Meteoric diagenesis and fluid-rock interaction in the Middle Permian Capitan backreef: Yates Formation, Slaughter Canyon, New Mexico

James W. Bishop, David A. Osleger, Isabel P. Montañez, and Dawn Y. Sumner

ABSTRACT

This study examines the geochemical record of diagenesis in the Middle Permian Yates shelf, exposed in Slaughter Canyon, New Mexico. This diagenetic history significantly modified lithologies, depositional fabrics, and pore systems. Early diagenesis was dominated during sea level highstands by marine cementation and reflux dolomitization, and during sea level lowstands by meteoric cementation and stabilization—the focus of this study. This early diagenesis variably overprinted primary marine isotopic signatures, potentially leading to erroneous chemostratigraphic correlations or paleoclimate reconstructions.

Four correlative sections through one m-scale cycle were analyzed for their $\delta^{13}C$ and $\delta^{18}O$ values. They show significant (2–4‰) $\delta^{13}C$ and $\delta^{18}O$ variability in coeval, texturally well-preserved calcites. The $\delta^{13}C$ and $\delta^{18}O$ values of marine cements, brachiopods, bulk carbonate, micritic matrix, and the first generation of meteoric spar (from high to low values) delineate an “inverted J curve,” indicating the variable alteration of components by diagenetic fluids. Numerical models indicate that the observed stable isotope trend is most consistent with diagenetic alteration in a partially closed system by meteoric fluids mixed with a progressively diminishing contribution of recycled marine waters.

In the Yates shelf, marine cements provide a more robust primary isotopic record than micritic matrix; however, neither preserves primary seawater isotopic values. Furthermore, common criteria used to diagenetically screen samples proved inadequate (e.g., textural preservation, staining, luminescence, depletion near

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sequence boundaries). Instead, diagenetic resetting is resolved by analyzing multiple, closely spaced, independently correlated sections, and by delineating trends between primary and later diagenetic components in populations of isotopic data.

INTRODUCTION

Stable carbon ($\delta^{13}$C) and oxygen ($\delta^{18}$O) isotope values from carbonate sediments are used extensively to reconstruct the past climate of the Earth and to correlate outcrops or wells. For the Paleozoic and the Precambrian, the absence of oceanic crust and associated deep sea sediments requires that many climate reconstructions be derived from carbonate platforms of marginal continental basins and epeiric seas. Increasingly, stable isotope data are also used to correlate disparate outcrops and/or wells in the subsurface, where seismic or biostratigraphic data may be insufficient (e.g., Vahrenkamp, 1996; Katz et al., 2007; Pollitt et al., 2012; Playton et al., 2013). However, isotopic values in platform strata are particularly susceptible to diagenetic resetting by evolved marine pore waters, by meteoric fluids during changes in relative sea level, and by saline brines and meteoric waters during their protracted burial and uplift histories (e.g., Moore, 1989, 2001; Choquette and James, 1990; Swart and Eberli, 2005). Additionally, isotopic values of some epeiric sea carbonates vary significantly along bathymetric profiles (e.g., Holmden et al., 1998; Panchuk et al., 2005, 2006), reflecting isolated water masses on shallow shelves (Patterson and Walter, 1994b) and seafloor dissolution, precipitation, and recrystallization (Patterson and Walter, 1994a; James et al., 2005), which can lead to isotopic resetting (Walter et al., 2007). Thus, for accurate chemostratigraphic correlations, and paleoclimate and paleoceanographic interpretations, it is essential to test isotopic trends for both diagenetic alteration and spatial heterogeneity.

In this study, we examine the $\delta^{13}$C and $\delta^{18}$O of marine cements, brachiopods, spar cements, micritic matrix, and bulk carbonate from a dip transect of one fourth- to fifth-order Yates cycle in the Capitan backreef, Slaughter Canyon, Guadalupe Mountains, New Mexico (Figure 1). The Capitan backreef is an ideal natural laboratory to evaluate $\delta^{13}$C and $\delta^{18}$O variability in platform carbonates because of its superb outcrop exposure on the canyon walls of the Guadalupe Mountains, its well-constrained sequence-stratigraphic framework (Osleger, 1998; Osleger and Tinker, 1999), and its well-constrained paragenetic history (e.g., Mruk, 1989; Scholle et al., 1992).

The Capitan system has been a focal point of carbonate research for more than 80 yr and has nurtured fundamental...
advances in sequence stratigraphy, diagenesis, and geochemistry (e.g., King, 1948; Dunham, 1972; Hileman and Mazzullo, 1977; Harris and Grover, 1989; Hill, 1996; Saller et al., 1999), learnings that have been applied widely throughout the industry. Here, we focus on the geochemical characterization of the backreef strata, a topic that remains poorly understood. This study has implications for hydrocarbon exploration and production, both within the Permian Basin and elsewhere. In the subsurface, siliciclastic sands of the Yates Formation, along with subordinate platform interior facies, are the main hydrocarbon-bearing reservoirs, whereas backreef and reefal facies commonly are strong aquifers used

Figure 1. (A) Map of the Permian Basin. The heavy box outlines the study area in the Guadalupe Mountains. During the Guadalupian, the Delaware Basin was connected to the Marfa Basin and the Panthalassic ocean through either the Hovey or the Diablo channel (Hill, 1999). (B) Schematic of Guadalupian deposition preserved in the Guadalupe Mountains. The Capitan backreef is subdivided into three composite sequences: the Seven Rivers, the Yates, and the Tansill. The study interval (heavy box) consists of the upper cycle in the Yates 2 high-frequency sequences (HFS) in Slaughter Canyon (Osleger, 1998). Modified from Weidlich and Fagerstrom (1999); used with SEPM permission. (C) Basemap of Slaughter Canyon, showing sections measured by Osleger (1998). This study examines sections 2 to 5. Map image, grid, roads, and washes derived from the U.S. Geological Survey Quadrangle Maps for Serpentine Bends (USGS, 2011) and Grapevine Draw (USGS, 2010). Universal Transverse Mercator, Zone 13S. (D) West-facing wall of Slaughter Canyon, showing the locations of sections 2 to 5. Image: Google, TerraMetrics © 2013. Mts. = Mountains.
as a water source for secondary recovery throughout the Delaware Basin (Ward et al., 1986; Hill, 1996). This study evaluates the origin of a major porosity-occluding cement within this aquifer, using stable isotope proxies. Although this cement has been recognized for decades, relatively little is known of its timing and distribution—a common problem within the industry, which hampers the prediction of porosity-occluding phases. Geochemical analysis helps identify cements and better understand their origin and timing—goals that improve the delineation of diagenetic geobodies that can be used in reservoir modeling. Additionally, this study assesses how faithfully these rocks preserve primary δ13C and δ18O values—the underpinning for chemostratigraphy, a methodology increasingly being used within the industry to correlate wells.

In this article, we first review the Yates backreef stratigraphic framework and describe the paragenetic history, supplementing our observations with those of other authors. We then present our isotopic data in the context of this stratigraphic and paragenetic framework. Finally, we use numerical models of fluid-rock interaction, using the methodology of Banner and Hanson (1990), to explain the distribution of isotopic data. These models simulate iterative equilibration of rock with its continually recharged pore fluid, resulting in incremental geochemical alteration. They allow a comparison of resulting fluid-rock interaction curves (a time series) with populations of geochemical data, taken to represent samples that have equilibrated with pore fluids a varying number of times.

**GEOLOGIC BACKGROUND**

**Basin Geography**

The Delaware Basin formed when the Mississippian to Early Permian Ouachita orogeny subdivided the ancestral Permian Basin into highlands and smaller basins. During the Capitanian and Ochoan (Middle to Late Permian), the Delaware Basin was more than 500 m (>1640 ft) deep and connected by a channel to the Marfa Basin and the global Panthalassic Ocean (Figure 1A; Hill, 1996, 1999). The massive Capitan reef formed in late Capitanian time and prograded into the basin during global regression (Ross and Ross, 1987a, b; Jin et al., 1994). Capitan stratigraphy is subdivided into the Seven Rivers, Yates, and Tansill Formations based on backreef sedimentation (Figure 1B). For most of its development, the Capitan reef formed a marginal mound in tens-of-meters water depth at the shelf edge, seaward and downdip of a pisolite shelf crest (Dunham, 1972; Osleger, 1998; Tinker, 1998). By later Tansill-equivalent time of deposition, it likely formed a barrier at least locally (e.g., Kirkland et al., 1999). Flow through the channel from the Marfa Basin was progressively restricted during Ochoan time, and the basin filled with thick bedded evaporites (Anderson and Dean, 1995).

This study focuses on Yates strata exposed in the Guadalupe Mountains (Figure 1), a triangular block tilted during Neogene Basin and Range tectonism (Hill, 1996). The basin-facing southeastern margin is now exposed because of differential erosion of reef-tract and basin deposits. Here, we examine Yates outcrops on the northeastern wall of the Slaughter Canyon.

**Stratigraphic Framework**

Slaughter Canyon contains seismic-scale outcrops that are well constrained in a high-resolution sequence-stratigraphic model (Osleger, 1998). The Yates composite sequence has been subdivided into high-frequency sequences (HFSs) and cycles, which have been correlated 3 km (1.9 mi) along shelf transects, and 25 to 80 km (16–50 mi) along strike (Garber et al., 1989; Osleger, 1998; Tinker, 1998; Osleger and Tinker, 1999). Each HFS is estimated to have lasted 100 to 400 k.y. (Borer and Harris, 1991b; Osleger, 1998; Tinker, 1998). We focus on the uppermost cycle in the Yates 2 HFS (equal to G23 in Harman, 2011, and Yates 3 HFS in Tinker, 1998, and Osleger and Tinker, 1999). Given that four major cycles exist within this HFS, we estimate a duration of 25 to 100 k.y. for accumulation of the interval studied.

During deposition of the Yates 2 HFS, the shoreline consisted of an oncoidal, fenestral pisolite crest with tepee structures, sheet cracks, and tidal laminites. Behind this shelf crest was a broad, shallow, evaporative lagoon. Basinward, the shelf crest passed into skeletal and locally oolitic packstones and...
grainstones and, finally, to the boundstones of the Capitan reef. In the immediate backreef, reef boundstones interdigitate with poorly sorted massive packstones and grainstones. These backreef strata dip up to 14° toward the basin, showing the classic fall-in geometry of the Permian reef (e.g., Pray and Esteban, 1977). The origin of basinward dips in the fall-in beds is controversial (e.g., Saller, 1996; Osleger, 1998; Tinker, 1998; Harwood and Kendall, 1999; Osleger and Tinker, 1999; Hunt et al., 2002; Kosa and Hunt, 2006; Resor and Flodin, 2010). The existing dips likely reflect depositional geometries enhanced by syn- to postdepositional fractures and faulting (e.g., Rush and Kerans, 2010). Cycle caps are commonly overlain by siliciclastics that moved across the shelf during lowstands and were reworked during ensuing transgressions (Borer and Harris, 1989, 1991a).

METHODS

In the chosen cycle, four correlative sections were measured, corresponding to Osleger’s (1998) sections 2 to 5. One hundred sixty-four samples were collected, at approximately 1-m (3-ft) intervals in sections 3 to 5 and at 0.5-m (1.5-ft) intervals in section 2. Samples were thin sectioned, stained with Alizarin Red-S and potassium ferricyanide (Dickson, 1965), and petrographically examined under transmitted light and cathodoluminescence (CL) using a Technosyn cold CL scope (model 8200 Mk II), operated at 10 to 15 kV with a current of 400 to 600 μA.

After diagenetic screening, powders were drilled for stable isotope analyses. For bulk carbonates, powders were drilled from thin-section billets, using a drill press with a 100-μm bit. For individual components, selected areas were microdrilled from approximately 70-μm-thick sections using a fully automated Merchantek micromilling system with approximately 20-μm spatial resolution. Powders of 15 to 150 μg were roasted for 30 min at 375°C in vacuo to remove organic volatiles. Carbon and oxygen stable isotope values were determined using a Fisons Optima isotope ratio mass spectrometer with a 90°C isocarb common acid bath autocalibrate system in the Stan Margolis Stable Isotope Laboratory, University of California Davis. Values are reported relative to Peedee belemnite using standard delta notation. One-sigma analytical precision for both δ¹⁸O and δ¹³C is more than ± 0.1‰.

CARBONATE CEMENT PARAGENESIS

Carbonate cements were distinguished based on their morphology, staining, CL, inclusions, and texture. They are divided into marine cements, late calcite cements, and dolomites. Each will be described here and then interpreted in the context of this and previous diagenetic studies of the Capitan.

Marine Cements

Marine cements are generally bladed to fibrous, rich in inclusions, and form pre-compaction isopachous coatings around grains (Figure 2). These cements precipitated very soon after deposition because the strata that host them are commonly crosscut by fractures that can be traced to cycle bounding surfaces. Their large volume in subhorizontal sheet cracks and decimeter-scale reef crypts requires an origin before significant burial and compaction. Although in each case primary textures can be well preserved, they have undoubtedly undergone various degrees of recrystallization (e.g., from metastable to stable mineralogies) and geochemical alteration. Isotopic values for marine cements have overlapping fields that range from 0‰ to 6‰ in δ¹³C and −6‰ to 0‰ in δ¹⁸O (Figures 3, 4).

Neomorphosed Botryoids

Botryoids composed of neomorphic calcite fill fractures in the pisolite facies and sheet cracks in tepees. Botryoids range in size from hundreds of micrometers to several centimeters. Where micrite drapes botryoids, it defines constituent crystal pseudomorphs with square-tipped or (rarely) featherlike
**Figure 2.** Photomicrographs of carbonate cements.

(A) Transmitted light photomicrograph of radiaxial fibrous calcite lining a primary pore in reef boundstone. Radiaxial fibrous calcite has divergent subcrystals and pendulum extinction. Crystal terminations are typically scalenohedral but can be flat topped (arrow). The red box outlines the area in B. (B) Transmitted light photomicrograph showing curved cleavage planes, diagnostic of radiaxial fibrous calcite.

(C and D) Paired transmitted light and cathode-luminescence (CL) photomicrographs. Inclusion-poor isopachous fibrous calcite (arrows at terminations) coating a micritic sphere. Limpid bladed crystals and weakly developed 120° compromise boundaries suggest a neomorphic fabric and original aragonite or high-magnesium calcite composition. Long-exposure time (4 s) on the CL photomicrograph accentuates the patchy dull luminescence of this sample. (E and F) Paired transmitted light and CL (2-s exposure) photomicrographs of micritized coated algal grains, consisting of fabric retentive dolomite replaced by red-luminescent fabric destructive dolomite (FDD). Primary pores are filled by two generations of spar: CS1 has nonluminescent to dully luminescent zones, locally corroded; porosity occluding CS2 has moderate to brightly luminescent zones. (G and H) Paired transmitted light and long-exposure (4 s) CL photomicrographs. The primary pore is coated by dense fibrous marine cements, capped by inclusion-rich prismatic (IRP) cement (arrows). Prismatic terminations of IRP are overgrown by zoned CS1, and remaining porosity is filled by non- to dully luminescent CS3.
Figure 3. Stratigraphic distribution of component and bulk carbonate $\delta^{13}C$ and $\delta^{18}O$ values from Slaughter Canyon. The inset shows a schematic depositional profile (from Osleger, 1998; this study). Spaced 200 to 500 m (656–1640 ft) apart, the four columns define a northwest (shoreward section 2) to southeast (basinward section 5) transect. Columns are correlated using siliciclastic sands that mark cycle bases (yellow), with some uncertainty where sands filter into reefal facies. In each column, matrix samples are more depleted in $^{13}C$ and $\delta^{18}O$ than marine cement and brachiopod samples. Bulk carbonate values typically fall between matrix and marine cements. Over a meter or two stratigraphically, $\delta^{13}C$ and $\delta^{18}O$ variability exceeds 2‰ for both matrix and cements. No correlation of isotopic trends is apparent between sections. HFS = high-frequency sequence; PDB = Peedee belemnite.
terminations. Neomorphic crystals consist of a patchwork of small (50–300 μm) mosaic calcite. Numerous elongate microinclusions impart a fibrous texture to the botryoids. Botryoids have a patchy dull luminescence.

Neomorphosed botryoids are interpreted as aragonite replaced by calcite, based on their characteristic square-tipped to featherlike terminations and mosaic replacement textures (e.g., Sandberg, 1985). The presence of micrite drapes suggests that these cements were synsedimentary. Neomorphosed botryoids are widely reported from Capitan reef facies, where they are intergrown with Archaeolithoporella, and from the pisolite crest facies tract, where primary aragonite is locally preserved (Chafetz et al., 2008). The presence of micritic drapes (this study), their intergrowth with Archaeolithoporella (Given and Lohmann, 1985, 1986), their reworking (Harwood and Kendall, 1999), and their significant volumetric contribution to reef crypts (>50%; Mruk, 1989) all suggest that neomorphosed botryoids were a synsedimentary marine cement.

Figure 4. (A) Isotope data, plotted by component. Marine cements, brachiopods, matrix, bulk carbonate, and spar CS1 plot along an inverted J curve (outlined), indicating fluid-rock interaction. In general, marine cements are less altered than matrix; bulk carbonates plot intermediate to these values, reflecting that they are a physical mixture of these two components. Calcite spar 1 plots as the depleted end member, indicating that it precipitated from diagenetic fluids under mostly fluid-buffered conditions. Values for dolomites are consistent with those measured elsewhere in the Capitan and attributed to refluxing mesosaline waters from the carbonate lagoon (Melim and Scholle, 2002). (B) Early cements are isotopically indistinguishable and overlap those of normal marine brachiopods, suggesting similar original values and comparable susceptibilities to fluid-rock alteration. All cements were likely marine, including inclusion-rich prismatic calcite (IRP), which, elsewhere, was interpreted as a mixing zone cement (e.g., Mruk, 1989).

IFC = isopachous fibrous calcite; RFC = radial fibrous calcite; FRD = fabric retentive dolomite; FDD = fabric destructive dolomite; PDB = Peedee belemnite.
Isopachous Fibrous Calcite

Isopachous fibrous calcite (IFC) commonly forms the first generation of cements in sheet cracks and around primary pores in grainstones or well-washed areas of packstones (Figure 2C, D). These cements form isopachous rinds as much as several hundreds of micrometers thick. In large pores, these rinds are commonly stacked, forming crusts as much as 2 mm thick. Locally, crusts contain peloids and skeletal debris. Isopachous fibrous calcite consists of turbid, radial fibrous calcite crystals, typically approximately 100 μm in length. Locally, these crystals are inclusion free, bladed, and/or have scalenohedral terminations. They stain pink with Dickson’s solution and commonly have no or patchy dull luminescence.

Isopachous fibrous calcite is interpreted as neomorphic calcite cement. The paucity of microdolomite inclusions suggests either that this cement was originally relatively low in Mg, or that it exsolved Mg in an open system (Meyers and Lohmann, 1977). Sediment within crusts of IFC suggests that IFC grew syndepositionally. Similar cements were found coating primary pores in the Yates backreef (Mutti and Simo, 1993) and the Yates-equivalent reef (Mruk, 1989), where they were interpreted as former high-magnesium calcite (HMC) cement. In Tansill backreef facies, similar isopachous crusts with square or acute-pointed terminations were inferred as aragonitic pseudomorphs (Mazzullo, 1999). In this study, bladed, inclusion-free, limpid crystals suggest a neomorphic fabric and an original mineralogy of either HMC or aragonite (e.g., Figure 2C, D). Only one sample contained IFC with feathery terminations, which might support a primary aragonite origin.

Radiaxial Fibrous Calcite and Fascicular Optic Calcite

Primary pores and secondary fractures are commonly lined by turbid crystals of radiaxial fibrous calcite (RFC) and rarely fascicular optic calcite (FOC) (Kendall, 1985). Radiaxial fibrous calcite and FOC commonly form the first generation of pore-lining cement, or they encrust thin rinds of IFC. These cements are abundant in primary pores where the reef interfingers with the fall-in beds, and in primary pores and early fractures of the pisolite crest facies tract. Radiaxial fibrous calcite forms columnar crystals as much as 3 mm long, containing divergent subcrystals. Convergent optic axes create distinctive concave twin planes and extinction that sweeps like a pendulum through the crystal (Figure 2A, B). Rarely, RFC is intergrown with FOC, which has divergent optic axes, convex twin planes, and extinction that sweeps radially through the crystal. Both RFC and FOC typically have scalenohedral crystal terminations. Crystals are turbid because of abundant inclusions, which are distributed throughout and define fibrous relics. Inclusions generally fall into two size classes: larger 5- to 40-μm inclusions, and smaller <5-μm inclusions that impart a dusty character. Larger inclusions are anhedral to euhedral dolomite. Smaller inclusions are locally identifiable as dolomite rhombs but more commonly are elongate zones with dark inclusion walls. These smaller elongate microinclusions impart the relict fibrous texture. Radiaxial fibrous calcite and FOC commonly have no or patchy dull luminescence. Larger dolomite microinclusions can exhibit moderate luminescence.

Radiaxial fibrous calcite and FOC are interpreted as original calcite cements that formed during very shallow burial in marine pore waters. An original mineralogy as HMC is probable, given the abundance of dolomite microinclusions (Meyers and Lohmann, 1977). A marine origin is suggested by the fibrous texture and elevated Sr (Rahnis and Kirkland, 1999). In addition, neptunian fissures related to cycle bounding surfaces commonly fractured strata containing voluminous early RFC and FOC pore-lining cement, suggesting that the cements formed during the sea level cycle that deposited the sediments. Because RFC and FOC locally fill moldic pores, we infer that they formed postdepositionally, a conclusion supported by the absence of micritic drapes, interred skeletal debris, biotic encrustation, or reworking of these cements (in contrast with neomorphosed botryoids and IFC). A primary origin may be suggested by curved twin planes and unaligned optic axes, which are energetically unfavorable and unlikely to result from replacement (Kendall, 1985). In contrast, Rahnis and Kirkland (1999) concluded that RFC and FOC are products of recrystallization because of an uneven distribution of dolomite microinclusions (cf. Wilson and Dickson, 1996; Richter et al., 2011). The stable isotope data in this study support a variably long history of diagenetic resetting, despite well-preserved textures (see below).
Inclusion-Rich Prismatic Calcite

Inclusion-rich prismatic calcite fills moldic porosity and commonly forms isopachous coatings around primary pores, nucleating on sedimentary particles and on earlier cement generations (e.g., IFC, RFC, FOC). Inclusion-rich prismatic calcite forms bladed to equant crystals, which are defined by inclusions delineating rhombic to scalenohedral terminations (Figure 2G, H). However, only rarely do inclusion-rich prismatic (IRP) margins constitute crystal boundaries. More typically, IRP syntaxially overgrows earlier cements (especially RFC) and/or is syntaxially overgrown by zoned calcite spar (CS). Boundaries between IRP and calcite spar 1 (CS1) are delineated by a change in the concentration of micro- (20 μm) dolomite or fluid inclusions, and by CL zoning (Figure 2G, H). Locally, the morphologies of IRP and RFC are difficult to distinguish, and IRP appears to have curved twin planes (possibly an oblique cut through RFC). Inclusion-rich prismatic calcite typically has patchy dull to moderate luminescence.

Inclusion-rich prismatic calcite is interpreted as an original HMC cement that precipitated postdepositionally from marine-derived pore waters. An origin during shallow burial is suggested because IRP fills moldic pores, formed before significant compaction (cf. CS1), and is locally the earliest and most voluminous cement phase in rocks that host neptunian fissures tied to cycle bounding surfaces.

Other scientists have interpreted that IRP precipitated from meteoric-marine waters in a mixing zone, based on the presence at IRP terminations of microinclusions of dolomite (dolomite necklaces) and/or kaolinite, inferred to have formed under meteoric influence (e.g., Mazzullo, 1999; Rahnis and Kirkland, 1999). A mixing zone origin has also been suggested because IRP fills after blocky calcite (CS1) that is inferred to be meteoric and because IRP is absent from growth framework pores in the reef—observations consistent with a mixed water origin (Mruk, 1989; Mutti and Simo, 1993; Mazzullo, 1999; Rahnis and Kirkland, 1999). A mixing zone origin has also been suggested because IRP precipitated after fibrous marine cements but before blocky calcite (CS1) that is inferred to be meteoric and because IRP is absent from growth framework pores in the reef—observations consistent with a mixed water origin (Mruk, 1989; Mutti and Simo, 1993; Mazzullo, 1999; Rahnis and Kirkland, 1999). Dolomite necklaces at IRP terminations and intergrown kaolinite books were not observed in this study. Also, IRP fills primary pores in backreef strata (Mutti and Simo, 1993; this study), and the trend of δ18O and δ13C values for IRP calcites are indistinguishable from demonstrably marine cements, suggesting that they shared a common origin and diagenetic history (see below). We propose that IRP calcite likely precipitated from marine-derived pore waters but was overprinted along with other marine cements during subsequent fluid-rock interaction.

Late Calcite Cements

Late calcite cements from backreef and reef facies were subdivided based on CL zonation and on episodes of dissolution. Previous studies of reefal diagenesis have also used isotopic ranges as criteria (e.g., Given and Lohmann, 1985, 1986; Mruk, 1989).

Calcite Spar 1

Calcite spar 1 fills primary and secondary porosity in all facies, where it commonly syntaxially overgrew IRP and locally filled porosity around fractured substrates (Figure 2E–H). Calcite spar 1 forms equant to bladed, limpid crystals, as much as 500 μm in length. Calcite spar 1 has repeating subzones of nonluminescence and moderate luminescence. Isotopic values for CS1 (n = 10) range from 1‰ to −4‰ in δ13C and −5‰ to −8‰ in δ18O (Figures 3, 4).

Calcite spar 1 is interpreted as a Permian meteoric phreatic cement on the basis of its paragenetic timing, distribution across the Capitan, and geochemistry (Pingitore and Goodell, 1979; Given and Lohmann, 1985, 1986; Mruk, 1989; Scholle et al., 1992). Calcite spar 1 formed after initial compaction and dissolution (i.e., in skeletal molds or on leached, fractured, and compacted cement substrates; Mruk, 1989), demonstrating a later origin than the IRP calcite. Calcite spar 1 is abundant in pores in the backreef and reef but has not been observed in lower forereef strata (Given and Lohmann, 1986; Mruk, 1989; Melim and Scholle, 1999), suggesting precipitation from a meteoric lens that did not extend to the lower forereef. It is unlikely to have formed from basinal fluids expelled from compacting clastics, given its low Fe content and relatively simple CL zonation (i.e., not sector zoned). It also has isotopic values more depleted in δ13C and δ18O than those of calcite cements in Yates-equivalent basinal sandstones (δ13C of −1.8‰ to −3‰; δ18O of −4.5‰ to −6.3‰; Dutton, 2008). Finally, CS1 is unlikely to have been
derived from evaporatively concentrated seawater, given its depleted $\delta^{18}O$ values. Thus, we conclude that CS1 is a meteoric phreatic cement. Given and Lohmann (1986) argued a meteoric origin for CS1 based on finding higher $\delta^{13}C$ values more basinward along a paleoslope traverse (from reef to forereef). This $\delta^{13}C$ enrichment was attributed to greater rock buffering of the fluid and an increased residence time as fluids moved downslope. Although we broadly agree with a meteoric phreatic origin, our isotopic data imply a secondary influence of marine waters in the origin of CS1 (discussed below).

Calcite Spar 2
In primary and secondary porosity of all facies, calcite spar 2 (CS2) commonly forms equant crystals (Figure 2E, F). The interface between CS1 and CS2 is typically marked by the corrosion and fracturing of CS1, or locally, CS2 syntaxially overgrows CS1. Calcite spar 2 consists of nonferroan (pink-staining) crystals with some inclusions and is subzoned, moderately to brightly luminescent. Isotopic values for CS2 ($n = 2$) range from 2.3‰ to 3.1‰ in $\delta^{13}C$ and $-2.3‰$ to $-11.1‰$ in $\delta^{18}O$ (Figures 3, 4).

Calcite spar 2 formed after compaction and is interpreted as a Cenozoic meteoric spar that likely replaced Ochoan evaporites (Scholle et al., 1992).

Calcite Spar 3
Calcite spar 3 (CS3) fills primary and secondary porosity in all facies, where it commonly cements fractured CS1 and CS2 cements (Figure 2G, H). Calcite spar 3 forms a nonferroan (pink staining), locally dusty, equant, locally poikilotopic spar that is nonluminescent to dully luminescent. Calcite spar 3 is commonly intergrown with kaolinite, which luminesces blue. Isotopic values for CS3 ($n = 2$) range from $-3.7‰$ to $-5.0‰$ in $\delta^{13}C$ and $-7.5‰$ to $-9.2‰$ in $\delta^{18}O$ (Figures 3, 4).

Calcite spar 3 is interpreted as a Cenozoic meteoric spar that replaced evaporites (Scholle et al., 1992).

Dolomite
Dolomite is pervasive in the pisolite crest facies tract and abundant near cycle tops in the backreef (Mutti and Simo, 1993). Dolomite in the forereef and reef occurs preferentially around early fractures and neptunian dikes (Melim and Scholle, 1995, 1999). Initial precipitation has been attributed to meteoric–marine mixing zone conditions (Mruk, 1989; Mazzullo, 1999; Rahnis and Kirkland, 1999), and to reflux (Mutti and Simo, 1993) from a mesosaline carbonate lagoon (Melim and Scholle, 1995, 1999, 2002).

Fabric Retentive Dolomite
Fabric retentive dolomite (FRD) consists of turbid, anhedral to subhedral, aphanocrystalline to finely crystalline (1–30 μm) dolomite that replaces skeletal and nonskeletal grains. Fabric retentive dolomite is abundant in the pisolite crest facies tract and in shelf facies beneath cycle tops. This dolomite has irregular to locally planar boundaries and is dully orange to nonluminescent. Isotopic values for FRD ($n = 3$) range from 6.1‰ to 6.3‰ in $\delta^{13}C$ and 1.4‰ to 2.1‰ in $\delta^{18}O$ (Figures 3, 4).

Fabric retentive dolomite is interpreted as an early replacement texture. Its association with the pisolite crest facies tract and cycle tops suggests that it formed from concentrated marine waters because of seepage reflux or tidal pumping (cyclic dolomitization of Montañez and Read, 1992; Mutti and Simo, 1993). A petrographically and isotopically similar dolomite from the reef and forereef was interpreted (Melim and Scholle, 1995, 1999, 2002) to result from the reflux of mesosaline waters from the restricted carbonate lagoon.

Fabric Destructive Dolomite
Fabric destructive dolomite (FDD) consists of very fine to medium crystalline (10–250 μm), anhedral to euhedral dolomite. It replaces grains, matrix, and cement throughout the pisolite crest facies tract but is concentrated near cycle tops farther outboard. Fabric destructive dolomite has planar crystal faces and luminesces bright red (Figure 2E, F). Isotopic values for FDD ($n = 2$) range from 5.5‰ to 5.9‰ in $\delta^{13}C$ and $-0.5‰$ to $-1.8‰$ in $\delta^{18}O$ (Figures 3, 4).

Fabric destructive dolomite likely formed as a replacement of FRD. Melim and Scholle (1995; 2002) interpreted FDD as forming during burial as it postulates some stylolitization and has significantly lower $\delta^{18}O$ values than FRD, possibly reflecting higher temperatures.
CARBON AND OXYGEN ISOTOPE COMPOSITIONS

The aforementioned carbonate components were analyzed for their stable isotopic composition to evaluate the magnitude and causes of isotopic variability in carbonate strata deposited during a discrete time interval. Figure 3 shows isotopic trends from marine cements, matrix, brachiopods, and bulk carbonate in four correlated sections. Closely spaced samples have isotopic values that vary by as much as 2‰ in both δ13C and δ18O. Depleted carbon and oxygen isotopic signatures, common beneath meteoric exposure horizons (cf. Allan and Mathews, 1982; Goldstein, 1991; Algeo et al., 1992; Bishop et al., 2009), are not observed at the cycle boundaries. In contrast, δ13C and δ18O values in calcites commonly increase approaching cycle (and HFS) boundaries (Figure 3), demonstrating that proximity to the HFS boundary does not control isotopic depletion.

Excluding dolomites and CS2 and CS3, all data plot as an inverted J curve in δ13C-δ18O space, with partially overlapping fields of (from highest to lowest) marine cements, brachiopods, bulk carbonate, micritic matrix, and CS1 (Figure 4). Calcite spar 2 (n = 2) plots off the J curve, and CS3 (n = 2) plots near CS1.

Dolomites are enriched in 13C by as much as 0.5‰ and in 18O by as much as 4‰, relative to the highest marine cements. These values fall within the fields of dolomites previously analyzed from the backreef, reef, and forereef (Mutti and Simo, 1993; Melim and Scholle, 1995; Hill, 1996) and are consistent with precipitation from mesosaline waters that refluxed from the carbonate lagoon (Melim and Scholle, 1995, 2002).

Values for neomorphosed botryoids, IFC, RFC, and IRP are indistinguishable from one another, consistent with a common origin as marine cements that were subsequently diagenetically altered. This includes IRP, which previously was interpreted as a product of meteoric-marine mixing (Mruk, 1989; Mutti and Simo, 1993; Rahnis and Kirkland, 1999). In a single thin section, multiple samples of the same cement phase have less than 0.5‰ variability (δ13C and δ18O), whereas different marine cement phases have less than 1‰ variability. Isotopic values for brachiopods fall within the marine cement field (Figures 3, 4). Values for marine cements and brachiopods show no systematic variation with depositional (Dunham) texture or facies (Figure 5), and they do not vary systematically with the degree of inferred textural preservation (fibrous texture) or chemical preservation (luminescence, staining).

Micritic matrix is depleted in 13C and 18O relative to marine cements (Figure 4). Although data fields overlap (Figure 4), matrix values are consistently more depleted than marine cements, both stratigraphically and within individual samples (Figure 3). Within the same hand sample, bulk carbonate values typically fall between matrix and marine cement values, in part reflecting the physical mixing of these phases in bulk samples.

Calcite spar cements are depleted in both 13C and 18O relative to the other components (Figure 4). Calcite spar 1 has relatively consistent δ18O and variable δ13C values; two samples of CS2 suggest highly variable isotopic values, and two samples of CS3 have similar values to CS1. Calcite spar 1 shows slightly depleted δ18O values in more landward sections (Figure 6). These results are consistent with published values for CS1, CS2, and CS3 (Given and Lohmann, 1985, 1986; Mruk, 1989; Scholle et al., 1992; Mutti and Simo, 1993; Hill, 1996; Mazzullo, 1999).

DISCUSSION

Shape of the Capitan J Curve

The inverted J curve delineated by Capitan samples is indicative of diagenetic alteration governed by variable degrees of fluid-rock interaction (e.g., Meyers and Lohmann, 1985; Lohmann, 1988; Banner and Hanson, 1990). Because of the different relative concentrations of carbon and oxygen in CaCO3 versus pore waters, isotopic equilibration between diagenetic fluids and carbonate components occurs at lower fluid:rock ratios for δ18O than for δ13C, resulting in distinctive alteration trends—the inverted J (Figures 4, 7).

In the Capitan data set, marine cements and brachiopods have the highest isotopic values, similar to those reported from least altered brachiopods in the Delaware Basin (Korte et al., 2005). Matrix values are lower, suggesting that matrix underwent more
extensive fluid-rock interaction. This trend likely reflects some combination of high depositional porosity, permeability, and reactive surface area in the precursor lime mud.

The degree of fluid-rock interaction (isotopic depletion) does not correlate with depositional (Dunham) texture or facies (Figure 5), as reported elsewhere (e.g., Batt et al., 2008). This suggests that petrophysical properties (which likely controlled the degree of fluid-rock interaction) were not governed by small-scale rock fabric (matrix flow). Interestingly, Melim and Scholle (1999, 2002) demonstrated that the pathways for dolomitizing fluid in slope sediments were governed by secondary fractures and sand-filled neptunian dykes. The alteration of marine cements may have been controlled by similar secondary fluid pathways. Alternatively, fluid-rock interaction might have been dictated by smaller (nanometer to micrometer) scale characteristics, below the resolution captured by Dunham textures, possibly related to microporosity and/or the reactive surface area of crystals.

Calcite spar 1 defines the diagenetic ($^{13}$C- and $^{18}$O-depleted) end member for the J curve.

Figure 5. (A and B) Crossplots showing matrix (A) and marine cements (B), distinguished by the depositional texture of the sample from which they were micro-sampled. Overlapping values indicate that the depositional texture exerted no significant control over the degree of fluid-rock interaction. (C) Crossplot showing matrix, marine cements, brachiopods, and bulk carbonate plotted according to their facies belts (reef, open shelf, oolitic shelf, or pisolite [pis.] crest). Overlapping fields suggest little control of facies over the degree of fluid-rock interaction. PDB = Peedee belemnite.

Figure 6. Calcite spar 1 sorted according to section. More basinward section (LS) has slightly enriched $\delta^{18}$O values for a given $\delta^{13}$C. PDB = Peedee belemnite.
This suggests one of two scenarios. (1) Calcite spar 1 may have precipitated in equilibrium with marine waters and was subsequently the most-altered phase during fluid-rock interaction. This seems unlikely given its primary calcite mineralogy, blocky texture with low surface area:volume ratio, and preserved constructional luminescence. (2) More likely, CS1 precipitated from diageneric fluids moderately rock buffered for $\delta^{13}$C and fluid buffered for $\delta^{18}$O.

The Capitan J curve has a conspicuously shallow arc, which presents a conundrum. The diageneric end member (CS1) was undoubtedly a meteoric phase—a conclusion supported by its distribution across the platform, its timing relative to compaction-dissolution, its trace-minor element distribution, and its isotopic signatures. Meteoric fluids typically are initially highly $^{13}$C depleted (from soil-respired CO$_2$) with low dissolved inorganic carbon (DIC), and they evolve to become more DIC rich and more $^{13}$C rich by interaction with carbonate sediments. At face value, the very shallow arc of the Capitan J curve would suggest fluid-rock interaction with a fluid rich in DIC, yet still highly depleted in $\delta^{13}$C. How could this occur with a meteoric fluid?

Numerical models can help elucidate controls on this J curve. A first test is to evaluate the impact of low-resolution sampling, which may have analyzed mixtures of minerals that fall on different parts of an inverted J curve. Such a scenario is supported by the relative position of components, where the multi-component or most mixed samples (matrix and bulk carbonate) hold more average isotopic values, relative to the end members (CS1 and marine cements). Typically, mineral mixtures have been interpreted as combining a pristine phase and a diageneric phase to create a single mixing line (i.e., a straight line in $\delta^{13}$C-$\delta^{18}$O space; Given and Lohmann, 1985, 1986; Banner and Hanson, 1990; Metzger and Fike, 2013). However, mixing might also overprint a fluid-rock interaction curve (Figure 7). To test this hypothesis, we randomly sampled two points along the standard J curve (from fluid-rock interaction models below) and combined them in random proportions. Repeating this process several thousand times yields a data field with a distinctive triangular spread, in which the boundaries are delineated by the original J curve and a linear mixture of the two end members. This distinctive data field is not observed in the Capitan data. Additionally, any mineral mixing should also incorporate other late diageneric phases, such as CS2 and CS3, which can have significantly different isotopic values. As a result, we conclude that mineral mixing controls little of the shape of the isotopic data, and the remaining discussion will focus on how fluid-rock interaction parameters impact the shape of the J curve.

**Figure 7.** Numerical models of diagenesis using meteoric water. (A) The two end-member trends commonly observed in diagenesis. Fluid-rock interaction proceeds by the iterative equilibration of a rock with successive pore volumes of diagenetic fluid, where $n$ is the number of time steps. The distinctive inverted J curve results because fluids and limestones have different ratios of C and O. A mixing line results when analyzed samples contain a physical mixture of different phases. (B) A distinctive triangular data field results when mineral mixing is superimposed on a fluid-rock interaction curve. The data field was constructed using the base-case fluid-rock interaction curve and the RAND function of Excel. Two samples were selected randomly from the 60,000 time steps and were then mixed in a random proportion. The resultant data field is clearly different from the observed Capitan J curve. PDB = Peedee belemnite.
Numerical Models of Fluid-Rock Interaction

To better understand the anomalous shape of the observed J curve in the Capitan, we used simple numerical models of fluid-rock interaction, using the methodology of Banner and Hanson (1990). Fluid-rock interaction is modeled beginning with a rock volume of calcite and a pore volume of fluid, both with specified isotopic signatures. In each time step, the isotopic signatures of rock and pore-fluid equilibrate by means of mass balance, with no change in porosity. In the subsequent time step, the pore fluid is replaced by a fresh volume of the unmodified fluid, and as much as 60,000 iterations are performed. This methodology simulates the iterative equilibration of rock with pore fluid; it allows the user to vary porosity, initial rock isotopic values, diagenetic fluid isotopic values, DIC in the fluid, and how open or closed the system is to new fluids. In general, the fluid-rock interaction models demonstrate that limestone δ18O approaches equilibrium with bulk fluid values after tens of iterations (time steps), whereas δ13C values require several thousand iterations to approach equilibrium with bulk fluid values (Lohmann, 1988; Banner and Hanson, 1990).

The shape of the J curve is not significantly impacted by changes to porosity, permeability, and static temperature, or by modeling of a simple closed system. Porosity and permeability control the rate at which a rock volume moves along the J curve (Figure 8A); higher porosity requires fewer time steps (iterations) to equilibrate rock with pore fluid, whereas higher permeability lowers the duration of each time step (iteration). A simple closed system can be modeled by retaining some diagenetic fluid from the previous model time step. This has a similar effect to using a lower porosity because the retained fluid is already in equilibrium with the rock (Figure 8D). Temperature changes impact δ18O but not δ13C (Figure 8B). Choosing a different temperature moves the diagenetic endpoint of the fluid-rock interaction curve but does not change its shape. A sinusoidally fluctuating temperature causes significant variability in δ18O values, creating a horizontal spread in the data (Figure 8B). However, neither approach simulates the observed data field.

With simple diagenetic fluids, the shape of the J curve (i.e., steepness of the arc) is most readily influenced by varying DIC (Banner and Hanson, 1990). During equilibration, the fluid:limestone ratio for O is much higher than for C; thus, the limestone δ18O approaches equilibrium with fluid values much more rapidly (at earlier time steps) than δ13C, resulting in a steep J curve. Because the C and O concentration in the host rock and the O concentration in the fluid are constants (by chemical formula), any change in the arc of the J curve depends on the DIC of the fluid—a higher DIC leads to an earlier δ13C equilibration and to more gently arcing J curves (Figure 8C). However, within the sensitivities examined here, DIC would need to be 50,000 ppm, an unreasonable concentration (nearly half that of solid calcite), to generate the J curve observed in the Capitan data (Figure 8C).

Ultimately, the most effective way to model a J curve with a very shallow arc is to incorporate a changing diagenetic fluid end-member value (Figure 9). This is accomplished by having variable mixtures of fluids—meteoric and marine—making up the fluid end member. The isotopic signature of the mixed fluid is dependent on the initial δ13C and δ18O of the meteoric and marine waters, their DIC concentrations, and their relative proportions in the mixture (Figure 9A). Given a particular ratio of meteoric-to-marine DIC (e.g., the 10:1 ratio in Figure 9A), a family of J curves can be generated with different diagenetic end members based on the volumes of fluid mixed (e.g., Figure 9B). Although each J curve approaches a different diagenetic end member, each retains the typical steep curve, contrary to the gentle arc of the Capitan data. Notably, relatively low DIC concentrations in the marine fluid bring the fluid end member into high δ18O-low δ13C space (Figure 9A), relevant to the development of the observed Capitan J curve.

The best-fit models for the Capitan system systematically vary the diagenetic end-member fluid composition through a model run by changing the proportion of meteoric and marine waters over time. Geologic scenarios that can be modeled are (1) rhythmically alternating marine and meteoric waters, (2) a progressively diminishing marine contribution over time, and (3) a diminishing marine contribution over time in a partially closed system.

1. Rhythmically changing the proportion of meteoric and marine waters might simulate high-frequency
sea level fluctuations exposing and flooding the shelf. Given a range of frequencies (18, 36, or 180 time steps), \( \delta^{18}O \) equilibrates with the diagenetic fluid over the course of each cycle (within approximately 10 time steps) but \( \delta^{13}C \) slowly equilibrates with the long-term average composition. This results in a broad swath of \( \delta^{18}O \) values (Figure 9C), not observed in the Capitan data.

2. The evolution of the pore fluid can also be modeled as a gradual change from marine water to fully meteoric water. Such a system might reflect lingering marine waters in poorly connected, more microporous parts of the rock. A linear decline in the marine contribution leads to a smooth curve with relatively high \( \delta^{18}O \) (Figure 9D). The shape of these curves depends on both the number of time steps before the marine influence is lost and the ratio of meteoric DIC to marine DIC. Crucially, this model can simulate the gentle J curve seen in the Capitan data. Modifying the trend of diminishing marine influence (e.g., from linear to exponential) would also change the shape of this curve. Given that this model requires remnant marine fluids to be retained in later time steps, it would also be expected that aged groundwaters play a function in later diagenesis. This more geologically reasonable scenario is explored below.

3. A final model simulates a partially closed system by retaining some pore fluids from earlier time steps (Figure 9E, 3F). Each pore volume of fluid...
Figure 9. Mixtures of meteoric and marine fluids. (A) Diagenetic fluid composition, shown as a series of mixing lines, where fluids are a combination of meteoric and marine waters with different ratios of dissolved inorganic carbon (DIC). When DIC_{meteoric} > DIC_{marine}, concave-up curves result; when DIC_{meteoric} < DIC_{marine}, convex-up curves result. (B) A suite of J curves using different proportions of meteoric and marine waters, each produced by fluids that have a 10:1 ratio of DIC_{meteoric} > DIC_{marine} (dark blue line in Figure 9A). Varying the proportion of meteoric and marine waters causes a shift in the diagenetic end member, which tracks the 10:1 fluid curve seen in A. (C) Within a model run, proportions of meteoric and marine fluid can be varied sinusoidally, here, with a period of 18, 36, or 180 time steps. Because of the rapid equilibration with fluid δ^{18}O, these curves have extreme high-frequency changes in δ^{18}O and relatively slow δ^{13}C equilibration. Note that graphs are plotted from decimated model output that does not show the full fluid-rock interaction pathway. (D) Models with diagenetic fluids that have a progressively decreasing marine contribution—a linear decrease from 100% to 0% marine, over a varying number of time steps and with different meteoric to marine DIC ratios. Relatively heavy δ^{18}O values result from a steady decrease in the marine contribution to diagenetic fluids. (E) Family of curves that result from mixtures of marine and meteoric waters in a partially closed system with a varying time lag. Initially, the partially closed system retains marine waters in the pore spaces but, after a designated time step, incorporates aged diagenetic fluid output from an earlier time step (defined by a lag time). For example, in the first 500 time steps, diagenetic fluids are 50% fresh meteoric water and 50% marine water. At time step 501, diagenetic fluids are 50% fresh meteoric fluid and 50% water output from time step 1. Similarly, time step 502 incorporates water output from time step 2. This lag time serves to extend the influence of marine waters from earlier time steps in a hydrologically reasonable way. (F) Family of models using a 500-time step lag time with different proportions of recycled fluid. Different proportions of recycled fluid change how smooth or steplike the resulting curves are. The best-fit models have lag times of approximately 500 samples and 40% to 98% recycled fluid. PDB = Peebeee belemnite.
has some proportion of aged fluid. Initially, this is marine water, not fully flushed from the pore space. After a time lag (e.g., 500 time steps), the aged fluid becomes the fluid output from a designated earlier time step (e.g., beginning with time-step 1). The time lag is applied to represent a somewhat closed system, where aged groundwaters are contributed from somewhere up hydraulic gradient (updip). Because of the marine contribution, earlier time steps equilibrate with a relatively enriched δ¹⁸Ofluid, and the character of this fluid is retained in later time steps by recycling aged groundwaters. The change in fluid composition at the time lag creates a stairstep in the curve, which is repeated at regular intervals. The steepness of the arc of these curves depends on the proportion of recycled fluid (Figure 9F) and the length of the time lag (Figure 9E). Longer time lags (Figure 9E) lead to more gentle curves because the effect of enriched δ¹⁸O from marine waters is retained in the system longer. Higher proportions of recycled fluid (Figure 9F) require more time steps for equilibration, leading to a more gently arced curve by shrinking the stairsteps caused by the time lag. Critically, models of mixed diagenetic fluids in a partially closed system lead to isotopic curves that very closely mimic those of the Capitan data set. These models likely represent a more realistic diagenetic evolution, where pore fluids are not pure end members but have previously evolved through fluid-rock interaction updip of the equilibrating host rock being modeled.

Limitations to Approach

Several limitations to the aforementioned numerical modeling approach are observed. First, the models do not consider the effects of pH on δ¹³C and δ¹⁸O values (Spero et al., 1997, Zeebe, 1999; Zeebe and Wolf-Gladrow, 2001); we assume pH is generally rock buffered. Second, the models do not evaluate the impact of variable mineralogy on the isotopic signature or primary sediment reactivity. Isotopic values of aragonite, calcite, and high-Mg calcite in equilibrium with the same fluid vary by as much as a few per mil (e.g., Gonzalez and Lohmann, 1985; Jimenez-Lopez et al., 2004, 2005). Although such variability would affect the original sediment values, we presume that all reactions move toward calcite, diminishing the impact in later time steps. Additionally, the general shape of the model output curve should be equally valid for a range of primary isotopic values. Thus, in this study, a cloud of primary isotopic signatures (with a suite of fluid-rock interaction curves) has been modeled as a single primary value (with a single fluid-rock interaction curve).

Variability in mineralogy and thus reactivity among components in a carbonate deposit (cf. Maliva, 1998) can be modeled as an equilibration of each component with a different number of pore-fluid volumes. This range of volumes likely relates in part to the variability in the true number of available pore-fluid volumes (i.e., porosity and permeability at the sample scale) and to the efficiency of fluid-rock interaction (sensu Cander, 1995)—the proportion of available pore-fluid volumes that actually reacts, which also depends on reactive surface area, mineral density, and dissolution-precipitation kinetics. That all Capitan components fall on the same general C-O isotopic trend suggests that this issue has little bearing on the shape of the fluid-rock interaction curve modeled here.

Finally, the question remains whether it is reasonable that Capitan backreef cement fabrics underwent thousands of isotopic equilibration events. Neomorphosed botryoids were obviously altered from aragonite to calcite. Some debate on whether fibrous calcites (e.g., RFC, FOC) are primary or alteration fabrics exists (Wilson and Dickson, 1996; Richter et al., 2011). Here, we infer from the Capitan J curve that these cements underwent repeated incremental isotopic exchange with pore fluids, whether or not the cements actually underwent wholesale recrystallization. Note that RFC and FOC typically display patchy dull luminescence, instead of constructional banding, and have scattered microdolomite inclusions. Such fabrics suggest that cations such as Mn, Fe, and Mg were mobilized during diagenesis and, at least locally, the crystallographic structure has been modified.

Implications for Fluid Behavior and Paragenesis

The stable isotope data and fluid-rock interaction models described above have implications for the Yates paragenesis, the primary isotopic signature of
Permian seawater, and the hydrology of the Capitan system. Specifically, they imply that (1) IRP was likely a marine cement, (2) CS1 formed after most fluid-rock interaction had occurred, (3) fluid-rock interaction in the Yates 2 HFS occurred during a younger (Yates or Tansill-equivalent), longer-lived sea level lowstand, (4) mixing lines between intergrown spar and neomorphosed botryoidal aragonite do not converge on a primary seawater value (cf. Given and Lohmann, 1985, 1986), and (5) the observed fluid-rock interaction required either long-lived exposure (>100 k.y.) or high permeabilities (at least tens of millidarcies).

1. 2. The timing of the precipitation of IRP and CS1 has been much debated (see above). Inclusion-rich prismatic calcite is likely a marine cement, given that its isotopic range is similar to other marine phases. Along with the other marine cements, it underwent fluid-rock interaction during meteoric diagenesis and now shares a primary marine end member. In contrast, CS1 likely precipitated directly from meteoric fluids (after marine fluid was flushed from the system), with moderate rock buffering for δ¹³C.

3. This study also places constraints on which subaerial exposure horizon is responsible for meteoric spar CS1 (and concomitant fluid-rock interaction). Calcite spar I formed after some compaction and prior to Ochoan evaporite precipitation. Additionally, CS1 is present in Seven Rivers, Yates, and Tansill strata, with similar stable isotopic values (e.g., Mruk, 1989; Hill, 1996; this study). Characteristic isotopic signatures for subaerial exposure are not observed at cycle tops or HFS boundaries in the Yates or Seven Rivers Formations (this study and our unpublished McKittrick Canyon data). Also, CS1 has not been observed overgrown by marine cements. These factors all suggest that CS1 is associated with a lower order younger sequence boundary, probably near the top of the Yates or the top of the Tansill.

4. Given and Lohmann (1985, 1986) derived a primary isotopic value for Permian seawater. They collected samples of recrystallized botryoidal aragonite along a bathymetric profile from reef to forereef. Intergrown neomorphosed aragonite and luminescent blocky spar in each of these samples generated a distinct mixing line, which had different diagenetic endpoint values in samples from different positions along the bathymetric profile. Primary end-point values for all samples converged on a single point (δ¹³C = 5.3‰; δ¹⁸O = −2.5‰), interpreted as a primary marine signature. However, this convergent point lies on the fluid-rock interaction curve documented here, suggesting that it is a diagenetically modified value for neomorphosed aragonite. Indeed, where primary aragonite has been found in parts of botryoidal cements in Yates and Tansill Formation tepees, neomorphosed parts of the botryoids exhibit significantly altered (by as much as approximately 3‰) δ¹⁸O values (Chafetz et al., 2008). Furthermore, given the fluid-rock interaction demonstrated here, it would be highly unlikely that aragonite neomorphosed to calcite in completely rock-buffered waters, whereas intergrown luminescent spar precipitated from waters entirely fluid buffered.

5. Finally, the data and models above place constraints on the hydrology of the subaerially exposed Capitan system. Given a range of likely subaerial exposure times (20 k.y.–1 m.y.), it is possible to calculate the fluid flow through a 1-m³ (35-ft³) volume of rock, where flow is fluid volume (gross rock volume × porosity × model iterations) divided by the duration of exposure (Figure 10). The effects of porosity and model iterations mostly counteract one another because higher porosities require fewer model iterations to throughput a similar volume of diagenetic fluid. As a result, in our models, the overall fluid flow is mostly dependent on the duration of exposure. Fluid flow can also be constrained using Darcy’s law, where flow is modeled as a local meteoric lens, several meters thick and 3 km (9843 ft) from the recharge zone (a position equivalent to the pisolite crest in older sequences). Flow is thus chiefly reliant on the permeability of early exposed sediment and the height of the meteoric lens, which is limited by the overall drop in sea level, here considered as much as 50 m (164 ft). Capitan back-reef and reef rocks currently have approximately 2% to 15% porosity and permeabilities that range from a few to several thousand millidarcies (Ward et al., 1986; Garber et al., 1989; Tinker, 1998). However, it is difficult to predict the exact values prior to significant compaction and spar precipitation, and these properties likely evolved significantly during meteoric diagenesis. Nevertheless, this simplified
model suggests that short (<100 k.y.) durations of exposure would have required high permeabilities (tens to thousands of millidarcies), whereas longer duration (>200 k.y.) exposure, more consistent with exposure near the end of the Yates deposition or near the end of the Tansill deposition, would have required lower permeabilities (<1–100 md). Cander (1995) introduced reaction efficiency (reactive fluid flux divided by total fluid flux) to better conceptualize the proportion of available pore fluid that actually reacts during fluid-rock interaction. In the Capitan system, given a 10- to 50-m (33–164-ft) thick meteoric lens, exposure times of 200 to 500 k.y., and a permeability of 0.1 to 1 d, reaction efficiencies would range between 0.2 and 0.0001. This implies that between 1 of 5 and 1 of 10,000 pore volumes of available fluid actually reacted during diagenesis. In summary, given reasonable durations of exposure and ranges of permeability, a broad array of reaction efficiencies is plausible, and sufficient volumes of pore fluid were available to generate the Capitan J curve.

CONCLUSIONS AND IMPLICATIONS
The Capitan backreef underwent significant fluid-rock interaction during shallow burial. These fluids
repeatedly equilibrated with platform sediments and cements, and precipitated early diagenetic spar (CS1). The anomalous shallow arc to the J curve, however, suggests that two secondary processes were also important. (1) Early diagenetic fluids were mostly fresh meteoric waters but with a contribution from lingering marine waters that diminished over time. The resultant fluid was initially $^{18}$O enriched relative to the pure meteoric input, contributing to the observed shallow arc of the J curve. (2) The system likely was partially closed, with early pore fluids recycled into subsequent generations of diagenetic fluids. Initially, these recycled fluids were remnant marine waters but later were likely aged meteoric fluids that had already reacted updip. This scenario suggests a dynamic spatial and temporal evolution of groundwaters and the carbonate sediments with which they interact—an aspect of diagenesis not readily incorporated into published fluid-rock interaction models.

This study highlights the complex diagenetic evolution of the Yates backreef, an important aquifer in the Delaware Basin. During shallow burial, geochemically important processes included reflux dolomitization and meteoric cementation and stabilization. These processes not only generated different isotopic signatures, but also created diagenetic geobodies that differ markedly in their physical character and timing. Cementation by porosity occluding CS1 and stabilization of much of the reef and fall-in beds occurred during sea level lowstand, likely a (single?) protracted exposure event (e.g., near the end of the Yates or Tansill deposition). This event occurred long after deposition, cementing a relatively thick sedimentary section—tens to hundreds? of meters of reef and backreef in the Yates, Seven Rivers, and, possibly, Tansill. In contrast, dolomite is pervasive in the shelf crest, concentrated at cycle tops in the fall-in beds, and focused around fractures and neptunian dykes in the forereef (Melim and Scholle, 1999). Dolomitization occurred when the shelf was flooded and circulation restricted, allowing the reflux of mesosaline lagoonal waters. These conditions existed repeatedly during sea level highstands (of cycles and HFSs), leading to multiple overprinted dolomitization events (e.g., Garcia-Fresca et al., 2012). Thus, geobodies for dolomites and for meteoric cements differ not only in their distribution (thickness, shape, location), but also in their number and timing. Such conceptual models for diagenetic geobodies can be used in geocellular reservoir models—for example, to condition training images for multiple-point statistics and facies distribution modeling (Murphy-Bishop et al., 2008; Kenter et al., 2010).

Interaction between the Yates shelf and meteoric fluids drove significant $\delta^{13}$C and $\delta^{18}$O variability (as much as 4‰) over short lateral and stratigraphic distances. This variability exists between different components (e.g., marine cements vs. matrix) of the same sample and the same components of coeval samples from different sections. These trends mask any primary isotopic variability, even in samples screened for diagenesis. This study thus suggests that extensive fluid-rock interaction and isotopic resetting can occur at very local scales in seemingly well-preserved samples (original textures, low Fe, low Mn).

This finding has implications for the studies of paleoclimatology and chemostratigraphy (e.g., using isotope curves to correlate wells). In many high-resolution chemostratigraphic studies, muddy matrix and/or bulk carbonate are inferred to be rock buffered for $\delta^{13}$C during diagenesis and to archive a robust record of secular seawater change (e.g., Saltzman, 2003, 2005, Payne et al., 2004; Halverson et al., 2005; Maloof et al., 2005; Katz et al., 2007; Batt et al., 2008). This inference is commonly based on the preservation of correlated large-magnitude isotope excursions, by the absence of isotopic depletion approaching exposure horizons and by petrographic or geochemical screening of samples (e.g., Metzger and Fike, 2013). However, each of these conditions is met in this study, where isotopic values are heavily diagenetically overprinted.

Isotopic results from Capitan strata provide useful criteria to use for diagenetic resetting in future chemostratigraphic studies. The Capitan example suggests that marine cements and brachiopods are more resistant than matrix (or bulk carbonate) during fluid-rock interaction and may capture a more robust chemostratigraphic record. This trend was likely driven by higher interparticle porosity, permeability, and/or reactive surface area in lime muds soon after deposition. However, although marine cements record the least altered isotopic values, they mostly do...
not preserve primary $\delta^{13}$C and $\delta^{18}$O values. In addition, the preservation of depositional texture, nonluminescence to dull luminescence, and low Fe contents proved to be poor arbiters of isotopic preservation in both matrix and marine cements (cf. Rush and Chafetz, 1990). More careful and extensive, multi-component sampling is likely required to screen for diagenetic effects. In sediments prone to meteoric diagenesis, non-marine spar cements should be sampled for each sea level lowstand to distinguish different generations of spars and associated episodes of fluid-rock interaction. Finally, multiple parallel sections served to highlight that isotopic variability was representative of neither secular trends nor diagenetic alteration at adjacent subaerial exposure horizons. This suggests that for subsurface well correlations, $\delta^{13}$C and $\delta^{18}$O chemostratigraphy should not solely be relied upon but interpreted in concert with other independent chronostratigraphic proxies (e.g., Playton et al., 2013). Similarly, for ground truthing future paleoclimate studies, independently correlated, closely spaced sections may be necessary to avoid more equivocal wiggle matching and the interpretation of erroneous secular trends.

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