Diagenetic controls on the isotopic composition of carbonateassociated sulphate in the Permian Capitan Reef Complex, West Texas

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ABSTRACT

Late Palaeozoic-age strata from the Capitan Reef in west Texas show faciesdependent heterogeneity in the sulphur isotopic composition of carbonateassociated sulphate, which is trace sulphate incorporated into carbonate minerals that is often used to reconstruct the sulphur isotopic composition of ancient seawater. However, diagenetic pore fluid processes may influence the sulphur isotopic composition of carbonate-associated sulphate. These processes variously modify the sulphur isotopic composition of incorporated sulphate from syndepositional seawater in shelf crest, outer shelf, shelf margin and slope depositional settings. This study used a new multicollector inductively-coupled plasma mass spectrometry technique to determine the sulphur isotopic composition of samples of individual depositional and diagenetic textures. Carbonate rocks representing peritidal facies in the Yates and Tansill formations preserve the sulphur isotopic composition of Guadalupian seawater sulphate despite alteration of the carbon and oxygen isotopic compositions by meteoric and dolomitizing diagenetic processes. However, sulphur isotopic data indicate that limestones deposited in reef and slope facies in the Capitan and Bell Canyon formations largely incorporate sulphate from anoxic marinephreatic pore fluids isotopically modified from seawater by microbial sulphate reduction, despite generally preserving the carbon and oxygen isotopic compositions of Permian seawater. Some early and all late meteoric calcite cements have carbonate-associated sulphate with a sulphur isotopic composition distinct from that of Permian seawater. Detailed petrographic and sedimentary context for carbonate-associated sulphate analyses will allow for improved reconstructions of ancient seawater composition and diagenetic conditions in ancient carbonate platforms. The results of this study indicate that carbonate rocks that diagenetically stabilize in high-energy environments without pore fluid sulphate gradients can provide a robust archive of ancient seawater's sulphur isotopic composition.

Keywords Carbonate-associated sulphate, diagenesis, Guadalupe Mountains, Palaeozoic seawater, Permian Reef, stable isotopes.

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INTRODUCTION

Sulphate - a metabolically-available, major ion in seawater – links the cycles of carbon, oxygen and iron through Earth's oceans (Garrels & Lerman, 1984; Bottrell & Newton, 2006). Small amounts are incorporated into the lattice of carbonate minerals [called carbonate-associated sulphate (CAS); Burdett et al., 1989; Kampschulte & Strauss, 2004] and its sulphur isotopic composition [reported in δ^{34} S notation as part-per-thousand changes in 34 S/ 32 S from the Vienna-Canyon Diablo Troilite (V-CDT) reference standard] may track that of the ancient seawater from which the minerals precipitated. A history of the δ^{34} S of seawater sulphate constrains ancient biogeochemical budgets because secular enrichment in the $\delta^{34}S$ of seawater sulphate represents increased burial of sulphide minerals with lower δ^{34} S produced by anoxic microbial sulphate reduction (Garrels & Lerman, 1984).

In Precambrian through to early Mesozoic successions, CAS data have highly variable isotopic compositions, especially during biotic crises (Kah et al., 2004; Newton et al., 2004; Gill et al., 2007, 2011b; Marenco et al., 2008; Li et al., 2009; John et al., 2010; Loyd et al., 2012b; Thompson & Kah, 2012; Wotte et al., 2012; Yan et al., 2013; Song et al., 2014; Algeo et al., 2015; Sim et al., 2015; L. Zhang et al., 2015; Bernasconi et al., 2017; Schobben et al., 2017; Witts et al., 2018). If representative of seawater, these data imply a small marine sulphate reservoir that could change rapidly or have spatial gradients. However, only a few studies have systematically examined the role of depositional setting, including overprinting diagenetic regimes, on the isotopic composition of CAS (Marenco et al., 2008; Wotte et al., 2012; Osburn et al., 2015), despite chemostratigraphic records being constructed from various palaeoenvironments. Was Palaeozoic seawater sulphate indeed heterogeneous?

Carbonate-associated sulphate in recent biogenic carbonate accurately preserves the δ^{34} S of modern seawater (Burdett *et al.*, 1989; Kampschulte *et al.*, 2001; Paris *et al.*, 2014b; Rennie *et al.*, 2018) and well-preserved biogenic carbonate, especially low-magnesium calcite in brachiopods and belemnites, may robustly preserve the composition of ancient seawater (Kampschulte & Strauss, 2004; Gill *et al.*, 2011a; Newton *et al.*, 2011; Wu *et al.*, 2014; Present *et al.*, 2015). Unfortunately, such well-preserved fossiliferous material is rare in the geological record and absent in Precambrian strata. Therefore, CAS in bulk carbonate rock is an attractive proxy for reconstructing the isotopic composition of ancient seawater because carbonates are widelydeposited in space and time in the rock record. Studies of CAS in bulk carbonate material have concluded that early diagenetic processes such as neomorphism, dolomitization and authigenic cementation may incorporate sulphate from diagenetically-modified or non-seawater fluids (Goldberg et al., 2005; Riccardi et al., 2006; Gill et al., 2008; Lovd et al., 2012a; Rennie & Turchyn, 2014; Baldermann et al., 2015; Present et al., 2015; Feng et al., 2016; Fichtner et al., 2017). Screening for the effect of such processes typically entails textural, trace metal, and carbon and oxygen isotope analyses associated with meteoric or burial diagenesis that may not correlate with sulphur isotope alteration (Goldberg et al., 2005; Gill et al., 2011a, 2011b; Yan et al., 2013; Fichtner et al., 2017). Because the early diagenetic history of a carbonate rock typically varies with its depositional setting, a thorough accounting of early diagenetic effects on CAS δ^{34} S requires detailed sedimentological context.

To discern the sulphur isotope composition of ancient seawater when biogenic calcite is unavailable or poorly preserved, CAS analyses are here considered in the context of a regional depositional facies model and diagenetic framework. The CAS and carbonate carbon and oxygen isotope results are reported from the late Guadalupian-age platform and slope carbonates of the Capitan Reef in the Permian Basin, West Texas, USA. In outcrop, detailed biostratigraphic and sequence stratigraphic models tightly constrain shelf to basin correlations (Silver & Todd, 1969; Tyrrell, 1969; Borer & Harris, 1991; Osleger, 1998; Kerans & Tinker et al., 1999; Sarg et al., 1999; Wilde et al., 1999; Lambert et al., 2002; Rush & Kerans, 2010). This framework allows comparison of the δ^{34} S of CAS in carbonates deposited in the same body of water, but in different depositional settings. Further, welldocumented petrographic and geochemical features in these carbonates record diverse diagenetic processes during deposition, burial and uplift (Newell et al., 1953; Mazzullo & Cys et al., 1977; Schmidt, 1977; Yurewicz, 1977; Given & Lohmann, 1986; Garber et al., 1989; Mruk, 1989; Scholle et al., 1992; Mutti & Simo, 1993, 1994; Mazzullo, 1999; Melim & Scholle *et al.*, 1999; Frost *et al.*, 2012; Budd *et al.*, 2013; Bishop *et al.*, 2014). Understanding the depositional environments and diagenetic regimes that affect CAS allows further exploration of the expression of sedimentary biogeochemical processes in the rock record.

GEOLOGICAL AND GEOCHEMICAL SETTING

The Capitan Reef rims a mixed carbonate and siliciclastic shelf that surrounded the restricted, epeiric seawater of the Delaware Basin during the late Guadalupian Epoch (Fig. 1A) (Lang, 1937; King, 1942; Ward *et al.*, 1986). Following burial, Cenozoic extension exhumed part of the Capitan Reef in the Northwest Shelf province of the Delaware Basin; it is exposed as largely structurallyintact outcrop in western Texas and southern New Mexico in the Guadalupe Mountains (Lang, 1937; King, 1942, 1948). Detailed biostratigraphic and sequence stratigraphic work allows precise correlation of lithostratigraphic units and timelines from shelf to basin (Fig. 2) (Silver & Todd, 1969; Tyrrell, 1969; Borer & Harris, 1991; Osleger, 1998; Kerans & Tinker *et al.*, 1999; Sarg *et al.*, 1999; Wilde *et al.*, 1999; Lambert *et al.*, 2002; Rush & Kerans, 2010). Samples for this study were collected from the Yates, Tansill, Capitan and Bell Canyon formations, whose stratigraphy and diagenesis are described below.

The northern wall of North McKittrick Canyon, in Guadalupe Mountains National Park, hosts a well-exposed shelf to basin transect made accessible by the Permian Reef Geology Trail (Fig. 1B) (King. 1942; Newell et al., 1953; Bebout & Kerans, 1993). Well-bedded shelf dolomites and sandstones of the Yates Formation interfinger with massive and poorly-bedded reef and slope dolomitic limestones of the middle Capitan Formation, which in turn pass laterally into well-bedded basinal limestones and sandstones of the Bell Canvon Formation (Fig. 2) (King, 1942; Babcock & Yurewicz et al., 1989). Dolomites of the Yates Formation interfinger updip to the north-west with well-bedded evaporite-rich lagoonal facies (King, 1942; Borer & Harris, 1991). The Capitan and Bell Canyon formations are overlain by thick, basin-filling



Fig. 1. (A) Palaeogeography of the Delaware Basin during deposition of the upper Capitan Formation reef showing the location of the Permian Reef shelf margin in outcrop (solid line) and the subsurface (dashed line) (modified from Ward *et al.*, 1986). The arrow shows the location of McKittrick Canyon in the Guadalupe Mountains, west Texas. (B) Map of North McKittrick Canyon in the Guadalupe Mountains National Park showing the locations of measured stratigraphic sections on Wilderness Ridge (WR), McKittrick Peak (MP), Capitan Formation Slope (CS) and Bell Canyon Formation toe of slope (TS). Dots on the cliff (CC) indicate sample positions from the massive facies of Capitan Formation that were collected without a measured stratigraphic section. Map assembled using topographic data from Ryan *et al.* (2009) and Google Satellite imagery from 1 October 2014. Sample grid references are tabulated in Table S1.



Fig. 2. Correlation of lithostratigraphy, biostratigraphy and sequence stratigraphy of the Guadalupian-age strata modified from Tinker (1998), Kerans *et al.* (1999) and Rush & Kerans (2010). White lines show the locations of measured stratigraphic sections on Wilderness Ridge (WR), McKittrick Peak (MP), Capitan Formation Slope (CS) and Bell Canyon Formation toe of slope (TS). White box indicates where on the Capitan Formation cliffs (CC) samples from the massive reef facies were collected without a measured stratigraphic section. Fusilinid zones from Wilde *et al.* (1999). Absolute ages based on conodont biostratigraphy by Lambert *et al.* (2002) and updated to the ICS v2016/04 timescale (Cohen *et al.*, 2013; updated). Abbreviations: *C., Codonofusiella*; Fm., formation; L. Cap., Late Capitanian; Lop., Lopingian; Ls., limestone; M., Middle Capitanian; Mbr., member; *P., Paradoxiella*; *R., Reichelina*; Word., Wordian; Wuch., Wuchiapingian.

evaporites of the Castile Formation, and the Yates Formation is overlain by more shelf deposits of the Tansill Formation, which interfingers with the upper Capitan Formation (DeFord & Riggs, 1941; King, 1942; Babcock & Yurewicz *et al.*, 1989). The Yates Formation overlies older shelf deposits of the Seven Rivers Formation (King, 1942).

Two informal lithostratigraphic units – the 'Hairpin' and the 'Triplet' – in the upper Yates Formation record sea-level changes on the shelf (Neese & Schwartz *et al.*, 1977). The Hairpin dolomite is correlated through the Capitan Formation and into the McCombs Limestone Member of the Bell Canyon Formation (Newell *et al.*, 1953; King & Newell, 1956; Osleger, 1998; Tinker, 1998; Kerans & Tinker *et al.*, 1999; Osleger & Tinker *et al.*, 1999; Kerans & Kempter, 2002; Rush & Kerans, 2010). The unconformably-overlying Triplet consists of a lower sandstone unit, a middle dolomite

unit and an upper sandstone unit (Neese & Schwartz *et al.*, 1977). The lower and middle units of the Triplet correlate to a limestone tongue in the Bell Canyon Formation known as the McKittrick Canyon Limestone (Brown, 1996; Wilde *et al.*, 1999; Rush & Kerans, 2010). The upper sandstone unit of the Triplet and the overlying basal dolomite unit of the Tansill Formation correlate to the Lamar Limestone Member of the Bell Canyon Formation (Tyrrell, 1969).

Each set of genetically-related strata (i.e. the Hairpin with the McCombs Limestone, the lower and middle Triplet with the McKittrick Limestone and the upper Triplet and basal Tansill with the Lamar Limestone) is a locally unconformity-bounded package called a high frequency sequence (HFS) composed of higher-order cycle sets; they are the Guadalupian 25 (G25), Guadalupian 26 (G26) and Guadalupian 27 (G27) HFSs, respectively (Tinker, 1998; Osleger & Tinker et al., 1999; Kerans & Kempter, 2002; Rush & Kerans, 2010). High frequency sequences represent fourth-order cyclic accommodation fluctuations and record deposition over ca 100 to 650 kyr (Goldhammer et al., 1990; Borer & Harris, 1991; Rush & Kerans, 2010). Third-order cycles, which are comprised of multiple HFSs and are called composite sequences (CSs), represent 1 to 3 Myr of deposition (Goldhammer et al., 1990; Tinker, 1998). The G25 HFS is the last sequence of the Permian CS 13, with a major unconformity at the top of the Hairpin unit separating it from the overlying G26 and G27 HFSs of the Permian CS 14 (Tinker, 1998; Kerans & Tinker et al., 1999; Osleger & Tinker et al., 1999; Kerans & Kempter, 2002; Rush & Kerans, 2010).

Tinker (1998) classified McKittrick Canyon facies by their lithology, texture, grain composition and sedimentary structures. Some of these include barrier island tepee-pisolite complexes foreshore grainstones and rudstones and (Fig. 3A); shelf algal and coated grain grainstones, rudstones and packstones (Fig. 3B); shelf margin skeletal-peloid wackestones and reef boundstones and framestones (Fig. 3C); and slope conglomerates, rudstones and lithoclast packstones (Fig. 3D) (Dunham, 1972; Esteban & Pray et al., 1983: Garber et al., 1989: Borer & Harris, 1991; Mutti & Simo et al., 1993; Tinker, 1998). Early diagenetic and shallow burial processes varied with stratigraphic position and included neomorphism and dissolution of aragonite or high-Mg calcite grains; precipitation of aragonite, calcite, dolomite and anhydrite cements; silicification; mimetic dolomitization; and compaction

and fracturing (Newell *et al.*, 1953; Mazzullo & Cys *et al.*, 1977; Schmidt, 1977; Yurewicz, 1977; Given & Lohmann, 1986; Garber *et al.*, 1989; Mruk, 1989; Mutti & Simo *et al.*, 1993; Mazzullo, 1999; Melim & Scholle *et al.*, 1999; Frost *et al.*, 2012; Budd *et al.*, 2013; Bishop *et al.*, 2014). Deeper burial diagenetic processes included further fabric destructive dolomite recrystallization and anhydrite and carbonate dissolution (Schmidt, 1977; Garber *et al.*, 1989; Mutti & Simo, 1993, 1994; Melim & Scholle *et al.*, 1999; Budd *et al.*, 2013). During uplift of the Guadalupe Mountains, further calcite spar precipitation replaced evaporite cements (Schmidt, 1977; Mruk, 1989; Scholle *et al.*, 1992; Mazzullo, 1999).

The δ^{34} S of sulphate in Delaware Basin seawater can be constrained to about 8 to 10% V-CDT by the composition of bedded evaporites in the inner shelf facies of the Seven Rivers Formation (Sarg, 1981) and varved evaporites in the Castile Formation (Thode et al., 1961; Holser & Kaplan, 1966; Hill, 1990; Leslie et al., 1997; Kirkland et al., 2000). These formations both pre-date and post-date deposition of G25–G27-age strata, suggesting that Delaware Basin seawater sulphate's δ^{34} S remained constant through deposition of Guadalupian strata. Data from the Seven Rivers Formation and the Castile Formation evaporites are also consistent with other major middle and late-Permian-age evaporite deposits, indicating that 10% is a reasonable δ^{34} S composition for global ocean sulphate (Claypool *et al.*, 1980).

The reef facies contains abundant early marine cements (Fig. 3C), syndepositional brittle fractures and evidence for failure of the shelf margin that suggest unusually high carbonate saturation states for Phanerozoic basins (Babcock & Yurewicz et al., 1989; Mruk, 1989; Grotzinger & Knoll, 1995; Stanton & Pray, 2004; Rush & Kerans, 2010; Frost et al., 2012; Budd et al., 2013). Given & Lohmann (1985) measured the isotopic compositions of early marine cements in the Capitan Formation; the carbon and oxygen isotopic compositions are reported in δ^{13} C and δ^{18} O notation as part-per-thousand changes in ¹³C/¹²C and ¹⁸O/¹⁶O from the Pee Dee Belemnite (PDB) reference standard. These authors argue that the δ^{18} O of primary aragonite marine cements was ca - 3%PDB, in agreement with data from well-preserved and globally distributed Capitanian brachiopods (Korte et al., 2005). Therefore, normal Capitanian marine conditions included warmer seawater and/or a lower δ^{18} O of seawater than the modern ocean (Given & Lohmann, 1985; Korte et al., 2005). The δ^{13} C of Delaware Basin primary



Fig. 3. Outcrop photographs of typical lithologies in each facies tract. (A) Dolomite cross-bedded oncoid-*Poly-diexodina* rudstone in the shelf crest facies tract. (B) Dolomite fenestral coated grain-mollusc packstone/grainstone capping a cycle set in the outer shelf facies tract. Many fenestrae are solution-enlarged and filled by sparry calcite. (C) Limestone cement-sponge boundstone in the reef facies of the shelf margin facies tract. A sponge (s) is encrusted by *Archaeolithoporella* and botryoidal cements (ALP). Internal cavities in the reef are filled by wackestone (ws), isopachous cement (i) and late poikilitic calcite spar (p). (D) Limestone lithoclast-skeletal packstone/grainstone gravity flow beds (grey) interbedded with dolomitic laminated mudstone–wackestone (beige) from the toe of slope in the slope facies tract.

marine cements and brachiopods are 5 to 7‰ PDB, which are among the highest of those found in Phanerozoic strata (Given & Lohmann, 1985; Mutti & Simo *et al.*, 1993; Korte *et al.*, 2005; Chafetz *et al.*, 2008). These δ^{13} C values are higher than contemporaneous Tethyan samples and may represent effects of restriction in the Delaware Basin or a difference between the Tethyan and Panthalassic seawater compositions (Korte *et al.*, 2005).

METHODS

One hundred and nine samples were collected from four measured stratigraphic sections (Fig. 1B) in the Yates, Tansill, Capitan and Bell Canyon formations spanning strata from the Hairpin unit to the lower Tansill Formation (i.e. fron the G25 through to the G27 HFS) and their correlative down-dip strata, and assorted samples from G26 and G27-equivalent massive facies of the Capitan Formation (Fig. 2). The current study sampled to survey the range of facies identified by Tinker (1998) (Fig. 4) and grouped samples by facies tracts, which are associated facies and successions of facies that characterize an energy, accommodation and sediment supply regime (Tinker, 1998; Rush & Kerans, 2010). Polished slabs were prepared, and a handheld rotary micro-drill was used to collect 262 subsamples of 5 to 20 mg of various diagenetic and sedimentary textures. Sub-samples were analyzed for carbonate carbon and oxygen isotopic composition, CAS concentration and CAS sulphur isotopic composition.

For carbonate carbon and oxygen isotope analysis, 50 to 200 µg of each sub-sample was weighed into 12 ml Labco Exetainer vials (Labco Limited, Lampeter, Wales, UK), which were then sealed with septum caps and flushed for 5 min with helium. The carbonate was digested for >2 h at 72°C by adding 50 to 100 µl of 85% phosphoric acid through the septum cap with a syringe and needle. The evolved CO_2 was analyzed with a Thermo Fisher Scientific GasBench II maintained at 72°C coupled to a Thermo Fisher Scientific Delta V Plus isotope ratio mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The carbon and oxygen isotopic compositions of the evolved CO₂ were determined relative to the Vienna-Pee Dee Belemnite (V-PDB) reference standard by normalization to a laboratory CO₂ tank that was calibrated against the NBS-19 international calcite reference material. The oxygen isotopic composition of the dissolved carbonate was calculated from the acid fractionation factor of calcite dissolution at 72°C. Some samples were a mixture of calcite and dolomite, so reported δ^{18} O values may be as much as 1.3% too high if they were pure dolomite (Kim et al., 2015). Accuracy was monitored by running two in-house calcite standards in triplicate at the beginning and end of each analytical session. Precision was monitored by running a third in-house dolomite standard between every five samples and was typically better than 0.2% for $\delta^{13}C$ and 0.3% for $\delta^{18}O$ $[1\sigma \text{ standard deviations (SD)}].$

The remaining carbonate powder was then pre-cleaned of soluble sulphates by ultra-sonicating in 10% NaCl and rinsing three times with ultra-pure water (18.2 Ω cm resistivity), centrifuging and discarding the supernatant with a pipette between each rinse. Samples were then transferred to acid-clean micro-centrifuge vials, dissolved in trace metal-clean 0.5 N hydrochloric acid, centrifuged and pipetted away from any insoluble residue (Present et al., 2015). Sulphate was purified from its cation matrix by anion exchange chromatography (Das et al., 2012; Paris et al., 2014a), after which its concentration was determined by ion chromatography using a Dionex ICS-3000 system (Thermo Fisher Scientific) using three in-house concentration standards to assess accuracy and precision, which were better than 0.5% (1 σ relative SD) (Paris et al., 2013; Present et al., 2015). The CAS concentrations were calculated from the measured sulphate amount, and from the dry

weights of the cleaned powder and the insoluble residue. Measuring sulphate concentrations after column purification permits improved intensity matching of samples to a bracketing standard for mass spectrometry but may bias CAS concentration measurements towards lower values because a small amount of dissolved carbonate liquid remained with the insoluble residue (<10 μ l of the 1 ml used to dissolve samples remained in the vials, i.e. <1% of the sample).

Carbonate-associated sulphate δ^{34} S was determined using a Thermo Fisher Scientific Neptune Plus multi-collector inductively-coupled plasma mass spectrometer with a Cetac Aridus II desolvating spray chamber (CETAC Technologies, Omaha, NE, USA) by matrix matching and sample-standard bracketing with an in-house Na₂SO₄ standard (Paris *et al.*, 2013, 2014a). Samples contained 3 to 550 nmol sulphate (typically ca 50 nmol) and full procedural blanks were 0.33 ± 0.23 nmol (1 σ SD). The long-term δ^{34} S reproducibility of 18 nmol sulphate replicates from a dissolved deep sea coral consistency standard was 0.31% (1 σ SD) and was 0.28% (1 σ SD) for 280 nmol sulphate replicates of a diluted seawater consistency standard. Reported precisions of isotope measurements (Table S1) combine instrument stability, reproducibility of the same sulphate solution within an analytical session, and propagated uncertainty from subtracting the procedural blank composition and amount.

RESULTS

A full list of petrographic descriptions and geochemical results is given in Table S1. The CAS δ^{34} S data from McKittrick Canyon are highly variable, ranging from -4.7% to +25.2%. Most data from a given hand sample are isotopically similar and vary by only a few permil. Early diagenetic cements, such as isopachous and botryoidal cements, are of similar δ^{34} S to the allochems in the same hand sample (δ^{34} S for these cements, plotted as gold stars in Fig. 4, generally overlap red squares or purple circles representing the δ^{34} S of shelf margin and shelf crest facies; examples of polished slabs are shown in Fig. 5). However, late, poikilitic calcite spar in vuggy, fracture and breccia pores is as much as 15% more enriched in ${}^{34}S$ than earlier depositional textures from the same hand sample (Fig. 5A, and represented by green



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Fig. 4. Measured stratigraphic sections and geochemical data from McKittrick Canyon. Facies are codified corresponding to Tinker (1998). Grey bars denote the δ^{34} S range of Delaware Basin evaporites in the Seven Rivers and Castile formations (Thode *et al.*, 1961; Holser & Kaplan, 1966; Sarg, 1981; Hill, 1990; Kirkland *et al.*, 2000). The solid red line represents a timeline at the top of composite sequence 13, and the dashed red line represents a timeline at the top of shown in Fig. 5 are annotated. Samples from the massive shelf margin facies of the Capitan Formation were collected from the top and base of cliffy outcrops without measured sections, but timelines were biostratigraphically determined to be sub-vertical (Fig. 2) (Kerans *et al.*, 2013), so longitude was used as a proxy for age instead of stratigraphic height; the vertical axis is scaled to the easting in metres. BS, boundstone; GS, grainstone; MS, mudstone; PS, packstone; RS, rudstone; WS, wackestone.

triangles in Fig. 4 that always plot at higher δ^{34} S than specimens from the same hand sample). Facies tract - and therefore depositional environment - better predicts a sample's CAS δ^{34} S than stratigraphic position. For example, the full range of CAS δ^{34} S is expressed by the five sections sampled within the G26 HFS (Fig. 4). Similarly, sponge-cement boundstones (facies OS0 at the base of the McKittrick Peak section and samples from the Capitan Cliffs in Fig. 4) or peritidal grainstones/rudstones (facies SC6, SC7 and SC8 in the Wilderness Ridge and McKittrick Peak sections in Fig. 4) are each of similar isotopic composition, regardless of the HFS in which they deposited. Barring the latest calcite spars, the δ^{34} S data cluster into distinct populations governed by their depositional facies tract (Fig. 6A). Samples from the shelf crest and outer shelf facies tracts have a mean δ^{34} S of 9.6%. Samples from the shelf margin (reef) facies tract have a mean of 13.2% and samples from the slope facies tract are highly variable, ranging from 6.1 to 19.3%. Within each facies tract, $\delta^{34}S$ data are not correlated with carbonate δ^{18} O (Fig. 7A).

Sulphate concentrations in the samples also vary. Most samples average about 400 ppm (i.e. $\mu g SO_4^{2-}$ per g soluble carbonate), but the late poikilitic calcite spar averages 200 ppm sulphate and well-bedded toe of slope limestones contain an average of 2600 ppm sulphate (Fig. 6B).

The carbonate δ^{13} C and δ^{18} O compositions of the samples reflect trends in previously published data: peritidal dolomites in the Yates and Tansill formations have the highest compositions (δ^{13} C is between 2‰ and 7‰, and δ^{18} O is between 0‰ and 4‰) and subtidal limestones in the Capitan and Bell Canyon formations are generally lower (Fig. 7B) (Given & Lohmann, 1985, 1986; Mutti & Simo *et al.*, 1994; Mazzullo, 1999; Melim & Scholle, 2002; Chafetz *et al.*, 2008; Frost *et al.*, 2012; Budd *et al.*, 2013; Loyd *et al.*, 2013). Trends towards δ^{13} C as low as -8‰ and δ^{18} O as low as -9‰ reflect the physical admixture or sampling of calcite precipitated from meteoric and burial fluids (meteoric and burial calcite cements plotted as yellow stars in Fig. 7B bound the scatter of analyses of each facies) (Given & Lohmann, 1986). Calcite spars with the lowest δ^{18} O, between -11% and -16% (green triangles in Fig. 7B), are the latest calcite generation in the Guadalupe Mountains (Scholle *et al.*, 1992; Mazzullo, 1999).

DISCUSSION

Evidence for carbonate-associated sulphate incorporation during diagenesis

The δ^{34} S of carbonate-associated sulphate (CAS) in the shelf crest and outer shelf facies tracts are the only samples that record the sulphur isotopic composition of Delaware Basin seawater (Fig. 6A), inferred to have been 8 to 10% from published analyses of sulphate evaporites in the Seven Rivers Formation and the Castile Formation (Thode et al., 1961; Holser & Kaplan, 1966; Sarg, 1981; Hill, 1990; Leslie et al., 1997; Kirkland et al., 2000). In allochems and early diagenetic cements deposited contemporaneously during the G26 HFS, the δ^{34} S of CAS increases from ca 10% in peritidal carbonates in the Yates Formation to ca 13‰ in sub-wave base limestones in the Capitan Formation, and can be as high as 19‰ in deep, basinal limestones in the Bell Canyon Formation (Fig. 4). During deposition of the G26 high frequency sequence (HFS), there was ca 30 m of relief between the foreshore facies in the Yates Formation and the shelf margin massive reef facies (Fig. 2) (Babcock & Yurewicz et al., 1989; Kerans et al., 2013) and ca 600 m of relief between the foreshore facies and the toe of slope facies (Newell et al., 1953). Two hypotheses may explain this shelf to basin gradient in the δ^{34} S of CAS: it may represent a depth gradient of the $\delta^{34}S$ of Delaware Basin seawater or facies-dependent diagenetic control on the δ^{34} S of sulphate incorporated as CAS. Higher δ^{34} S of sulphate may be



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Fig. 5. Polished slabs annotated with isotopic data for micro-drilled sub-samples identified with letters corresponding to Table S1. (A) Cement boundstone from a vertical syndepositional fracture in a tepee structure in the Hairpin unit (sample MC-187; 39.4 m in the McKittrick Peak section). Botryoidal aragonite is neomorphosed to brown calcite pseudospar (b, c and j), and appears beige where dolomitized (a, g, h and i). Isopachous calcite marine cement (f), neomorphosed aragonite marine cement and dolomitized aragonite marine cements all preserve the $\delta^{34}S$ and $\delta^{13}C$ of the Delaware Basin seawater ($\delta^{34}S \approx 10\%$, $\delta^{13}C \approx 6\%$), but the $\delta^{18}O$ of the dolomite is higher, reflecting precipitation from evaporated seawater. Moulds of aragonite needles in dolomitized botryoids at the top of the slab (a and g) indicate that some dolomitization preceded neomorphism, but most calcite pseudospar and dolomite retain the aragonite botryoidal fabric. Equant calcite fills secondary pores created during dissolution after dolomitization (d), and has a higher δ^{34} S and lower δ^{13} C and δ^{18} O created by microbial sulphate reduction (MSR) in a meteoric-phreatic groundwater lens. Poikilitic calcite spar (e) has dramatically higher δ^{34} S and lower δ^{18} O reflecting hotter telogenetic meteoric fluids. (B) Cement-*Tubiphytes* boundstone from the G26-age reef facies of the Capitan Formation (sample MC099 collected at UTM Zone 13R 522856 m E, 3439789 m N). Sponges (S) and Tubiphytes (T) are encrusted by brown calcitic Archaeolithoporella (A), partially-dolomitized calcite pseudospar after botryoidal aragonite, and isopachous fibrous calcite marine cements (I). Unlike on the shelf, the neomorphosed (c) and dolomitized (a) cements in the reef have higher δ^{34} S than Delaware Basin seawater. The equant calcite (d) has lower δ^{34} S than the marine cements (b and c), but is also higher than the composition of seawater, suggesting less efficient MSR in the meteoric-phreatic fluids than in the marine-phreatic pore fluids. (C) Lithoclast-bioclast rudstone from the G26-age toe of slope facies in the Bell Canyon Formation (sample MC017; 3.1 m in the toe of slope section). Bioclasts include reef-derived bryozoan, brachiopod, crinoid and Tubiphytes fragments. Lithoclasts are bioclast wackestones that include the same assemblage. The δ^{34} S of the lithoclasts (a) and bioclasts (b) match other matrix and grain analyses from the toe of slope and are the highest non-sparry calcite compositions measured, indicating that carbonate-associated sulphate (CAS) is incorporated from pore fluids into the re-deposited grains during early marine diagenesis. (D) Oncoid rudstone from the shelf crest foreshore facies in the Tansill Formation (sample MC052; 27 m in the Wilderness Ridge section). Isopachous calcite marine cement (d) lines interparticle pores between pink dolomitized oncoids and aggregate grains (a and b). Both components preserve the $\delta^{34}S$ of Delaware Basin seawater, despite alteration of δ^{18} and enrichment in transition metals as evidenced by the pink colouration during dolomitization. The isotopic composition of poikilitic calcite spar that fills remaining interparticle pores was not analyzed in this sample. (E) Lithoclast rudstone at the top of the G26-age slope (sample MC213; 22.5 m in the Capitan Formation Slope section). Lithoclasts (dashed outline) are reef-derived Archaeolithoporella boundstone (Lb), spicule-bryozoan-ostracod grainstone (Lg), peloid packstone (Lp) and laminated mudstone (Lm). The finergrained mudstone and packstone lithoclasts are selectively dolomitized (c and d), and the siltstone matrix is dolomite-cemented (a). These dolomitic components largely preserve the $\delta^{34}S$ of Delaware Basin seawater, although some (d) are slightly isotopically-depleted and may have incorporated re-oxidized sulphide during early diagenesis. The δ^{34} S compositions of lime boundstone and grainstone lithoclasts (e and f) are higher than that of seawater. Late poikilitic calcite spar (b) has the highest δ^{34} S.



Fig. 6. Box plots of geochemical data from each facies tract and stage of diagenesis. Data for marine cements, equant calcite and poikilitic calcite is aggregated from all facies tracts. Boxes denote interquartile range and median, whiskers (dotted lines) span the range of data within 50% of the interquartile range, and crosses mark outliers beyond the whiskers. Grey bars denote estimates of the isotopic composition of carbonates precipitated from normal late Permian seawater: δ^{13} C and δ^{18} O ranges are of brachiopod calcite and well-preserved marine cements (Given & Lohmann, 1986; Korte *et al.*, 2005), and δ^{34} S range is of Delaware Basin evaporites in the Seven Rivers and Castile formations (Thode *et al.*, 1961; Holser & Kaplan, 1966; Sarg, 1981; Hill, 1990; Kirkland *et al.*, 2000): (A) δ^{34} S of CAS; (B) CAS concentration; (C) δ^{13} C; (D) δ^{18} O.



Fig. 7. Carbon, oxygen and sulphur isotope cross-plots. Grey bars denote estimates of the isotopic composition of carbonates precipitated from normal late Permian seawater (sources described in caption to Fig. 6). (A) δ^{18} O versus δ^{34} S. (B) δ^{18} O versus δ^{13} C. (C) and (D) Interpretation of isotope data that represent a physical mixture of carbonates formed in equilibrium with marine or meteoric end-member fluids. Carbonates formed from unaltered marine, meteoric and burial fluids have compositions of the blue star, yellow dot and green field, respectively. The fluids may evolve through physical and/or biogeochemical processes described by the arrows, such that meteoric or marine end-member carbonates can have a range of compositions along the vectors. Evaporation, sulphide oxidation, microbial sulphate reduction (MSR) and photosynthesis may affect the δ^{13} C, δ^{18} O and/or δ^{34} S of seawater or seawater-derived fluids, such that carbonate precipited at equilibrium from those fluids falls along the blue arrows. Similarly, sulphide oxidation, MSR and water-rock reactions will alter the isotopic compositions of meteoric-derived fluid with soil carbon; additionally, the temperature of precipitation will affect the δ^{18} O of carbonate precipitated from the fluid. Taken together, these processes permit a range of meteoric end-member carbonates along the yellow arrows. Therefore, physical mixtures of carbonates that sample various amounts of each carbonate precipitated along the diagenetic vectors fill the light blue field. V-CDT, Vienna-Canyon Diablo Troilite; V-PDB, Vienna-Pee Dee Belemnite.



Fig. 8. Paragenetic sequence of processes influencing the texture and chemical composition of the Capitan Reef complex, from deposition in the marine environment to progressively more recent diagenetic events, simplified from Melim *et al.* (1999). Brackets indicate the integrated set of diagenetic processes represented by the textures in each panel in Fig. 9.

developed by microbial sulphate reduction (MSR), which preferentially leads to the fixation of low- δ^{34} S sulphur in sulphide minerals and leaves the residual sulphate enriched in ³⁴S (Thode *et al.*, 1961). Microbial sulphate reduction can only occur in anoxic conditions, thereby implying a chemocline in the water column above the reef facies if the depth gradient in the water column hypothesis is correct.

However, a shallow chemocline above the shelf margin is precluded by abundant reefbenthic heterotrophic dwelling animals. Although cryptic encrusters such as Tubiphytes and Archaeolithoporella become increasingly abundant towards the upper Capitan Formation, sponges, bryozoans, brachiopods, corals, molluscs and crinoids are found throughout the reef in life positions (Babcock & Yurewicz et al., 1989; Fagerstrom & Weidlich, 1999; Weidlich & Fagerstrom et al., 1999). These organisms almost certainly could not have tolerated anoxic or sulphidic conditions (Grieshaber & Völkel, 1998; Theissen & Martin et al., 2008; Riedel et al., 2012; Mills et al., 2014). Therefore, the observed shelf to basin gradient in the δ^{34} S of CAS cannot represent a syndepositional depth gradient in the δ^{34} S of Delaware Basin seawater. Although a water-column chemocline may have developed below the shelf margin (because the slope and toe of slope facies lack fossils in their life position), the CAS in many shelf to upper slope samples must incorporate an isotopically-distinct, diagenetic source of sulphate.

Carbonate-associated sulphate in diagenetic and primary carbonates

To examine the controls on the $\delta^{34}S$ of CAS, the following discussion is organized by stage of

diagenesis, in which each diagenetic process is examined from shelf to basin. Primary grains reflect their initial composition and the integrated effect of chemical exchange with fluids. Cements and spars reflect the composition of seawater, pore fluids and burial fluids whose composition evolved from biogeochemical reactions in the fluid or exchange with the rock. Samples that include a physical mixture of closely intergrown end-member carbonate phases may therefore have a wide range of isotopic compositions (Fig. 7C and D). Figure 8 is a simplified paragenetic sequence for the Capitan Reef complex in the Guadalupe Mountains based on previouslyreported petrographic and geochemical data. Samples analyzed for CAS experienced the integrated effect of multiple diagenetic processes during different but overlapping periods of time in different locations from shelf to basin. Figure 9 organizes the CAS δ^{34} S data by texture and facies tract to visualize where and when each diagenetic process preserves the δ^{34} S of seawater.

Early marine diagenesis

Excluding calcite spars, the relative homogeneity of the δ^{34} S of CAS in texturally-diverse samples within each facies tract – including the samples whose δ^{34} S is distinct from that of seawater – suggests that CAS includes sulphate incorporated during early diagenesis. The interquartile δ^{34} S of CAS in the shelf crest samples is similar to that in outer shelf samples, and distinct from the interquartile in the shelf margin, slope and toe of slope samples (Fig. 6). Additionally, the shelf samples that accurately preserve the δ^{34} S of Permian seawater formed in a different environment than the reef and slope samples whose compositions reflect carbon and oxygen isotopic equilibrium with Permian seawater (Fig. 7A and B).



The early marine diagenetic processes operating during CAS incorporation include marine isopachous calcite and aragonite cementation, botryoidal aragonite cementation and the neomorphic inversion of aragonite and high-magnesium calcite to low-magnesium calcite (Schmidt, 1977; Garber et al., 1989; Mutti & Simo et al., 1994; Mazzullo, 1999). Neomorphosed components include bioclasts and coated grains, which are now pervasively dolomitized in the shelf facies tracts and are predominately calcite elsewhere. Brown calcite pseudospar represents the neomorphic inversion of botryoidal aragonite (Mazzullo, 1980). In tepee structures in the shelf crest facies tract (Fig. 5A), the CAS in brown calcite records the $\delta^{34}S$ of seawater (red bars in Fig. 9A). In cavities in the shelf margin facies tract (Fig. 5B), the CAS in brown calcite has a higher $\tilde{\delta}^{34}S$ than seawater (purple bars in Fig. 9A). In both cases, the δ^{34} S of CAS in these early marine cements matches that of neomorphosed allochems and cements in the same hand samples, as well as that of micritic and peloidal matrix whose original mineralogy is unknown (Fig. 9B and C). Therefore, the δ^{34} S of CAS records the pore fluid sulphate during early cementation and neomorphism. The δ^{34} S of pore fluid sulphate matched that of seawater in the shelf crest and outer shelf facies tracts, but preferential consumption of low $\delta^{34}S$ pore fluid

Fig. 9. Histograms of the δ^{34} S of carbonate-associated sulphate (CAS) in depositional and diagenetic textures, with the colour of the bar corresponding to the facies tract from which the sample was collected. Grey bars denote the estimated δ^{34} S composition of Delaware Basin seawater (sources in caption to Fig. 4). (A) Calcitic early marine cements incorporate CAS from the seawater in which the aragonite botryoids precipitated and from the pore fluids in which the aragonite neomorphically inverted to brown calcite pseudospar. The pore fluid $\delta^{34}S$ was distilled towards higher compositions in the shelf margin by microbial sulphate reduction (MSR), but was unmodified from the seawater composition in the shelf crest. (B) Calcitic grains and micrite matrix incorporate CAS from the seawater in which the grains or mud precipitated, the pore fluids in which they were cemented and the pore fluids in which any aragonite neomorphically inverted to calcite. These pore fluids were distilled towards higher compositions by MSR. (C) Dolomitized early marine cements incorporate CAS from the dolomitizing fluids, in addition to the fluids responsible for the calcitic cements in (A). In the shelf crest, the cements were dolomitized by many pore volumes of a reducing fluid, but it was sulphate-poor or its δ^{34} S was not modified from that of seawater. Dolomitization in the reef and slope was fabricdestructive, and possibly preceded aragonite neomorphism. (D) Dolomitized grains and micrite matrix similarly incorporates CAS from seawater and the suite of earlier diagenetic regimes. The δ^{34} S of CAS lighter than seawater is generally associated with the finest-grained or most siliciclastic-rich facies, and may reflect the addition of low- δ^{34} S sulphate from reoxidized sulphides. (E) Equant calcite spar incorporated CAS from reducing meteoric groundwater. (F) Poikilitic calcite spar incorporated CAS from a much younger, extrabasinal, possibly Neogene meteoric groundwater. V-CDT, Vienna-Canyon Diablo Troilite.

sulphate by MSR distilled the residual sulphate towards higher compositions in the shelf margin and slope facies tracts (Fig. 7C).

Clasts and grains precipitated on the shelf and transported to deeper environments during deposition provide further evidence of CAS incorporation post-dating primary carbonate precipitation. For example, bryozoan fragments and lime wackestone lithoclasts derived from the shelf margin and redeposited in the toe of slope have δ^{34} S of CAS of 16 to 17‰ (Fig. 5C), which is comparable to other CAS analyses from the toe of slope but higher than those in the shelf margin (Fig. 6).

Dolomitization

Allochems, micrite and cements in the shelf crest and outer shelf facies tracts are now fabric-retentively dolomitized (Fig. 5D), likely by reflux dolomitization following marine cementation (Adams & Rhodes, 1960; Melim & Scholle, 2002; Frost *et al.*, 2012). The δ^{34} S of CAS in partially dolomitized botryoidal cements (Fig. 5A) matches that of the brown calcite pseudospar (the range of red bars in Fig. 9A overlaps that in Fig. 9C and D). Therefore, dolomitization on the shelf does not appear to have changed the δ^{34} S of CAS incorporated during earlier stages of marine diagenesis, which preserved the δ^{34} S of seawater (Fig. 9D). This may be because the dolomitizing fluids were sulphate-poor, or because the δ^{34} S of their sulphate was not modified from that of seawater.

Some packstone-grainstone beds in the slope facies tract and high-permeability regions of the shelf margin facies tract are discordantly dolomitized as well (Frost et al., 2012). Slope mimetic dolomite and dolomite-cemented siltstones have CAS with δ^{34} S that is ca 10% (Fig. 5E), matching the isotopic composition of seawater despite a diagenetic increase of δ^{34} S in calcitic specimens, including limestone lithoclasts, from the same facies. Therefore, in the shelf margin and slope facies tracts, dolomitization likely began before most neomorphism and marine cementation; this is consistent with prior observations of mouldic fibrous pores in dolomitized botryoids in the shelf margin and mimetic replacement of aragonite at the crystal scale (Mutti & Simo et al., 1994; Melim & Scholle, 2002). This early dolomitization of the slope occurred with fluids with a $\delta^{34}S$ composition similar to that of seawater sulphate (black bars in Fig. 9D). Aragonite neomorphism and early marine cementation in the shelf margin and slope facies tracts likely followed dolomitization, after enrichment of pore fluid sulphate δ^{34} S could occur (black bars in Fig. 9B). Cementation of the shelf crest and outer shelf preceded cementation of the shelf margin and slope, with reflux dolomitization occurring in the interim.

The limestones from the shelf margin and slope facies tracts represent the carbon and oxygen isotopic compositions of the Delaware Basin well (Given & Lohmann, 1985; Korte *et al.*, 2005) but they are not useful for chemostratigraphic reconstructions of seawater sulphate (Fig. 7). Samples with δ^{34} S of CAS most distinct from syndepositional seawater were deposited in the toe of slope. Within each facies tract, there is weak correlation between δ^{34} S and δ^{18} O or δ^{13} C, which is often used to geochemically screen samples for diagenetic alteration. However, the diagenetic processes that influence the δ^{18} O and δ^{13} C of carbonate are different than those that

influence the δ^{34} S of CAS. Carbonate-associated sulphate in samples from the coarse-grained, high-porosity shelf facies best preserve the $\delta^{34}S$ of seawater sulphate, despite a complicated diagenetic history that includes early marine cemendolomitization. tation and Dolomitization increased the δ^{18} O of the carbonate (Fig. 7C and D; Mutti & Simo et al., 1994), likely by the flushing of many pore volumes with evaporated mesosaline brines (Melim & Scholle, 2002), but evaporation to mesosaline concentrations and precipitation of gypsum modifies the δ^{34} S of sulphate in the brine by <0.5‰ (Raab & Spiro, 1991). Carbonate sediments deposited in lower-energy, deeper reef and slope environments generally preserve primary δ^{18} O and δ^{13} C compositions that match late Permian brachiopod calcite and marine cements (Given & Lohmann, 1985; Korte et al., 2005). Neomorphism and marine phreatic (botryoidal and isopachous) cementation in these environments coincided with MSR that led to increase in the δ^{34} S of pore fluids and CAS, but these processes do not fractionate carbon or oxygen isotopes (Fig. 7C).

Early burial–meteoric diagenesis

In the shelf, shelf margin and slope facies tracts, a generation of equant calcite spar post-dates a dissolution event following early marine cementation. This equant calcite fills primary pores including fenestrae, secondary pores in neomorphosed botrvoidal cements, mouldic pores formed by dissolution of aragonite allochems and evaporites and pores in breccia that line some syndepositional fractures (Given & Lohmann, 1986; Mruk, 1989; Mutti & Simo et al., 1993; Budd *et al.*, 2013). It has a δ^{34} S of CAS between 10% and 18%, except for a single analysis of an early generation of calcite filling a solution-enlarged vug that is -4.6% (Fig. 9E). Based on its equant, inclusion-rich texture, δ^{18} O near 8‰ and variable δ^{13} C, it likely corresponds to calcite 'Spar I' in the Capitan Formation as defined by Mruk (1989) and Given & Lohmann (1986) and identified as sparry calcite cathodoluminescence zone CLI in the Yates Formation by Mutti et al. (1993). It crystallized from meteoric-phreatic fluids, probably during lowstands between HFSs (Given & Lohmann, 1986; Mruk, 1989; Mazzullo, 1999; Budd et al., 2013; Bishop et al., 2014), so its δ^{34} S of CAS that is higher than Guadalupian seawater δ^{34} S may represent active MSR in this groundwater lens (Fig. 7C).

A subset of equant calcite samples from the shelf crest, outer shelf and slope facies tracts

incorporate CAS with lower δ^{34} S than contemporaneous seawater, which probably reflect incorporation of reoxidized sulphide. Many of these samples' δ^{18} O and δ^{13} C compositions are largely indistinguishable from the other samples in each facies tract (Fig. 7A and B). This lack of variability may be because sulphide oxidation locally produces high acidity that would dissolve nearby carbonate, strongly rock-buffering the carbon and oxygen isotopic composition (Fig. 7C) (Walter et al., 1993). In the shelf crest and outer shelf facies tracts, samples with low δ^{34} S are also among the finest-grained supratidal evaporitic mudstones, fenestral algal-coated grain packstones and siliciclastic-rich packstones that cap depositional cycles. The lowest δ^{34} S composition, -4.6%, is in a cloudy calcite cement similar to Spar I that rims a solutionenlarged vug in a fenestral packstone. Meteoric vadose pendant cements in some samples are likely related to recent outcrop weathering, but other samples lack such cements. Therefore, there may have also been Permian-age oxidizing meteoric diagenesis, which would have reoxidized low δ^{34} S sedimentary sulphide minerals. Gypsum with both low and high δ^{34} S has been observed and similarly interpreted in Seven Rivers Formation lagoonal evaporites (Sarg, 1981). Additionally, in the slope, some dolomitized peloidal grainstones and fine-grained packstones have low δ^{34} S of CAS (Fig. 5E and black bars in Fig. 9D), consistent with incorporation of sulphate with anomalously-low δ^{34} S into CAS during dolomitization (Marenco et al., 2008; Present et al., 2015; Fichtner et al., 2017).

Late burial-meteoric diagenesis

Carbonate-associated sulphate with the highest δ^{34} S compositions is in late-stage poikilitic calcite spar that fills interparticle and fracture pores (Fig. 5A and E). The δ^{34} S of CAS is as high as 25% (Fig. 9F), which is as much as 15%higher than early diagenetic textures in the same hand sample (Fig. 5A). This calcite spar is only observed in the uplifted outcrops of the Guadalupe mountains, and replaces anhydrite cements that are only observed in subsurface drill core (Garber et al., 1989; Mruk, 1989; Scholle et al., 1992; Mazzullo, 1999; Budd et al., 2013). It corresponds to calcite 'Spar II' as defined by Given & Lohmann (1986), 'Spars II and III' as defined by Mruk (1989), and sparry calcite cathodoluminescence zones CLII and CLIII defined by Mutti et al. (1993). The poikilitic spars with the highest δ^{34} S have end-member δ^{18} O and δ^{13} C compositions with lower δ^{18} O and higher δ^{13} C than early diagenetic equant calcite spars, representing more rock-buffering and warmer meteoric basinal fluids (Fig. 7; Budd *et al.*, 2013; Loyd *et al.*, 2013). Despite replacing Capitanian or Ochoan-age anhydrite cement, the distinct δ^{34} S of CAS in these spars suggests a non-Permian source for the sulphate associated with meteoric groundwater advection during burial and uplift. The lack of Permian δ^{34} S compositions is particularly surprising because the poikilitic spar includes anhydrite inclusions indicative of a direct replacement (Scholle *et al.*, 1992).

Implications for carbonate-associated sulphate chemostratigraphy

Fine-grained limestones and micritic textures are frequently sampled in CAS chemostratigraphy studies because, in some depositional environments, the CAS in primary aragonite mud represents a dominant mass fraction of the total CAS in recrystallized and cemented carbonate (Lyons et al., 2004; Rennie & Turchyn, 2014). However, in environments with high sedimentation rates or high organic carbon fluxes, CAS measurably incorporates diagenetically-enriched pore fluid sulphate during recrystallization and cementation (Loyd et al., 2012a; Rennie & Turchyn, 2014). Fine-grained slope or basinal limestones therefore may be poor archives of ancient seawater sulphate. Peritidal fine-grained limestones, on the other hand, may incorporate isotopically-light sulphate that is the product of re-oxidized sulphide and pyrite during early meteoric or dolomitizing diagenesis (Marenco et al., 2008; Present et al., 2015; Fichtner et al., 2017). Meteoric replacement of biogenic aragonite leaches sulphate without fractionating its isotopes if the meteoric fluids are sulphate-poor (Gill et al., 2008), but organicrich, fine-grained carbonate sediments are pyriterich (Ku et al., 1999; Crémière et al., 2017), providing a source of isotopically-light sulphur that would be mobile during early diagenesis.

Covariation between trace or minor element concentrations and stable isotope data is often used to geochemically screen samples for diagenetic alteration of primary seawater compositions because many diagenetic processes re-equilibrate a sample towards a diagenetic end-member composition with a distinct thermodynamic equilibrium composition (Brand & Veizer, 1980, 1981). However, the early marine diagenetic processes that incorporate high- δ^{34} S sulphate into a carbonate mineral (MSR coincident with marine-phreatic cementation or recrystallization) occur in a pore fluid environment without δ^{18} O gradients from seawater. Pore fluids may exhibit δ^{13} C gradients driven by the respiration of organic carbon during MSR, but the much greater mass of marine-derived carbon (12%) relative to CAS (<1%) in the initial carbonate suggests that covariation between δ^{13} C and δ^{34} S is not a sensitive indicator of marine diagenetic alteration of CAS. Meteoric and burial diagenetic end-member compositions indeed create δ^{18} O and δ^{13} C covariation with δ^{34} S (Fig. 7), but the 'primary', marine-derived carbon and oxygen end-member in the reef and slope facies tracts still incorporated diagenetic sulphate.

In other words, the diagenetic end-members that affect carbon and oxygen isotopes are formed at different times and by different biogeochemical processes than those that affect sulphur isotopes. Consequently, screening samples for chemostratigraphy using δ^{13} C and δ^{18} O may not capture important diagenetic alteration of δ^{34} S. Increasing rock-buffering of meteoric fluids creates the classic 'inverted J-curve' that defines the meteoric-phreatic diagenetic end-member affecting carbon and oxygen isotopes (Lohmann, 1982). The data in Fig. 7 represent physical mixtures between microscopically-intergrown calcite crystals that formed from the meteoric and the marine end-member fluids. However, the marine end-member for sulphur isotopes can vary independently of biogeochemical processes affecting carbon or oxygen isotopes.

Additionally, in a low-energy depositional environment without pore fluid advection, the pore fluid minor and trace elements will equilibrate with the carbonate sediment. Constituents that are abundant in the pore fluid but not in the solid - such as sulphate - will dominate the carbonate phase's composition without measurable covariation with common diagenetic proxy elements such as strontium (which is abundant in the carbonate but not the fluid). Covariation with redox-sensitive trace elements such as manganese and iron (which are abundant in reduced fluids compared to the primary carbonate) will depend on the unknowable primary ratio of sulphur, oxygen, carbon and metals in the ancient depositional environment. Further study of the trace element distribution of the Permian Reef may help to identify depositional environments and diagenetic regimes where such elements predict CAS diagenetic alteration, but their enrichment is not a clear indication of CAS alteration. For example, metal enrichment evidenced by pink-orange colouration in many

carbonates in the Yates and Tansill formations (for example, Fig. 5D) indicates that reducing conditions during dolomitization led to incorporation of ferrous iron, which was later oxidized, but the fluids were evidently not carrying sulphate fractionated from seawater.

Previously published bulk rock CAS data from Guadalupian successions have a large δ^{34} S variability. Sparse biogenic carbonate data includes one analysis of brachiopod calcite that is 11.0%and another that is 14.9% (Kampschulte & Strauss, 2004; Wu et al., 2014). Bulk carbonate analyses from limestones deposited in the Tethvan Ocean in South China include δ^{34} S excursions from -40% to +40% (Li *et al.,* 2009; Yan et al., 2013) that are well beyond the range of all other Palaeozoic CAS and evaporite data; if these CAS data accurately reflect the δ^{34} S of Tethyan seawater, then they imply periods of heavily stratified oceans with heterogeneous sulphate concentrations. Data from the current study, although temporally-restricted to the time represented by two to three high-freqency sequences (HFS) ($ca \ 10^6$ years), suggests that variable diagenetic regimes can contribute to observed CAS variability. Extremely high δ^{34} S of CAS measurements may reflect periods of intense pore fluid sulphate reduction driven by high organic carbon burial fluxes and exacerbated by low bottomwater oxygen concentrations (Yan et al., 2013). Extremely negative δ^{34} S of CAS measurements may reflect local re-oxidation of sulphide in shallowly buried sediments as the chemocline in the sediments or water column episodically shoaled and deepened (Riccardi et al., 2006; Li et al., 2009; Yan et al., 2013; G. Zhang et al., 2015).

For future CAS chemostratigraphy studies where well-preserved biogenic calcite is unavailable, coarse-grained carbonates deposited in highenergy peritidal depositional environments might provide the best record of seawater sulphate. Organic carbon in high-energy settings is rapidly consumed by aerobic and suboxic processes in the pore fluids of mobile sediments (Aller et al., 2004). If these processes consume sufficient organic matter, the availability of organic matter for MSR will limit the development of pore fluid sulphate δ^{34} S gradients in lower sediments (Aller et al., 2010). Sediments in high-energy settings also do not accumulate large aqueous sulphide or pyrite reservoirs (Aller et al., 2004) that may be easily re-oxidized during dolomitization or meteoric diagenesis. However, sediments in such environments form porous and permeable grainstones and matrix-poor rudstones whose δ^{18} O may be fluid-buffered and dramatically different from that precipitated from syndepositional seawater. Despite this, carbonate rocks deposited in highenergy environments may have the best chance of preserving original seawater δ^{34} S in CAS.

CONCLUSIONS

By comparing the $\delta^{34}S$ of carbonate-associated sulphate (CAS) along a shelf to basin transect of carbonate rocks synchronously deposited in peritidal to deep environments, this study demonstrates that carbonate-associated sulphate may incorporate diagenetic sources of sulphate that are isotopically distinct from synsedimentary seawater. Fine-grained facies deposited in lowenergy environments, which are often targeted in isotope chemostratigraphy studies because they are more rock-buffered during early and burial diagenesis, are most likely to incorporate δ^{34} S reflecting residual pore fluid sulphate. In contrast, early diagenesis of grainy sediments including marine cementation, fabric-retentive dolomitization and neomorphism - deposited in high-energy depositional settings appears to incorporate pore fluid sulphate with seawaterlike δ^{34} S into carbonate-associated sulphate.

These results show that δ^{34} S variability of carbonate-associated sulphate may not necessarily indicate heterogeneity or rapid changes in the δ^{34} S of ancient seawater caused by widespread euxinic conditions. While carbonate-associated sulphate in peritidal, high-energy grainstones and rudstones in the shelf crest and outer shelf accurately record the δ^{34} S of Delaware Basin seawater sulphate, δ^{34} S of carbonate-associated sulphate in the deeper facies constrains the timing and conditions of diagenesis in the Capitan Reef. Limestones in the shelf margin and slope facies tracts have heavier δ^{34} S compositions reflecting neomorphism and cementation in a regime of active microbial sulphate reduction (MSR). However, because many dolomites associated with high-permeability regions in the shelf margin and slope facies tract incorporate carbonate-associated sulphate with $\delta^{34}\hat{S}$ similar to or even lighter than seawater, dolomitization in these environments must have at least partially preceded neomorphism and cementation. Sparry calcite cements formed during meteoric diagenesis range from seawater-like compositions up to 8% heavier, indicating active microbial sulphate reduction in the groundwater present during cementation. Burial meteoric fluids that replaced

evaporite cements during uplift incorporate high- δ^{34} S sulphate from an isotopically-distinct fluid.

Physical admixture of the sparry calcite cements into neomorphic components creates covariation between δ^{34} S and δ^{18} O, but such vectors are not produced during early marine diagenesis. Therefore, the absence of covariation between δ^{34} S and δ^{18} O is not an adequate geochemical screening method for determining primary seawater δ^{34} S. Sulphur isotope chemostratigraphy intended to reconstruct ancient seawater composition and biogeochemical fluxes must consider early diagenetic processes in the sedimentary environment.

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Supporting Information

Additional information may be found online in the Supporting Information section at the end of the article:

 Table S1.
 Sample locations, descriptions, and geochemical data.