

## SUPPLEMENTAL MATERIAL

# Middle Oxfordian carbon cycle perturbation expressed in the Smackover Formation, USA

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### S1. Methodology

Although ditch-cutting samples comprise of a depth composite (10-30 feet; 3 -10 m) and are lower sample resolution, in the absence of core they have been independently established as reliable material for carbon isotope stratigraphy (see Metzger, 2014; Eldrett et al. 2021). The ditch-cuttings in this study were washed and cleaned to limit the impact of drilling mud contamination. Samples were also screened for additives such as Loss-Control Materials, cements and any obvious caving material.

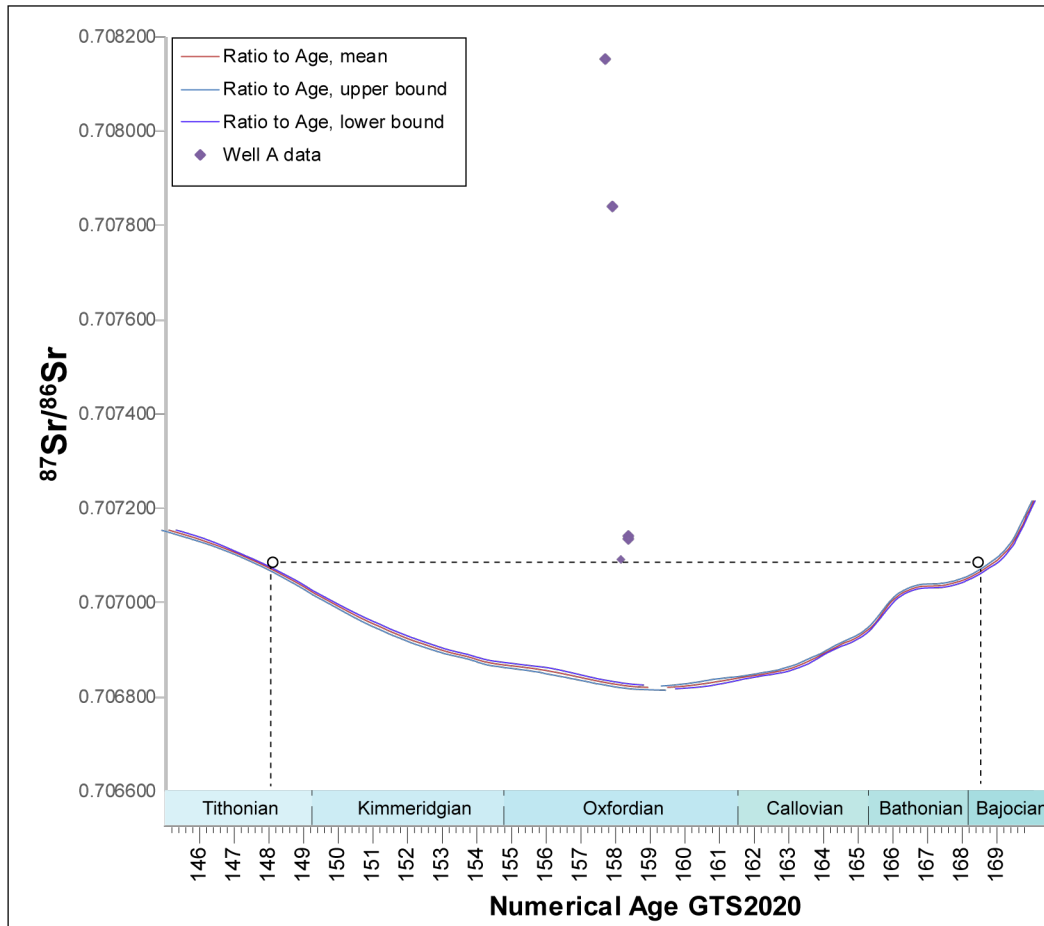
For  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{18}\text{O}_{\text{carb}}$  analyses, an aliquot of sample material was reacted with phosphoric acid using a common acid bath at 90°C and the  $\text{CO}_2$  released was analyzed using a Finnigan-MAT 251. The data were calibrated using NBS-19 (National Bureau of Standards-19;  $\delta^{13}\text{C} = 1.95\text{‰}$ ;  $\delta^{18}\text{O} = -2.2\text{‰}$ ) and reported relative to Vienna Pee Dee Belemnite (V-PDB) using the conventional notation. In-house reference material (OCC;  $\delta^{13}\text{C} = 3.01\text{‰}$ ;  $\delta^{18}\text{O} = -5.28\text{‰}$ ) was used for quality assurance purposes and to report instrument precision. Replicate analyses yielded a precision  $< 0.1\text{‰}$  for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. Errors are reported as 1 S.D.

For  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  analyses, organic material was isolated via dissolution in 5 % HCl acid, the resultant residual was combusted in a Costech ECS 4010 (Costech Analytical Technologies, Inc.). For isotopic measurement, the  $\text{CO}_2$  gas produced was transferred to a continuous flow isotope-ratio mass spectrometer (Thermo Delta V Advantage) at RMAS, Florida, USA. The reproducibility of  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  values is  $\pm 0.4\text{‰}$  as indicated by the standard deviation of replicate analyses of an internal standard of glycine ( $n=54$ ,  $\delta^{13}\text{C}_{\text{org}} = -31.8\text{‰}$ ;  $\delta^{15}\text{N} = -1\text{‰}$  V-PDB). All  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  data are reported relative to the V-PDB scale using the conventional notation and defined for organic carbon as the  $\delta^{13}\text{C}$  value of graphite (USGS24) =  $-16.05\text{‰}$  versus V-PDB (Coplen et al., 2006). Weights and percentages of insoluble residue (after HCl treatment) and total organic matter (TOC) were calculated following the methods of Oehlert et al. (2012). The standard deviation of these analyses is 0.4 wt% based upon repeated analyses of glycine ( $n=54$ ). Carbon : Nitrogen (C:N) ratios for the samples were calculated from the standard weight.

Strontium isotopes ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) were measured on six samples using a ThermoFisher Scientific Neptune Plus multi-collection inductively coupled plasma mass spectrometer (MC-ICP-MS) at the University of Miami. All measured Sr isotope ratios were normalized to  $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$  to correct for instrumental mass bias (see Pourmand et al. 2014). NIST SRM-987 was run as a reference standard and the long-term average on this instrument was:  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710256 \pm 0.000022$  (2SD).

## S2. $^{87}\text{Sr}/^{86}\text{Sr}$ Results

Possible  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio to age for Well A was calculated by comparing the measured data to the global  $^{87}\text{Sr}/^{86}\text{Sr}$  loess smoothed database (McArthur et al. 2020). This fit provides an age either of Tithonian or Bajocian for the measured  $^{87}\text{Sr}/^{86}\text{Sr}$  values from well A (see Figure S1). However, both of these estimates are not supported by the regional geology and available biostratigraphic data (see Hammes et al. 2011; Pindell et al. 2020), indicating that all measured  $^{87}\text{Sr}/^{86}\text{Sr}$  values from the Smackover Fm. are highly radiogenic compared to Late Jurassic global seawater (McArthur et al. 2020). Therefore, these data were excluded from further interpretation and not part of the main text.



**Figure S1.**  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope data from the Smackover Fm. Well A plotted against the global  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope loess curve (McArthur et al. 2020). Well A data points plotted according to the carbonate isotope age model, corresponding with the Oxfordian Stage as supported by regional biostratigraphic data and regional perspective. Dashed line represents the possible ratio to age fit to the loess smoothed database (McArthur et al. 2020).

### **S3. Regional Stratigraphic Framework**

There have been numerous studies on the stratigraphy, sedimentology and depositional evolution of the Late Jurassic Smackover Fm (i.e. Imlay, 1941; 1945; Mancini & Benson, 1980; Baria et al. 1982; Benson, 1988; Prather, 1992; Young and Oloriz, 1993; Hart & Balch, 2000; Parcell, 2003; Macini et al. 1990; 1998; 2004; 2006; 2008; 2019). These integrated regional well log and core studies have provided a detailed stratigraphic framework for the US Gulf Coast region. Within this stratigraphic framework, the Smackover Fm. represents the second-order transgressive – regressive (T-R) cycle comprising a transgressive systems tract (TST) and highstand systems tract (HST) (Macini et al. 1990; Prather, 1992; Goldhammer 1998; Galloway, 2008; Hammes et al. 2011). The Smackover is considered Middle to Late Oxfordian in age based on the occurrence of ammonites throughout sections onshore (Imlay, 1941, 1945; Imlay and Herman, 1984; Young and Oloriz, 1993) and the occurrence of Oxfordian planktonic foraminifera recovered from either the upper carbonate unit of the Smackover Fm. or from the overlying Gilmer Limestone unit in offshore wells from the Appomattox Field (Godo, 2017). However, in the studied wells, the Smackover Fm. is devoid of age diagnostic macro- and micro-fossils. Therefore, to provide independent age constraints to the generated carbon isotope ( $\delta^{13}\text{C}$ ) profiles, the studied wells were correlated using the sequence stratigraphic framework to onshore sections from Louisiana and Alabama that recover diverse ammonite fauna throughout Smackover Fm. The stratigraphic framework and correlation are provided in **Figure S2** and detailed below.

The sequence stratigraphic correlation provided (**Fig. S2**) here spans sections across the Smackover carbonate ramp from inner ramp (Little Cedar Creek and Appleton Fields; Alabama); middle-outer ramp (i.e. Cotton Valley Field, Louisiana), outer ramp (Gulf of Mexico, this study) to basinal settings (Ek-Balam Field, Campeche, Mexico). The interpretations presented here are based on core descriptions and analyses, petrophysical logs and seismic interpretation and follow the interpretations made by previous authors as detailed below.

#### **Little Cedar Creek Field, Alabama**

Little Cedar Creek Field is located in southeastern Conecuh County, Alabama. Unconformably overlying the alluvial Norphlet Fm, the Smackover Fm is characterized by a transgressive subtidal lime mudstone and dolomudstone to wackestone overlain by a clotted peloidal thrombolite boundstone (Mancini et al. 2008). Thrombolitic boundstones from the

Smackover Fm., are generally interpreted as initiating during sea-level rise and generally within an inner ramp setting with water depths of less than 9m (Baria et al. 1982; Mancini et al. 2004). The thrombolites at the Little Cedar Creek field are interpreted as being developed farther up the depositional dip than other discovered microbolites in the eastern Gulf coastal plain in water depths < 3m and close proximity to the Oxfordian paleo-shoreline (Mancini et al., 2006). The maximum flooding surface is located above this interval within a deeper water to subtidal lime mudstone, with the subsequent regressive highstand systems tract comprising high-energy peloidal and ooid grainstone and packstones (Mancini et al. 2008). The Haynesville Fm. directly overlies the Smackover Fm. with the Buckner anhydrite absent in this location.

### **Appleton Field, Alabama**

The Smackover Fm. penetrated in the Appleton Field in southern Alabama was deposited ontop of a paleotopographic basement high in the inner part of a carbonate ramp in the Conecuh Embayment (Benson et al. 1997). Directly ontop of basement are microbial reef boundstones/bindstones that are interpreted to be deposited above an amalgamated sequence boundary, transgressive surface and maximum flooding surface (Parcell, 2003) (see **Fig. S2**) with the entire section representing an early highstand systems tract (regressive phase; Mancini et al. 2008). The microbial reef facies are overlain by shoaling-upward cycles consisting of ooid–oncoid–peloid grainstones and packstones capped by wackestones and mudstones of the upper Smackover and interpreted as shoal and tidal flat facies (Hart and Balch, 2000; Parcell, 2003). While the skeletal wackestones, peloidal–oncoidal packstones/wackestones, and algal laminites were being deposited in progressively shallower waters around the basement paleohighs, laminated mudstones indicative of deeper- or less energetic water were deposited off-structure (Mancini et al. 1998). The Smackover sequence is capped by sabkha evaporites of the Buckner Fm. which appear conformable and form part of the latest regressive phase of the Smackover 2<sup>nd</sup> order sequence (Mancini et al. 1990; Prather, 1992; Hart and Balch, 2000, Parcell, 2003).

### **Cotton Valley Field, Louisiana**

The Cotton Valley field is located on a very prominent domal anticline near the northern edge of the North Louisiana Interior Salt Dome Basin. This study uses sedimentologic and biostratigraphic data available from core material from the A.J. Hodges no 1 Pardee-Calloway borehole, Cotton Valley Field (after Young and Oloriz, 1993). The majority of the core comprises laminated lime mudstones interpreted as outer ramp depositional environment (3450m – 3700m). According to the scheme of Prather (1992) and Mancini et al. (2008), the laminated lime mudstone interval is considered to be transgressive, with the maximum flooding surface placed within interval (this study places it at 3520 m). A regressive sequence is interpreted above this interval, with the upper 50m (3400m – 3450m) of the Smackover at this location consisting of high energy oolitic grainstones characteristic of an inner ramp deposition (Young and Oloriz, 1993). The recovery of ammonites such as *Dichotomoceras*, *Dichotomosphinctes* gr. *anconensis* and *Cubaochetoceras* from “3510 m and below must be referred to Middle Oxfordian” (Young

and Oloriz, 1993). In particular, the occurrence in the basal Smackover of the ammonite genera *Gregoryceras* and *Ochetoceras* provides constraint of the transgressive phase of the basal Smackover Fm. to the Middle Oxfordian *transversarium* zone. A number of ammonites from between depths of 3470m and 3505 m can be considered Late Oxfordian, with the grainstones of the top 50m barren in ammonites (Young and Oloriz, 1993).

### **Gulf of Mexico, USA.**

The three proprietary wells labelled “A”, “B” and “C” recover a complete Smackover sequence from the outer ramp setting, offshore Gulf of Mexico. The facies from the Smackover Fm. in these wells are consistent and can be assigned the following units in ascending order after Godo (2017): a carbonate unit rich in pyrite, termed the ‘Pydol’ ii) a laminated lime mudstone with intervals of algal laminated layers termed the basal carbonate; iii) a middle marl member comprising laminated lime-calcareous-argillaceous mudstones/marls and iv) a carbonate rich upper member. Following the sequence stratigraphic framework of Mancini et al., (1990; 2008); Prather (1992) the Pydol and basal carbonate units are assigned to the transgressive systems tract, with the overlying high TOC middle marl unit representing the maximum flooding of the ramp. The upper part of the middle marl and upper carbonate unit represents the regression phase or highstand systems tract (HST).

### **Ek Balam Field, Mexico.**

The Ek-Balam field is a major oil and gas field in the offshore Campeche Bay, Mexico. The Middle to Late Jurassic interval is characterized by three units from oldest to youngest: (i) aeolian sandstones assigned to the Bacab Formation; ii) an evaporitic sabkha unit termed the Tson anhydrite (uppermost part of the Bacab Formation) and iii) calcareous marine mudstone and shale unit assigned to the Ek-Balam Fm (Cantú-Chapa, 2009; Snedden et al. 2020). The Bacab and Tson anhydrite member are interpreted as regressive sequences capped by a sequence boundary, with a sharp contact between the Tson anhydrite member and the overlying Ek-Balam Fm (Cantú-Chapa, 2009). The marine shales of the Ek-Balam Fm. are interpreted as a transgressive cycle with the maximum flooding surface in the middle of the Formation (~4515 m in Balam 101 well). The upper part of the Ek-Balam Fm. exhibits a coarsening upwards cycle with calcareous shales indicative of shelfal depositional environment and assigned to the regressive sequence.

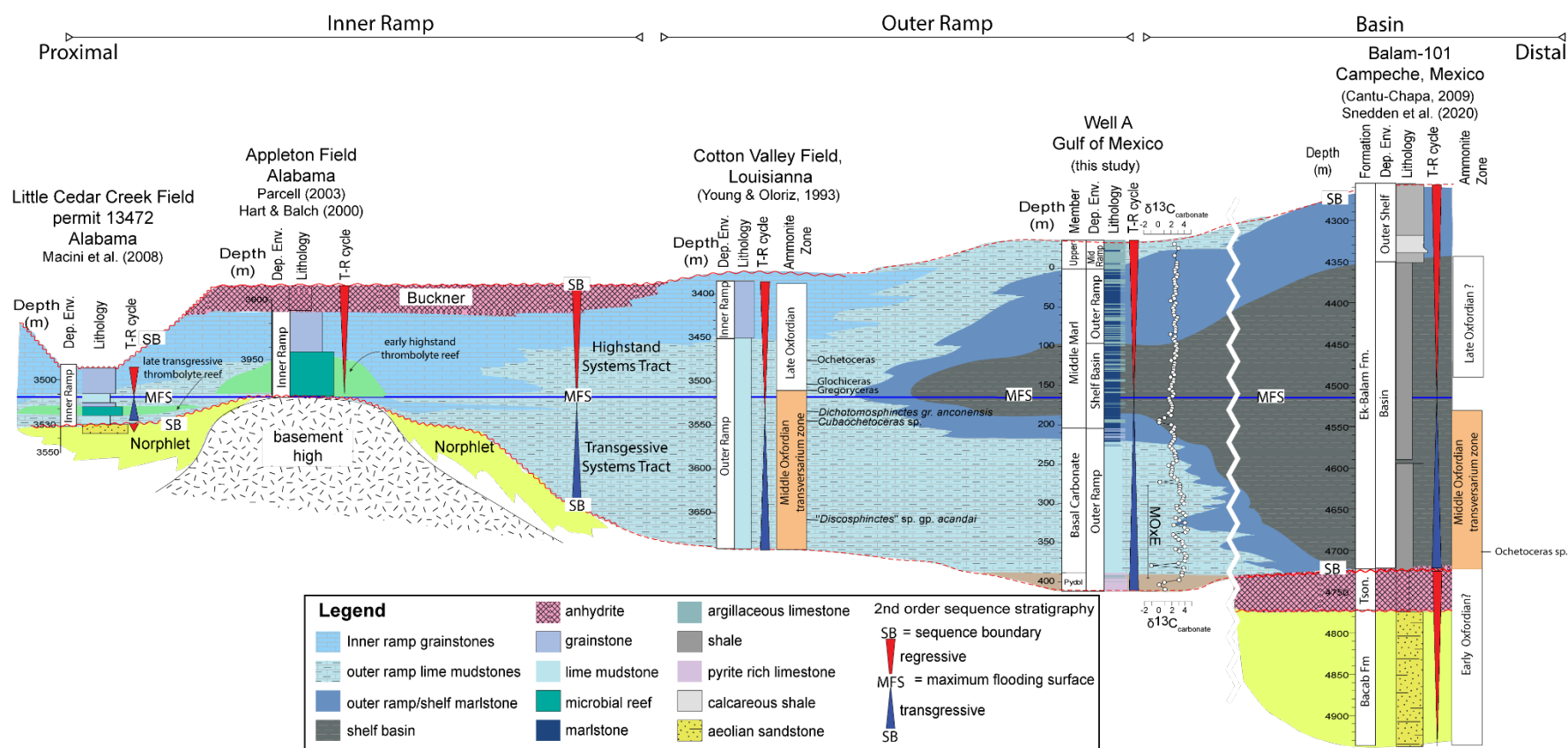
The Ek-Balam Fm. contains numerous ammonites, including a specimen of *Ochetoceras* sp. (Balam 101 well; Cantú-Chapa, 2001) and specimens of *Ochetoceras rioslopezi* n. sp., *Glochiceras* sp., and fragments of *Ochetoceratinae* and *Perisphinctidae* (Maloob 406 well; Cantú-Chapa, 2009). Based on stratigraphic correlation of these ammonite fauna occurrences with other localities, Cantú-Chapa (2009) assigned the lower transgressive sequence of the Ek-Balam Fm. to the Middle Oxfordian *transversarium* ammonite zone. A Late Oxfordian age for the regressive upper Ek-Balam Fm. is supported by the occurrence of Oxfordian foraminifera

(*Globigerina oxfordiana*) in the nearby Chac-1 well (Ornelas-Sánchez et al. 1993; in Snedden et al. 2020). The sandstones of the underlying Bacab Formation are devoid of marine fossils, so Cantú-Chapa (2009) inferred an Early Oxfordian age based on stratigraphic position below the ammonites recovered from the Ek-Balam shales.

### **Regional Correlation**

The regional sequence stratigraphic framework (**Fig. S2**) illustrates the relationship between proximal and distal depositional environments and provides a correlation between the onshore and offshore sections. The Smackover can be divided into a transgressive – regressive cycle, with the transgression mostly associated with the lower Smackover (Pydol and basal carbonate unit) with the maximum flooding surface in the middle marl unit. Distally, the marls recorded in the studied wells laterally grade into deeper marine shales. Inboard within the inner ramp, the maximum flooding surface corresponds with the most inboard extent of laminated lime mudstones and on paleotopographic highs is recorded as an amalgamated surface. The regressive phase of the Smackover Fm. records a shallowing-up sequence with higher energy oncoid–peloid grainstones in the inner ramp, prograding outboard and laterally grading into argillaceous limestones and calcareous mudstones/marls in the basinal setting. The regressive phase is ultimately capped with sabkha evaporites deposited inboard (Buckner anhydrite) before the start of the next 2<sup>nd</sup> order sequence (Haynesville).

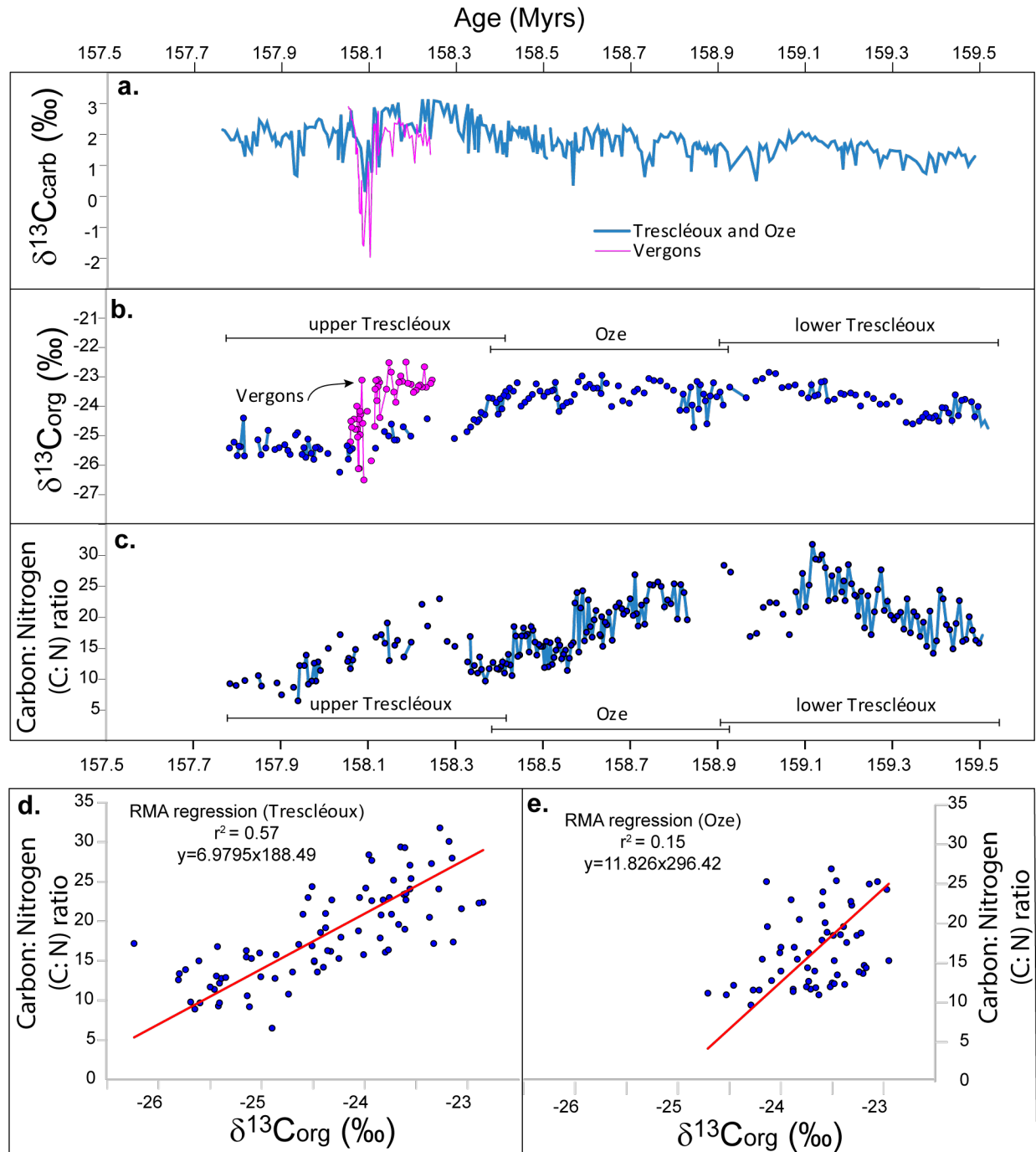
Therefore, using the sequence stratigraphic framework the studied wells offshore were correlated to onshore sections from Louisiana that recover diverse ammonite fauna throughout Smackover Fm. (Imlay and Herman, 1984; Young and Oloriz, 1993), including the genera *Ochetoceras* and *Gregoryceras* from the basal carbonate unit, constraining this unit both onshore and in the studied wells to the Middle Oxfordian *transversarium* zone (Young and Oloriz, 1993) and laterally equivalent to the basinal shales of the Ek-Balam Fm., offshore Mexico (Cantú-Chapa, 2009).



**Figure S2.** Sequence stratigraphic correlation between the studied wells in the Gulf of Mexico (well A illustrated here) and other representative Smackover sections onshore Louisiana and Alabama following the interpretations of Young and Oloriz (1993); Hart and Balch (2000); Parcell (2003) and Mancini et al. (2008). These are also compared to the Balam Field using the interpretation of Cantú-Chapa (2009). The studied sections are flattened on the maximum flooding surface. Lithology and depositional environment key plotted in the legend. Ammonite data and interpretations are from Young and Oloriz (1993; Cotton Valley Field) and Cantú-Chapa (2009; Balam Field, Campeche, Mexico) and provide constraints to the studied sections through the sequence stratigraphic correlation. See text for discussion of the sections.

#### S4. $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ Divergence

The positive  $\delta^{13}\text{C}_{\text{carb}}$  shift recorded in the Pydol – basal carbonate units are also mirrored in the paired  $\delta^{13}\text{C}_{\text{org}}$  record indicating a strong primary coupling between the two carbon pools. This observation is consistent with paired  $\delta^{13}\text{C}$  records from the Isle of Skye (UK; Pearce et al. 2005, Nunn et al. 2009), but contrasts with those from the Subalpine Basin (Louis-Schmid et al, 2007b). The decline  $\delta^{13}\text{C}_{\text{org}}$  values from the Subalpine Basin is interpreted to reflect increased isotopic fractionation between carbonate and marine organic matter due to an increase in atmospheric  $\text{pCO}_2$  (Louis-Schmid et al, 2007b). The interpretation of Louis-Schmid et al. (2007b) assumed that the  $\delta^{13}\text{C}_{\text{org}}$  values from the two studied localities (Trescléoux and Oze) did not reflect different contributions of marine and terrestrial organic matter as indicated by the lack of covariance between the C:N record and  $\delta^{13}\text{C}_{\text{org}}$  values (Louis-Schmid et al, 2007b). However, covariance plot between C:N and  $\delta^{13}\text{C}_{\text{org}}$  values from the Trescléoux section indicates a strong and significant co-variance ( $r^2 = 0.57$ ; P-value  $< 0.05$ ; **Figure S3**). The C:N-record, if interpreted in terms of organic matter source, indicates that organic matter in the lower part of the Trescléoux section is predominantly terrestrially derived, whilst the upper part that records the decline in  $\delta^{13}\text{C}_{\text{org}}$  values is predominantly marine derived (Louis-Schmid et al, 2007b). Therefore, the decline in  $\delta^{13}\text{C}_{\text{org}}$  values from the Subalpine Basin may reflect local changes in organic matter source rather than shifts in the global carbon pool due to changes in  $\text{pCO}_2$ . This interpretation is further supported by the overall high  $\delta^{13}\text{C}_{\text{org}}$  values from the Vergons section, ~100km away within the Subalpine Basin, SE France (Padden, 2001). Although C:N data is not available for the Vergons section, the  $\delta^{13}\text{C}_{\text{org}}$  profile mirrors the  $\delta^{13}\text{C}_{\text{carb}}$  profile with high values in the Middle Oxfordian *transversarium* zone, punctuated by an abrupt ~2‰ negative isotope excursion (Padden et al. 2001) indicating coupling between the two carbon pools and consistent with both the records from the Isle of Skye (UK; Pearce et al. 2005, Nunn et al. 2009) and the Smackover Fm. (this study).



**Figure S3.** Data from Subalpine Basin: Trescléoux and Oze (after Louis-Schmid et al, 2007b); Vergons (after Padden, 2001). Data is plotted against age (Myrs) using the age calibration of Gradstein et al. (2020). **a.**  $\delta^{13}\text{C}_{\text{carb}}$  values for all three sections showing the correlation between Trescléoux/Oze and Vergons. **b.**  $\delta^{13}\text{C}_{\text{org}}$  values; the composite record from Trescléoux/Oze is broken down into the respective three measured sections: upper and lower Trescléoux with the intervening section from Oze (after Louis-Schmid et al, 2007b). **c.** The C:N ratio from the Trescléoux and Oze sections (after Louis-Schmid et al, 2007b). **d.** Covariance plot between

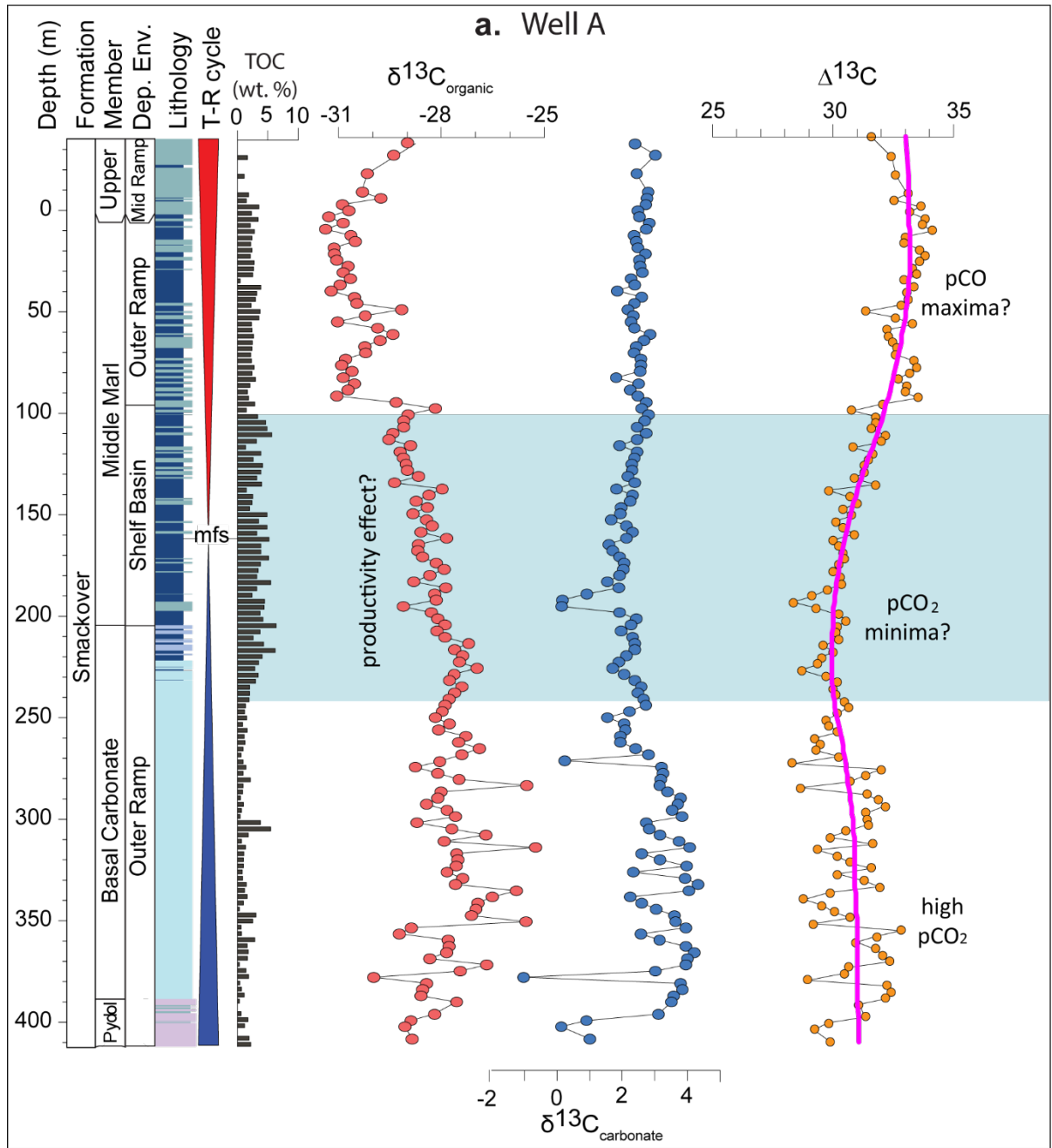
$\delta^{13}\text{C}_{\text{org}}$  and C:N ratio for the Trescléoux section; **e.** Covariance plot between  $\delta^{13}\text{C}_{\text{org}}$  and C:N ratio for the Oze section. For both **d-e**, regression lines after Reduced Major Axis Regression (RMA) with  $r^2$  values are plotted

The middle marl unit records a divergence between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$ , with  $\delta^{13}\text{C}_{\text{org}}$  values remaining high and decrease up-section as  $\delta^{13}\text{C}_{\text{carb}}$  values are relatively low and increase up-section (Well A; 200m – 90m). There are several possible explanations for this divergence such as: i) reduced isotopic fractionation between dissolved inorganic carbon and marine organic matter as a consequence of  $\text{CO}_2$  drawdown (supported by lower  $\Delta^{13}\text{C}$  values), and/or ii) enhanced marine productivity and burial of  $^{12}\text{C}$  enriched organic matter (supported by higher TOC and  $\delta^{15}\text{N}$  values) during maximum flooding of the ramp.

- i) Given the relationship between atmospheric  $\text{CO}_2$  ( $\epsilon_p$ ) and  $p\text{CO}_2$ , stratigraphic variation in the offset between covarying  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  curves, expressed by  $\Delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ), offers a potential tool for tracing palaeo- $p\text{CO}_2$  change (cf. Kump & Arthur, 1999; Jarvis et al., 2011, 2015). Therefore, to help understand whether  $\text{CO}_2$  drawdown was responsible for the observed divergence between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  in the middle marl unit,  $\Delta^{13}\text{C}$  was calculated and variations were investigated (**Fig S4**). The  $\Delta^{13}\text{C}$  profile does indeed show a minimum ( $\sim 30\text{‰}$ ) in the interval between 200m – 90m, suggestive of  $p\text{CO}_2$  drawdown that may be responsible for reduced isotopic fractionation between dissolved inorganic carbon and marine organic matter resulting in relatively enriched  $\delta^{13}\text{C}_{\text{org}}$  values recorded in this interval. This approach has uncertainties and assumes: (1) no significant diagenetic alteration of the carbonate or organic carbon  $\delta^{13}\text{C}$  values, or a uniform systematic overprinting of these; (2) an overwhelmingly marine or terrestrial organic matter fraction, or a constant proportion of these; and (3) limited temporally restricted productivity effects (Jarvis et al. 2011, 2015). At least the first two assumptions appear to be correct for the middle marl interval, with a lack of  $\delta^{13}\text{C}_{\text{carb}} - \delta^{18}\text{O}_{\text{carb}}$  covariance indicating minimal diagenetic overprint on the carbonate fraction, and a relatively stable Carbon : Nitrogen (C:N) ratio indicating constant proportion of marine and terrestrial organic matter.
- ii) It is also possible that the divergence between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  may be due to regionally increased marine organic matter productivity, or temporally restricted productivity effects. Increased organic matter productivity is supported by the high TOC (mean  $\sim 4$  wt. %) and an increase in  $\delta^{15}\text{N}$  values from  $\sim 0$  ‰ to  $\sim 1.2$  ‰. This interval is interpreted to reflect the maximum flooding of the ramp/shelf, which could result in enhanced nutrient supply and associated increase in marine productivity with greater burial and preservation of organic material in the sediment as reflected by an increase in  $\delta^{13}\text{C}$  values (Jenkyns, 1996; Louis-Schmid et al. 2007) and potentially a drawdown of  $p\text{CO}_2$  (Jarvis et al. 2011, 2015). However, the higher  $\delta^{13}\text{C}_{\text{org}}$  values are not reflected in the  $\delta^{13}\text{C}_{\text{carb}}$  profile suggesting that the impact was not uniform between the organic and inorganic carbon pools. During the maximum

submergence of the Smackover ramp, microbial thrombolytic reefs developed inboard (Mancini and Parcell, 2001; Mancini et al. 2008; Mancini et al. 2018) and this shift in reef community may have impacted fractionation pathways of organic and carbonate matter and may result in a de-coupling of the carbon isotopic signature? Additional research would be required to ascertain the  $\delta^{13}\text{C}$  value and impact of different reef types on the regional and global carbon cycle.

The uppermost middle marl unit and upper carbonate unit (-30m to 90m) is characterized by low  $\delta^{13}\text{C}_{\text{org}}$  values (mean = -30.5 ‰; S.D. = 0.6‰), while  $\delta^{13}\text{C}_{\text{carb}}$  values remain steady (mean = 2.5‰; S.D = 0.25‰). The  $\Delta^{13}\text{C}$  values shows a significant positive increase indicative of  $\text{pCO}_2$  maximum. The divergence between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values in this interval could therefore be explained by increased isotopic fractionation between dissolved inorganic carbon and marine organic matter as a consequence of increased  $\text{pCO}_2$  concentrations. Therefore, the maximum in  $\text{pCO}_2$  postdates the MOxE positive  $\delta^{13}\text{C}$  excursion. This interval also exhibits a stronger covariance between  $\delta^{13}\text{C}_{\text{org}}$  and C: N values ( $r^2 = 0.49$ ; P-value = 0.08; main text Fig.3) indicating that organic matter source may also have contributed to the lower  $\delta^{13}\text{C}_{\text{org}}$  values.



**Figure S4.** Data from well A showing vertical profiles in TOC,  $\delta^{13}\text{C}_{\text{carb}}$ ,  $\delta^{13}\text{C}_{\text{org}}$  and  $\Delta^{13}\text{C}$ , with values in  $\Delta^{13}\text{C}$  possibly a proxy for atmospheric  $\text{pCO}_2$  (see Jarvis et al. 2011, 2015). Divergence between  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  recorded between 200m and 90m depth, with elevated  $\delta^{13}\text{C}_{\text{org}}$  values compared to  $\delta^{13}\text{C}_{\text{carb}}$  resulting in low  $\Delta^{13}\text{C}$ . Interval shaded in blue corresponds with interval of higher TOC and may reflect increased marine organic matter production and preservation.

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