et al. (1966) documented the oxygen and hydrogen isotopic composition of saline formation waters in the Illinois, Michigan, and Alberta sedimentary basins, and concluded that despite elevated salinities, subsurface waters in these basins were largely derived from local meteoric water. The oxygen isotope composition was considered to have evolved to more positive values via equilibration with carbonate minerals, while hydrogen isotope composition was relatively unaffected. More recently, the changes in oxygen and hydrogen isotopic compositions that accompany seawater evaporation have become recognized. At early stages of evaporation, residual waters can acquire a heavy isotopic composition, a trend which later reverses itself during more advanced stages of evaporation (Sofer and Gat, 1972; Holser, 1979; Pierre et al., 1984; Knauth and Beeunas, 1986). This trend has important implications for the origin of basinal waters because it permits waters with more negative δD and δ18O values to be generated by extreme evaporation of seawater as well as by meteoric water invasion.

Equilibration of water with feldspars and clay minerals can also affect water composition, sometimes producing significant depletion in δD and enrichment of δ18O values of the residual fluid (Yeh, 1980; Suchek and Land, 1983). Importantly, the low water-rock ratio characteristic of sedimentary strata can be coupled with massive mineralogical transformations during burial diagenesis, suggesting that the latter processes override any primary signal in shale-rich, siliciclastic sections of sedimentary basins, such as the upper Gulf Coast (e.g., Yeh, 1980).

Application of boron isotopic systematics may permit advances to be made in distinguishing between marine and nonmarine solute sources. Swihart et al. (1986) showed that marine evaporites may be differentiated from nonmarine evaporites because of the large difference in B isotopic compositions of seawater and average continental crust. Seawater has an almost constant δ11B (+40%), which is controlled by B adsorption onto detrital clays, weathering of oceanic crust, and clay authigenesis (Schwarz et al., 1969; Spivack and Edmond, 1987; Spivack et al., 1987). In contrast, B in the continental crust has lower δ11B (-8 to +2%), and seawater also tend to have a light boron isotopic composition (δ11B = +15% for desorbable B) relative to seawater. Macpherson and Land (1989) and Vengosh et al. (1989, 1991a,b) have analyzed the boron isotopic composition of various natural waters from surface and subsurface environments and noted large variations in δ11B which are attributed to the source of boron. Few formation waters and surface lakes analyzed to date have δ11B values more positive than seawater. However, δ11B significantly greater than +40% is characteristic of Dead Sea brines. Because of the elevated salinity, unusually high Br content and similar overall geochemistry, the Smackover Formation Waters have been likened to Dead Sea brines (Carpenter and Trout, 1978). It has been suggested that both waters have been partially derived from seawater evaporation and modified by later diagenetic processes including evaporite dissolution and recrystallization.

The oxygen, hydrogen, and strontium isotopic compositions of Smackover Formation waters in southwest Arkansas and central Mississippi have been investigated by Knauth et al. (1980), Kharkaka et al. (1987), and Stueber et al. (1984), but isotopic trends have not been integrated with element chemistry, and the boron isotopic composition of these brines has not been reported. The present-day oxygen and hydrogen isotopic composition of Smackover Formation brines in MS has been modeled as seawater evaporated beyond halite facies, subsequently isotopically modified by exchange with the host rock and by mixing with meteoric water (Kharkaka et al., 1987). Stueber et al. (1984) measured the strontium isotopic composition of Smackover Formation brines in southwest Arkansas and found considerable variation in 87Sr/86Sr ratios, with values ranging from 0.7071 to
0.7101 and most samples being significantly enriched in $^{87}$Sr relative to Jurassic-age seawater. Enrichment in $^{87}$Sr was attributed to detrital clastic mineral sources, but STUEBER et al. (1984) concluded that the observed regional heterogeneity was the result of random geochemical processes. The data we present will show that the geochemistry of Smackover Formation waters in southwest Arkansas indeed varies systematically in response to diagenetic and mixing events. The "ground truth" isotopic heterogeneity in formation waters of this relatively simple oolitic reservoir has important implications for regional hydrogeochemical modeling from Sr and other isotope systems in rock-based studies.

THE STUDY AREA

Geological Framework

The southwest Arkansas shelf is located near the updip limit of Jurassic sedimentation and is bounded by the east Texas, northern Louisiana, and central Mississippi salt basins, and the Sabine and Monroe uplifts. Figure 1 shows the study area in southwest Arkansas and gives the locations of samples analyzed for strontium, oxygen, and hydrogen isotopic composition relative to two dominant fault systems. The South Arkansas Fault system and the Louisiana State Line Graben were active during the Jurassic and are genetically related to deformation of the underlying Louann Salt (BISHOP, 1973). Both fault systems are potential sites for large-scale vertical migration of fluids (MCCAIG, 1988; HOOPER, 1991). Portions of the South Arkansas Fault system (in Miller, Lafayette, and Nevada counties) extend to the surface (HALEY et al., 1976). Faults associated with the Louisiana State Line Graben do not have surface expression but may extend to greater depths and may be related to older, previously existing zones of deformation (BISHOP, 1973).

The Upper Smackover Formation mostly consists of oolitic and algal carbonate grainstones. However, in some areas the high-energy carbonates grade into more carbonate mud-rich facies or into clastic facies (e.g., CHIMENE, 1976), and in structurally high locations Smackover Formation carbonates are completely absent (GREEN, 1989). The thicker, Lower Smackover Formation is made up of argillaceous and organic-rich mudstones and is thought to be a major source of hydrocarbons (e.g., SASSEN et al., 1987). The Smackover Formation is underlain by a thick sequence of clastics and evaporites (Fig. 2), which include, in ascending order from the basement, the red beds of the Eagle Mills Formation, the Werner Anhydrite, the Louann Salt, which locally contains bittern salts (EUSTICE, 1990), and subarkosic sandstones of the Norphlet Formation. Shales and anhydrite of the Buckner and Haynesville formations directly overlie the Smackover Formation and the Jurassic section terminates with sands and shales of the Cotton Valley Group (BISHOP, 1967; DICKINSON, 1968; COLLINS, 1980).

Jurassic strata are relatively undeformed and consist of east-west striking beds gently dipping to the south. The Louann Formation lacks large salt domes, but salt swells in the southern portion of the study area probably contributed to local perturbations in Smackover Formation structure. The Louann Formation is absent west and north of the South Arkansas Fault in Miller County (COLLINS, 1980). Burial depths to the top of the Smackover Formation vary from approximately 1300 m in the north to 3250 m in the south and corresponding formation temperatures (obtained from petrophysical logs) range from 60 to 105°C. These bottom hole temperatures may be affected by drilling conditions and drilling fluids and are therefore probably minimum values; however, they represent our best estimate of in situ reservoir conditions.

Diagenetic minerals in the Upper Smackover Formation occur as replacements of matrix or previously formed diagenetic phases, or as pore-filling cements, and include carbonates, sulfates, sulfides, and minor amounts of quartz, kaolinite, and clay minerals. The Sr isotopic composition of calcites, dolomites and S minerals has been integrated with petrographic relations to constrain strontium isotopic evolution...
during progressive burial diagenesis (Moldovanyi et al., 1990; Dworkin, 1991). Precipitation of calcite, anhydrite, and pyrite represent pre-compaction diagenetic processes (<500 m burial). Moderately radiogenic dolomite, sphalerite, and galena are intermediate in the diagenetic sequence, while fracture and vug-filling calcite, marcasite, native sulfur, and celestite are the latest diagenetic minerals present pre-compaction diagenetic processes (~500 m burial). Modernization and recrystallization of carbonates, sulfate dissolution/precipitation, illitization of smectite, and albition of Ca-richfeldspars (Carpenter and Trout, 1978; Moldovanyi and Walter, 1992). Smackover Formation waters also have anomalously high bromide concentrations relative to evaporated seawater. Bromide enrichment in these formation waters could be due to seawater evaporation, recrystallization of halite (Stoessell and Moore, 1983; Land et al., 1988), or to the dissolution of bittern salts deposited in this interior salt basin (Land and Prezbindowski, 1981). However, Smackover Formation brines with elevated bromide content are not correspondingly enriched in elements associated with simple dissolution of bittern salts (e.g., K, Rb, B), thereby suggesting that Br enrichment occurred in response to the recrystallization of underlying Louann Salt (Moldovanyi and Walter, 1992).

Lower salinity waters from certain Smackover reservoirs associated with the South Arkansas Fault have elevated Cl/Br ratios (up to 2.5X higher than average) which are consistent with halite dissolution. Undersaturated meteoric waters were likely recharged to the Smackover Formation through faults having surface expression. Elevated Cl/Br ratios in waters near the Louisiana State Line Graben are likely also related to proximity to the Louann Formation and to halite dissolution associated with water migration along faults, but there is no evidence of meteoric recharge.

A striking characteristic of Smackover Formation water geochemistry is the variability in H2S concentrations. H2S-rich waters occur in the center of the study area, within a narrow east-west trending belt (Fig. 3a). Concentrations of dissolved sulfide range from <10 to >600 mg/L and are highest at the western end of the study area, near the South Arkansas Fault system. Boron and alkali metals are typically enriched in H2S-rich waters and exhibit strong geochemical and spatial relations to H2S content (Fig. 3b). The relations among B, alkali metals, and H2S contents suggest that Smackover Formation brines have likely mixed with waters from deeper-seated strata undergoing siliciclastic diagenesis at higher temperatures (Moldovanyi and Walter, 1992). Two major fault systems bounding the study area are the most likely large-scale fluid migration paths.

**TECHNIQUES AND ANALYTICAL RESULTS**

Formation water samples were collected and analyzed for major, minor, and trace element composition using field and laboratory techniques described in Moldovanyi and Walter (1992). Samples identified numerically in Fig. 1 were selected for various isotopic analyses. Most samples are from reservoirs in oolitic carbonate reservoirs on the Arkansas shelf. Two samples, one from east Texas (#43) and one from west Arkansas (#44), are from, or are in close proximity to, siliciclastic reservoirs of equivalent Jurassic age. The host rock at these sites consists of sandstones and red beds eroded from an igneous intrusion in the immediate vicinity (Green, 1989). Results of Sr, B, O, and H isotopic analyses of Smackover Formation waters are given in Table 1.

Strontium isotopic analyses were conducted on 49 filtered and acidified brine samples using a VG 154 thermal emission mass spectrometer at Washington University, following procedures described in Popp et al. (1986) and Moldovanyi et al. (1990). Brines were analyzed in triple or single collector mode and analytical uncertainty of all samples is better than 0.00005 ± 2σ. 87Sr/86Sr ratios were adjusted relative to the conventional ratio of 0.71014 for NBS-987. Actual measured values for NBS-987 were 0.71025 ± 2σ in triple collector Faraday mode and 0.71019 ± 2σ in Daly mode.

Rubidium concentrations were determined by isotope dilution in single-collector mode using a Daly detector in pulse-counting mode and are precise to 0.5%. Potential contributions to 87Sr from in situ decay of Rb, evaluated assuming a maximum age of 160 m.y., would decrease Sr isotope ratios by 9.5 × 10⁻⁵ in waters with highest Rb/Sr and 0.7 × 10⁻⁵ in waters with lowest Rb/Sr. As the majority of samples have contributions between 1.3 and 3.3 × 10⁻⁵, similar to analytical uncertainty, in situ growth of 87Sr is insignificant.

Eighteen water samples were selected from the subset for B isotopic analyses. Boron isotopic analyses were performed at the University of Texas by trimethylborine distillation, and analysis as the Cs-metaborate ion (MacPherson, 1989). Boron isotopic data are given in standard δ notation, relative to NBS borate SRM 951, and are reproducible to ±0.5%.

Oxygen and hydrogen isotopic analyses were performed at Arizona State University on 27 filtered samples collected in glass bottles with no head space. Oxygen isotopes were measured using the CO₂ equilibration method (Epstein and Mayeda, 1953), with a reproducibility of ±0.5%. Oxygen isotopic ratios have been converted from measured activities to concentrations, correcting for compositional effects using equations of Sorensen and Gat (1972). Hydrogen isotopic ratios, measured using the heated capillary method described in Knauth and Beenen (1986), are reported in concentration units and are precise to ±1‰. O and H isotopic compositions are given in standard δ notation relative to SMOW.
Strontium Isotope Composition

Strontium isotope ratios of Smackover Formation waters measured in this study range from 0.70743 to 0.71071 (Table 1) and are similar to the range observed by Stueber et al. (1984). All samples are more radiogenic than Jurassic-age marine carbonate (0.7068 to 0.7072; Burke et al., 1982) and considerable variation in ⁸⁷Sr/⁸⁶Sr ratios occurs within and between H²S-rich and H₂S-free waters across the relatively small study area. Sr isotope ratios can vary dramatically among adjacent brine samples (Fig. 4a,b), although mean ⁸⁷Sr/⁸⁶Sr ratios of H₂S-rich and H₂S-free waters are not significantly different (0.70898 ± 0.00088 and 0.70863 ± 0.00060, respectively). In both H₂S-free and H₂S-rich oolitic carbonate reservoirs, ⁸⁷Sr/⁸⁶Sr ratios are independent of bromide content and other major ion concentrations, and show no trend with δ¹⁸O and δD.

Within the H₂S-rich belt, formation waters are generally more radiogenic than the H₂S-free brines sampled north and south of the belt (Fig. 4a,b). A frequency plot of ⁸⁷Sr/⁸⁶Sr ratios in H₂S-rich brines confirms the heterogeneous nature of these fluids and shows the even distribution of ⁸⁷Sr/⁸⁶Sr ratios (Fig. 4a). Formation waters from the western part of the study area are more radiogenic than brines sampled at the northeastern extension of the belt. This regional gradient is also apparent in H₂S and alkali element concentrations. Figure 5 shows the strong relation between ⁸⁷Sr/⁸⁶Sr ratios and H₂S concentrations.
As a group, H$_2$S-free brines are somewhat less radiogenic and more homogeneous in their Sr isotope composition than H$_2$S-rich brines, and do not exhibit a regional gradient (Fig 4b). As the frequency plot in Fig. 4b indicates, most $^{87}$Sr/$^{86}$Sr ratios in H$_2$S-free brines fall in the range between 0.7085 to 0.7090. Two samples from east Texas and west Arkansas (43 and 44 in Table 1) have unusually elevated $^{87}$Sr/$^{86}$Sr ratios (0.71044 and 0.71071, respectively) for H$_2$S-free brines. Such radiogenic values likely reflect enhanced water-rock interactions with siliciclastic reservoirs known to be present in the Smackover Formation at these locations. Because of their intimate association with siliciclastics rather than oolitic carbonate reservoirs, these two water samples are excluded from further discussion.

Two-component mixing models assume that resulting mixtures are not altered after the mixing event has occurred (e.g., FAURE, 1986). Water-rock interactions involving addition or removal of Sr after mixing can disrupt a linear relation between $^{87}$Sr/$^{86}$Sr and 1/Sr that would result from mixing two components. Smackover Formation brines contain 400 to 2950 mg/L Sr, more than ten times higher than predicted from theoretical seawater evaporation trajectories, and this enrichment most likely results from water-rock interaction with the host limestones and/or adjacent anhydrites and siliciclastic minerals (CARPENTER and TROUT, 1978; MOLDOVANYI and WALTER, 1992).

Strontium substitutes for Ca in calcite, barite, gypsum, and anhydrite, and is a major element in celestite and strontianite. Given the presence of these minerals in the host rocks (e.g., MOORE and DRUCKMAN, 1981; SWIRYDZUK, 1988; MOLDOVANYI et al., 1990), control on Sr concentration by mineral equilibria in Smackover Formation waters is reasonable. In fact, results of geochemical modeling of aqueous
species distributions using the code SOLMINEQ.88 (Khara- 
Raka et al., 1988) indicate that Smackover Formation waters 
are near equilibrium with respect to anhydrite and celestite 
(Moldovanyi and Walter, 1992).

Mixing in Smackover Formation brines is better evaluated 
by considering the relation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and B, 
Li, K, and Rb concentrations. These species (B and alkali 
metals) are less likely to be affected by water-rock interactions 
with Upper Smackover Formation reservoir rocks since these 
elements are not involved in carbonate or sulfate mineral 
equilibria. Scatter diagrams of $^{87}\text{Sr}/^{86}\text{Sr}$ versus B and alkali 
metals show strong relations, but only in H$_2$S-rich waters 
(Fig. 7). Sulfide-rich waters show a hyperbolic relation

![Graph](image-url)

**Fig. 4.** Regional variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in H$_2$S-rich (a) and H$_2$S-free (b) brines from the Arkansas shelf. Mean $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Smackover brines are given in text. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Jurassic-age marine carbonate range from 0.7068 to 0.7072 (Burke et al., 1982).

![Graph](image-url)

**Fig. 5.** $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. H$_2$S concentrations in H$_2$S-rich formation waters. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Jurassic-age marine carbonate range from 0.7068 to 0.7072 (Burke et al., 1982).
between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and B and alkali metal content, while H$_2$S-free waters have uniformly low B and alkali metal content despite a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The difference in trends between H$_2$S-rich and H$_2$S-free waters suggests that reservoirs across the Arkansas shelf have not been uniformly affected by the processes controlling B and alkali metal concentrations and Sr isotopic composition.

The positive correlation between K and $^{87}\text{Sr}/^{86}\text{Sr}$ values could result from recrystallization of K-rich potash salts. Potash salts are unknown from the Louann Formation on the Arkansas shelf, but only a few wells have penetrated into the salt and little is known about its geochemistry. The lack of correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Br, which would also be enriched by dissolution or recrystallization of potash salts, is also inconsistent with recrystallization. The strong relation among $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and H$_2$S, B, Li, K, and Rb concentrations points to a common source of Sr and these species, and suggests that waters are sourced from deeper-seated evaporite and siliciclastic strata undergoing thermochemical sulfate reduction and diagenetic reactions at higher temperatures. Feldspars are common constituents of red beds and their alteration could be a source of radiogenic Sr and Rb to formation waters (e.g., Boles, 1982; Land, 1987; Russell et al., 1988). The significant enrichments in alkali metals, B, and $^{87}\text{Sr}$ in H$_2$S-rich formation waters in the vicinity of the South Arkansas Fault system suggest that these faults may be a conduit through which deeper-seated waters migrate into Upper Smackover reservoirs. The absence of the Louann Formation northwest of the fault zone places Smackover Formation waters in more direct proximity to the siliciclastics of the Norphlet and Eagle Mills formations. Gradients in Sr isotopic composition and trace element content suggest that waters enriched in $^{87}\text{Sr}$, B, and alkali metals have migrated eastward, following permeable pathways approximately parallel to regional strike.

Heterogeneities in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of H$_2$S-free formation waters have no apparent regional relation to major and minor element geochemistry of the brines and cannot be modeled in terms of two-component mixing. The four H$_2$S-free brine samples (#47, 53, 55, and 78 in Table 1) with unusually radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7091 to 0.7101) are not markedly enriched in B or alkali metal content. These waters are from reservoirs associated with a segment of the South Arkansas Fault in Lafayette County (Fig. 4b), suggesting that waters enriched in $^{87}\text{Sr}$, but not in H$_2$S, B, and alkali metals, may have migrated along the fault zone at this location. The

![Figure 6](image-url)  
**Fig. 6.** $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. $1/\text{Sr}$ showing absence of mixing relations in brines from oolitic carbonate reservoirs of the Smackover Formation. Open circles = H$_2$S-rich and black circles = H$_2$S-free formation waters. Radiogenic samples (#43, #44) from siliciclastic reservoirs in east Texas and west Arkansas have been excluded from the graph.  

![Figure 7](image-url)  
**Fig. 7.** $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. Li, B, K, and Rb concentrations in H$_2$S-rich (open circles) and H$_2$S-free waters (black circles) showing hyperbolic mixing relations in H$_2$S-rich waters. Note that despite the similar range in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, H$_2$S-free brines generally have lower and more uniform B and alkali metal contents. (H$_2$S-free samples #43 and #44 are not included in the diagrams). B and alkali metal concentrations from Moldovanayi and Walter (1992).


\[ \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \] ratios of formation waters from oolitic carbonate facies away from the fault are relatively invariant (mean = 0.70846 ± 0.0004). It is possible that variable degrees of local interactions with the clay-rich Lower Smackover may contribute to the smaller amplitude Sr isotopic heterogeneity in these brines.

Formation waters and diagenetic minerals in the Upper Smackover Formation in southwest Arkansas exhibit considerable heterogeneity in strontium isotopic compositions despite the relative homogeneity of the reservoir rock in which the waters and minerals are found. Geochemical relations and regional trends suggest that the Sr isotopic composition of these subsurface waters is controlled by carbonate and sulfate mineral diagenesis, and by mixing with waters which have interacted with silicate minerals in deeper and higher temperature regions of the sedimentary section, or with metamorphosed Paleozoic sediments. The results suggest that basinal waters, migrating through even a relatively small geographic area, are affected by processes acting on small spatial scales. The potential for small-scale spatial variations in \( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \) has important implications for the application of Sr isotope systematics in mineral paragenetic studies which attribute variations in \( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \) ratios to temporal trends. A uniform Sr reservoir present at a given time can seriously compromise assumptions involved in age-dating of diagenetic minerals. This is especially important in those studies where diagenetic minerals are correlated with host rocks and residual fluids in microscopic inclusions in order to date mineralization events and determine sources of fluids on a regional scale.

**BORON ISOTOPE SYSTEMATICS: BORON SOURCES AND BRINE EVOLUTION**

Boron contents and isotopic compositions of Smackover Formation brines are provided in Table 1. Boron concentrations range by nearly a factor of 10, from 35 to 350 mg/L. For reference, seawater of normal salinity has a boron content of about 5 mg/L. seawater evaporated to between halite and potash evaporite facies would contain between 48 and 170 mg/L B.

Boron isotope composition also ranges widely in the Smackover Formation brines, from +26 to +51% (Table 1). Modern ocean water has a \( \delta^{11}\text{B} \) value of +40% (SPIVACK et al., 1987), as does seawater experimentally evaporated to potash salt stage (Land, unpublished data). Thus, Smackover Formation brines are both isotopically enriched depleted by significant amounts relative to seawater. The majority of the samples have a B isotope composition heavier than seawater. There are still relatively few data on B contents and isotopic composition of subsurface or subaerial brines. Of the available data, only Dead Sea brines and some surficial Australian evaporated lakes have B isotope compositions heavier than modern ocean water (VENGOSH et al., 1989; 1991a,b); B isotope data from U.S. Gulf Coast formation waters (MACPHERSON and LAND, 1989; LAND and MACPHERSON, 1992), dominantly from Tertiary siliciclastic strata, tend to be significantly lighter than modern seawater (i.e., <40%). The same is true of B isotope compositions of Illinois Basin brines throughout the stratigraphic section (STUEBER et al., 1993).

Boron isotope composition is plotted vs. inverse B content in Fig. 8. A mixing relation is evident, such that brines with higher B contents have lower \( \delta^{11}\text{B} \) values. \( \text{H}_2\text{S} \)-rich brines all have \( \delta^{11}\text{B} \) values significantly lower than those of \( \text{H}_2\text{S} \)-free brines. There are variations in chloride content of Smackover brines from the southwest Arkansas shelf, brought about in part by meteoric recharge (MOLDOVANYI and WALTER, 1992). Thus, the mixing relation could be partially obscured by changes in B content. Nevertheless, it is apparent that B-enriched brines with lower \( \delta^{11}\text{B} \) values have mixed in variable proportions with brines relatively depleted in B and with \( \delta^{11}\text{B} \) values significantly enriched relative to modern ocean water.

Figure 9 shows the \( \delta^{11}\text{B} \) values of Smackover brines plotted versus Li, K, Rb, and B concentrations. Brines relatively depleted in \( ^{11}\text{B} \) also are enriched significantly in alkali elements. Simple dissolution of borates cannot account for high B concentrations because borate minerals analyzed to date have \( \delta^{11}\text{B} \) values near +30% (SWIHaRT et al., 1986; MACPHERSON, 1989). When combined with the relations between alkali elements, \( \text{H}_2\text{S} \), and radiogenic Sr, these data again suggest that the \( \text{H}_2\text{S} \)-enriched brine endmember likely evolved in chemical and isotopic composition in contact with feldspars and clay minerals undergoing diagenesis at higher temperatures and deeper in the section. These brines may have migrated into Smackover Formation reservoirs on the Arkansas shelf via the South Arkansas Fault system.

Clearly, B has undergone both isotopic and concentration evolution in Smackover Formation brines. Variations in B content in sediment porewaters may result from multiple processes. Shales are often enriched in B due to adsorption onto detrital clays in estuarine and marine environments (e.g., SPIVACK et al., 1987). During later stages of burial, the adsorbed B may be lost to solution as a result of shale dewatering and clay-mineral transformations, thereby increasing the B concentration of the porewaters (e.g., HARDER, 1970; PERRY, 1972). Some B of crustal composition, contained in the crystalline lattice of silicate minerals, may be released during dissolution. Boron may also be added to solution through interactions with borate minerals, such as boracite and danburite (MACPHERSON and LAND, 1989; SIMMONS, 1988). Alternatively, B levels may decrease if B is adsorbed or fixed onto the mineral lattice during clay mineral diagenesis (PERRY, 1972).

The Dead Sea brines have been interpreted as residual brines from marine halite deposits, enriched in B, which
have undergone bacterial sulfate reduction and early dolomitization (SASS and STARINKS, 1979; ZAK, 1974, 1980). VENGESH et al. (1991a) suggest that Dead Sea brines are depleted in B content relative to their degree of evaporative concentration because of B uptake onto clays with attendant boron isotope fractionation. Consistent with earlier work (SCHWARZ et al., 1969; SPIVACK and EDMOND, 1987), isotopically light B is preferentially adsorbed onto clays, resulting in water depleted in B, but enriched in $^{11}$B.

If Smackover Formation brines are considered to contain a primary evaporated seawater component, the degree of evaporation can be estimated assuming some conservative chemical species. Bromide in these brines is enriched above the degree of evaporation indicated from other proposed conservative parameters of seawater chemistry, such as the divalent cation function (CARPENTER, 1978). Nevertheless, on the assumption that Br remains the most nearly conservative element during seawater evaporation and water-rock interaction, we have normalized our B contents to Br. Our data are compared with data from other natural waters in Fig. 10. Smackover Formation brines have Br/B ratios up to four times those of modern seawater.

The Smackover Formation brine data in Fig. 10 form a better two-component mixing trend than the simple 1/B function plotted in Fig. 8 because the effect of meteoric dilution is removed. The position of Dead Sea brines at $\delta^{11}$B values up to +57% and Br/B ratios between 60 and 140 appears consistent with the evaporatively concentrated, B-depleted endmember of the two-component mixing trend, although there is considerable scatter in the mixing array. Importantly, the $^{11}$B-depleted, B-enriched endmember appears consistent with analyses reported by MACPHERSON and LAND (1989) and LAND and MACPHERSON (1992) for deep, saline formation waters from the Texas Gulf Coast section. Many of these brines are of the CaCl$_2$ type and are similar in overall chemistry to Smackover Formation waters. Thus, B enrichment in Smackover Formation brines could be similarly explained by release of $^{10}$B during higher temperature siliciclastic mineral diagenesis. This mechanism would also account for the other characteristics of this endmember, such as enrichments in Li, Rb, K, and $^{87}$Sr, and is consistent with H$_2$S-enrichment by abiotic sulfate reduction at elevated temperatures (e.g., ORR, 1974, 1977; POWELL and MACQUEEN, 1984).

Redbeds of the Norphlet and Eagle Mills formations contain abundant feldspars and clay minerals and are a likely source of K, Li, Rb, isotopically light B, and radiogenic Sr. Sulfates of the deep-seated Werner anhydrite are probably

![FIG. 9. $\delta^{11}$B vs. Li, B, K, and Rb concentrations in H$_2$S-rich (open circles) and H$_2$S-free (closed circles) brines. Alkali metal and B concentrations from MOLDOVANYI and WALTER (1992).](image)

![FIG. 10. $\delta^{11}$B vs. Br/B ratio in H$_2$S-rich (open circles) and H$_2$S-free (closed circles) Smackover Formation brines. Seawater (black diamond) is shown for reference. B-depleted Smackover brines are isotopically heavy, similar to Dead Sea brines (boxed area; from BENTOR, 1961; ZAK, 1974, 1980; VENGOSH et al., 1991a). Conversely, isotopically enriched samples are depleted in $^{11}$B, consistent with deep saline Vicksburg Formation (cross) and Edwards Formation (open box) brines from the Texas Gulf Coast (from MACPHERSON and LAND, 1989).](image)
undergoing thermal reduction, and hence, are a likely source of H₂S. Thus, waters circulating through these deeper formations interact with the rocks and become enriched in these species. The occurrence of highest ⁸⁷Sr/⁸⁶Sr ratios and Li and K concentrations at the northwestern end of this trend (Fig. 7) suggests that these “siliciclastic” fluids are possibly related to water migration along the more southwestern leg of the South Arkansas Fault. The tendency towards less radiogenic brine values in the south and east portions of the Arkansas shelf argues against the possibility of fluids entering via the Louisiana State Line Graben fault system.

Boron isotope systematics of Upper Jurassic Smackover Formation brines indicate that waters have been modified at various stages of the burial history. Porewaters of original marine composition could have been geochemically altered during shallow burial, as dense hypersaline Buckner Formation waters and possibly evolved brines from compaction of the underlying Louann Formation migrated into Upper Smackover Formation carbonates. Brine evolution has also been suggested from theREE composition of early calcite cements, which are enriched in heavy REEs and may have precipitated from waters depleted in light REEs, such as those associated with evaporite precipitation (MOLDOVANYI et al., 1990). In fact, it is conceivable that the Buckner depositional environment was much like the present-day Jordan Rift-Dead Sea setting, and that these fluids interacted with underlying evaporites and clastics much the same way that modern Dead Sea brines interact with associated sediments to produce the subsurface “rift valley” brines described by BENTOR (1969) and HARDIE (1990). The boron isotopic evolution was likely influenced by B depletion via uptake of ¹¹B by clay minerals, as has been shown in Australian salt lakes (VENGOSH et al., 1991b) and the Dead Sea (VENGOSH et al., 1991a).

Later, deeper burial processes have further modified the B content and boron isotopic composition of Upper Smackover Formation porewaters, although the effect appears to be somewhat less widespread than the earlier diagenetic modification. Deeply circulating waters, enriched in H₂S, B, Li, K, Rb, and radiogenic Sr released during high-temperature siliciclastic diagenetic reactions, have mixed with the resident Smackover Formation waters. The degree of mixing, as evidenced by ⁸⁷Sr/⁸⁶Sr and ¹³B ratios, is variable and probably controlled by permeability of the reservoir. The deep-seated endmember brine must have been significantly depleted in ¹¹B to produce a 15–20% shift in ¹³B in the brines. isotopically light B was probably derived from clay mineral transformations, feldspars, or from metamorphosed basement rocks.

**OXYGEN AND HYDROGEN ISOTOPE COMPOSITION: MIXING OF BRINES WITH METEORIC WATER AND WATER–ROCK INTERACTION**

Oxygen and hydrogen isotope compositions of Smackover Formation waters in southwest Arkansas (Table 1) are plotted relative to the meteoric water line (MWL) in Fig. 11. δ¹⁸O and δD values, ranging from +9% to +8% and -26% to -6%, respectively, show systematic regional trends (Fig. 12). These values are generally closer to the oxygen and hydrogen isotopic composition of seawater (SMOW) than are subsurface waters in many higher latitude intracratonic basins where δD values may be as low as -130% (HITCHON and FRIEDMAN, 1969). Within the study area, samples having lightest δ¹⁸O and δD isotopic composition correlate with relatively shallow burial depths (≤1750 m) and relatively low formation temperatures (average 65°C). These isotopically light waters are generally H₂S-free or contain only minor amounts of H₂S, have low TDS (as low as 150 g/L as compared to 360 g/L in most saline samples), and have mean δ¹⁸O and δD values of +2 ± 2% and -23 ± 3%, respectively. The remaining samples, from deeper (up to 3250 m) and hotter (up to 105°C) reservoirs, are comprised of both H₂S-rich and H₂S-free formation waters and generally have more positive mean δ¹⁸O and δD values (+6 ± 1% and -13 ± 3%, respectively).

**FIG. 11. δ¹⁸O vs. δD of Smackover Formation brines compared to SMOW and the global meteoric water line. Open circles = H₂S-rich and black circles = H₂S-free waters from the present study. Regression line represents best fit for data in southwest Arkansas and intersects MWL at approximately -5% ⁶¹⁸O and -30% ²H.**

Present-day meteoric waters in the U.S. Gulf Coast have average δ¹⁸O and δD ranges of approximately -3 to -4%, δ¹⁸O and -20 to -23% δD (CLAYTON et al., 1987; KHARAKA et al., 1987). Linear regression of Smackover Formation O and H isotope data for southwest Arkansas yields an intercept with the global meteoric water line of approximately -5% δ¹⁸O and -30% δD (Fig. 11). Given the scatter and the uncertainty of the fit (r = 0.6), this value is reasonably close to the composition present-day meteoric waters in the Gulf Coast.

Integration of elemental and stable isotope data, coupled with regional distribution of isotopically light waters in the vicinity of the South Arkansas Fault system, argue strongly for meteoric water mixing with the more saline endmember(s). We have already presented evidence that supports mixing within the saline brine endmember. δ¹¹B-depleted, H₂S-rich, and alkali-element-enriched fluids, flowing through deeper-seated sources undergoing higher-temperature diagenetic reactions, have apparently mixed into southwest Arkansas reservoirs. The isotopic composition of the meteoric endmember may be evaluated independently by integrating isotopic and elemental data. Regression of Ca vs. Cl concentrations shows that the brine compositions extrapolate to low Ca concentrations in the meteoric endmember (Fig. 13a). Meteoric waters should have relatively little Ca and Cl relative to the high Ca and Cl concentration of Smackover Formation
brines. At low Ca concentrations, the brines appear to contain approximately 45,000 mg/L Cl, likely due to halite dissolution during the downward migration of meteoric waters. Figures 13b and c show the relation between Ca content and δD and δ18O, respectively. Extrapolation of these data to low Ca concentration yields intercepts of −4% for δ18O and −36% for δD. This oxygen and hydrogen isotopic composition for the meteoric endmember is very close to the composition obtained by extrapolation to the global MWL line (Fig. 11). The “saline” endmember appears to have a δ18O value of +5 to +7‰ and a δD value of −5 to −10‰ based on the compositional data in Fig. 13b,c.

Although the timing of meteoric recharge is difficult to constrain, volcanic activity, uplift, and erosion in the area during the Cretaceous makes this a plausible time for meteoric recharge (SALVADOR, 1987; BYERLY, 1991). Since that time, the Smackover Formation has undergone continuous burial so that meteoric influx would be more limited. However, it appears that some meteoric water has penetrated locally to great depths and has significantly altered the isotopic and chemical composition of Smackover Formation brines in the immediate vicinity of the South Arkansas Fault. Meteoric infiltration subsequent to deposition of the Cretaceous Travis Peak sandstones has also been invoked to explain patterns and timing of sandstone diagenesis, including extensive quartz cementation (DUTTON and LAND, 1988).

The isotopic evolution of saline porewater within the Smackover Formation may have followed several paths. The stable isotopic composition of the isotopically heavy endmember could be related to evaporatively concentrated seawater. The stable isotopic composition of evaporating seawater defines a curved trajectory in δ18O and δD space (SOFER and GAT, 1975; HOLSER, 1979; PIERRE et al., 1984; KNAUTH and BEEUNAS, 1986). The exact position of the evaporation trajectory is difficult to model for ancient systems because climatic conditions (e.g., T °C, humidity) are largely unknown.

Regardless of the original H2O source, interactions between water, carbonate, and siliciclastic minerals at high temperatures can shift δ18O and δD values and the magnitude of the shift will depend on the water-rock ratio (e.g., SUCHEK and LAND, 1983; O'NEIL, 1987). These reactions generally tend to increase δ18O and decrease δD. Because O isotope equilibrium between water and carbonate minerals can in theory be achieved at sedimentary temperatures (e.g., CLAYTON et al., 1966; KHAHAKA and CAROTHERS, 1986; LONGSTAFFE, 1987; O'NEIL, 1987), and because δD values of formation waters may be influenced by other reactions involving isotopic exchange with H2S, hydrocarbons, and clay minerals, the potential effects of these processes on the oxygen and hydrogen isotopic composition of the saline Smackover Formation water must be considered.

The effect that carbonate water-rock equilibration has on the δ18O value of Smackover Formation waters can be evaluated from the published stable isotopic composition for grains, whole rock, and calcite cements from the study area (MOLDOVANYI et al., 1990). The mean δ18O of the primary framework grains (ooids, rhodoliths) is +27 ± 1‰ (SMOW).
Stable isotope compositions in Smackover brines

Whole-rock samples have a mean $\delta^{18}O$ of $+26 \pm 1\%$e, largely because of varying amounts of late-stage poikilitic calcite cements ($\pm 23 \pm 0.5\%e$, SMOW). In Fig. 14, we present a plot of $\delta^{18}O$ vs. temperature for formation water samples, superimposed on lines representing equilibrium conditions between formation water and calcite having $\delta^{18}O$ values of framework grains ($27\%$) and poikilitic calcite ($23\%$) within Smackover Formation reservoir rocks. Many waters are not in equilibrium with respect to either grains or whole rock. Most waters could be considered to represent equilibrium between the bracketing values of late-stage calcspar cements and the bulk rock. However, it is questionable whether the stable isotopic compositions of calcspar cements buffer the formation waters, or whether the values simply reflect equilibrium with respect to the formation water which may have other controls on its composition. Thus, although the data do not represent simple rock buffering of water oxygen isotope composition, isotopic exchange with the carbonate host rock has modified water compositions significantly.

Clay minerals, H$_2$S, and hydrocarbons are important hydrogen reservoirs. Experiments by O'NEIL and KARAKA (1976) demonstrate that H isotopic exchange between detrital clays and formation waters can occur at relatively low temperatures. YEH (1980) and SUCHAREK and LAND (1983) report significant and progressive enrichment in $\delta D$ of clays, and attendant decreases in $\delta D$ of shale-buffered porewaters. However, H exchange does not appear to be significant in other basinal settings with lower shale volumes (KARAKA and CAROTHERS, 1986). Isotopic exchange between H$_2$S and hydrogen in formation waters has been found to be locally significant in the Western Canada sedimentary basin at very high H$_2$S concentrations (HITCHON and FRIEDMAN, 1969). A plot of $\delta D$ vs. H$_2$S concentrations in Smackover Formation brines (Fig. 15) shows that $\delta D$ is apparently related to H$_2$S content in sour brines. However, many Smackover Formation waters with high levels of H$_2$S have virtually the same $\delta D$ value as samples with lower H$_2$S concentrations. A few H$_2$S-rich brines are significantly enriched in deuterium but the same is true for some H$_2$S-free brines (Table 1; Fig. 15). Thus, on a regional scale, $\delta D$ values simply are not controlled by H$_2$S content. This is likely due to the relatively low mass of dissolved sulfide gas relative to the mass of water, the dominant hydrogen reservoir (HITCHON and FRIEDMAN, 1969; KARAKA and CAROTHERS, 1986).

A summary diagram showing the potential for multiple evolution paths of the stable isotope composition of Smackover Formation waters is given in Fig. 16. The isotopically enriched endmember (also the saline endmember, see Figs. 13 and 15) is marked with an arrow.
**Fig. 16.** Stable isotopic composition of Smackover Formation brines relative to SMOW, global meteoric water line (MWL), and a schematic “hooked” evaporation trajectory. Arrows indicate the expected shifts in $\delta^{18}$O and $\delta^D$ during evaporation, rock-water interactions, and meteoric invasion. Dotted line represents the regression of Smackover Formation brine data.

$^{13}$b,c) could evolve from a variety of starting compositions and could follow various trajectories to its present-day composition. Water-rock interactions in carbonate or siliciclastic strata, depicted by radiating arrows, could involve water of SMOW-like compositions, evaporated seawater, or waters expelled from shales. Equilibration with siliciclastic and carbonate minerals would decrease $\delta^D$ and increase $\delta^{18}$O. However, given the paucity of shales in basal strata in southwest Arkansas and given the salinity/stable isotope relations in these brines, it seems that effects on $\delta^{18}$O from water-rock interactions with carbonates would likely be of greater significance than the effects on $\delta^D$ values.

Later meteoric water invasion along faults, decreasing $\delta^D$, $\delta^{18}$O, and Cl concentrations, is also indicated by the data. Importantly, it is less straightforward to invoke water-rock interactions solely with meteoric water, with subsequent evolution to its present composition through water-rock interactions. In that case, both $\delta^D$ and $\delta^{18}$O values would be expected to increase with progressive water-rock interactions, at odds with the reported burial geochemical trends in shales (e.g., YEH, 1980; SUCHECKI and LAND, 1983). Perhaps coincidentally, the $\delta^D$ value of the most saline brine endmember (about +10‰, Fig. 13c) corresponds to the evaporation trajectory positions within the halite facies of evaporative concentration of seawater, consistent with many other aspects of the elemental composition of these brines (MOLDOVANYI and WALTER, 1992).

**CONCLUSIONS**

Formation waters in Upper Jurassic Upper Smackover Formation carbonates exhibit striking variations in strontium, boron, oxygen, and hydrogen isotopic compositions within a small portion of the Gulf Coast basin in southwest Arkansas. The heterogeneities attest to the multiple geochemical processes which have influenced the isotopic composition of the formation waters. These processes potentially include evaporation of seawater to halite facies, meteoric water recharge, water-rock interactions during burial diagenesis, and mixing with hotter basinal brines undergoing reactions in deeper-seated siliciclastic strata.

Strontium isotope ratios of Smackover Formation waters are extremely heterogeneous and are generally significantly more radiogenic than Jurassic seawater. Values of $^{87}$Sr/$^{86}$Sr range from 0.70743 to 0.71071 and vary systematically across the study area. Most radiogenic $^{87}$Sr/$^{86}$Sr ratios are found in H$_2$S-rich brines and correlate with enrichments in Li, B, K, and Rb, consistent with input of radiogenic Sr and alkalies from siliciclastic sources. In contrast, H$_2$S-free waters have a more homogeneous Sr isotopic composition which probably represents an “un-mixed” endmember composition, in part controlled by diagenetic interaction with marine Jurassic $^{87}$Sr/$^{86}$Sr of the carbonate host rock. Strontium concentrations are buffered by sulfate mineral equilibria and preclude application of the relation $^{87}$Sr/$^{86}$Sr vs. $1/\text{Sr}$ as an accurate test of mixing phenomena.

Despite the absence of correlation between $^{87}$Sr/$^{86}$Sr ratios and $1/\text{Sr}$, hyperbolic relations between Sr isotopic ratios and H$_2$S, B, and alkali metals in H$_2$S-rich waters indicate mixing with waters which have experienced siliciclastic diagenetic reactions and sulfate reduction at elevated temperatures. Fluids charged with $^{87}$Sr, H$_2$S, B, and alkali metals probably gained access to the Smackover Formation reservoirs via the South Arkansas Fault zone and flowed toward the east along permeable pathways, mixing with the resident brine.

The boron isotopic composition of Smackover Formation brines in southwest Arkansas ranges from +26 to +50‰. Brines enriched in B relative to evaporation of seawater are depleted in $^{11}$B, while those depleted in boron are enriched in $^{11}$B. Relative to seawater, the boron isotopic composition of the brines has been altered by the preferential removal or addition of the light isotope, $^{10}$B, indicating that the dominant processes responsible for the isotopic composition of the brines involve boron derived from clay mineral transformations and/or crustal sources. Earliest diagenetic alteration of Smackover Formation carbonates and porewaters may have involved waters similar to Dead Sea brines in geochemical and boron isotopic composition. The Buckner depositional environment, from whence these waters may have been sourced, could have been very much like the modern Jordan Rift-Dead Sea area. A few Smackover Formation brine samples have $\delta^{11}$B similar to modern seawater and B concentrations which conford to predictions from evaporation trajectories. These could represent a less geochemically altered residual bittern.

The oxygen and hydrogen isotopic composition of Smackover Formation brines can be modeled in terms of an isotopically enriched brine and an isotopically-depleted meteoric endmember. The paucity of shales in the deep Gulf Coast sedimentary section in Arkansas suggests that local clay mineral diagenesis is not a major control on $\delta^D$ and $\delta^{18}$O values of the isotopically enriched endmember. Likewise, interactions with H$_2$S do not appear to account for the variability in the $\delta^D$ values of these brines because H$_2$S-free and H$_2$S-rich brines have a similar range of $\delta^D$ values. Water-rock interactions with carbonates, however, have significantly af-
 effected the oxygen isotope composition. Thus, the δD value appears of greater impor-
t in elucidating trends among stable isotopic compositions and the solutes of these brines, but is
difficult to interpret without knowing the flow path of the brines, and the minerals with which they have been in contact.

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