Cyclic Variation of Organic Carbon Isotope Ratio ($\delta^{13}C_{org}$) and the Total Organic Carbon (TOC) within the Barnett Shale (Texas, USA): A Signal of 3nd Order Sea Level Change in the Mississippian*

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Abstract

Seven wells (five in Tarrant County, one in Johnson County, one in Bosque County), covering approximately 100 km along the NNE-SSW trend of the axis of the Fort Worth Basin (Texas, USA), were selected for the measurement of total organic carbon (TOC) as well as organic carbon isotope ratio ($\delta^{13}C_{org}$) of the Mississippian Barnett Shale. The TOC and $\delta^{13}C_{org}$ value of 98 rock cuttings from 7 wells ranges from 1.3 to 6.2%, and -23.9 to -29.7‰ (means -27.4‰), respectively. If we assume $\delta^{13}C_{org}$ value of two end members, i.e. marine and continental organic matter, to be -22 and -30‰, respectively, our study indicates the dominance of continental type organic matter within the study area of the basin.

The systematic variation of TOC and $\delta^{13}C_{org}$ of each well reveals that the Barnett Shale is characterized by three major cycles. Each cycle is characterized by inverse correlation between TOC and $\delta^{13}C_{org}$. The trend of decreasing or increasing continental-type organic matter (increasing or decreasing value of $\delta^{13}C_{org}$) with decreasing or increasing TOC is unusual (Creaney and Passey, 1993). The TOC and $\delta^{13}C_{org}$ cycles can be correlated with the 3rd order global sea level curve. The study suggests that each sea level rise was tied with decreasing value of $\delta^{13}C_{org}$ and increasing value of TOC. The sea level rise within the basin may be due to positive water balance with an excess outflow of relatively low salinity surface water, which inhibited the haline circulation of the basin and made it more anoxic (e.g. present day Black Sea). The basin anoxia condition might have resulted from basin restriction due to increased tectonic activity along the Ouachita thrust (this time was characterized by increased tectonic activity along the Ouachita thrust due to the approach of the Laurentia towards Gondwana). On the other hand, the sea level rise as a result of deglaciation due to increased pCO_2 level, caused more input of continental type organic matter within the basin. The positive correlation between TOC and phosphate content along the depth profile from one well confirms this argument (more nutrient supply during sea level rise). Both pCO_2 rise and basin anoxia

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together increased the preservation possibility of continental type organic matter. Therefore, the TOC and $\delta^{13}C_{org}$ cycles within the Barnett Shale were the results of complex interplay among pCO_2, basin anoxia and tectonic activities.

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Cyclic variation of organic carbon isotope ratios ($\delta^{13}C_{org}$) and the total organic carbon (TOC) within the Barnett Shale (Texas, USA): A signal of 3rd order sea level change in the Mississippian

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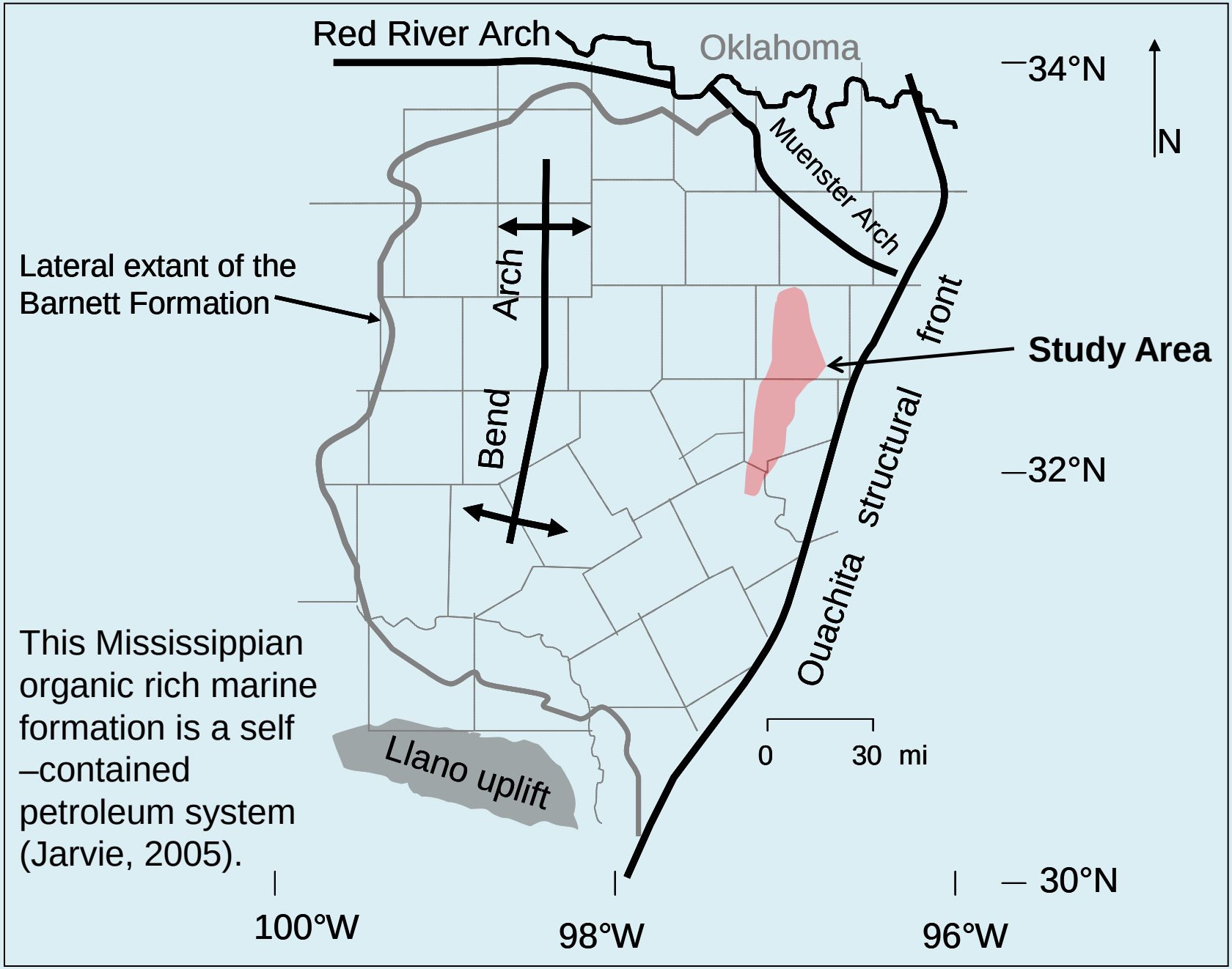
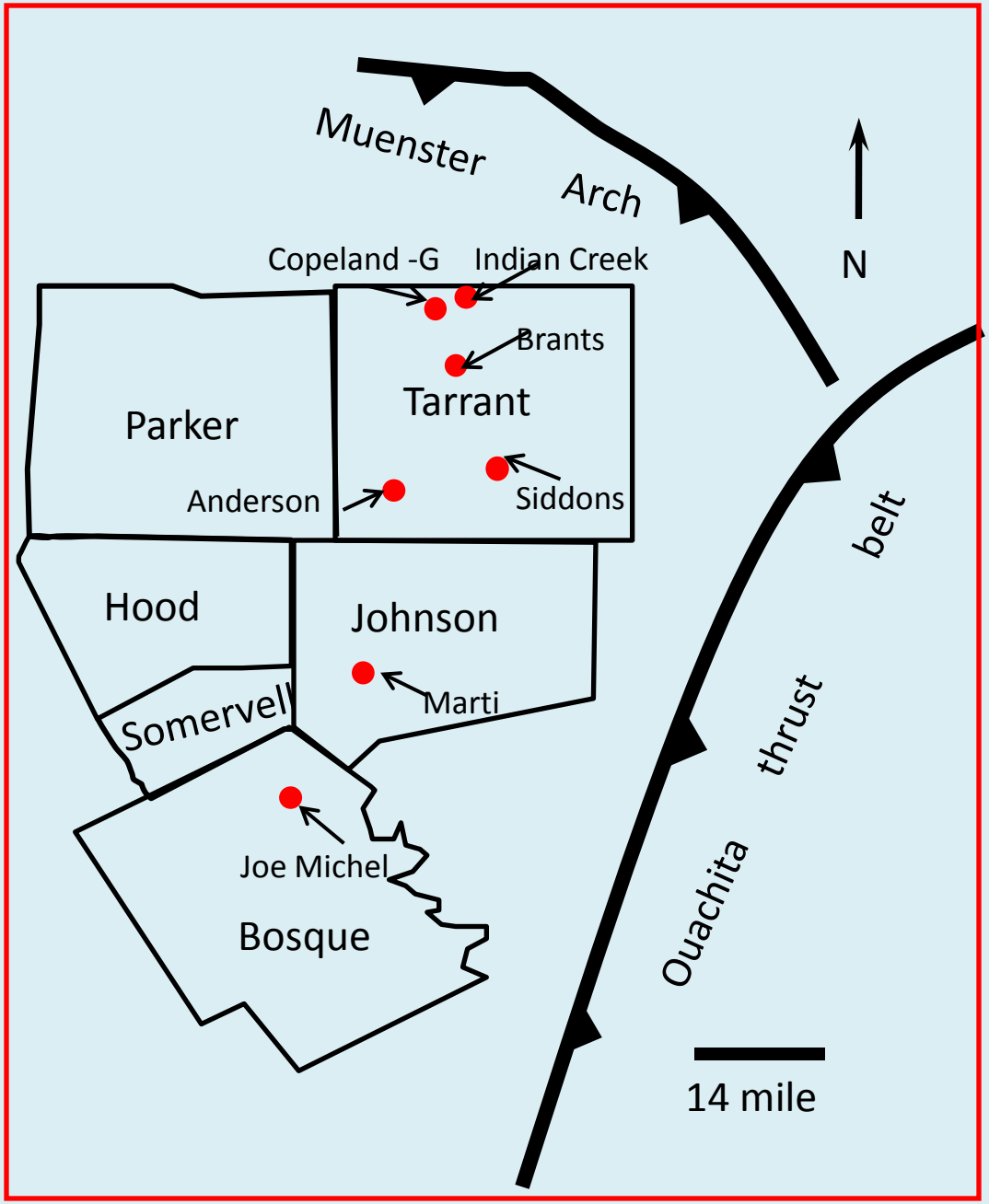
2) XTO Energy, Fort Worth, Tx

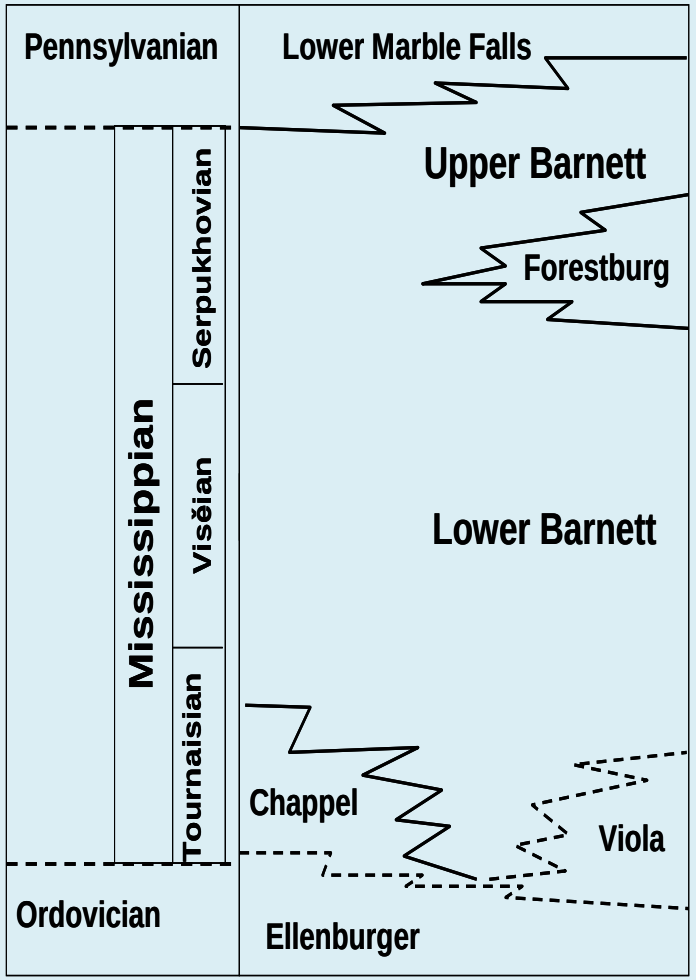
Acknowledgements: We acknowledge XTO Energy for providing rock cutting samples of the Barnett Formation



Modified from Hill et al., 2007

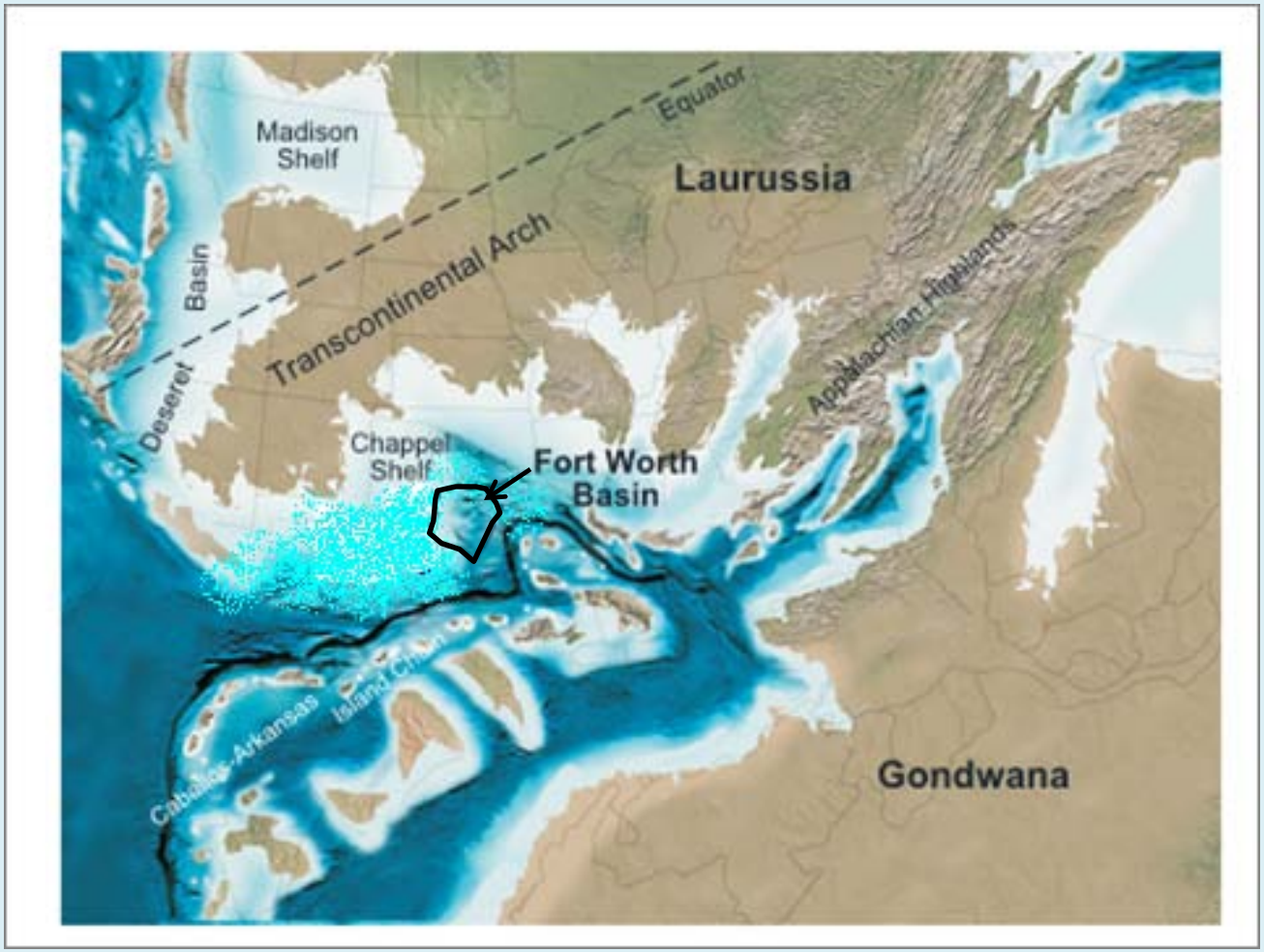
Well Locations





(Montgomery et al, 2005)

Regional paleogeography of the southern mid-continent region during late Mississippian showing the possible position of the Fort Worth Basin



The Barnett Formation was possibly deposited within a narrow foreland basin between the rapidly approaching continents of Laurussia and Gondwana during the Mississippian. (Hill et al., 2007; Blakey, 2005; Loucks and Ruppel, 2007).

(Modified from Loucks and Ruppel, 2007)

Principles

	$\delta^{13}C_{Org}$ (‰)	
C3 plant	**~(-28)**	Continental
C4 plant	(-10)- (-14)	
Marine phytoplankton	**~(-21)**	

$$\delta^{13}C = \left\{ \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} - 1 \right\} X1000$$

Produces continental $\delta^{13}C_{Org}$ (‰) ~ **-28**

Continental Plant → Use atmospheric CO_2 whose $\delta^{13}C$ ~(-7),for photosynthesis

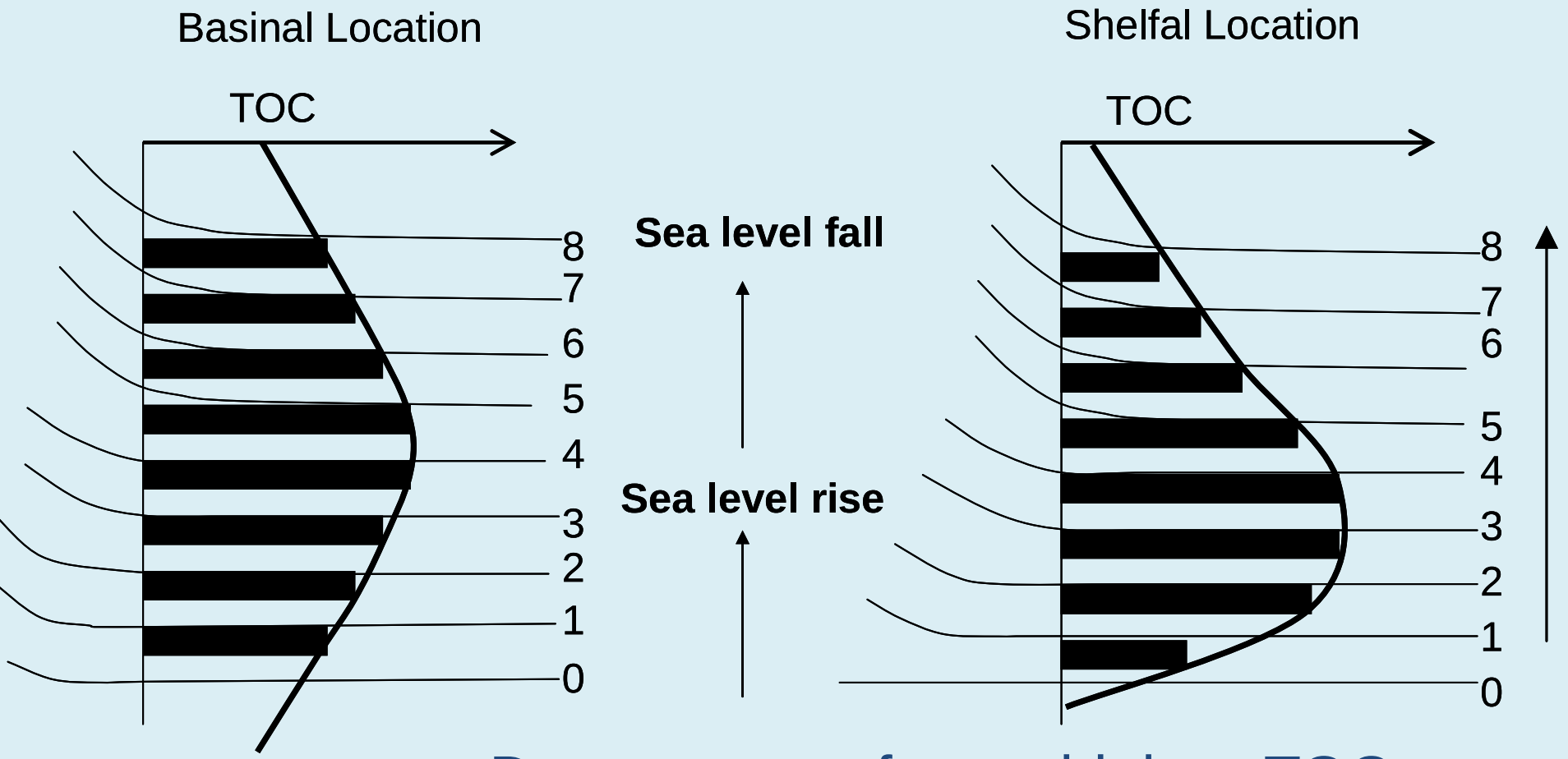
Marine phytoplankton → Use water dissolved $(HCO_3)^-$ whose $\delta^{13}C$ ~0, for photosynthesis

Fractionation between organic and inorganic carbon $\Delta^{13}C_{(Inorganic\text{-}organic)}$~21

Produces marine $\delta^{13}C_{Org}$ (‰) ~**-21**

(Meyers,1997)

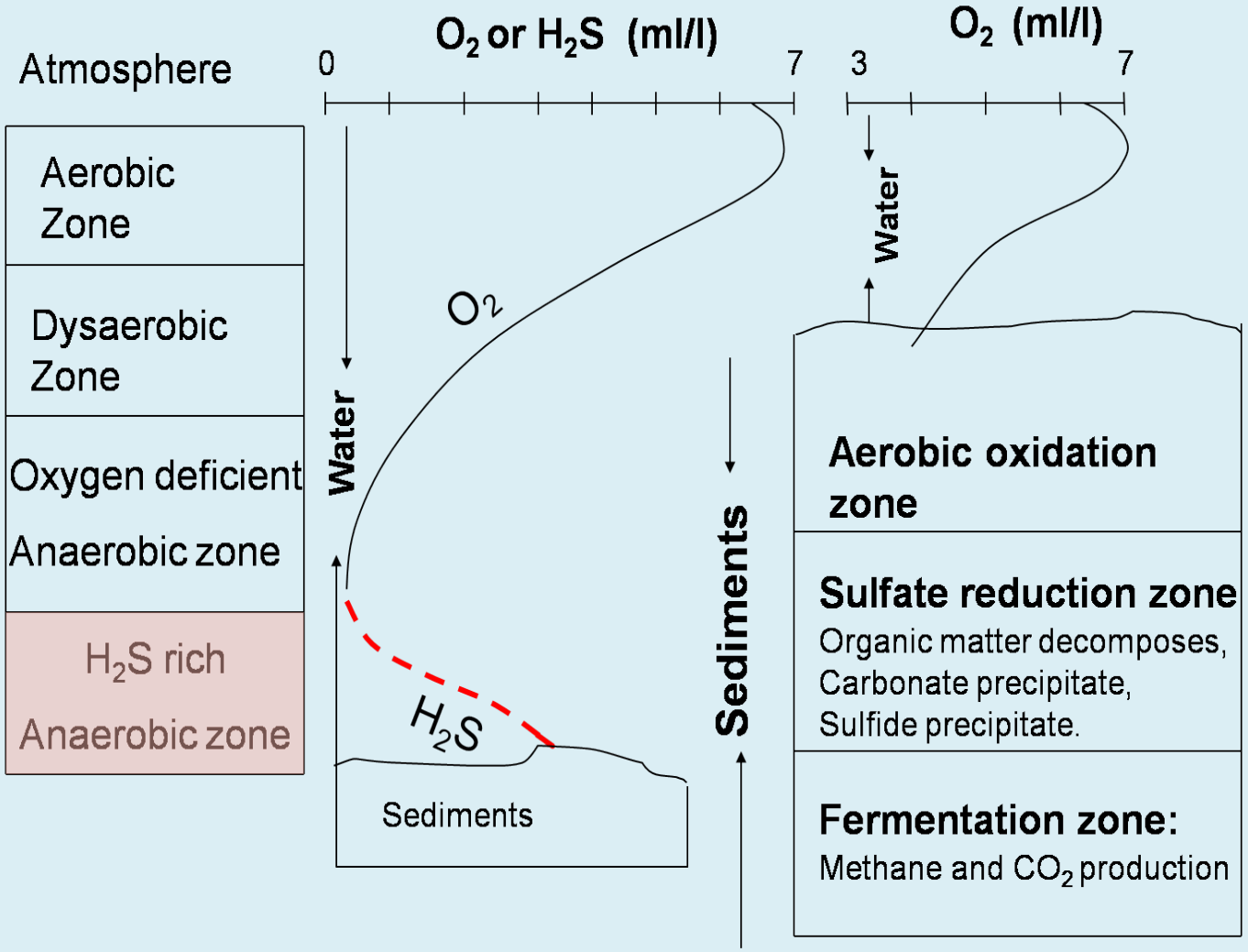
Variation of TOC-depth profile in response to sea level change and location within a basin



Deeper water favors higher TOC

(Modified from Creaney and Passey,1993)

Schematic representation of typical sedimentary environment

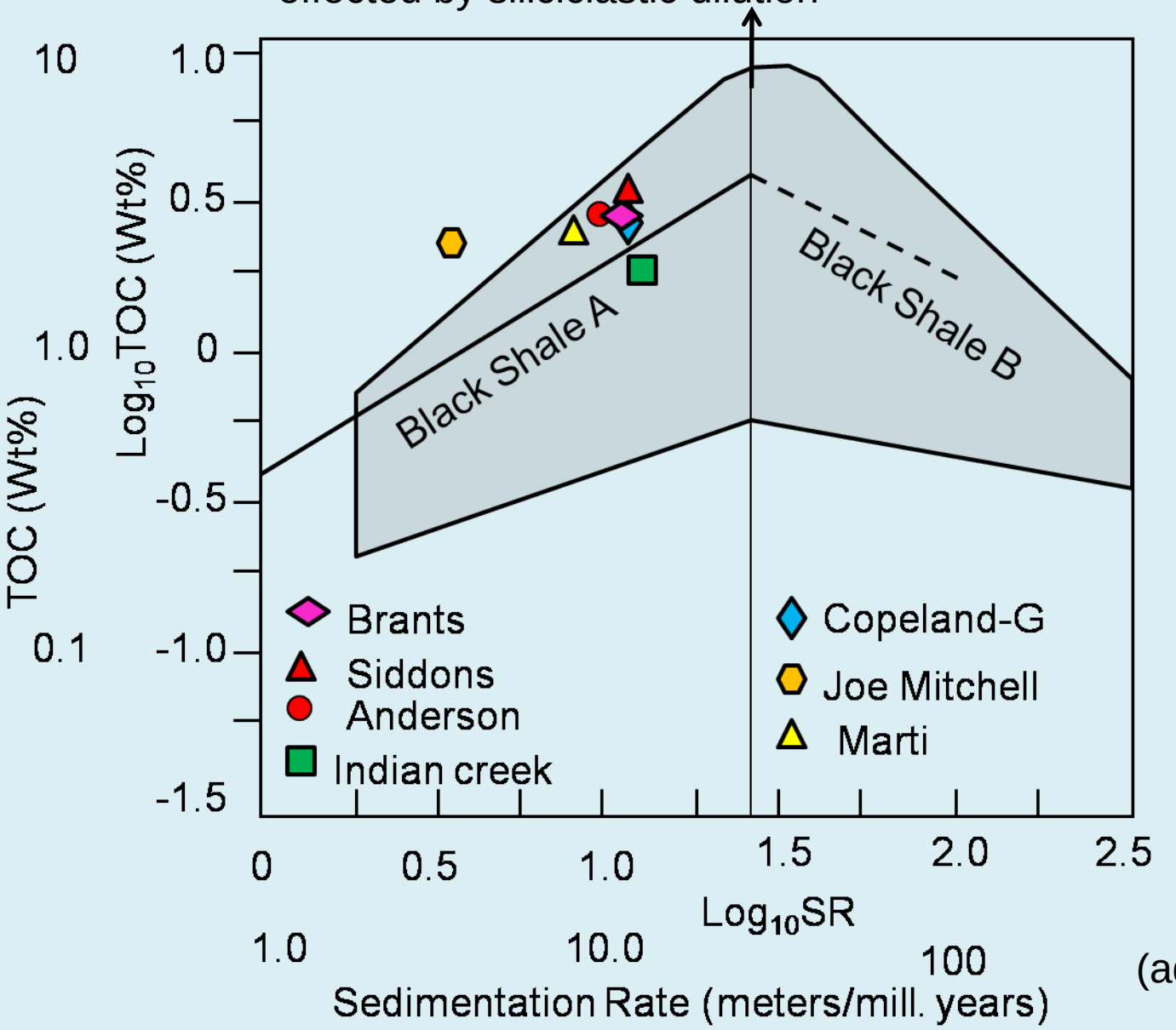


Organic matter preservation is favored by two major factors:

1) Smaller vertical extent of the aerobic zone
2) rapid passage of the sediments through the aerobic zone of intense organic degradation- high sedimentation rate

(modified from Caspers, 1957; Ibach, 1982; Didyk et al., 1978)

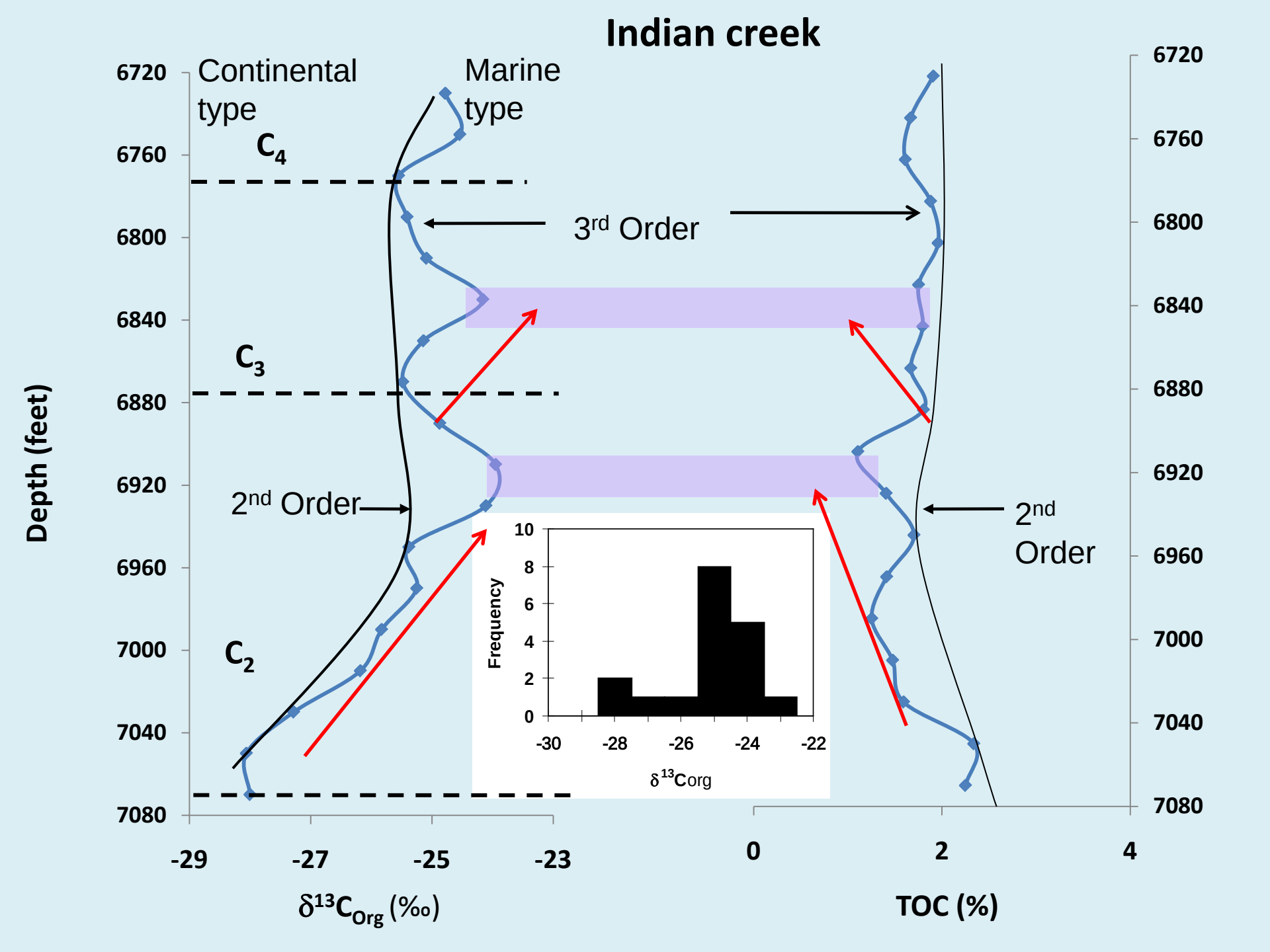
Relation between TOC and sedimentation rate

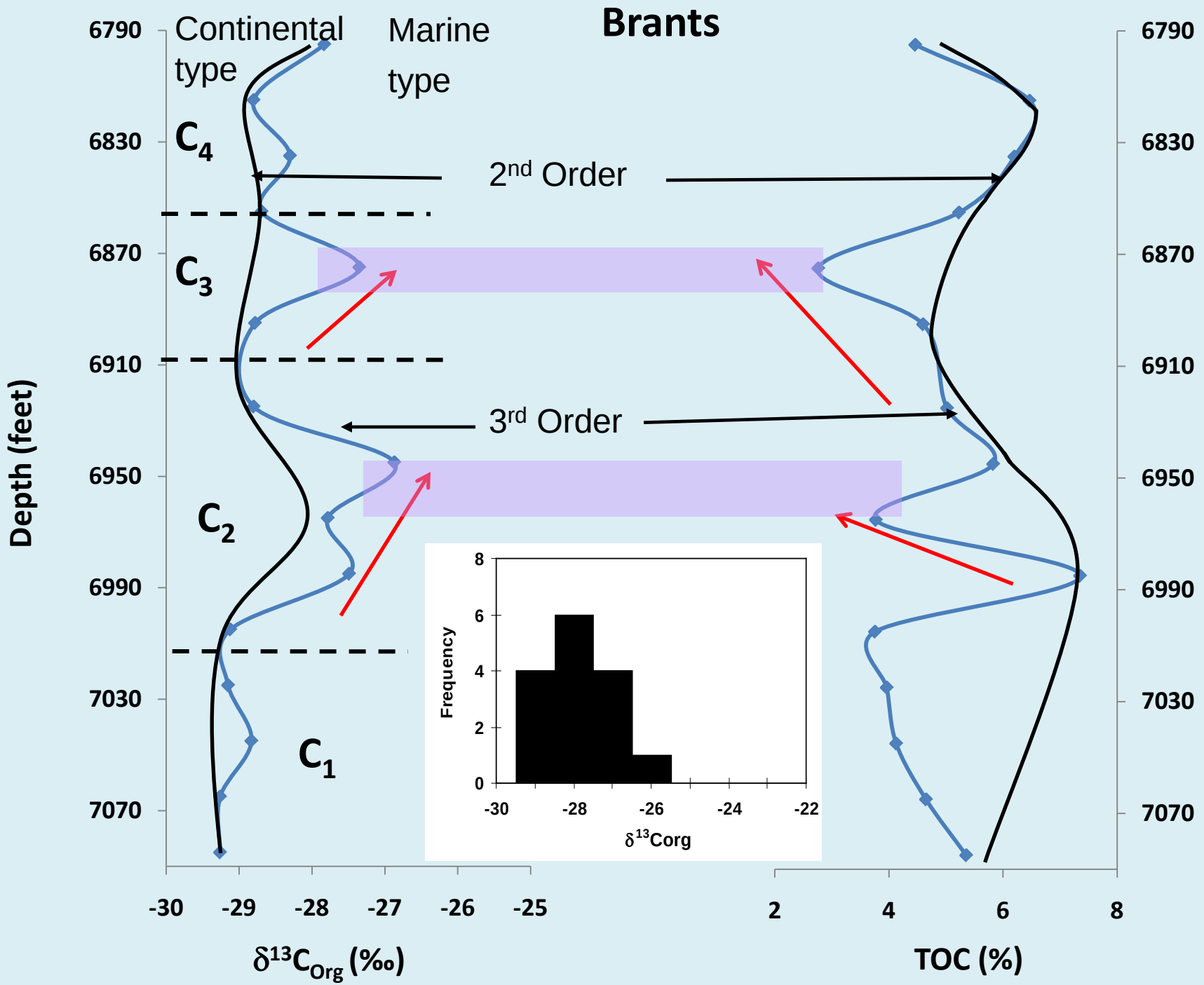


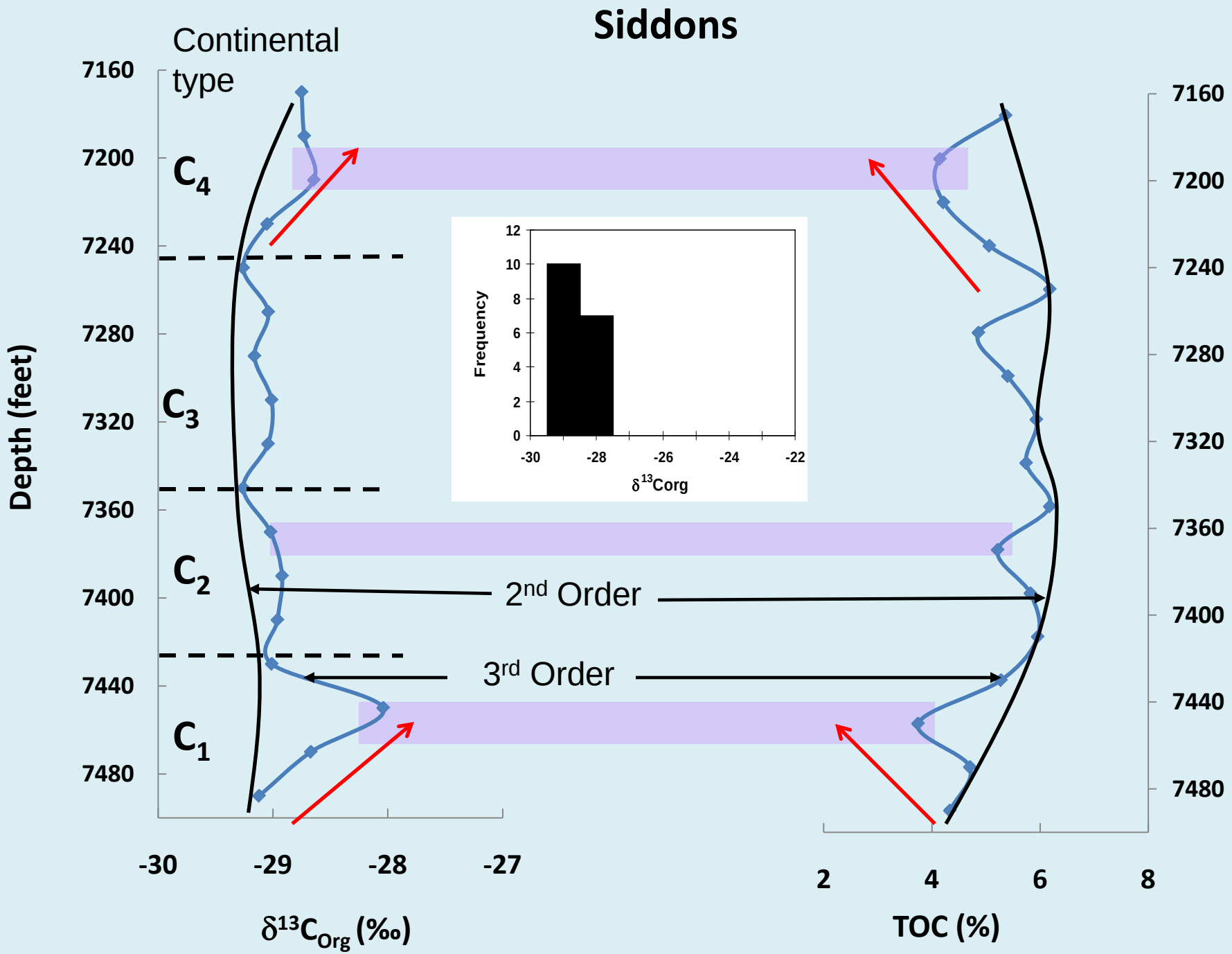
Black shale A: general trend of TOC-sedimentation rate in the field of low sedimentation rate.

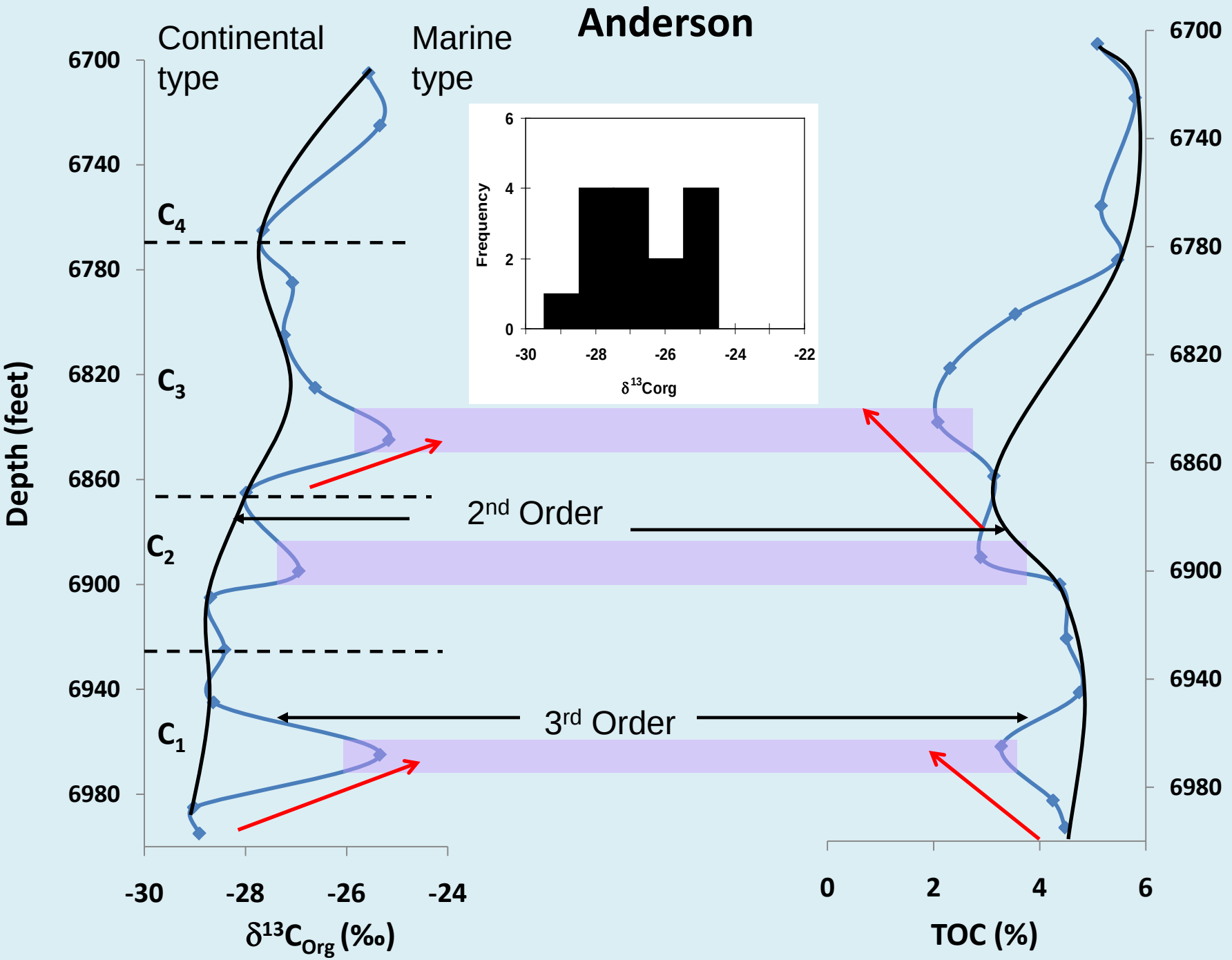
Black shale B Antithetic correlation between TOC-Sedimentation rate at higher sedimentation rate due to siliciclastic dilution.

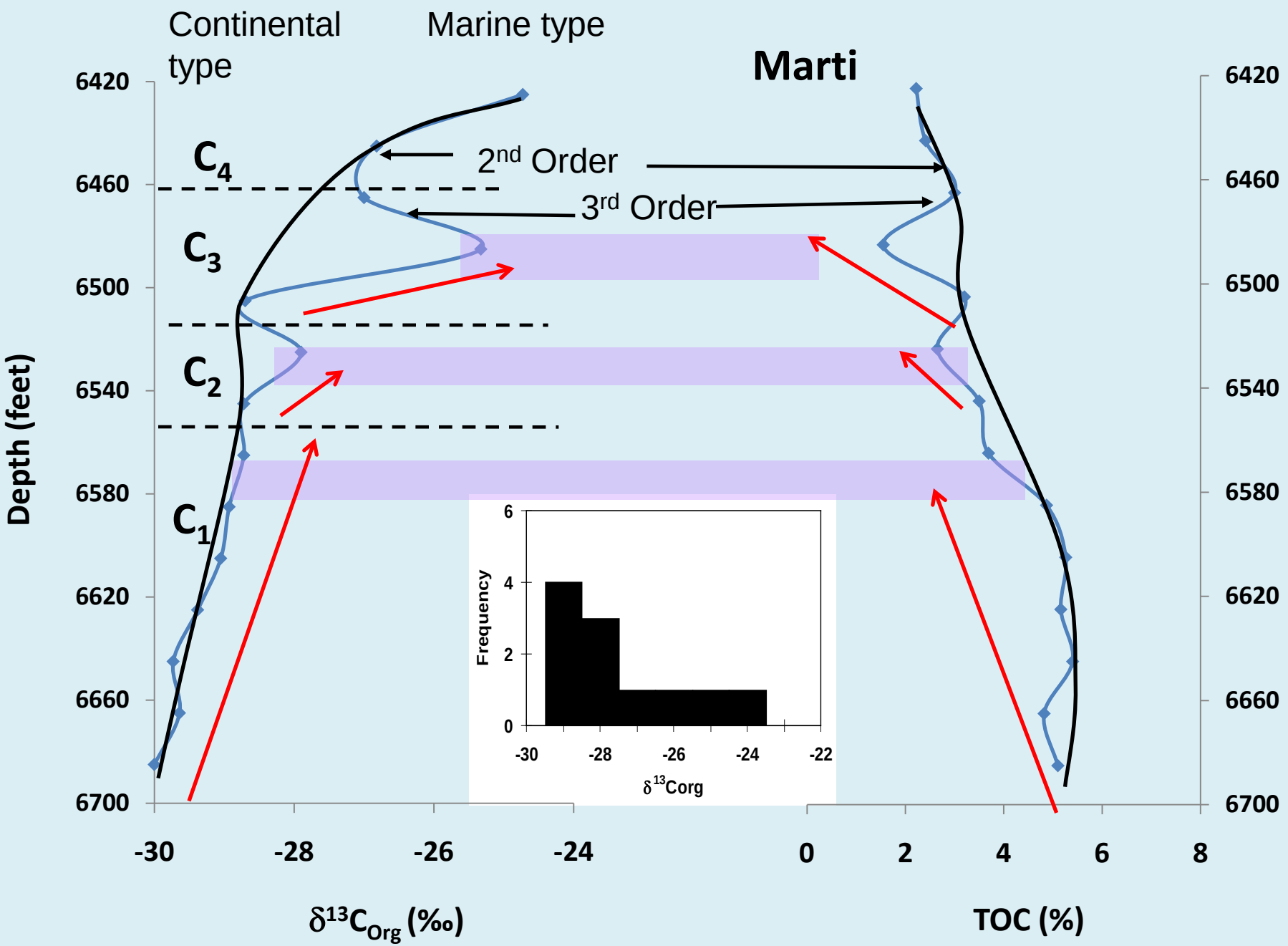
(adopted from Ibach,1982)

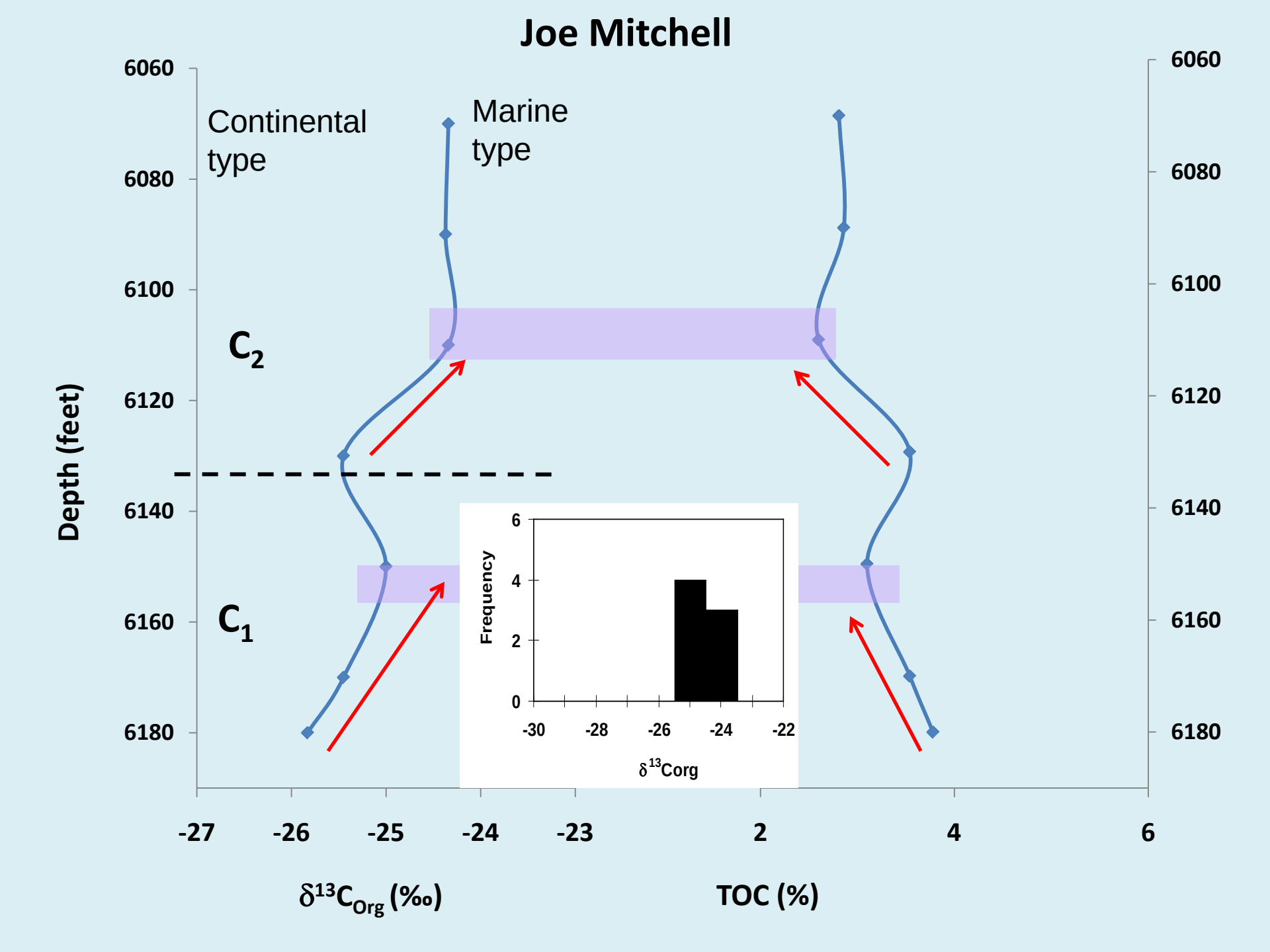

Indian creek
Continental type
Marine type
C4
C3
C2
3rd Order
2nd Order
2nd Order
Depth (feet)
6720
6760
6800
6840
6880
6920
6960
7000
7040
7080
-29
-27
-25
-23
δ13Corg (‰)
0
2
4
TOC (%)
Frequency
10
8
6
4
2
0
-30
-28
-26
-24
-22
δ13Corg

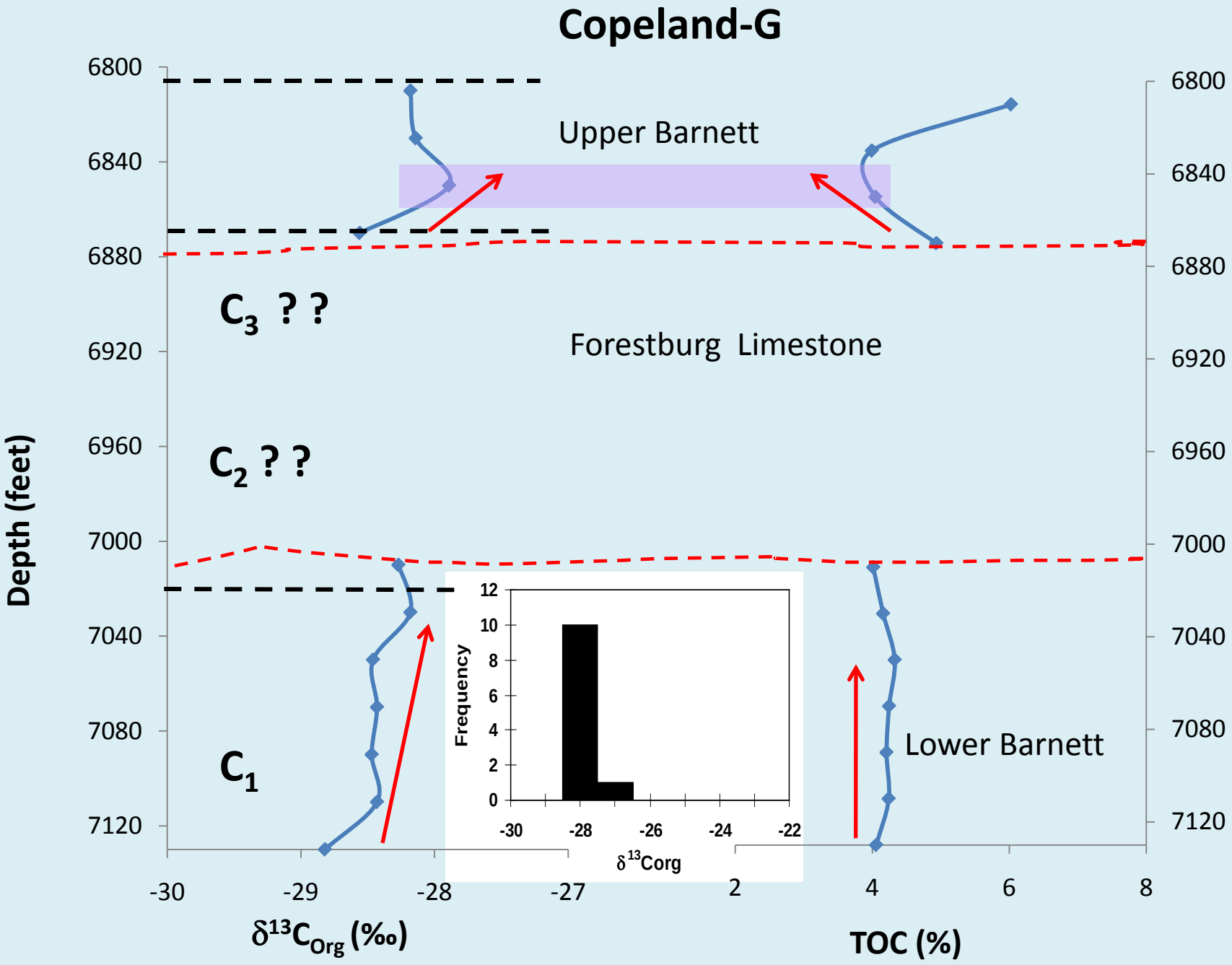

Brants
Continental type
Marine type
C_4
C_3
C_2
C_1
2nd Order
3rd Order
Depth (feet)
6790
6830
6870
6910
6950
6990
7030
7070
-30
-29
-28
-27
-26
-25
$\delta^{13}C_{Org}$ (‰)
2
4
6
8
TOC (%)
Frequency
0
2
4
6
8
-30
-28
-26
-24
-22
δ^{13}Corg

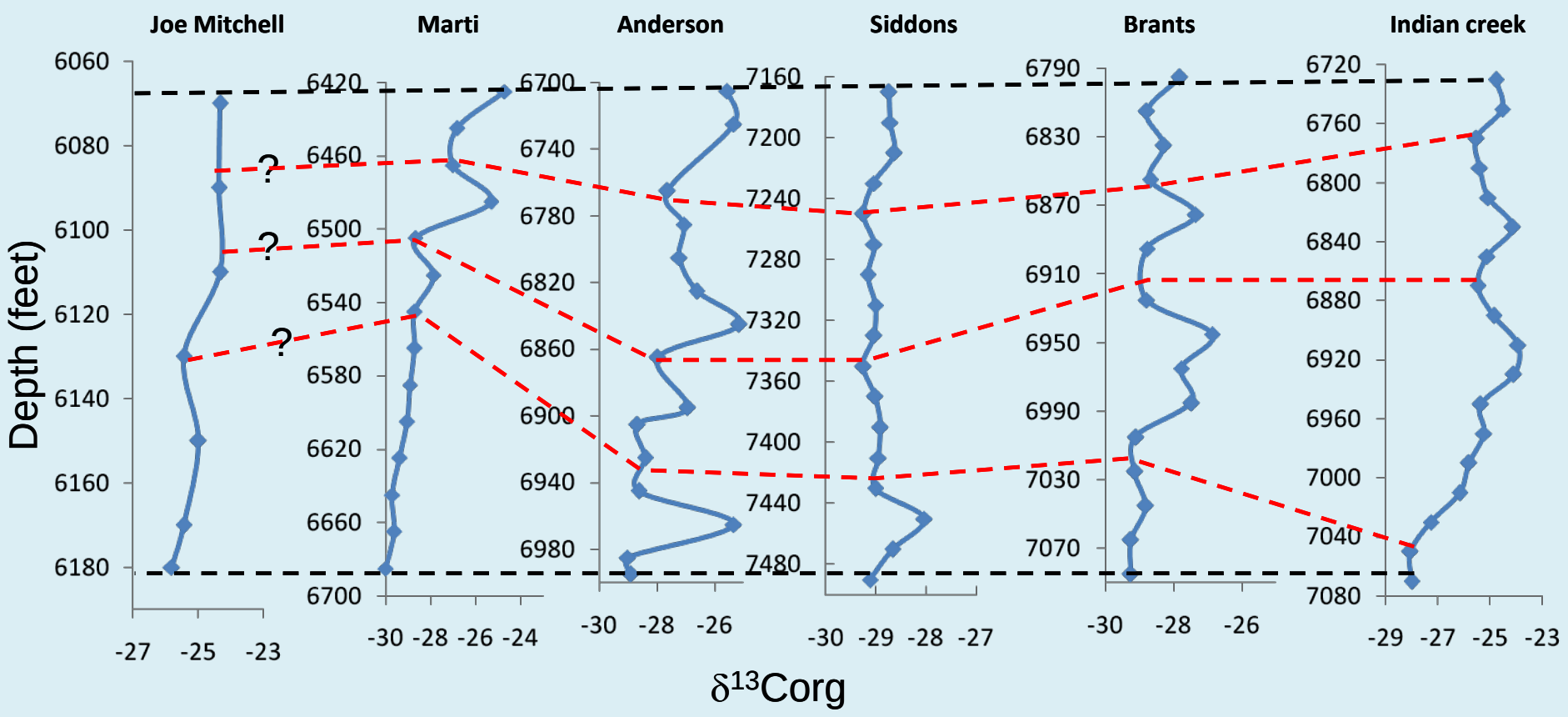

Siddons
Continental type
Depth (feet)
7160
7200
7240
7280
7320
7360
7400
7440
7480
C4
C3
C2
C1
2nd Order
3rd Order
Frequency
12
10
8
6
4
2
0
-30
-28
-26
-24
-22
δ13Corg
-30
-29
-28
-27
δ13COrg (‰)
2
4
6
8
TOC (%)


Anderson
Continental type
Marine type
6700
6740
6780
6820
6860
6900
6940
6980
Depth (feet)
C4
C3
C2
C1
2nd Order
3rd Order
Frequency
δ13Corg
-30
-28
-26
-24
-22
δ13COrg (‰)
0
2
4
6
TOC (%)


Continental type
Marine type
Marti
2nd Order
3rd Order
C4
C3
C2
C1
Depth (feet)
6420
6460
6500
6540
6580
6620
6660
6700
-30
-28
-26
-24
0
2
4
6
8
δ13Corg (‰)
TOC (%)
Frequency
6
4
2
0
-30
-28
-26
-24
-22
δ13Corg

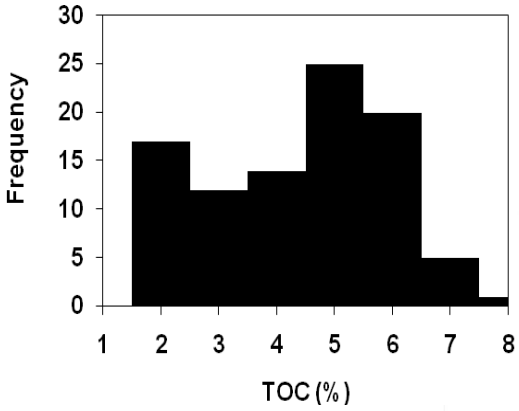

Joe Mitchell
Continental type
Marine type
C2
C1
Depth (feet)
6060
6080
6100
6120
6140
6160
6180
-27
-26
-25
-24
-23
2
4
6
δ13Corg (‰)
TOC (%)
Frequency
0
2
4
6
-30
-28
-26
-24
-22
δ13Corg

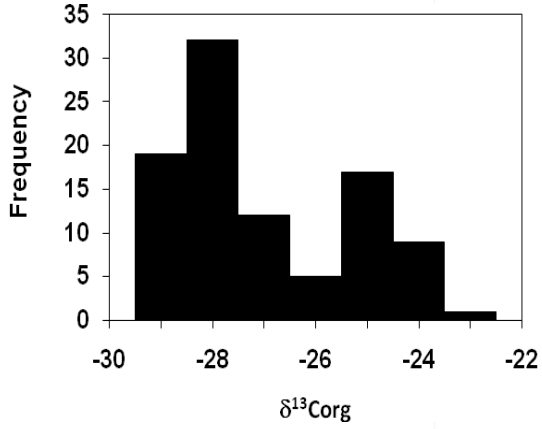

Copeland-G
Upper Barnett
Forestburg Limestone
Lower Barnett
C3 ? ?
C2 ? ?
C1
Depth (feet)
6800
6840
6880
6920
6960
7000
7040
7080
7120
-30
-29
-28
-27
2
4
6
8
δ13COrg (‰)
TOC (%)
Frequency
12
10
8
6
4
2
0
-30
-28
-26
-24
-22
δ13Corg

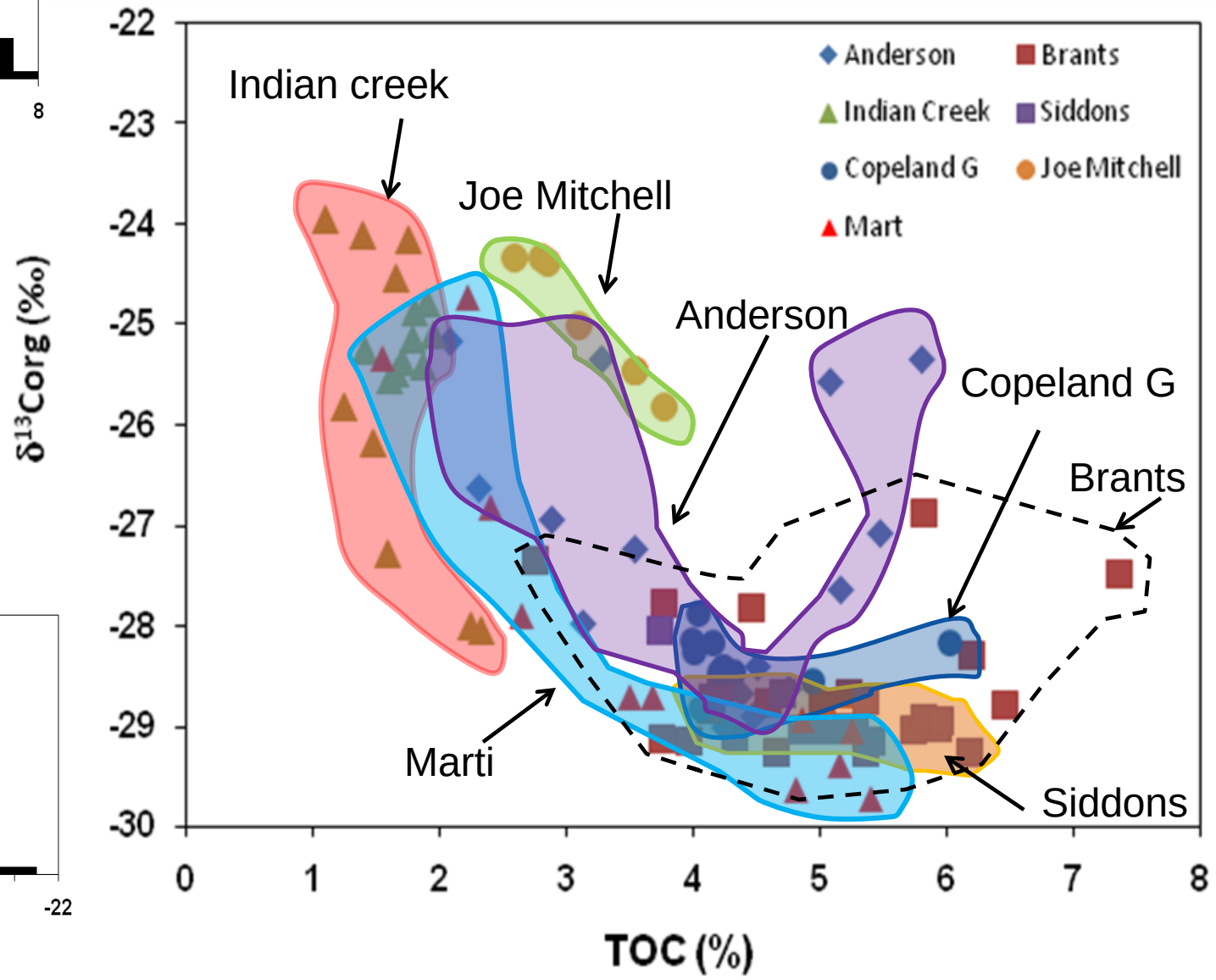


The correlation of the Barnett Formation within different wells. The correlation was done on the basis of already established cycles.

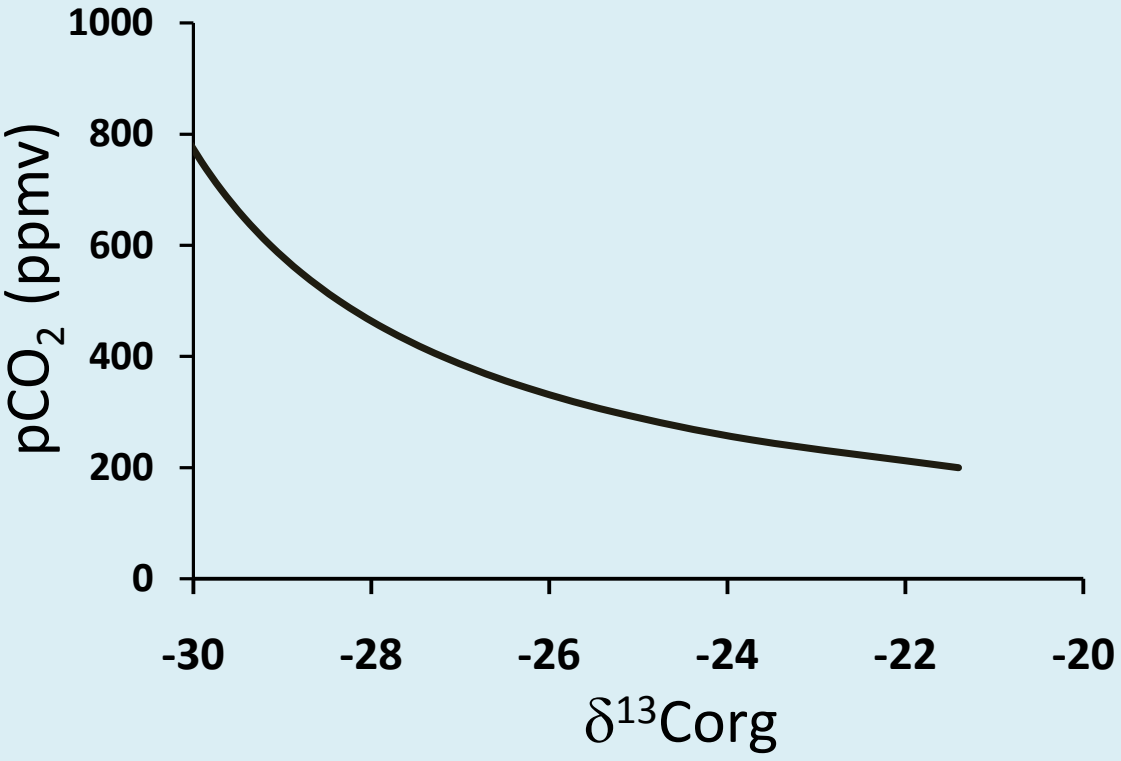
The diagram exhibits the antithetic relation between TOC and δ^{13}Corg of the Barnett Formation from seven wells







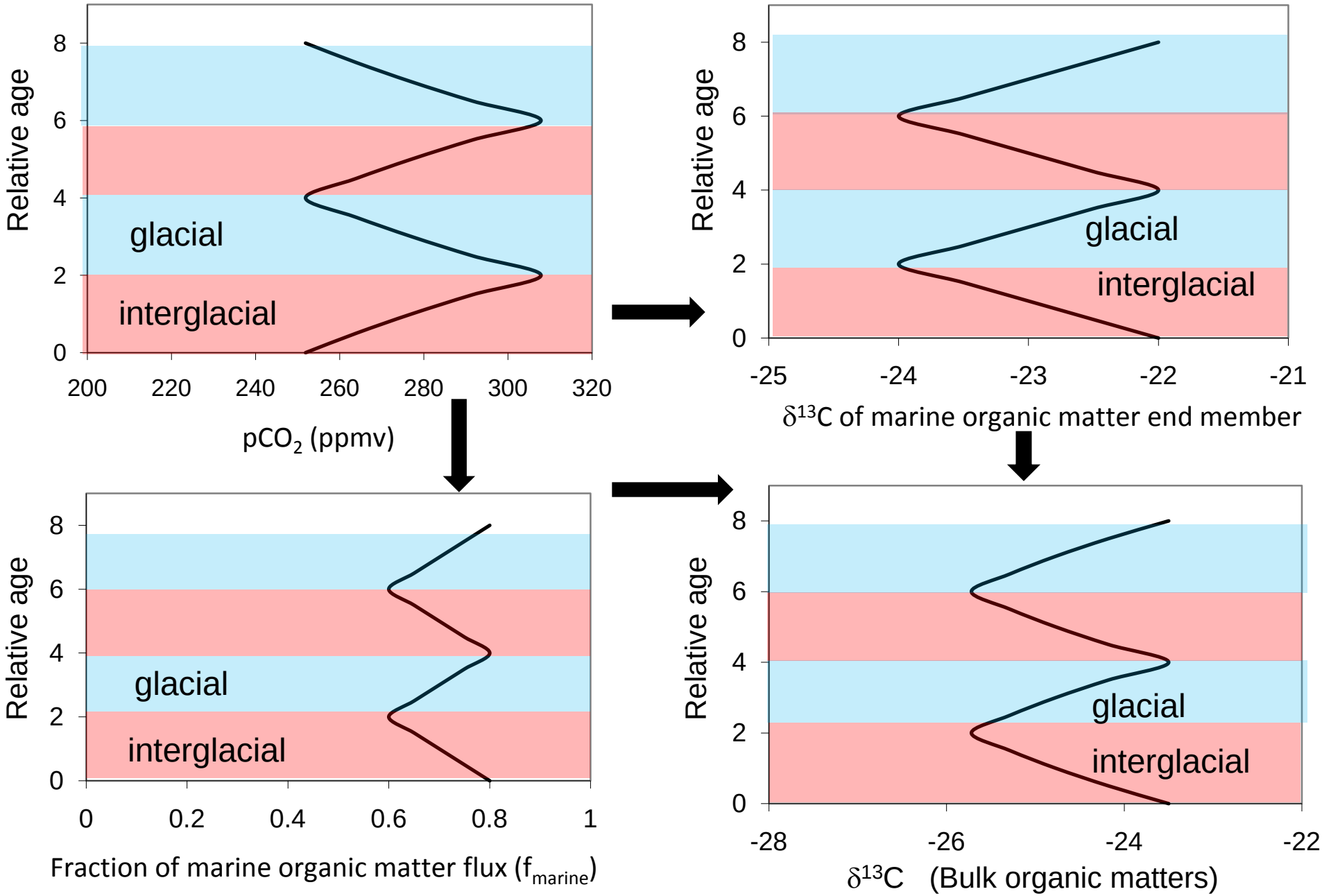
Relation between $\delta^{13}C$ and pCO_2



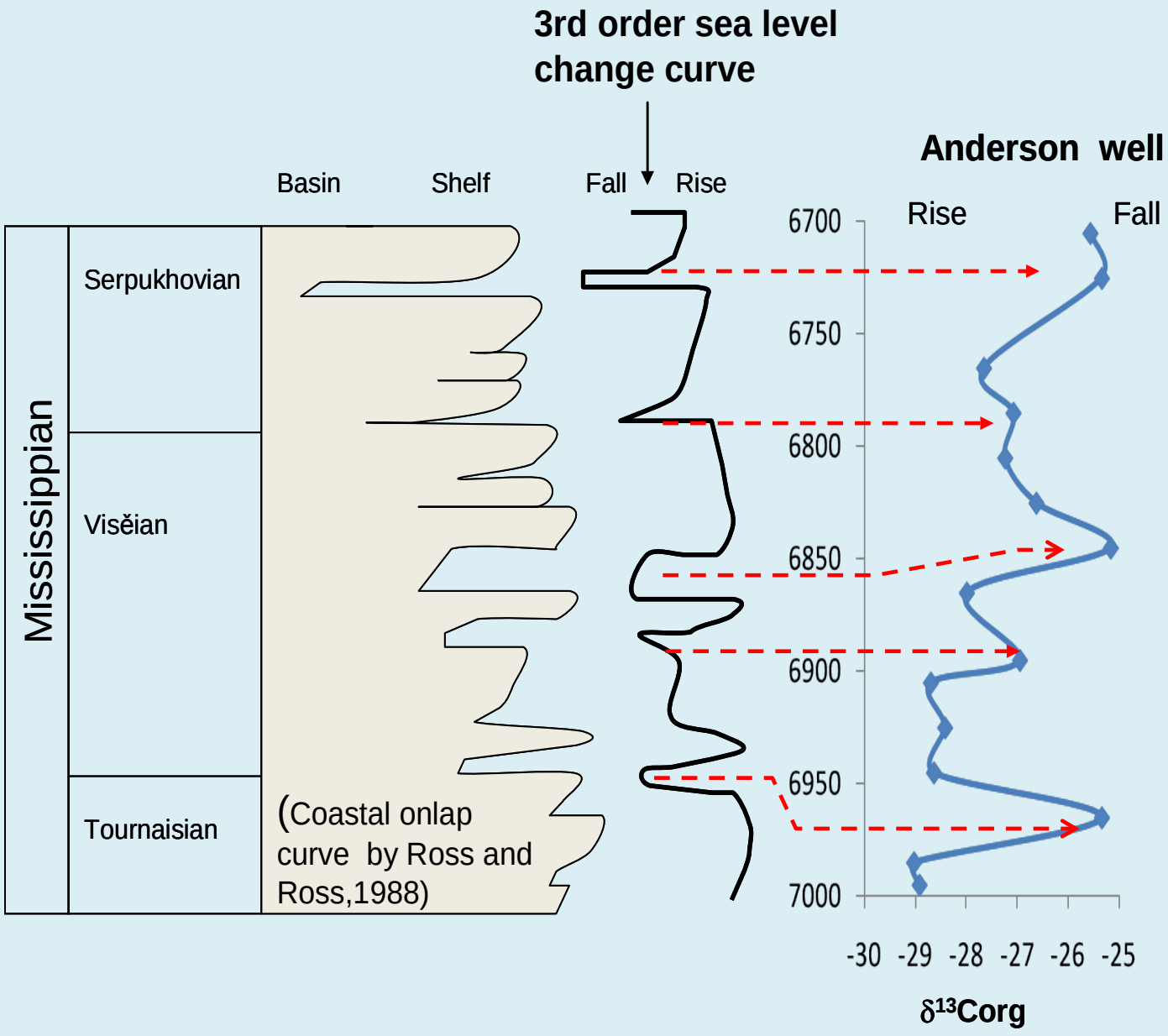
$$\delta^{13}C(org)-\delta^{13}C(carb)=\left[\frac{(159.5\,[PO_4])+38.99}{(0.034\,pCO_2)}\right]-33$$

Assuming constant $\delta^{13}C$ (carb)~0

(Kump and Arthur; 1999)



Model constraints: (1)Constant $\delta^{13}C$ of continental organic end member value.
(2) Constant phosphate concentration in the basin.



The diagram exhibits an overall similarity between 3rd order sea level change curve and $\delta^{13}C_{org}$ profile of the Barnett Formation.

Modern analogues

Black Sea

Present day anoxic condition established — 3,000 years ago

↑

Anoxic condition began to form — 7,000 years ago

Maximum organic carbon content change from 0.7 to 20%

↑

Rising Mediterranean waters began to invade the Black sea due to climatic warm-up. — 11,000 years ago

↑

Black sea (Fresh water Lake) — 22,000 years ago

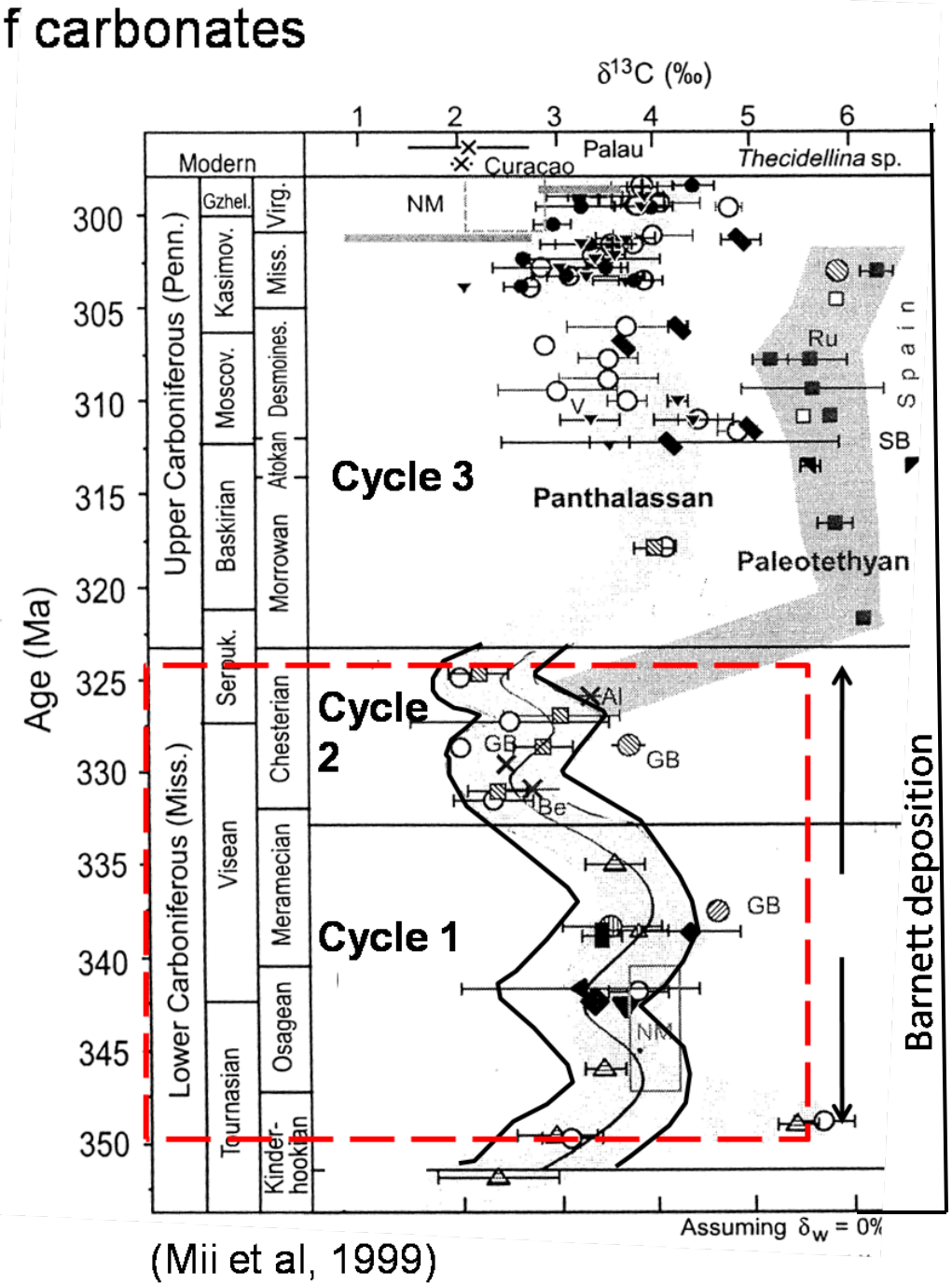
Eastern Mediterranean Sea

Intermittent anoxic condition prevailed 5 times during last 9000 years due to large and sudden influxes of fresh water from ice melting or precipitation

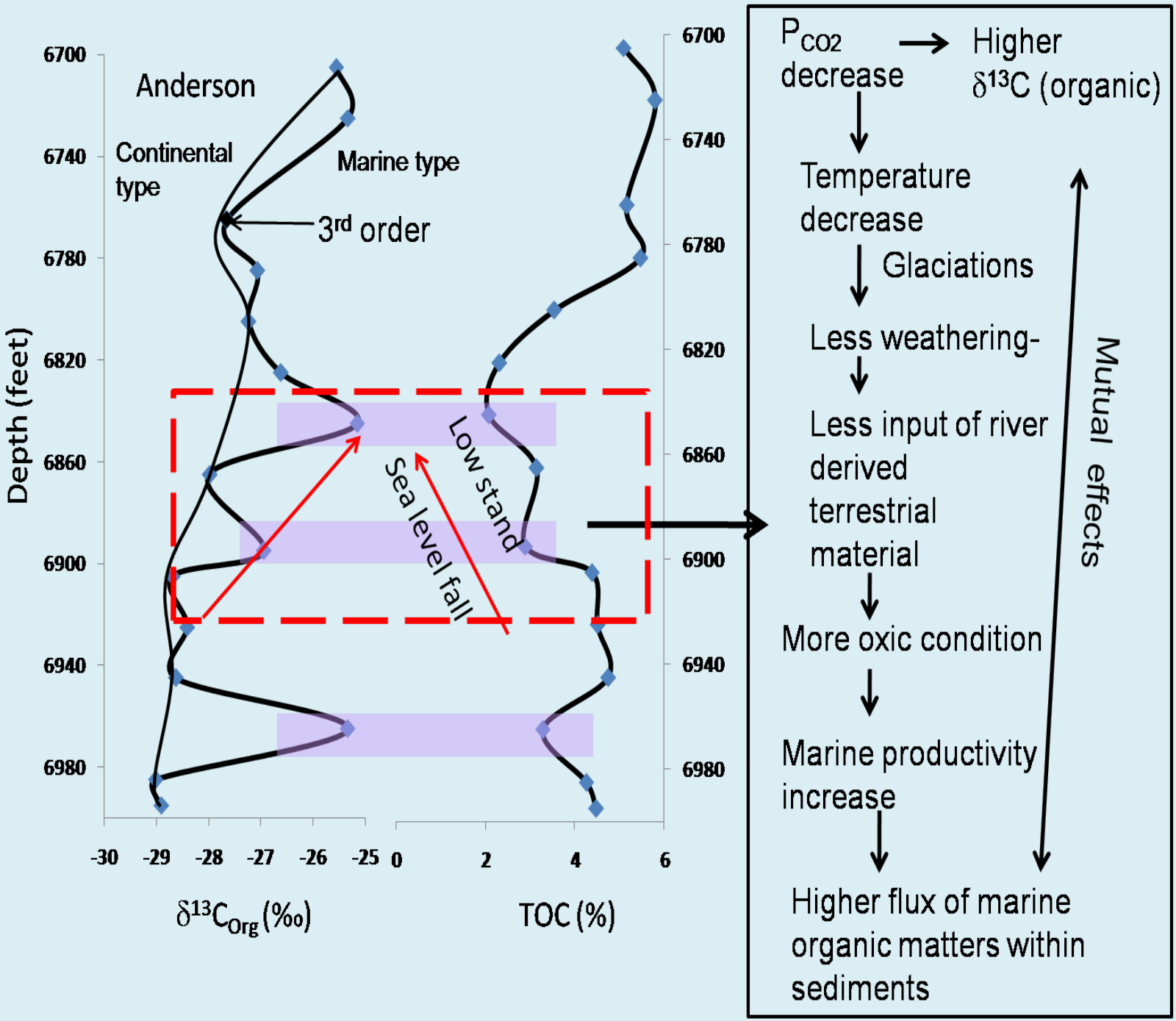
(Demaison and Moore, 1978)

Carbon isotope records of carbonates from North America

Carbon isotope data from North American Brachiopod shells also exhibit similar type of cyclicity during the Missippian.



(Mii et al, 1999)


Anderson
Continental type
Marine type
3rd order
Depth (feet)
6700
6740
6780
6820
6860
6900
6940
6980
Low stand
Sea level fall
-30
-29
-28
-27
-26
-25
0
2
4
6
δ13COrg (‰)
TOC (%)
PCO2 decrease
Higher δ13C (organic)
Temperature decrease
Glaciations
Less weathering-
Less input of river derived terrestrial material
More oxic condition
Marine productivity increase
Higher flux of marine organic matters within sediments
Mutual effects

Conclusions:

- Carbon isotope ratio of bulk organic matter from the Barnett Formation documented the paleoclimatic signature of the Mississippian.

- Our study reveals 3rd order sea level change during the Barnett formation.

- $\delta^{13}C_{org}$ and TOC can be used as geochemical correlation tool within organic rich shale/mudstone.