Presented at "Advances in the Understanding and Interpretation of Carbonates"
SEPM Conference held August 27-28, 2023, in Houston, TX
Convenors: Ted Playton and Paul (Mitch) Harris

Early Diagenesis in the Permian Reef

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Keywords: eodiagenesis, cementation, dolomitization, microbial sulfate reduction

Key Messages

- The Permian Reef Complex is dominated by carbonate cements, mud, and coated grains that record precipitation conditions and fluid-rock interactions.
- Isotope measurements (δ^{13}C, δ^{18}O, δ^{44}Ca, δ^{26}Mg, δ^{34}S, and Δ_{47}) show most components chemically equilibrated with marine-derived eodiagenetic fluids.
- Marine pore fluids in the reef facies were modified by microbial metabolisms.
- Fabric-retentive dolomitization occurred during earliest diagenesis.
- Carbonate bulk composition did not further evolve during recrystallization in a closed-system burial environment.
- Preservation of earliest chemical signatures permit interrogation of the biotic and environmental controls that interplay to create distinguishing features of the Permian Reef Complex.

Research Scope, Data and Results

The Permian Reef Complex (west Texas and New Mexico) is a Guadalupian carbonate-clastic platform that rimmed the Delaware Basin, with stunning outcrops in the Guadalupe Mountains and famous hydrocarbon productivity in the Permian Basin. After a century of research and production, several features of the Permian Reef Complex have become archetypal for modern and ancient carbonate platforms. These include cyclic reflux dolomitization, margin lithification and slope transport, reciprocal sedimentation, highstand supratidal polygonal sheet crack-pisolite facies, and a deep subtidal ecologic reef volumetrically dominated by mud and cement (e.g., Harris and Grover, 1989). Marine diagenetic processes penecontemporaneous with deposition control many of these striking aspects. A mechanistic understanding of the Permian Reef Complex's architecture requires examining the interplay between basin seawater composition, microbial and macrofaunal ecology, and sedimentologic processes.

Reef facies in the Capitan Formation have widespread aragonite cements encrusted by microbes and volumetrically less significant sponges, bryozoans, and algae (Mazzulo and Cys, 1977; Grotzinger and Knoll, 1995), now nearly all replaced by neomorphic calcite and dolomite. Shelf facies in the Yates and Tansill formations also have volumetrically dominant precipitated calcite and aragonite cements in polygonal sheet crack-pisolite complexes. These supratidal facies, as well as dolomite abundance in all shelf-top facies, increase in areal extent during highstand system tracts (Mutti and Simo, 1994; Rush and Kerans, 2010). The stratal geometries indicate recrystallization and dolomitization is driven by seepage of water from lagoons developed behind the supratidal complexes during highstands, resulting in fabric-retentive and fabric selective replacement of primary grains and cements (Adams and Rhodes, 1960; Mutti and Simo, 1994; Rush and Kerans, 2010).

We integrate petrographic, chemical imaging, and isotopic datasets (carbonate δ^{13}C, δ^{18}O, δ^{44}Ca, δ^{26}Mg; carbonate Δ_{47} clumping; carbonate-associated sulfate δ^{34}S)

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to investigate the interplay between biogeochemical processes, Delaware Basin seawater composition, and carbonate diagenesis during construction of the Permian Reef Complex and subsequent burial. High-resolution sections along a shelf-to-basin transect of time-equivalent strata in the Yates, Tansill, Capitan, and Bell Canyon formations were measured in McKittrick Canyon, Guadalupe Mountains National Park, TX. From 109 polished sample slabs, we micro-drilled 262 geochemical samples capturing a full paragenesis for each depositional facies (Present et al., 2019). The isotopic composition of carbonate mineral major elements (Ca, Mg, C, O) and clumped combinations (Δ_{47}) were used to constrain precipitation conditions and fluid-rock interactions. X-ray fluorescence maps by benchtop and synchrotron sources were used to produce a minor and trace element paragenesis. Combined with carbonate-associated sulfate $\delta^{34}S$ measurements, these data track microbial processes in pore fluids across depositional environments. Sediment and fluid interactions during neomorphism and dolomitization were quantified with a reactive-transport model constrained by the isotopic data (Bryant et al. 2022).

Carbonate $\delta^{13}C$ and $\delta^{18}O$ values of reef and slope facies match that of primary Permian seawater in the Delaware Basin, with variable admixture of lighter meteoric components (Fig. 1A). In shelf-top facies, higher values indicate evaporation of lagoonal waters and evolution of dissolved inorganic carbon by photosynthetic carbon fixing metabolisms. Reef and slope facies have more variable and lower $\delta^{13}C$ values across similar ranges of $\delta^{44}Ca$ values as shelf-top facies (Fig. 1B). Calcium isotopes are kinetically fractionated from seawater during aragonite cement precipitation and re-equilibrate towards higher seawater values during diagenesis if adequate seawater-derived fluids flush the pore system; thus, shelf-top environments were more thoroughly flushed by seawater during carbonate neomorphism and diagenesis than the reef and slope. Similarly, $\delta^{26}Mg$ values show that neomorphism of aragonite to calcite did not modify the isotopic composition of minor Mg substitution, and dolomitization occurred under near-surface equilibrium conditions. Clumped isotope Δ_{47} values, which decrease with increasing carbonate-water equilibration temperature, fully control $\delta^{18}O$ values of fluids in equilibrium with dolomite at all temperatures; thus, fluid-mineral exchange during dolomitization and limestone neomorphism occurred prior to burial, and burial diagenesis at elevated temperatures occurred under highly rock-buffered conditions that preserved near-surface chemical information (Fig. 1C). Carbonate-associated sulfate $\delta^{34}S$ values in shelf-top facies match that of Permian seawater sulfate, but are higher in reef and slope facies, indicating that pore fluids were modified by microbial sulfate reduction in deeper facies during earliest marine diagenesis (Fig. 1D).

These results indicate that polygonal sheet crack cements, pisoids, and other coated grains rapidly precipitated from a productive, evaporitic shelf-top carbonate factory. They were neomorphosed or dolomitized shortly after deposition by advective flow of marine-derived pore fluids. Fabric-retentive early dolomitization may have been favored by lower sulfate concentrations and aqueous sulfide catalysis, but the net effect of sulfate reduction on shelf-top pore fluids was small. Mud and cements in the reef and slope facies also neomorphosed prior to burial, but by sediment-buffered, sulfidic pore fluids in diffusive connection with seawater. A reaction-transport model shows that, to reconcile $\delta^{44}Ca$ and $\delta^{34}S$ isotopes, Delaware basin seawater needed a higher $[Ca^{2+}]/[SO_4^{2-}]$ ratio than modern seawater and unusually high rates of microbial sulfate reduction (Fig. 1D).

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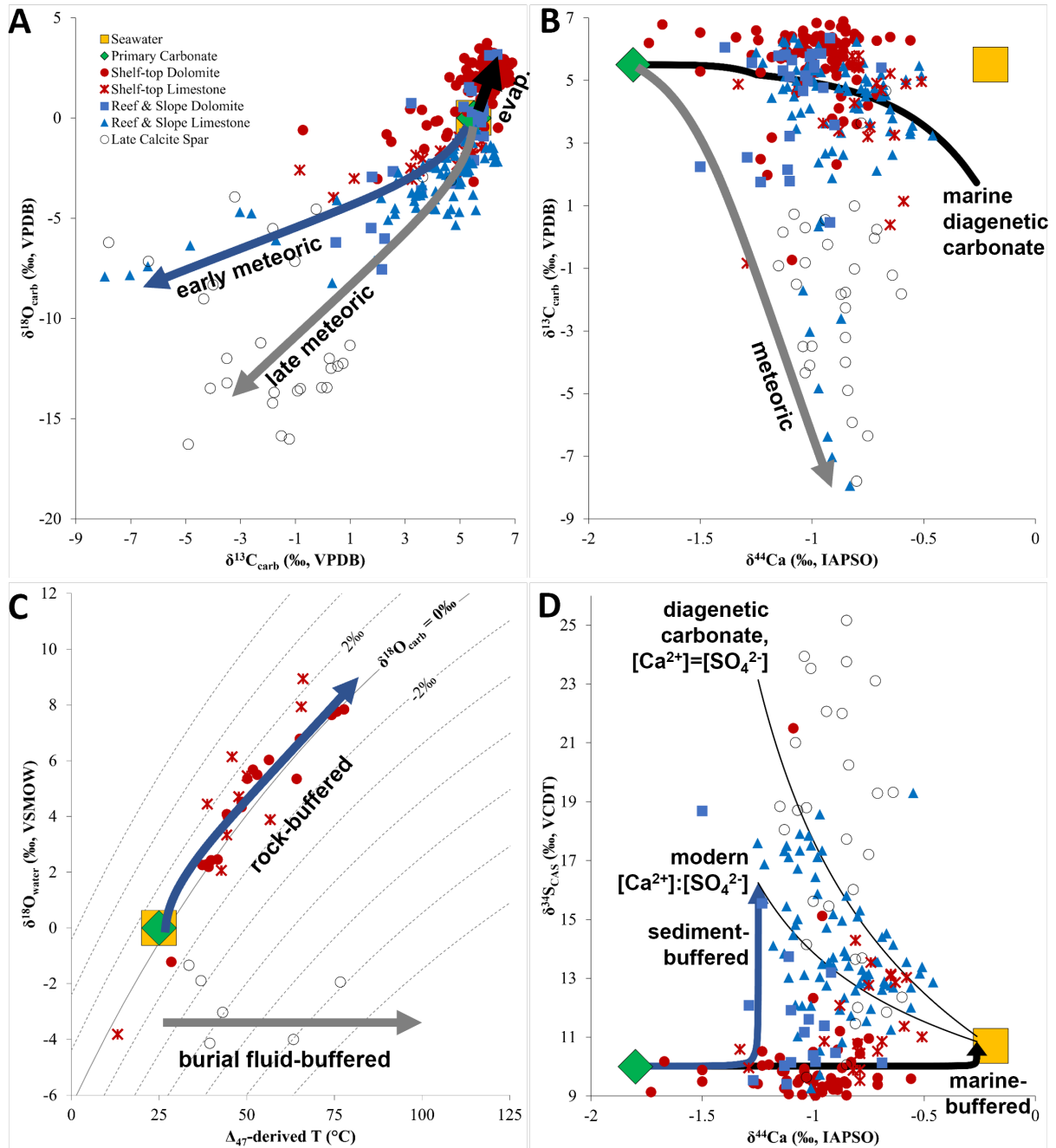Convenors: Ted Playton and Paul (Mitch) Harris

Figure 1. Isotopic tracers of primary and diagenetic processes acting on the Permian Reef Complex. (A) Carbonate $\delta^{13}C$ and $\delta^{18}O$ values predominantly reflect primary marine compositions, with higher values in shelf top settings and with variable admixture of lower $\delta^{18}O$ and $\delta^{13}C$ meteoric calcite. (B) Carbonate $\delta^{44}Ca$ values track seawater fluid availability as neomorphism and dolomitization occur, with less seawater advection and more diagenetic fluid evolution of $\delta^{13}C$ in reef and slope settings. (C) Dolomite Δ_{47}-derived equilibration temperatures and $\delta^{18}O$ values of water in equilibrium with measured dolomite $\delta^{18}O$ values. Burial fluids evolved in composition while dolomite $\delta^{18}O$ values preserved original compositions. (D) Carbonate-associated sulfate $\delta^{34}S$ values in the reef and slope incorporated pore fluids with sulfate modified by microbial sulfate reduction, requiring high rates of microbial sulfate reduction and higher $[Ca^{2+}]/[SO_4^{2-}]$ during early diagenesis.

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Significance

Integrated petrographic, stratigraphic, and petrographic data constrain the composition of marine fluids during deposition, as well as fluid flow and rock-water interactions during diagenesis. Together, these data explain distinctive features of the Permian Reef Complex. Grotzinger and Knoll (1995) enumerated several conditions favorable for widespread precipitation of marine carbonate cements in Precambrian and Permian reef complexes, including increased deepwater alkalinity due to microbial sulfate reduction and increased Ca fluxes due to supercontinent weathering. Here, these are quantitatively demonstrated as important factors in Permian Reef construction and early diagenesis.

These results also inform the use of diagenetic carbonate components as palaeoceanographic archives. Carbonate clumped and oxygen isotope data indicate that the Permian Reef Complex is a chemically stable archive of Permian environmental conditions, with mild and petrographically distinct burial diagenesis modifying porosity. Calcium isotope data indicate that shelf-top diagenesis was advective and dominated by seawater-derived lagoonal brines, and reef and slope diagenesis was diffusive and dominated by seawater-derived sulfidic pore fluids. This permits further understanding of ecologic and biogeochemical roles of microbes in the Permian Reef. Other platforms with extensive early diagenesis may be complicated but robust archives of ancient environments.

Biological (e.g., microbial metabolisms, encrusting and binding organisms) and environmental (e.g., seawater composition, climate) controls on pore fluid compositions during early diagenesis affect the carbonate factory's intensity, locus, and mineralogy. Future work will relate primary and diagenetic fluid composition to sedimentary structures and stratigraphic architecture.

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Introduction

The Permian Reef Complex (west Texas & New Mexico) is a Guadalupian carbonate-siliciclastic platform that rims the Delaware Basin, a Pangean epeiric sea (Fig. 1).

Marine diagenetic processes penecontemporaneous with deposition control many platform architectural features (Fig 2), including:
- Supratidal pisolite-sheet crack barrier island complexes
- Mimetic dolomitization by cyclic reflux of lagoonal fluids
- Deep subtidal margin reef dominated by precipitated mud and cement
- Reciprocal sedimentation and slope/basinal carbonate gravity deposits

Supratidal pisolite-polygonal sheet crack barrier

Fabric-selectively dolomitized shelf top

Subtidal mud & cement-dominated reef

Figure 2: Examples of distinctive early diagenetic features of the Permian Reef Complex.

We integrate petrographic, stratigraphic, and isotopic data to develop mechanistic links between basin seawater composition, microbial & macrofaunal ecology, and sedimentologic processes.

Study Area & Methods

- Near-continuous shelf-to-basin exposure of the Permian Reef Complex in McKittrick Canyon, Guadalupe Mountains National Park, TX (Fig. 1).
- Permian-age peritidal dolomites are directly correlatable to time-equivalent shelf-margin reef, slope, and basinal facies (Fig. 3).
- 206 5-10 mg micro-drilled carbonate samples from 121 polished slabs with facies-dependent paragenesis.
- Isotopic measurements of major elements in carbonate minerals, and carbonate-associated sulfate.

SHELF	MARGIN	BASIN
Tansill Fm.		
Yates Fm.	Capitan Formation	Bell Canyon Formation
Seven Rivers Fm.		
Queen Fm.	Goat Seep Fm.	Cherry Canyon Fm.

Figure 3: Facies model of the Permian Reef during deposition of the "Triplet" unit of the uppermost Yates Formation (Kerans 2012), and regional lithostratigraphy of the Permian Reef Complex.
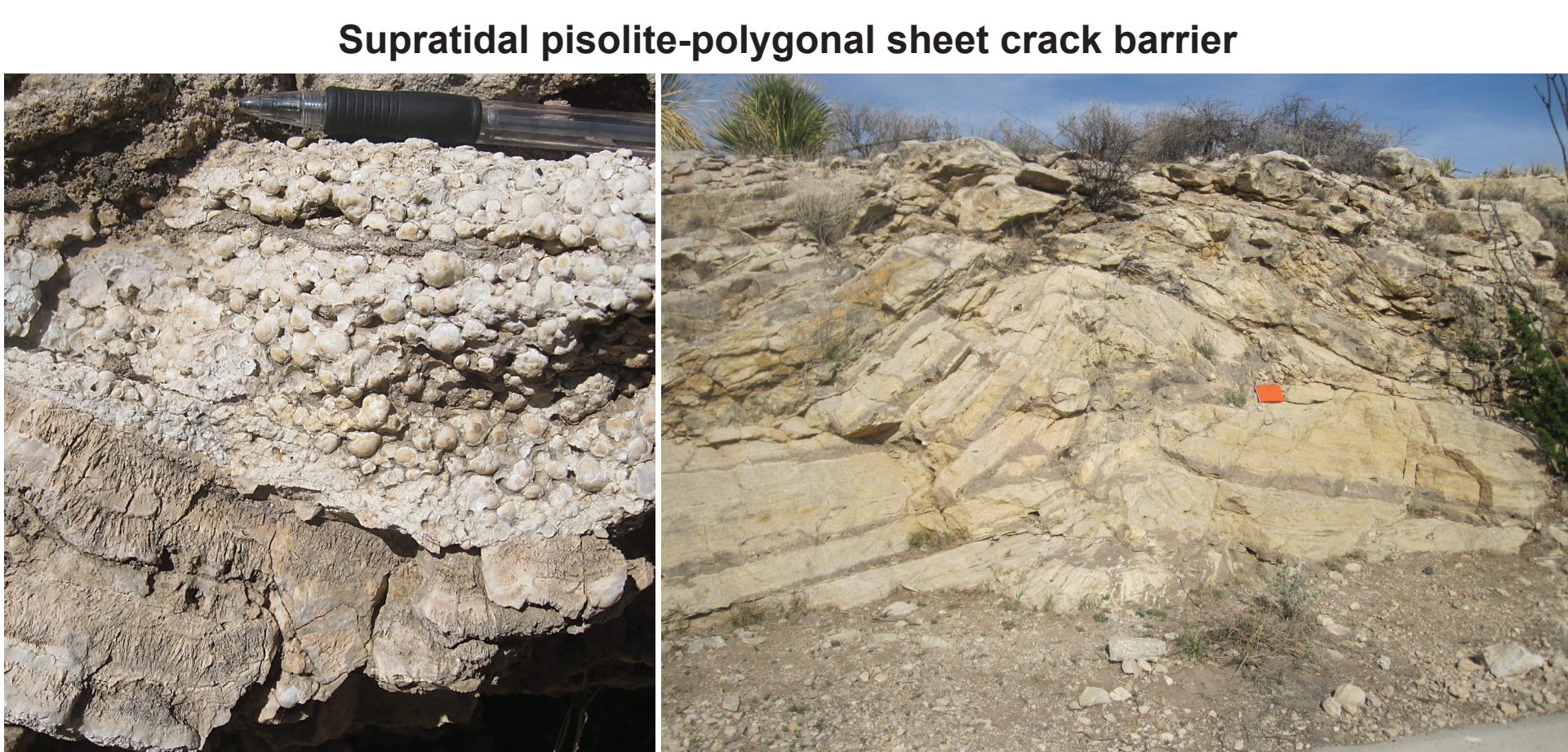
Figure 1: Photo-panorama of Yates, Tansill, Capitan, and Bell Canyon formations exposed in McKittrick Canyon. Inset: Regional map of Capitan Reef and the Delaware Basin in New Mexico and West Texas, modified from Ward et al. (1986).

Shelf-top dolomite derived from evaporitic, productive seawater

Dolomite stratal geometries are consistent with seepage reflux of evaporitic, lagoon-derived brines (Fig. 4).
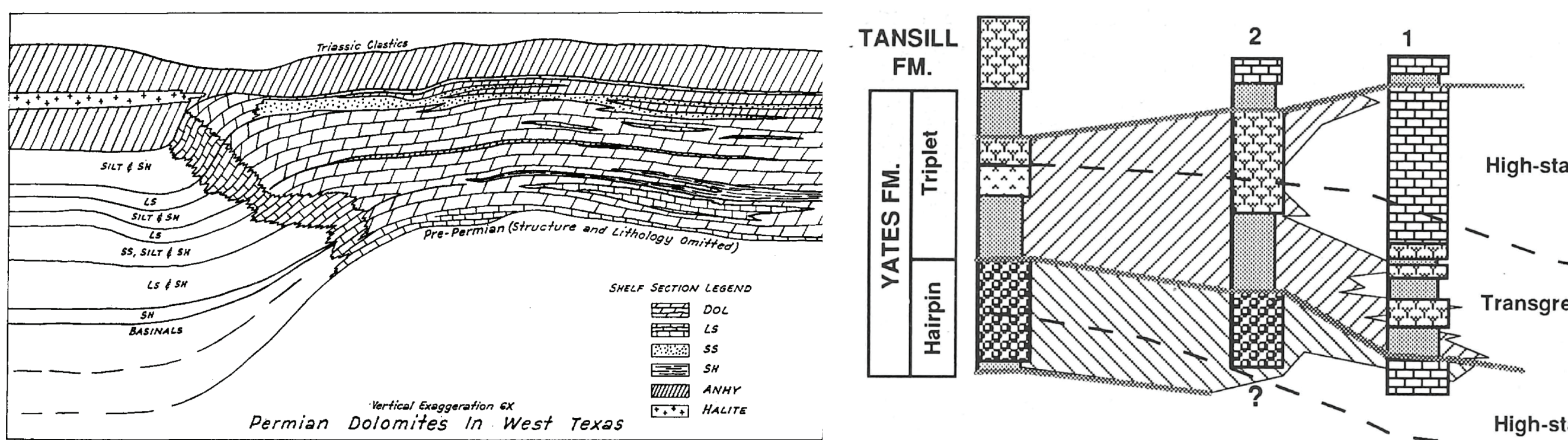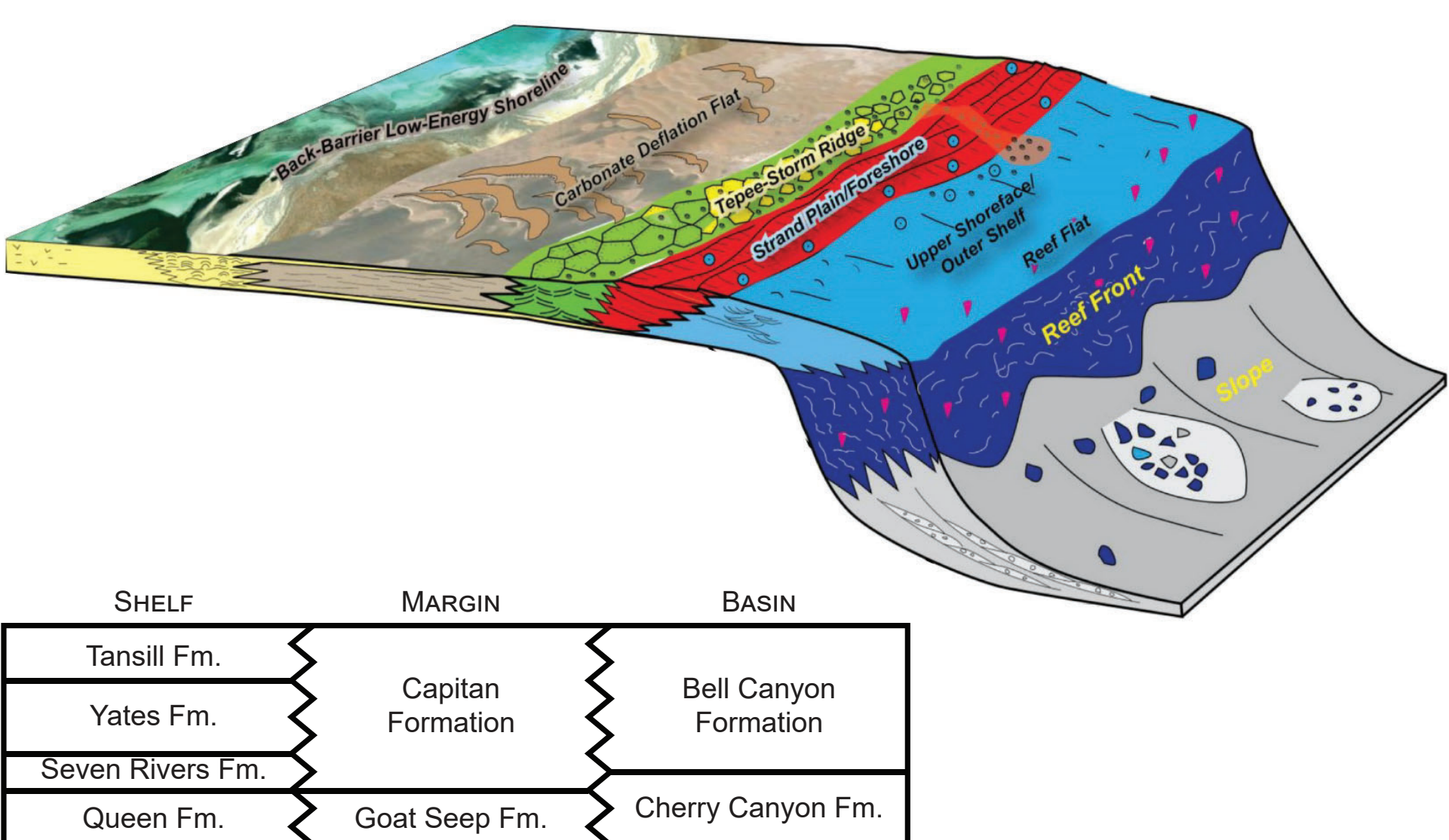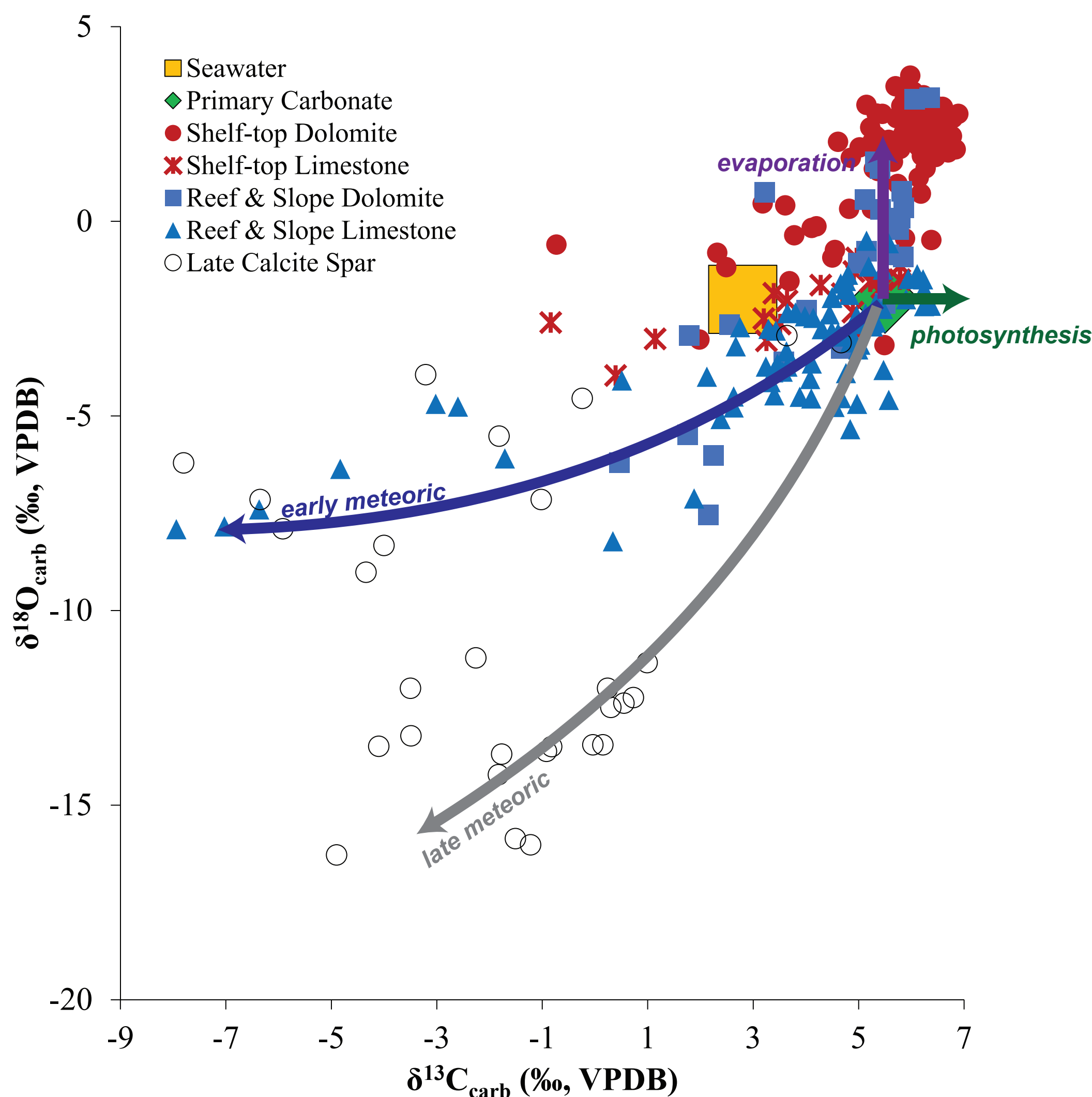
Left: shelf-top dolomite patterns recognized in the original seepage reflux dolomitization model by Adams & Rhodes (1960)

Right: dolomite extent increases as lagoon restriction increases through highstand system tracts (Mutti & Simo, 1994)

Figure 4: Stratal geometries of dolomite in the Permian Reef Complex.

Limestone δ13C and δ18O values formed near equilibrium with normal Permian seawater, with variable admixture of early and late meteoric components (Fig. 5).

Shelf-top dolomites have higher δ18O values that reflect evaporation of lagoon water.

Shelf-top dolomites have higher δ13C values that reflect photosynthetic uptake of dissolved inorganic carbon, indicating that the lagoon was a productive, saline environment.

The Mg isotopic compositions (δ26Mg) of carbonates are lower than that of Mg dissolved in water.

The lowest-δ26Mg dolomites are consistent with equilibrium mineral precipitation from seawater, but most dolomite δ26Mg values are distilled by precipitation along the seepage flow path.

Limestone δ26Mg values may be inherited from primary kinetic isotope fractionations, such as from bio-mediated or rapid inorganic precipitation. However, shelf-top calcites, which are predominantly early marine cements, may also have formed in equilibrium with seawater
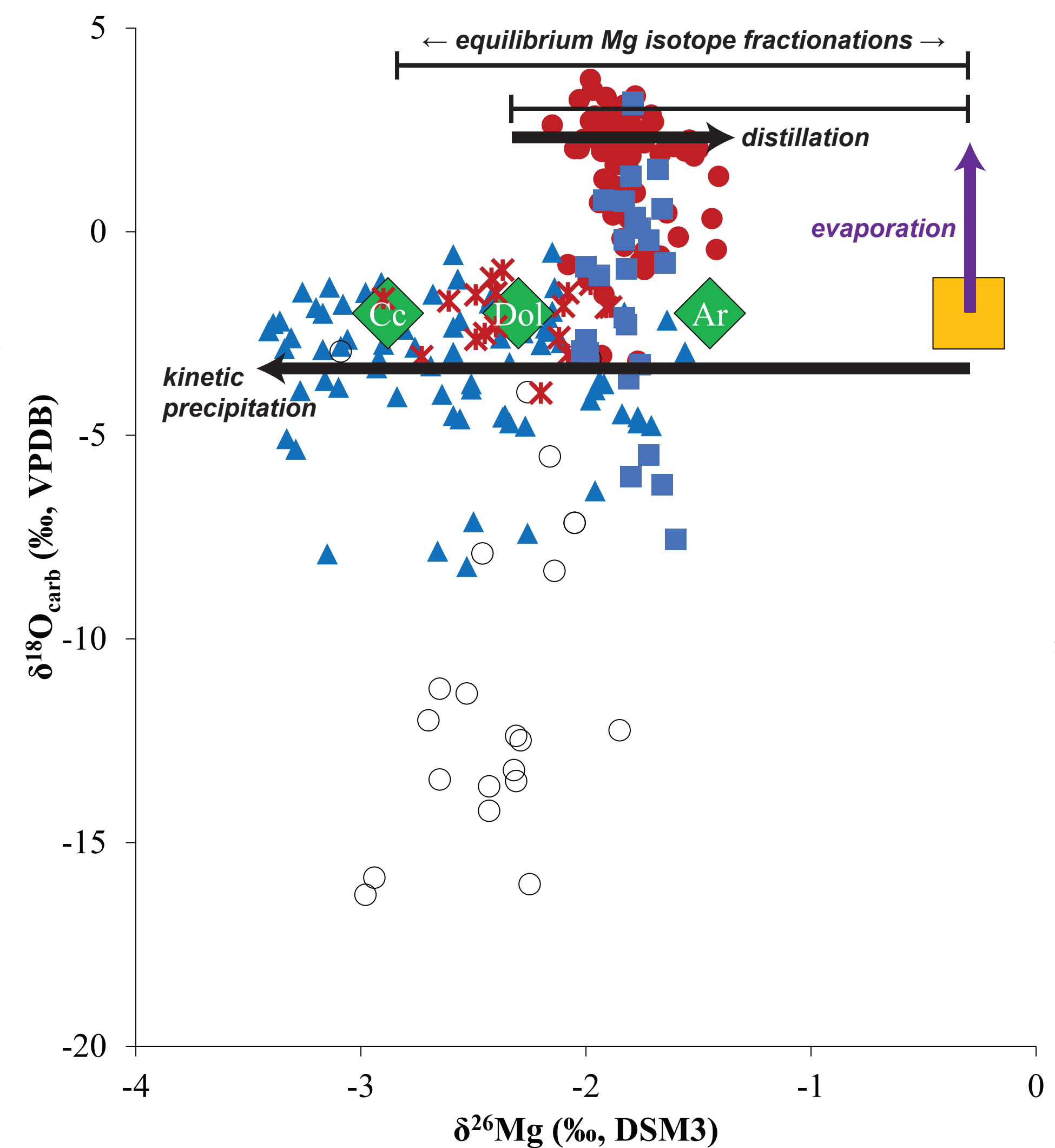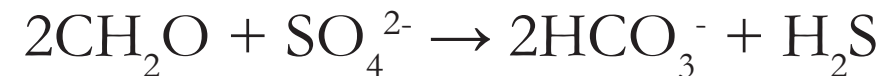
Figure 5: δ13C and δ18O of carbonates in McKittrick Canyon.

Figure 6: δ26Mg and δ18O of carbonates in McKittrick Canyon.

Microbial sulfate reduction modified reef & slope pore fluids

Sulfate is an important oxidant in seawater that anaerobic microorganisms use to respire organic carbon, producing sulfide and increasing carbonate mineral saturation:

$$2CH_2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$$

Microbial consumption of SO_4^{2-} increases the δ34S value of the residual.

Minor amounts of SO_4^{2-} are incorporated into carbonate minerals during precipitation & recrystallization as Carbonate-Associated Sulfate (CAS).

CAS records the δ34S value of the fluid from which the carbonate formed, providing a fingerprint of anoxic conditions and anaerobic microbial respiration.
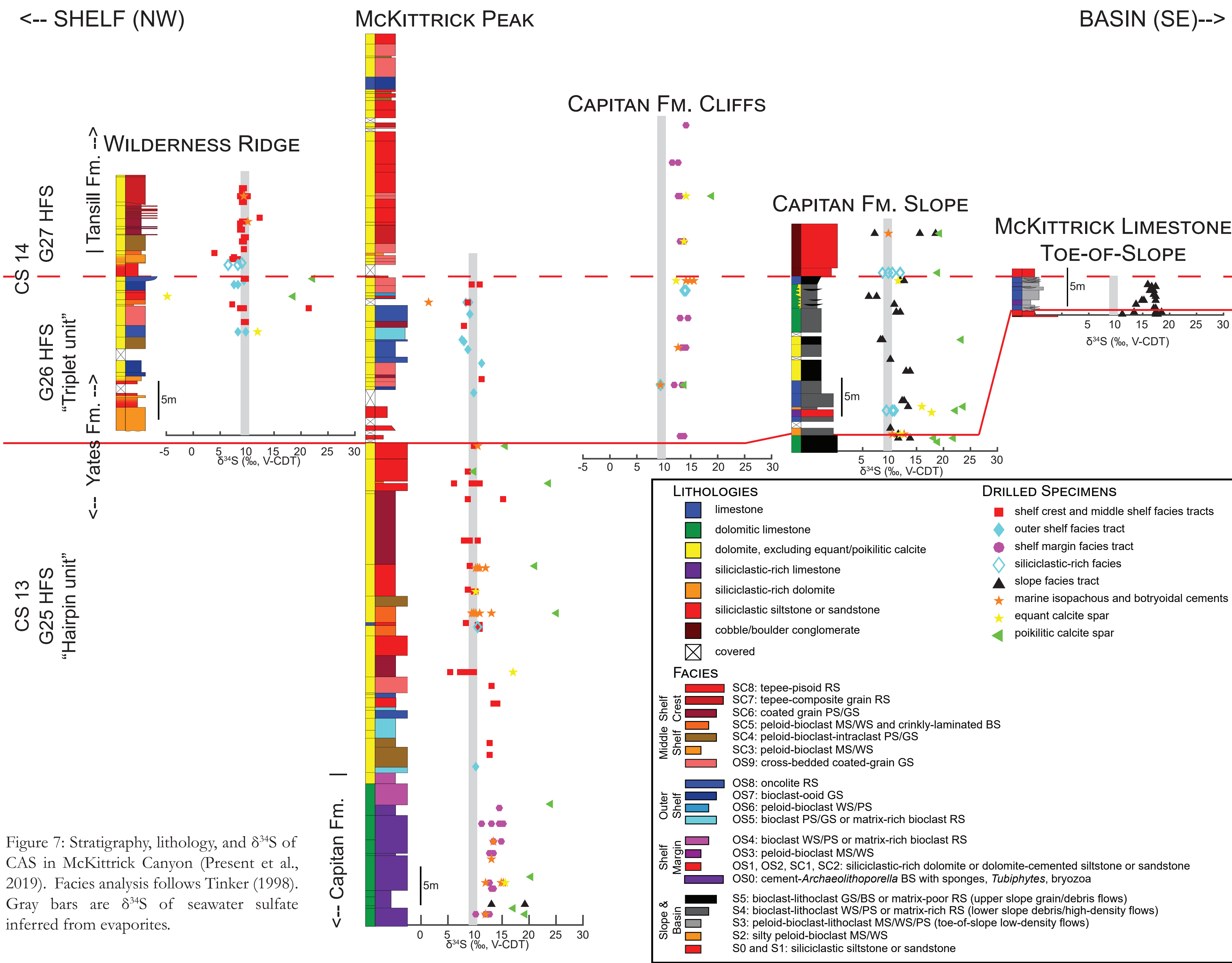
Figure 7: Stratigraphy, lithology, and δ34S of CAS in McKittrick Canyon (Present et al., 2022). Facies analysis follows Tinker (1998). Gray bars are δ34S of seawater sulfate inferred from evaporites.

LITHOLOGIES		DRILLED SPECIMENS	
	limestone	■	shelf crest and middle shelf facies tracts
	dolomitic limestone	●	outer shelf facies tract
	dolomite, excluding equant/poikilitic calcite	◆	shelf margin facies tract
	siliciclastic-rich limestone	◇	siliciclastic-rich facies
	siliciclastic-rich dolomite	▲	slope facies tract
	siliciclastic siltstone or sandstone	★	marine isopachous and botryoidal cements
	cobble/boulder conglomerate	✕	equant calcite spar
⊠	covered	◄	poikilitic calcite spar

FACIES

SC8: oncolite RS
SC7: tepee-composite grain RS/GS
SC6: coated-grain PS/GS
SC5: peloid-bioclast MS/WS and crinkly-laminated BS
SC4: peloid-bioclast-intraclast PS/GS
SC3: peloid-bioclast MS/WS
SC9: cross-bedded coated-grain GS

OS4: oncolite RS
OS7: bioclast-ooid GS
OS2: peloid-bioclast WS/PS
OS5: bioclast PS/GS or matrix-rich bioclast RS

OS4: bioclast WS/PS or matrix-rich bioclast RS
OS1, OS2, SC1, SC2: siliciclastic-rich dolomite or dolomite-cemented siltstone or sandstone
OS0: cement-rich/microbialite BS with sponges, Tubiphytes, bryozoa

S5: bioclast-lithoclast GS/BS or matrix-poor RS (upper slope grain/debris flows)
S4: bioclast-lithoclast WS/PS or matrix-rich RS (lower slope debris/high-density flows)
S3: peloid-bioclast-lithoclast MS/WS/PS (toe-of-slope low-density flows)
S2: silty peloid-bioclast MS/WS
S1 and S1: siliciclastic siltstone or sandstone

Limestone δ13C and δ18O values formed near equilibrium with normal Permian seawater, with variable admixture of early and late meteoric components (Fig. 5).

Shelf facies preserve the δ34S of seawater as inferred from evaporites (Fig. 8).

Limestones from the reef and slope are enriched in δ34S by as much as 10‰ from seawater by microbial sulfate reduction. Benthic animals in the reef preclude anoxic seawater, so increasing enrichment with depth must be diagenetic.

Re-oxidation of sulfide in shelf dolomites may have contributed to aragonite and calcite dissolution and dolomite replacement, but synchrotron XRF mapping indicates that dolomitizing fluids do not appear to have remobilized sulfate incorporated into depositional fabrics or modified during earlier marine phreatic diagenesis (Fig. 9).
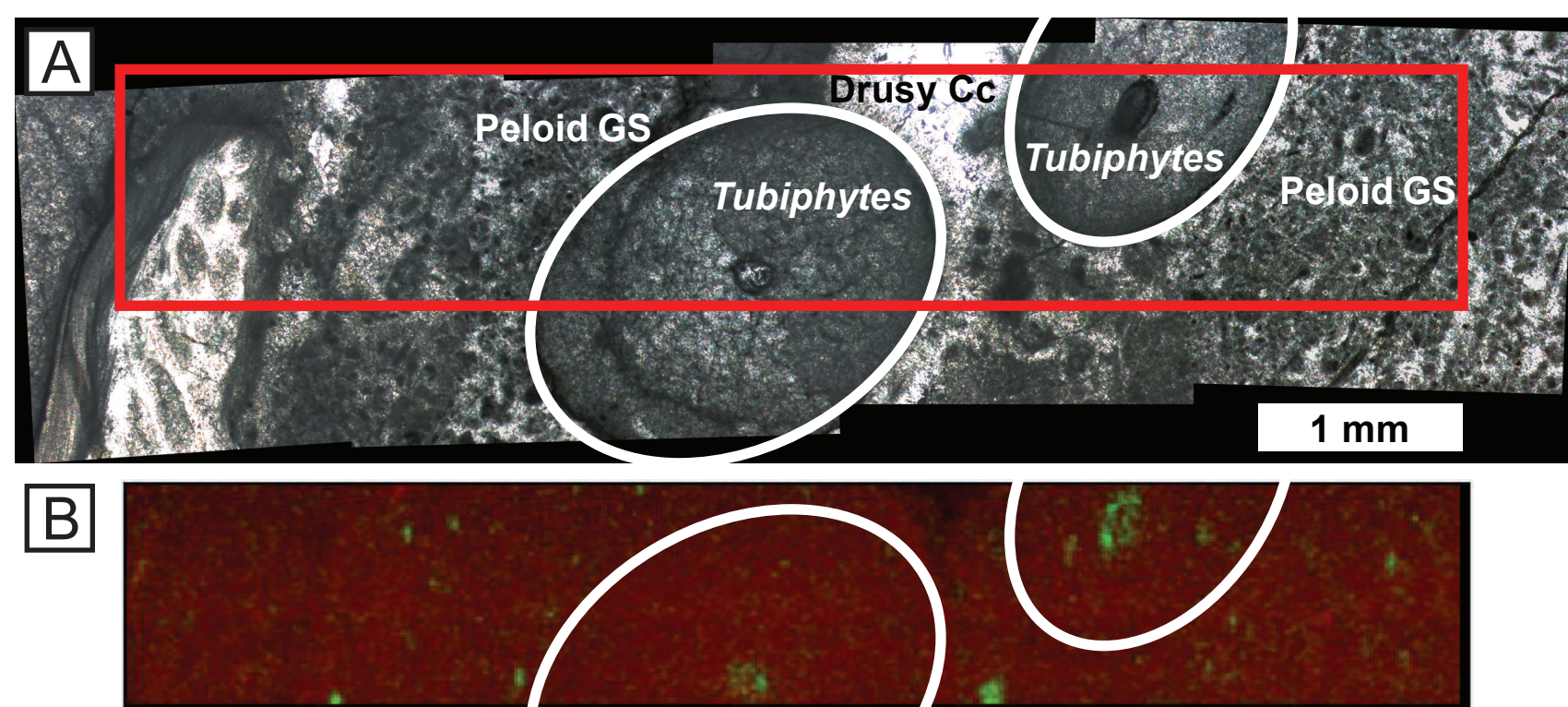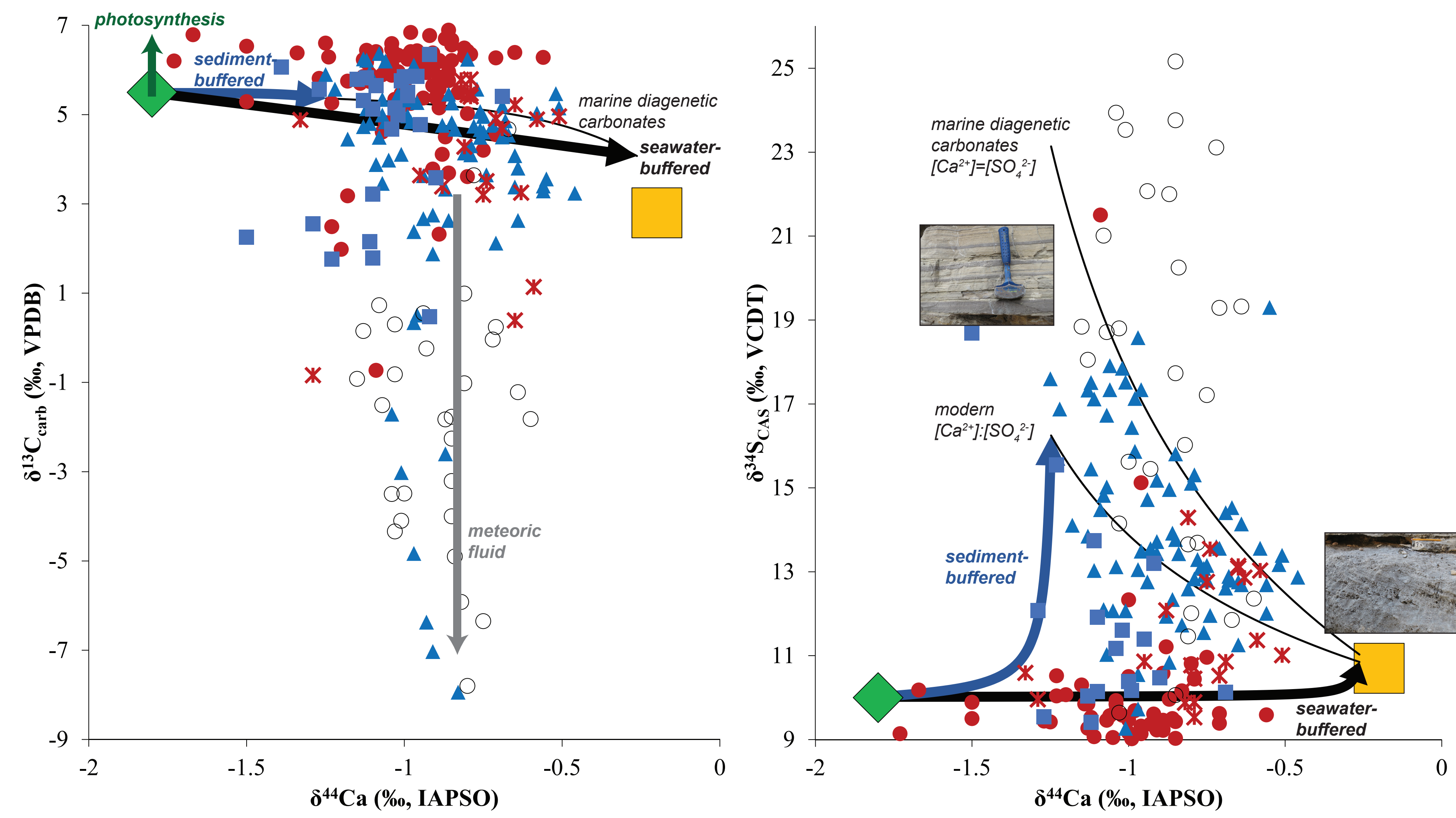
Figure 8: δ34S_CAS and δ18O of carbonates in McKittrick Canyon, and histogram showing facies dependence of CAS data color-coded as in Fig. 7.

Figure 9: (A) Thin section photomicrograph of Tubiphytes framestone from the reef. Peloidal grainstone cemented by equant calcite and drusy marine phreatic calcite fill the framework. (B) Map of SO_4^- and Mg distribution from synchrotron XRF. Minor dolomitization of some peloids and the cores of Tubiphytes does not control the distribution of SO_4^- in the sample, suggesting that CAS is incorporated during earliest marine diagenesis, prior to dolomitization.

Neomorphism & dolomitization occured in marine-derived fluids

Due to kinetic isotope fractionations, primary carbonates precipitate with a lower δ44Ca than seawater. Diagenetic carbonates form at equilibrium with Ca in pore fluids, which is not fractionating.

If fluids are sediment-buffered, then δ44Ca evolves little during diagenesis. However, if fluids are well-connected to seawater, then the primary kinetic δ44Ca signature is erased. This provides a tool to disentangle advective (seawater-buffered) vs. diffusive (sediment-buffered) marine diagenetic regimes (Fig. 10). A reactive transport model can quantify diagenetic carbonate compositions (Fig. 11).

Figure 10: δ44Ca composition of diagenetic carbonates and their trajectory towards seawater or sediment-buffered endmembers. Pore fluid δ13C changes little during marine diagenesis, but δ34S is a sensitive tracer of microbial sulfate reduction in marine sediments.

Figure 11: Carbonate diagenetic model scheme from Ahm et al. (2018) modified to track microbial sulfate reduction in pore fluids (Bryant et al., 2022).

Limestone facies are more sediment-buffered than dolomitized shelf facies, indicating that dolomite formed with more advection of seawater-derived calcium.

Higher δ34S of sediment-buffered facies requires high rates of microbial sulfate reduction compared to carbonate recrystallization rates.

Quantitatively explaining the highest δ34S values of sediment-buffered limestones requires subequal [Ca2+] and [SO4 2-], which is a lower [Ca2+]:[SO4 2-] than the modern ocean.

Rock-buffered burial preserved environmental compositions

Carbonate "clumped" isotopes (Δ47) are an independent metric of mineral-water equilibration temperatures. In combination with mineral δ18O values, they provide a means for calculating water δ18O values (Fig. 12).

Shelf-top dolomite and limestone both equilibrated with water at burial temperatures up to ~80 °C.

Water δ18O values evolved with burial recrystallization while mineral δ18O values retained their early marine diagenetic compositions.

Telogenetic calcite spar filled remaining porosity and equilibrated with warm meteoric groundwater.

Rock-buffered equilibration between carbonate minerals and miniscule volumes of burial fluids preserves other near-surface compositions because there is far more O in water than any other tracer.
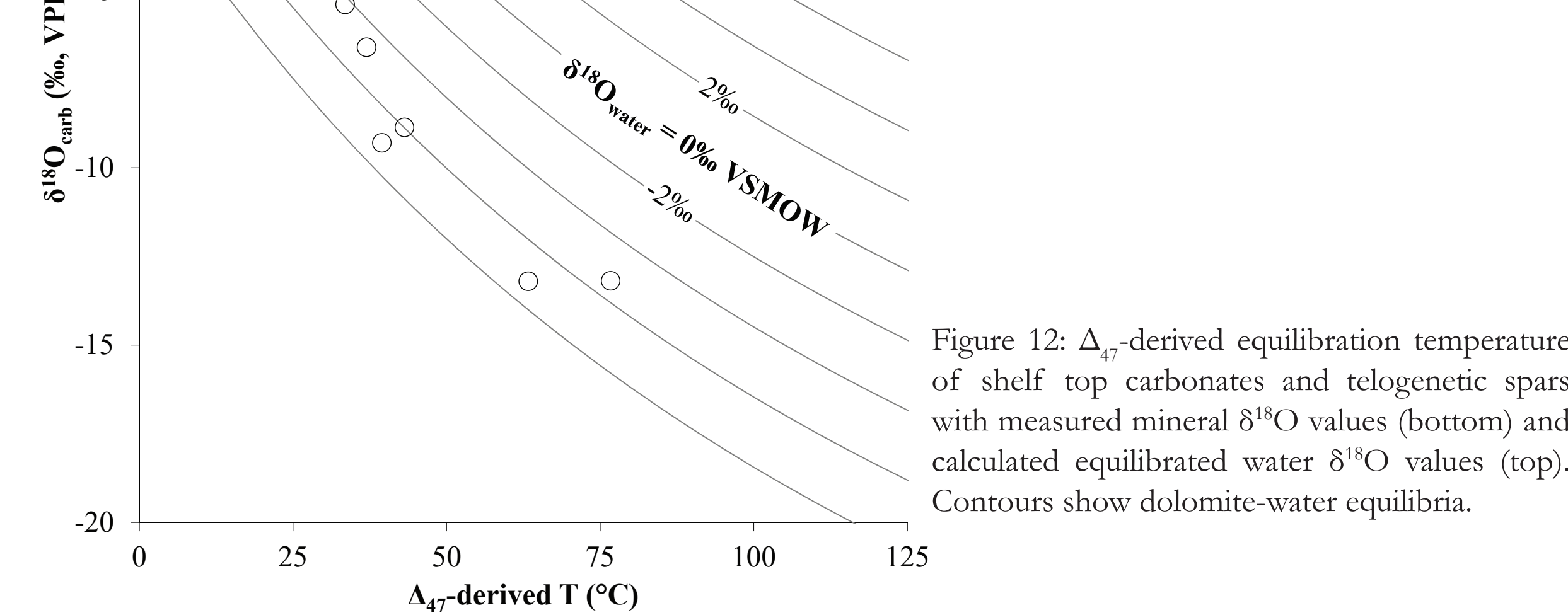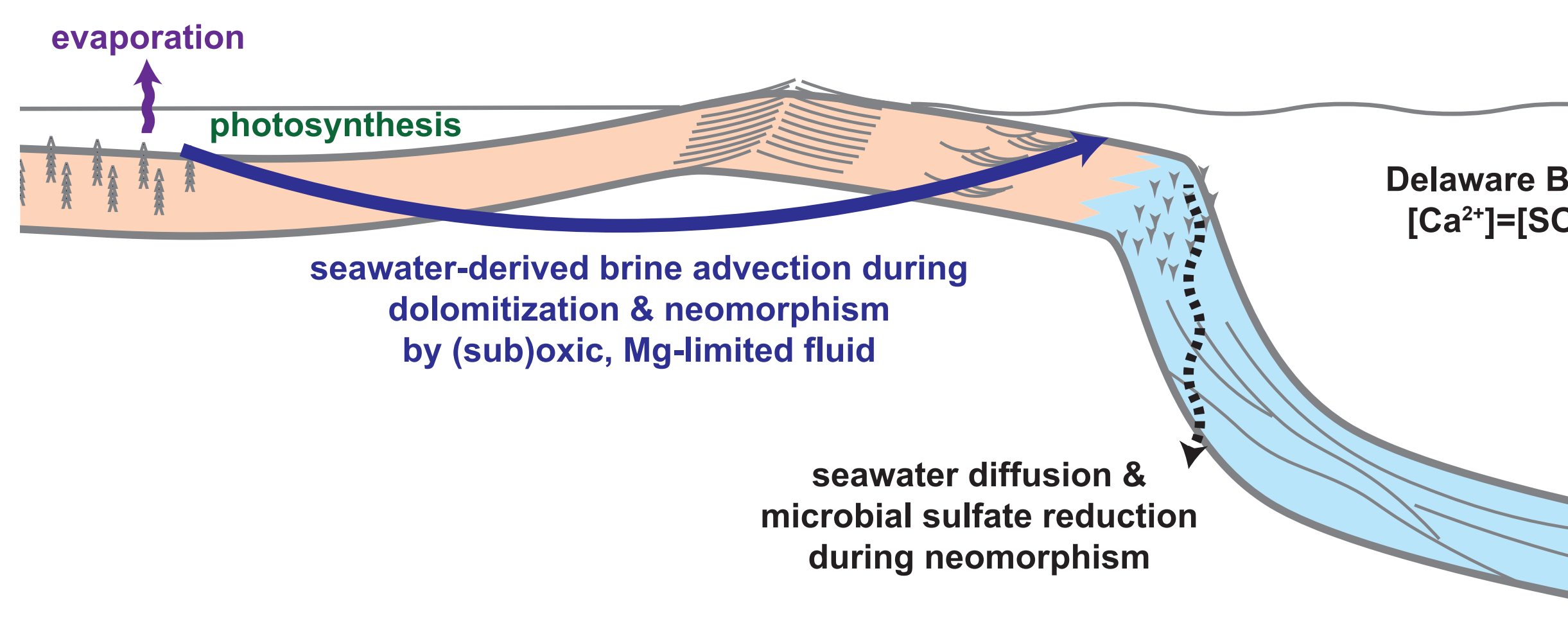
Figure 12: Δ47-derived equilibration temperature of shelf top carbonates and telogenetic spars with measured mineral δ18O values (bottom) and calculated equilibrated water δ18O values (top). Contours show dolomite-water equilibria.

Summary & Significance

- Integrated isotopic, stratigraphic, and petrographic data provide a pore fluid evolution model for the Permian Reef Complex (Fig. 13).

- Environmental (e.g., seawater composition, climate) and biological (e.g., primary productivity, anaerobic metabolisms) factors control early marine diagenetic processes that are integral to the Permian Reef Complex architecture.

seawater–derived brine advection during dolomitization & neomorphism by (sub)oxic, Mg–limited fluid

seawater diffusion & microbial sulfate reduction during neomorphism

Delaware Basin [Ca2+]=[SO4 2-]

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