New constraints on carbonate diagenesis from integrated Sr and S isotopic and rare earth element data, Jurassic Smackover Formation, U.S. Gulf Coast: a reply

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INTRODUCTION

Wade et al. (1992) raise two objections to our interpretation of diagenesis of the Jurassic Smackover Formation carbonates in southwest Arkansas: (1) timing and degree to which saline Louann or Buckner Formation brines were involved in the precipitation of equant calcite cements, and, (2) occurrence of, and controls on, thermochemical sulfate reduction within Smackover Formation reservoirs in southwest Arkansas. Wade et al. (1992) suggest that we have ignored stratigraphic relations and contend that our sample selection is biased. We welcome the opportunity to address their objections, to clarify our procedures and sampling philosophy, and to reiterate our original interpretation of the geochemical evolution of Smackover Formation carbonates. Our interpretations are based on the integration of systematic and significant geochemical trends among various trace element and isotope systems, and offer alternative mechanisms to explain trends not readily explained by models presented by Moore and Druckman (1981), Wagner and Matthews (1982), Moore (1985) and Humphrey et al. (1986). In addition, we were able to draw on the considerable interpretive insights made possible by our related investigation of regional variations in the geochemistry of Smackover Formation brines (Moldovanyi and Walter, 1991).

PRECIPITATION OF EQUANT CALCITE CEMENTS: TIMING AND WATER CHEMISTRY

A variably luminescent equant calcite cement fills inter- and intragranular pores, moldic pores, fractures, vugs and stylolitic seams. As with most calcite cements, genesis rarely is obvious from petrographic characteristics, because different diagenetic events can produce similar petrographic fabrics. Moldovanyi et al. (1990) confronted this situation while sampling the Smackover Formation carbonates across the southwest Arkansas shelf. We found that, despite the predictable regional diagenetic zonation (Moore and Druckman, 1981), generations of pore-filling equant cement could not be adequately categorized by petrography alone, and that certain generations of equant calcite commonly transcended the geographic diagenetic-zone boundaries.

Following the paragenetic sequence in Moore and Druckman (1981) and Moore (1985), Wade et al. (1992) adhere to the simple categorization scheme of "pre-" and "post-compaction" equant calcites. They state that these cements either occur mutually exclusive of one another or they are unrecognizably intermingled in cores of the "transitional" diagenetic zone. Furthermore, Wade et al. (1992) also claim that "pre-compaction" calcite is absent from the Smackover Formation in the "southern" zone. As Wade et al. (1992) must be aware, compaction in carbonates is in part controlled by depositional texture and stabilization history, which may vary considerably spatially, such that a particular generation of cement may be present in differentially compacted rocks.

For this reason, and because, as Wade et al. (1992) have acknowledged, pre- and post-compaction cements are often difficult to distinguish petrographically, we chose not to categorize cements in this manner. Instead, our hypothesis was that "early" and "late" generations of equant calcite might be better distinguished by integrating petrographic and cathodoluminescent properties with the more quantitative and unambiguous data on minor element and Sr, C and O isotope composition. Wade et al. (1992) suggest that we have not sampled "early" pre-compaction cements and imply that our characterization of these cements in cores from the southern zone is erroneous. In reality, our combined petrographic and geochemical

approach circumvents this problem and provides less ambiguous criteria with which to categorize cements across the *entire* study area. Although we did not sample calcites from the "northern" zone, the conclusions of our study are based on geochemical properties of those cements in the "transitional" and "southern" which we did sample.

Prior to our investigation, Sr isotope compositional data on the Smackover Formation from the Arkansas shelf were limited to analyses of "generic" calcite cements and framework grains by STUEBER *et al.* (1984). These data were integrated with existing, but unpaired, analyses of stable isotope and minor element data by MOORE (1985), who suggested that the Sr isotope compositions of equant ("poikilitic") calcite cements are geochemically "tied" to present-day subsurface Smackover brines. To obtain better temporal resolution, we microsampled non-luminescent and brightly luminescent equant calcite and calcites with unequivocal genesis (such as, for example, fracture-filling cement). A full suite of geochemical analyses (O, C, Sr isotopes; minor, trace, and rare earth elements) was performed on each sample to characterize the geochemical and isotopic composition of these end-member components. Geochemistry of original marine components was defined by analyzing primary grains (e.g. ooids and rhodoliths).

Equant calcite cements exhibit a large range in C and O isotope composition, with values ranging from approximately $-2‰$ to $-8‰$ $\delta^{18}O$ and $+4‰$ to $+1.8‰$ $\delta^{13}C$. The Sr content and $^{87}Sr/^{86}Sr$ ratios of equant cements vary from 40 to 600 ppm, and 0.70679 to 0.70964, respectively. For reference, the $^{87}Sr/^{86}Sr$ ratio for Jurassic seawater ranges from 0.7068 to 0.7072 (BURKE *et al.*, 1982), Correlation of these data and integration with petrographic and luminescent properties reveals systematic geochemical trends in all the cores analyzed (Figs 7–9 in MOLDOVANYI *et al.*, 1990): heavier O isotope composition is characteristic of cements with less radiogenic $^{87}Sr/^{86}Sr$ ratios and lower Sr content. These cements are also non-luminescent and occur in cores from the "transitional" (#1 Buchanan Heirs; #3 Nations) and "southern" (#1 Barnett Estates; #1 McMahen; Tract #22–3) diagenetic zones. In contrast, brightly luminescent calcite has $\delta^{18}O$ and $\delta^{13}C$ values as low as $-8‰$ and $+1.4‰$, respectively, and has $^{87}Sr/^{86}Sr$ ratios up to 0.70964. These luminescent calcite cements were identified in cores from the "transitional" (#3 Nations) and "southern" (#1 McMahen) diagenetic zones.

The wide range in Sr isotope and trace element composition of calcite cements requires that cementation occurred over a wide range of diagenetic conditions, a conclusion also reached by others investigating Smackover Formation diagenesis (e.g. MOORE and DRUCKMAN, 1981; WAGNER and MATTHEWS, 1982; HUMPHREY *et al.*, 1986). However, our more refined sampling of early generations of calcspar shows that a significant volume of cement was in place prior to the acquisition of radiogenic character in the fluids. Furthermore, our data document progressive geochemical evolution of primary grains, a process which results from the interaction with waters evolving chemically through progressive burial and water–rock interactions. This aspect of our model—the complex geochemical evolution of grains and cements—is at odds with existing models which suggest that many geochemical properties are inherited during early diagenesis and remain unchanged during subsequent stages of alteration.

As we suggested, the geochemistry of relatively "early" calcites (lower $^{87}Sr/^{86}Sr$ ratios, LREE enrichment) may be interpreted in several ways. We were cautious to avoid firm conclusions about early diagenetic fluid chemistries. Two possibilities were discussed in MOLDOVANYI *et al.* (1990): meteoric diagenesis vs diagenesis related to evaporatively concentrated brines. Meteoric influx is quite likely, especially in the northern portion of the study area, and in select areas of the southern diagenetic zone (such as

the Walker Creek Field). Meteoric water invasion is also supported by geochemical trends in formation brines (MOLDOVANYI and WALTER, 1990, 1991) but it is difficult to ascertain the timing of meteoric recharge relative to diagenesis.

Stratigraphic considerations (i.e. relations to the overlying Buckner Evaporites and underlying Louann Salt), and the stable isotope composition and REE concentrations of "early" calcites suggest that mixing with evaporatively concentrated brines may have played a role in generating fluids involved in precipitation of non-luminescent calcite cements. The non-luminescent, nonradiogenic "early" equant calcite cements also are depleted in light rare earth elements (LREE) and have a lighter O isotope composition relative to primary grains and brightly luminescent, radiogenic calcites. Depletion in LREE cannot be easily explained by meteoric diagenesis or local rock-buffering of REE. However, evaporites are commonly enriched in LREE (MORGAN and WANDLESS, 1980; WRIGHT, 1985). Seawater concentrated to the point of evaporite mineral precipitation would be expected to be depleted in LREE; calcite cements precipitating from these waters would acquire this REE pattern. Precipitation from hypersaline waters could also be consistent with the trend toward lighter O isotope composition evident in these cements (HOLSER, 1979; PIERRE *et al.*, 1984; KNAUTH and BEEUNAS, 1986). Several fault systems, such as the South Arkansas Fault System and the Louisiana State Line Graben, were already in place at the time of Smackover and Buckner deposition (TROELL and ROBINSON, 1987; BISHOP, 1973). Introduction of hypersaline brines would be facilitated by migration along these faults or by density-driven flow from Buckner brines into relatively porous Smackover strata.

Contrary to the allegations of WADE *et al.* (1992), we do not imply that these brines were "responsible for the stabilization of unstable Smackover ooid sands shortly after deposition", but the data do suggest that "early" calcite cements could have precipitated from fluids which had interacted with hypersaline brines. Our model *does not* rule out a continued involvement of saline fluids during burial diagenesis; it *does* suggest that mixing could have occurred earlier than previously thought. We close this section by reiterating that the "lack of firm constraints on REE fractionation coupled to the ambiguity in O and Sr isotopic trends makes it difficult to model the chemistry of early diagenetic waters" (direct quote from MOLDOVANYI *et al.*, 1990).

THERMOCHEMICAL SULFATE REDUCTION

WADE *et al.* (1992) express concern over our evaluation of the S isotope geochemistry of diagenetic S species and our interpretations regarding source and distribution of H_2S within reservoirs of the Upper Smackover Formation in southwest Arkansas. They base their objections on the premise that thermochemical sulfate reduction (TSR) will occur above "some minimum temperature" (providing sufficient SO_4, H_2S, and hydrocarbons are available). They insist that the S data presented by MOLDOVANYI *et al.* (1990) indicate that thermochemical sulfate reduction has occurred in close proximity to shallow Smackover Formation reservoirs on the southwest Arkansas shelf.

Although H_2S may be generated by high-temperature abiotic and/or low-temperature biological processes, large volumes of H_2S gas in hydrocarbon reservoirs are often explained in terms of thermochemical sulfate reduction (e.g. ORR, 1974, 1977). Many of the criteria proposed by

ORR (1974, 1977) for TSR are satisfied in Smackover For-
mation reservoirs: large volumes of H_2S, abundant organic
matter and S-rich source rocks, presence of native S, and
burial temperatures in the 80–100°C range. SASSEN (1988)
and CLAYPOOL and MANCINI (1989) invoke the TSR model
of ORR (1974, 1977) to explain the occurrence of H_2S in
deeper Smackover Formation reservoirs in the Mississippi
Salt Basin and in southwest Alabama, respectively. How-
ever, evidence supporting TSR in these instances did not
include integrated data on S isotope systematics of oils,
diagenetic minerals (sulfates and sulfides), and S-species in
brines.

Despite possibly permissive physical conditions for TSR
occurrence in Smackover Formation reservoirs in south-
west Arkansas, our more detailed S isotope data reveal
two important inconsistencies with the ORR (1974, 1977)
model. Unlike the classic examples of TSR at Pine Point,
Northwest Territories, Canada (POWELL and MACQUEEN,
1984) and Big Horn Basin, Wyoming (ORR, 1974), the S
isotope compositions of sulfide and sulfate minerals, S in
oils, and dissolved H_2S and SO_4 in brines of the Smackover
Formation vary widely and do not converge toward the S
isotope composition of coeval sulfate (MOLDOVANYI and
WALTER, 1988). Typically, $\delta^{34}S$ of brine H_2S averages
+17.8‰, but may be as low as −5.2‰, while the $\delta^{34}S$ of
brine SO_4 averages +21‰ but may be up to 10‰ heavier
than Jurassic seawater sulfate (16 ± 1.5‰; CLAYPOOL et al.,
1980). Pyrite, galena, sphalerite and marcasite have a
mean $\delta^{34}S$ of −16.8‰, +3.5‰, −1.0‰, and +6.9‰, re-
spectively. In contrast, native S, anhydrite, and celesite are
enriched in ^{34}S and have a mean $\delta^{34}S$ of +18.2‰, +20.8‰,
and 27.8‰, respectively.

The S isotope composition of S in crude oils from south-
west Arkansas is equally heterogeneous and ranges from
−4.5 to +4.4‰ (MOLDOVANYI and WALTER, 1988; MOLDO-
VANYI, 1990). The variability of $\delta^{34}S$ in these samples
suggests that S of variable isotope composition may have
been added from multiple external sources, and that there
has not been equilibration among the various S reservoirs
(e.g. minerals, oils and brine). WADE et al. (1992) claim
that S isotope homogeneity is not a requisite in all cases of
TSR. This may be so, but it has yet to be generally
accepted. We know of no instance in the literature where
such widely discordant isotope compositions among oils,
H_2S, and SO_4 were interpreted as evidence in favor of
TSR.

A second, even more compelling, inconsistency with the
ORR (1974) model pertains to the geographic distribution
of H_2S-rich reservoirs along the narrow east–west trending
belt within the study area and to the geochemical charac-
teristics of H_2S-rich brines. WADE et al. (1992) attribute the
distribution of H_2S to controls exerted by temperature and
by availability of SO_4. They suggest that the southern
boundary of the H_2S-rich belt is controlled by a change in
facies from anhydrite to non-evaporitic shale in the over-
lying Buckner Formation. However, they fail to explain
what controls the northern boundary, as well as to account
for the distribution of H_2S in Smackover Formation brines.

The relation between H_2S mole-% and depth depicted
by WADE et al. (1992) (their fig. 1) is based on unpublished
data from unidentified "representative Arkansas pet-
roleum reservoirs". From these data, they attempt to
establish upper and lower depth limits from 2.4 to 3 km for
our sulfide data. Our samples, taken from H_2S-rich reser-
voirs ranging in depth from 1.7 to 2.7 km, do not in fact
exhibit these trends. In Fig. 1 we show that H_2S-free
Smackover Formation brines from reservoirs overlain by
anhydritic Buckner facies occur over an overlapping depth
range with H_2S-rich reservoirs. Simple temperature and
lithological controls, thus, are not sufficient to explain H_2S
distribution. Moreover, it is not even apparent that H_2S
content of brines shows any clear increase with depth;
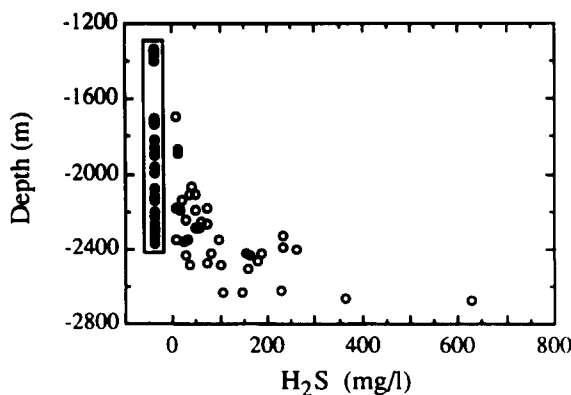there is no relation among H_2S or SO_4 concentrations and

FIG. 1. Depth and dissolved H_2S content of subsurface
formation waters in H_2S-rich (open circles) and H_2S-free
reservoirs (solid circles) in the Smackover Formation,
southwest Arkansas (after MOLDOVANYI, 1990). The
H_2S-free samples plotted are restricted to reservoirs from
the northern portion of the study area which are in contact
with anhydritic facies of the overlying Buckner Formation.
The H_2S-free formation waters overlap in production
depth with H_2S-rich formation waters. The trend in H_2S
content of sour brines with increasing reservoir depth is not
especially strong.

temperature in our formation water samples (MOLDOVANYI
and WALTER, 1991).

The distribution of H_2S, however, does follow a regional
east–west gradient in H_2S concentrations unrelated to res-
ervoir depth (MOLDOVANYI and WALTER, 1988). Highest
concentrations are found in the western and southwestern
end of the study area, along the southern margin of the
H_2S-belt (at Dorcheat–Macedonia field) and near the trace
of the South Arkansas Fault in Miller County (at Mars Hill
and McKamie-Patton fields) (MOLDOVANYI, 1990; CAR-
PENTER and TROUT, 1978). In addition, brines with elevated
concentrations of H_2S also have elevated levels of B, Li, K
and radiogenic Sr (MOLDOVANYI and WALTER, 1988). These
trends in brine geochemistry cannot be explained by the
facies patterns suggested by WADE et al. (1992).

In Fig. 2 we show data for Li and Rb contents of
H_2S-free formation water samples from reservoirs overlain
by evaporitic Buckner facies and compare these to
H_2S-rich formation water samples. Clearly, increase in
H_2S content is associated with elements exotic to the calci-
tic reservoir mineralogy. Because the brines with most
radiogenic Sr isotope composition typically have the isoto-
pically heaviest H_2S (MOLDOVANYI, 1990), it is likely that
H_2S was dominantly generated by TSR at higher tempera-
tures, in contact with siliciclastics deeper in the sedimen-
tary section. Taken together with the discordance in the S
isotope systematics among Smackover Formation oils,
brine H_2S and SO_4, and diagenetic sulfides, we cannot
envision a local source for H_2S. Thus, we reiterate our
original conclusion that H_2S was generated, likely by TSR,
deeper in the basin and subsequently migrated into upper
Smackover Formation reservoirs of the southwest Arkan-
sas shelf..

We hope that our comments have addressed the issues
raised by WADE et al. (1992) regarding the complex dia-
genetic history of the Smackover Formation and the con-
trols on regional geochemistry of Smackover Formation
waters. We feel we have demonstrated that integration of
elemental and isotopic data on discrete diagenetic com-
ponents as well as on present formation waters can provide
important new constraints on progressive burial diagenesis
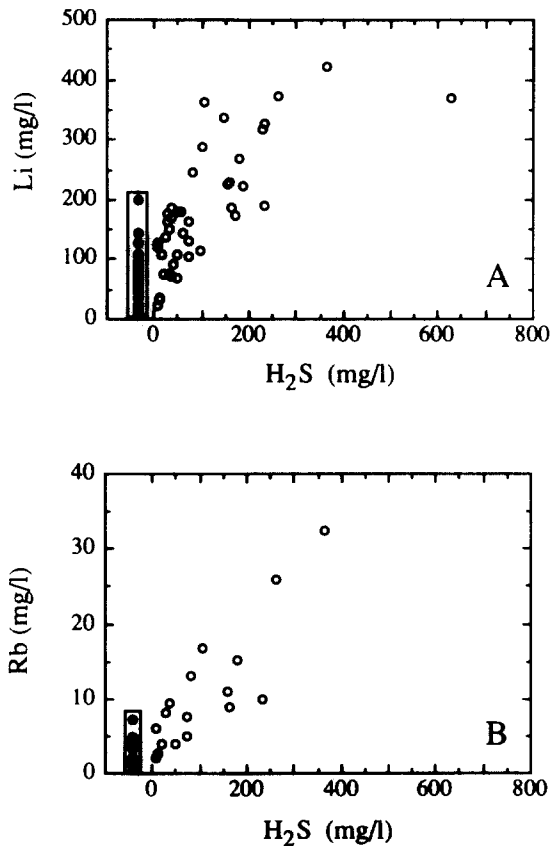
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Fig. 2. Content of Li (A) and Rb (B) in Smackover Formation brines from the southwest Arkansas shelf (oolitic facies) (after MOLDOVANYI, 1990). Samples are identified as H_2S-rich (open circles) and H_2S-free (solid circles). As in Fig. 1, H_2S-free samples are restricted to the northern portion of the shelf where Smackover Formation reservoirs are in contact with evaporitic facies of the overlying Buckner Formation. Lithium and Rb content of H_2S-free brines is lower than most H_2S-rich brines and there is a strong positive correlation between dissolved H_2S and Li and Rb concentrations.

of Smackover Formation carbonates and on the importance of water–rock interactions external to the carbonate reservoir.

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