# Anoxia and Euxinia (or not) in an Upper Devonian Black Shale: Woodford Shale, Permian Basin, West Texas*

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## Abstract

Black shales are commonly assumed to have been deposited in bottom waters are generally anoxic, if not euxinic. However it is now recognized that rich accumulations of organic matter can form in the presence of low levels of oxygen. We examine three types of evidence for euxinia in long cores from the Upper Devonian black shale sequences, the Woodford Shale in the Permian Basin, west Texas, USA, which contains one of the longest continuous records of black shale deposition. Total organic carbon (TOC) averages 5 to 6% in two long cores, reaching a maximum of 14%. We address trace metal concentrations, pyrite framboid sizes, and in a low maturity Woodford core, the concentration of the biomarker isorenieratane, which records the presence of green-sulfur bacteria in the water column. In the Woodford Shale, all parameters clearly record eugenic conditions in one relatively narrow interval: greatly elevated isorenieratane concentrations, which indicate the presence of sulfidic waters extending into the photic zone; small pyrite framboid sizes, which indicate precipitation of pyrite in the water column, and elevated Mo/Al ratios, consistent with euxinic conditions. But outside of this ~ 3 meter zone, evidence for strongly developed euxinia is generally lacking and is only supported by elevated Mo/Al ratios, despite the presence of strong enrichment in organic carbon. If euxinic bottom water developed, it was restricted to a thin layer at the base of the water column. We relate the development of bottom water euxinia to the flux of reactive iron into the basin, generally associated with detrital clays. Where the flux of iron is high, sulfide is scavenged from ocean water in the form of pyrite, preventing the development of a euxinic water column. Euxinia develops when $H_2S$ production outpaces reactive iron input, for example when clay flux is low during sea level transgressions or in carbonate-dominated depositional systems. Development of euxinia may reinforce the preservation of organic matter in sediments because of the toxicity of $H_2S$ to most burrowing organisms, and the euxinic interval of the Woodford has the highest TOC in the formation. However other intervals lacking a euxinic signature have comparable TOC, so that euxinia is not a prerequisite for development of rich source rocks.

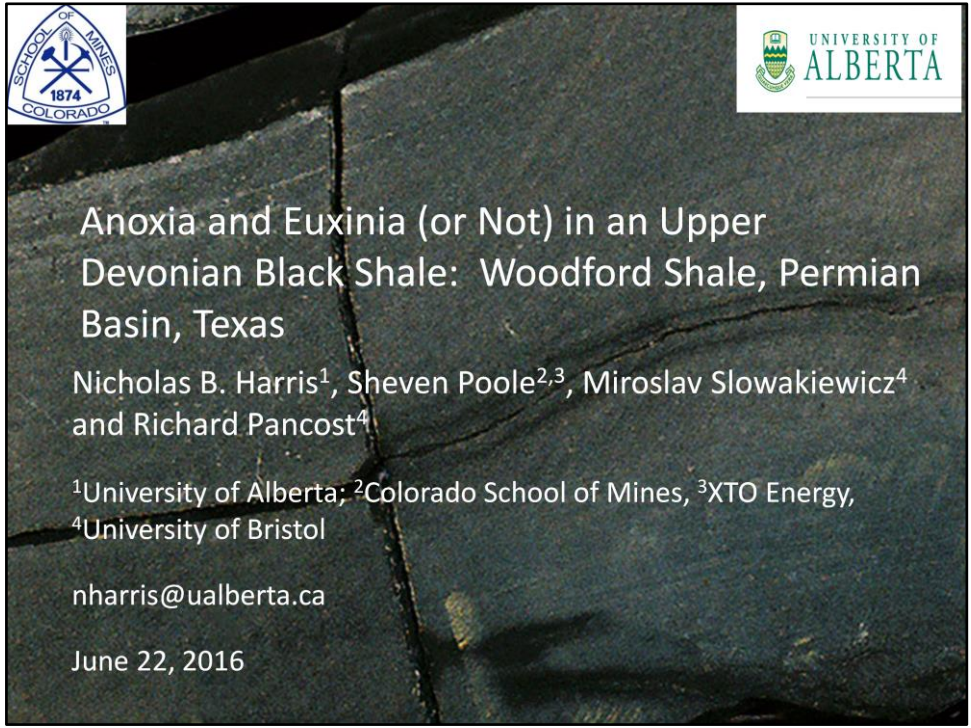
## Selected References


Goodfellow, W.D., and J.W. Lydon, 2007, Sedimentary Exhalative (SEDEX) Deposits, *in* W.D. Goodfellow (ed.), Mineral Deposits of Canada - A Synthesis of Major Deposit-Types, District Metallogeny, The Evolution of Geological Provinces, and Exploration Methods: Geological Association of Canada, p. 163-184.

Harris, N.B., 2014, Trace Elements and Basin Processes: Woodford Shale, Permian Basin, West Texas: AAPG Annual Convention and Exhibition, Pittsburgh, Pennsylvania, May 19-22, 2013, Search and Discovery Article #10573 (2014), Website accessed September 2016.

Hemmesch, N.T., N.B. Harris, C.A. Mnich, and D. Selby, 2014, A Sequence Stratigraphic Framework for the Upper Devonian Woodford Shale, Permian Basin, West Texas: AAPG Bulletin, v. 98/1, p. 23-47. DOI: 10.1306/05221312077

Wilkin, R.T., H.L. Barnes, and S.L. Brantley, 1996, The Size Distribution of Framboidal Pyrite in Modern Sediments: An Indicator of Redox Conditions: Geochimica et Cosmochimica Acta, v. 60/20, p. 3897-3912.



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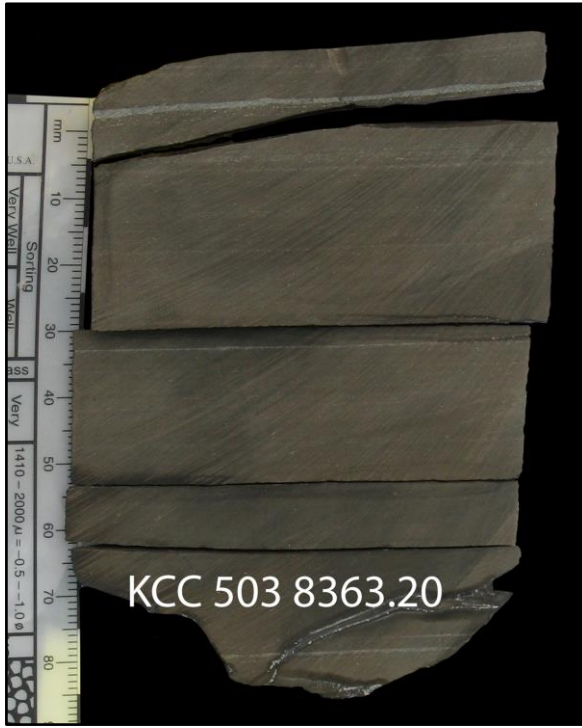
June 22, 2016




## Black Shales:

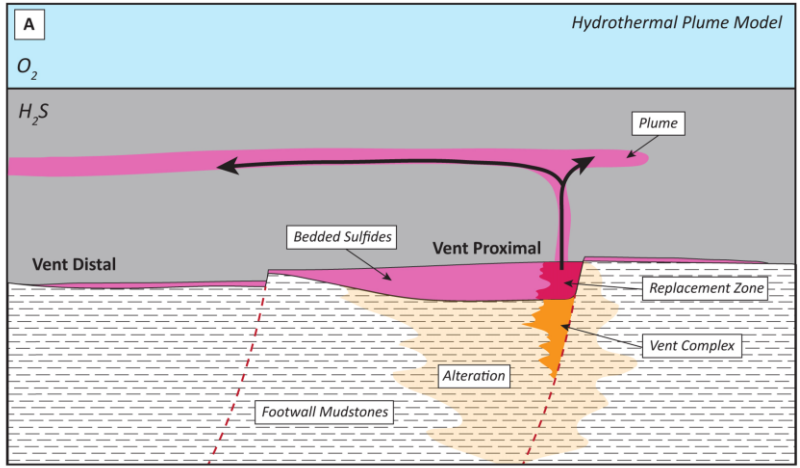
To a petroleum geologist:

- A source rock
- A reservoir

To an ore geologist

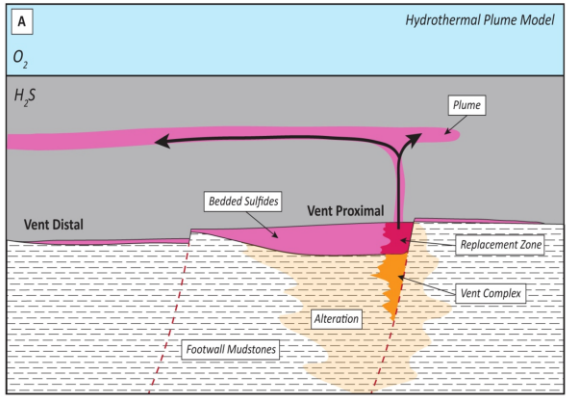
- A host for base metals

Model for Black Shale-Hosted SEDEX deposits - eruption of a metal-rich fluid plume into a euxinic water column




From Joseph Magnall, modified after Goodfellow and Lydon, 2007

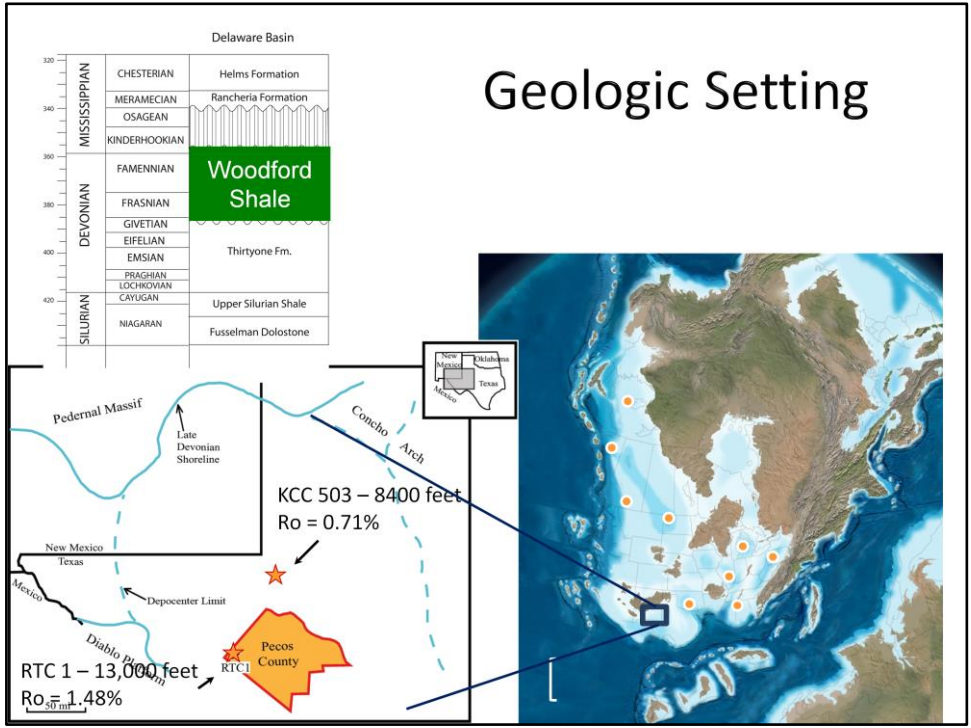
# Is persistent euxinia common in black shale basins?



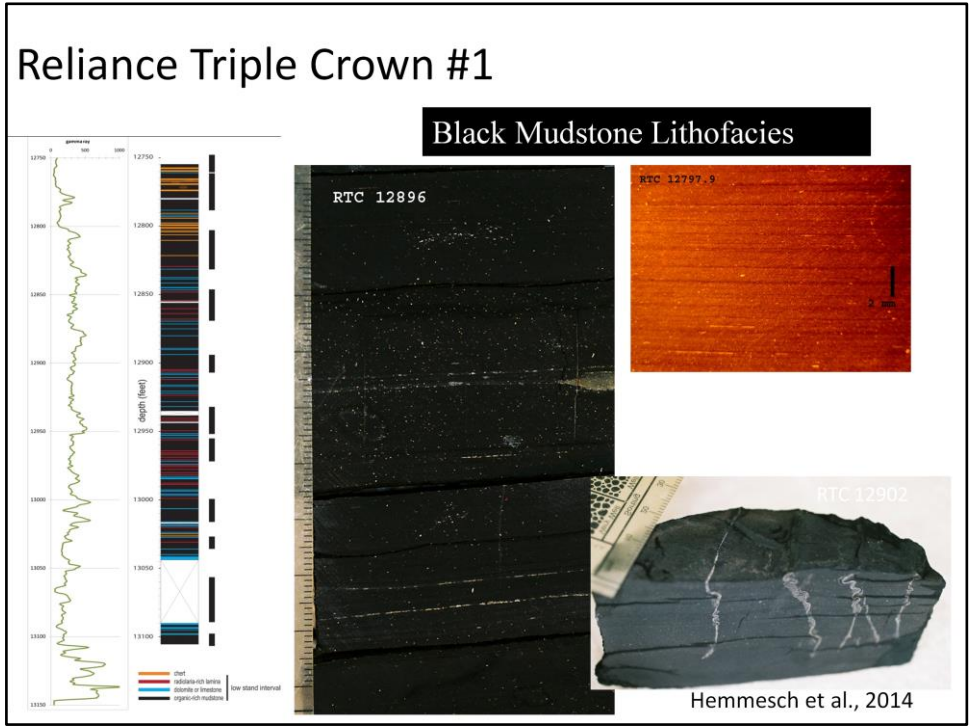

What types of evidence indicate euxinic conditions?

Does euxinia generally characterize continuous black sequences?

Do black shale formations differ in terms of redox / euxinia?

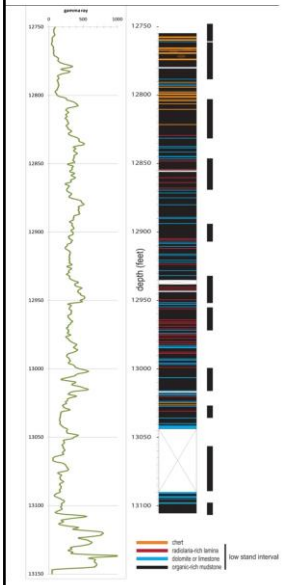


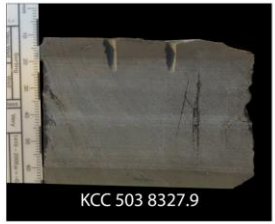

Presenter's notes: Our focus area is the Permian Basin in west Texas. For this study, we've been given access to a number of long cores by operators in the basin, indicated by the stars. In this talk, I'll be describing our observations in the RTC 1 core.



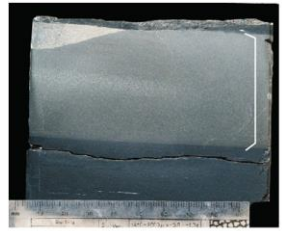

Presenter's notes: What did we see in the core? This is the PhD work of Nikki Hemmesch. Black shale, the classic laminated organic-rich dark rock, is the dominant lithology. That's the black rock in the facies column on the left hand side, and it amounts to more than 90% of the section.

# Minor lithofacies within the organic mudstone



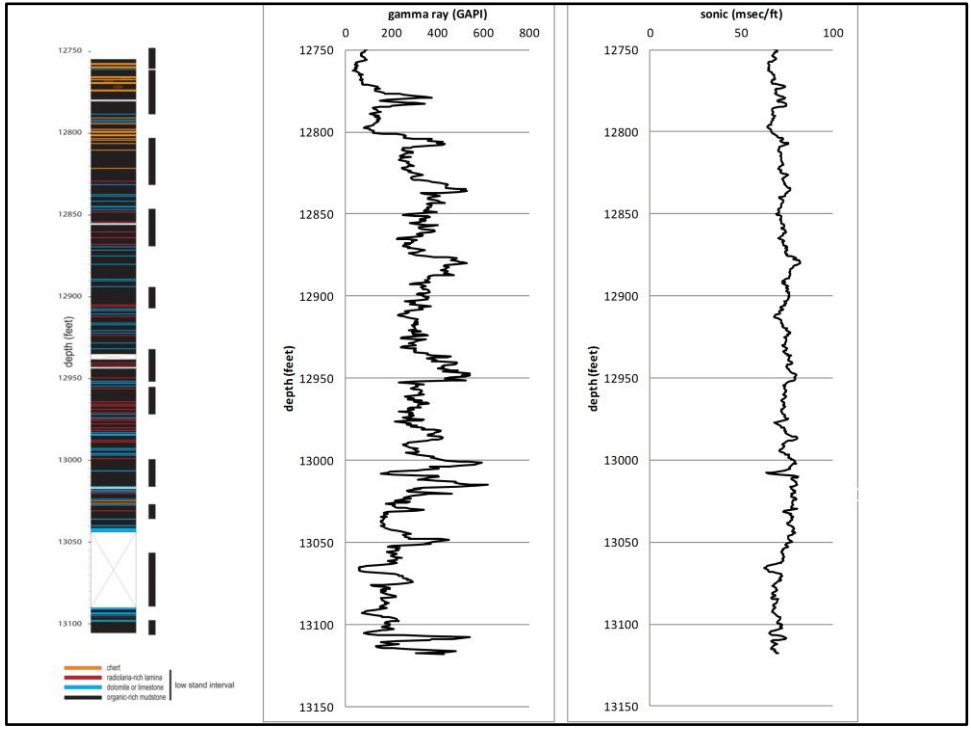



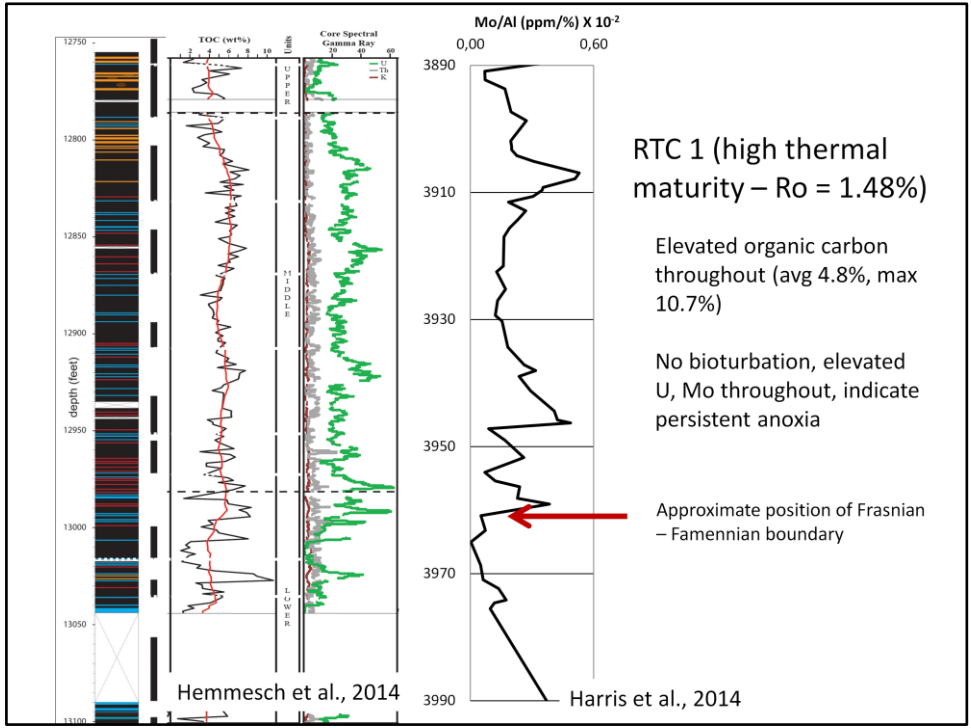

Chert beds (orange)



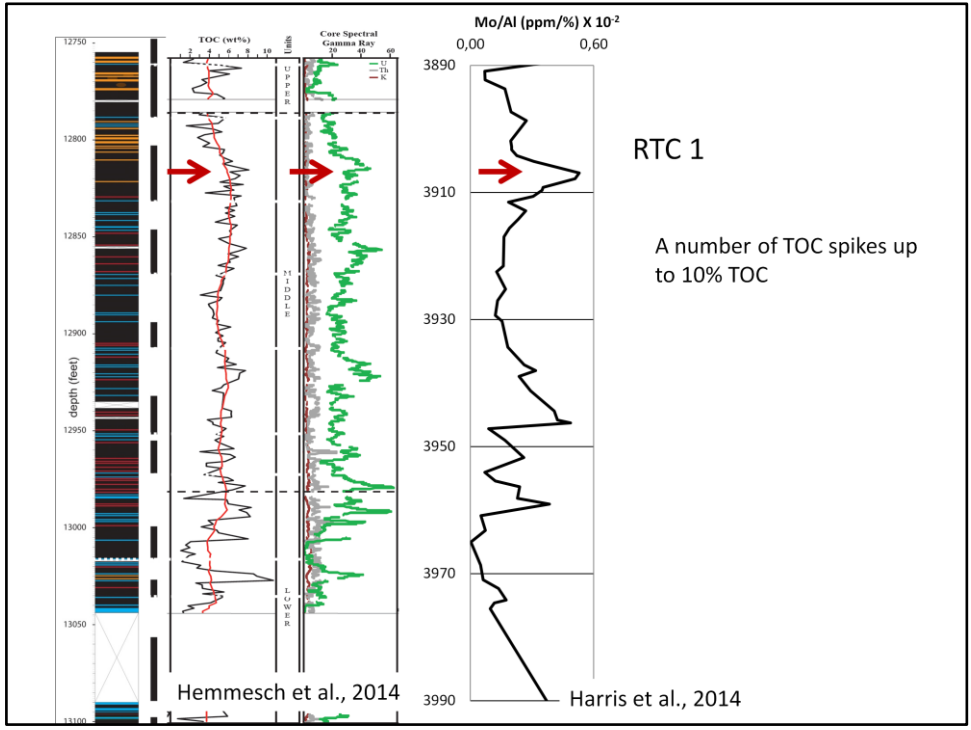
Dolomite beds (blue)

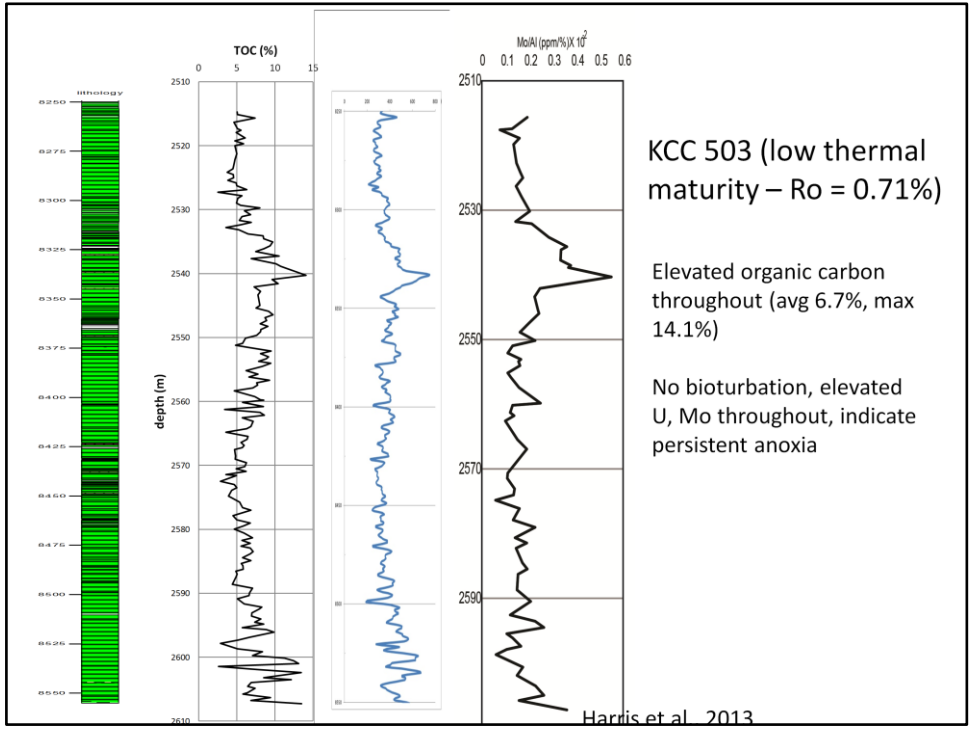

Radiolarian laminae (dark red)


depth (feet)
12750
12800
12850
12900
12950
13000
13050
13100
chert
radiolaria-rich lamina
dolomite or limestone
organic-rich mudstone
low stand interval
gamma ray (GAPI)
0
200
400
600
800
depth (feet)
12750
12800
12850
12900
12950
13000
13050
13100
13150
sonic (msec/ft)
0
50
100
depth (feet)
12750
12800
12850
12900
12950
13000
13050
13100
13150




Presenter's notes: We see at least 10 of these cycles in the RTC core. Given that the overall age span of the Woodford was 20 million years, these cycles represent periods of time on the order of 2 to 3 million years, so these would then be 3rd and 4th order sea level cycles.


depth (feet)
12750
12800
12850
12900
12950
13000
13050
13100
TOC (wt%)
Units
Core Spectral Gamma Ray
U
TH
K
UPPER
MIDDLE
LOWER
Mo/Al (ppm/%) X 10-2
0,00
0,60
3890
3910
3930
3950
3970
3990
RTC 1
A number of TOC spikes up to 10% TOC
Hemmesch et al., 2014
Harris et al., 2014

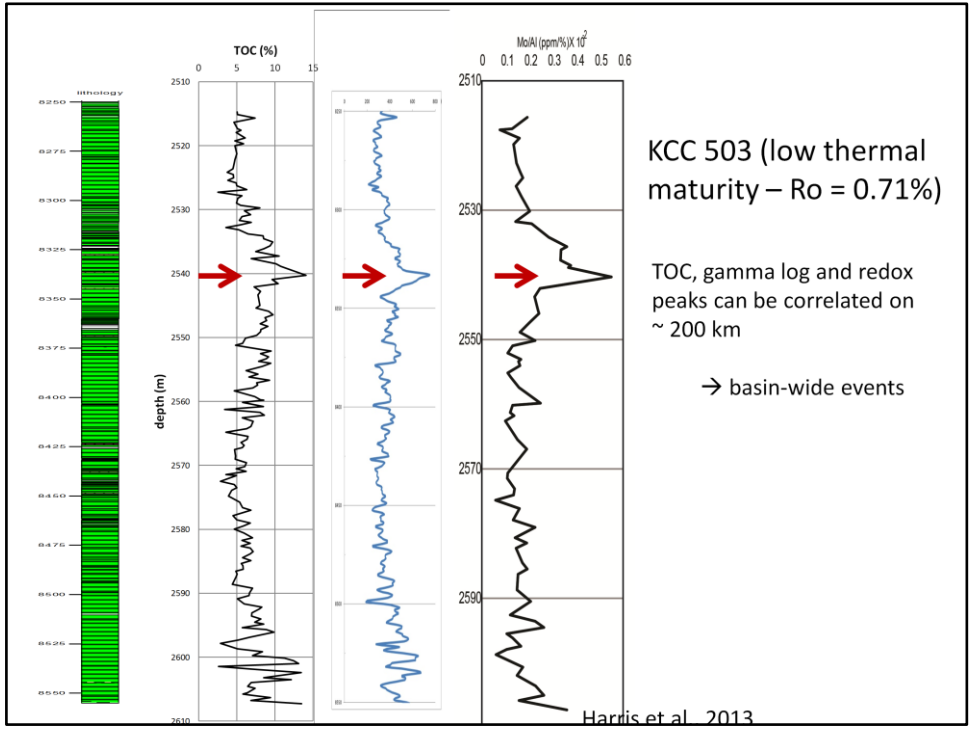



KCC 503 (low thermal maturity – Ro = 0.71%)

Elevated organic carbon throughout (avg 6.7%, max 14.1%)

No bioturbation, elevated U, Mo throughout, indicate persistent anoxia

Harris et al., 2013




KCC 503 (low thermal maturity – Ro = 0.71%)

TOC, gamma log and redox peaks can be correlated on ~ 200 km

→ basin-wide events

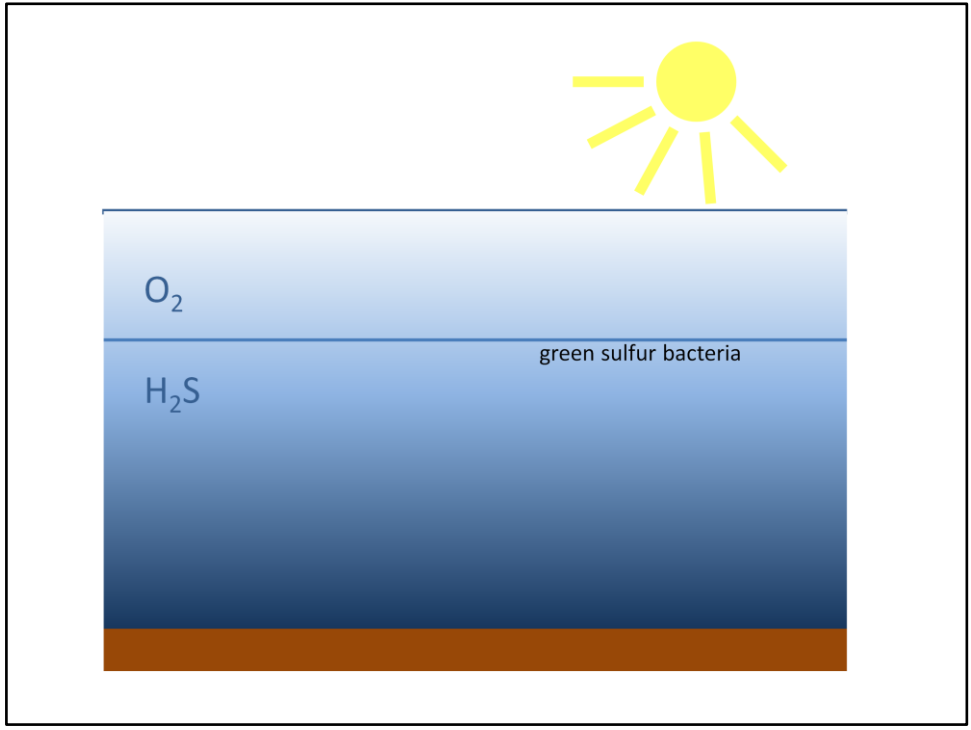
Harris et al., 2013

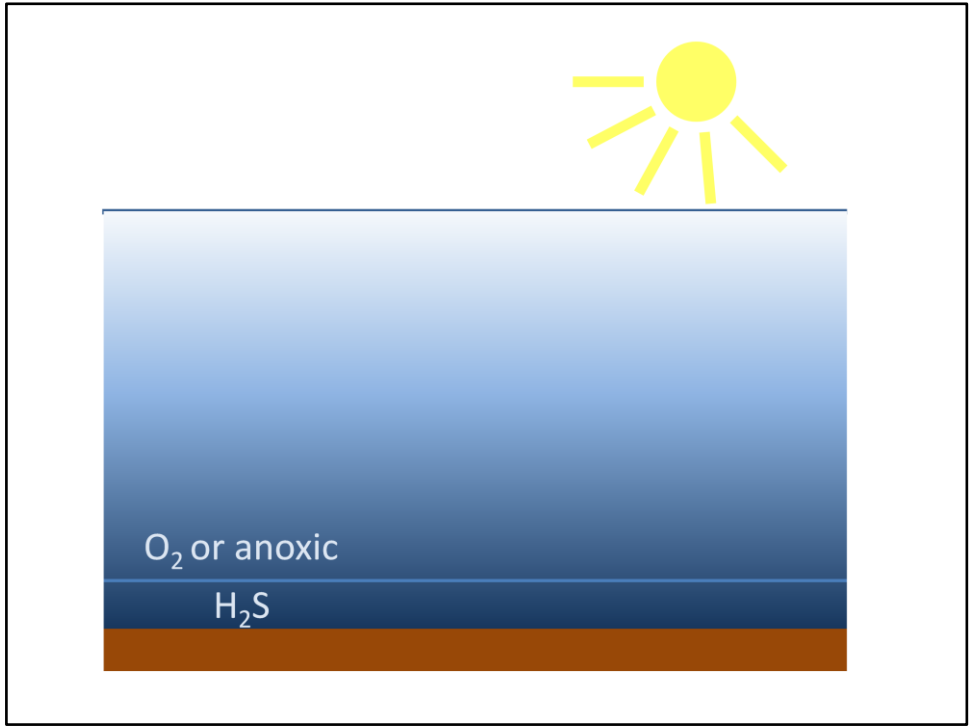
## Three proxies for euxinia

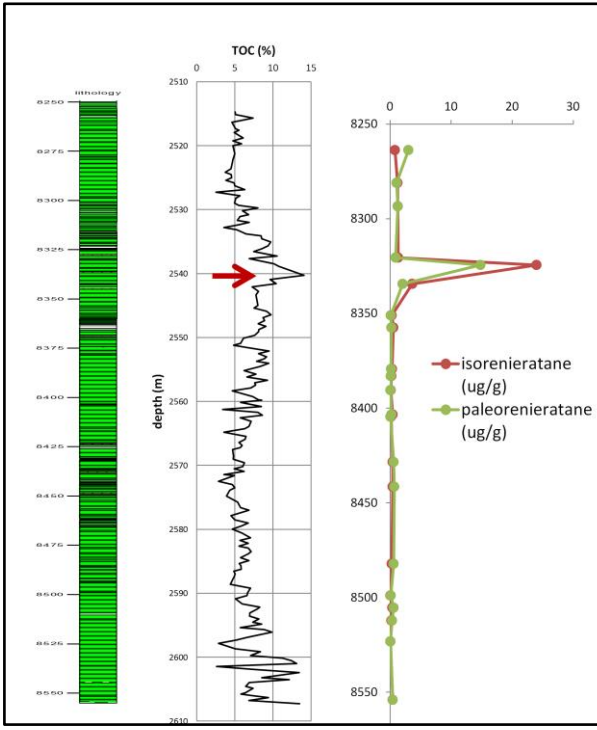
1) Biomarkers (isorenieratane and paleorenieratane) – green-sulfur bacteria within the photic zone

2) Pyrite framboid – size distribution (small, uniform size) indicates whether framboids formed within the water column

3) Mo enrichment versus U enrichment – higher Mo enrichment indicates excess sulfide


$O_2$
green sulfur bacteria
$H_2S$

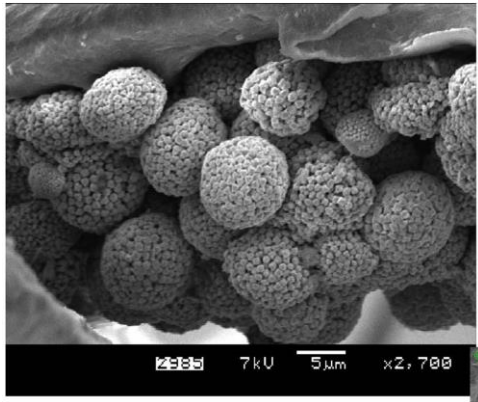

$O_2$ or anoxic
$H_2S$




## KCC 503 well

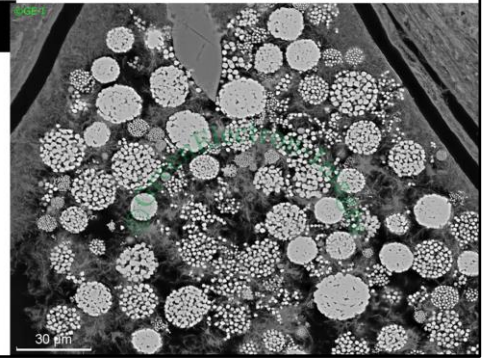
One period of euxinia within the photic zone (shallow level in water column)

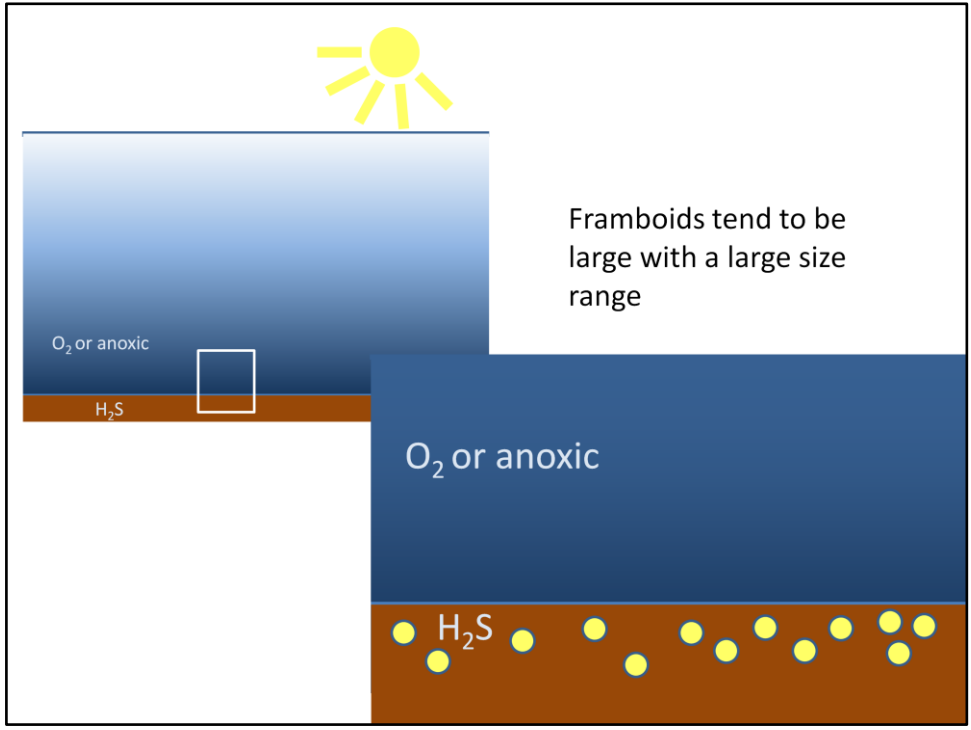
No clear correlation of TOC to isorenieratane → high TOC does not imply shallow euxinia

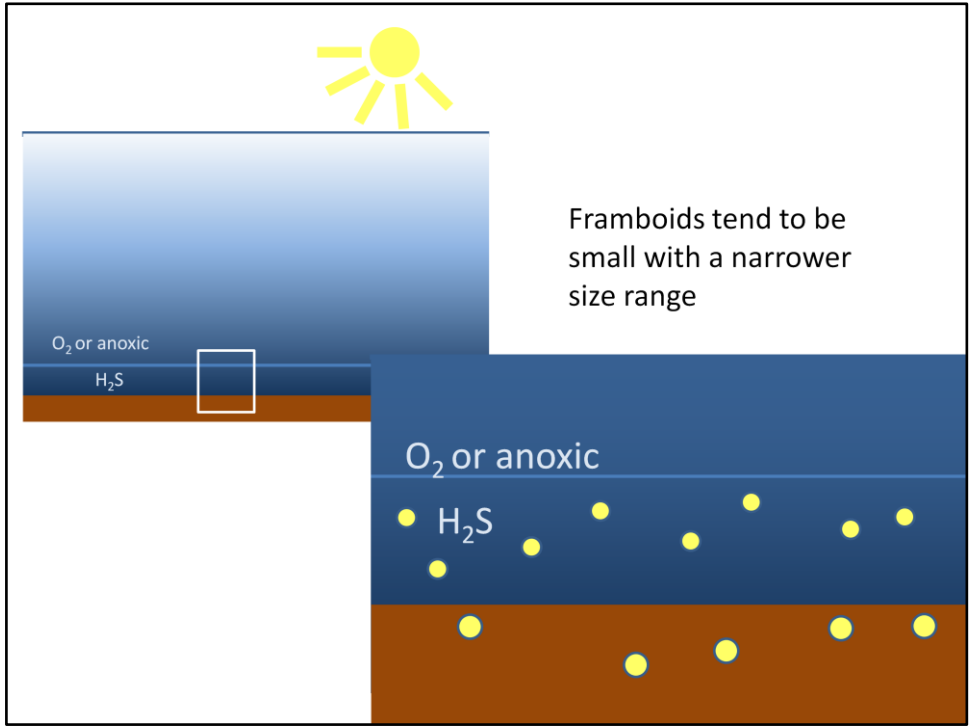


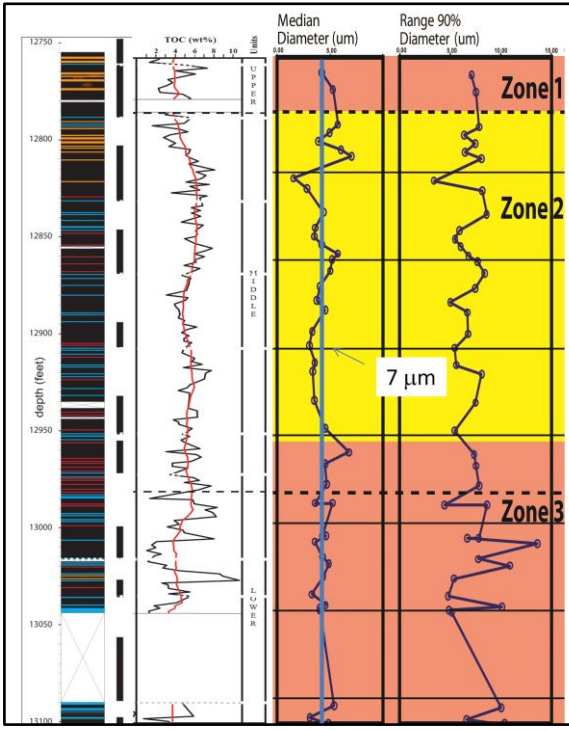

Pyrite framboids –

Aggregates of pyrite crystallites, common in sedimentary rocks



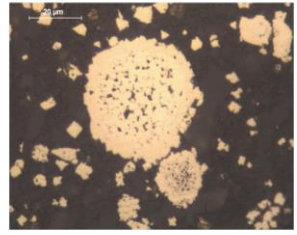

Framboids tend to be large with a large size range
$O_2$ or anoxic
$H_2S$
$O_2$ or anoxic
$H_2S$

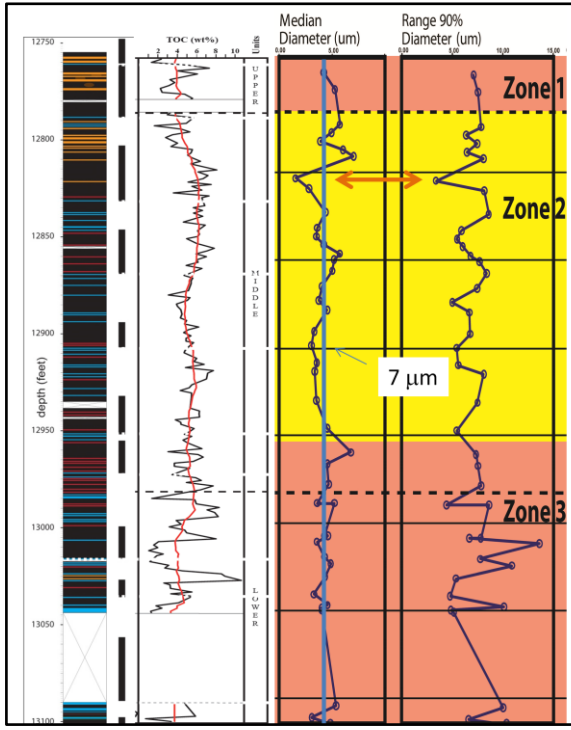

Framboids tend to be small with a narrower size range
$O_2$ or anoxic
$H_2S$
$O_2$ or anoxic
$H_2S$




## RTC 1 well

Framboids that form in the water column are typically smaller and are fairly uniform in size → indicate euxinia (Wilkin et al., 1996)

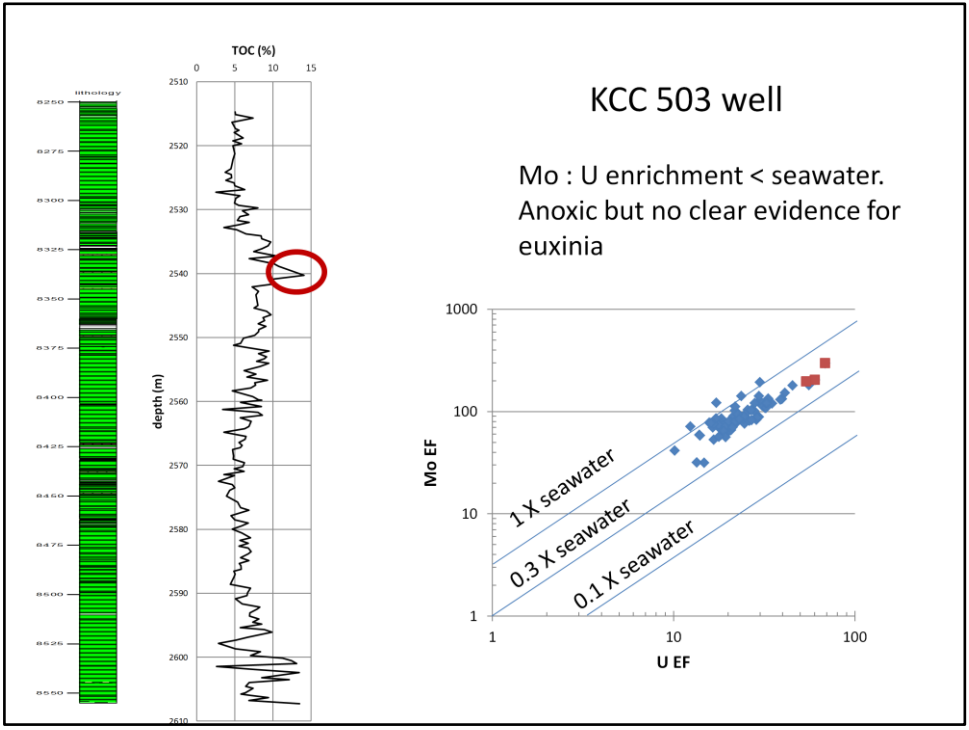


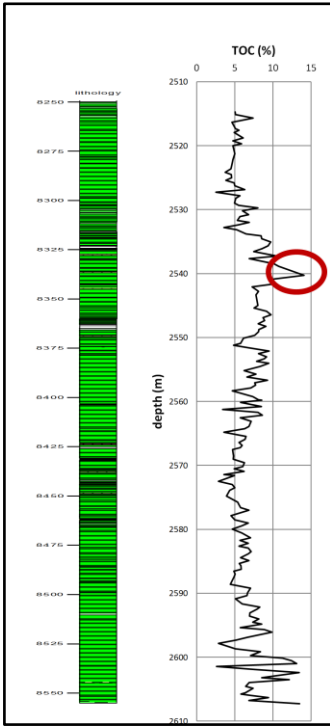



## RTC 1 well

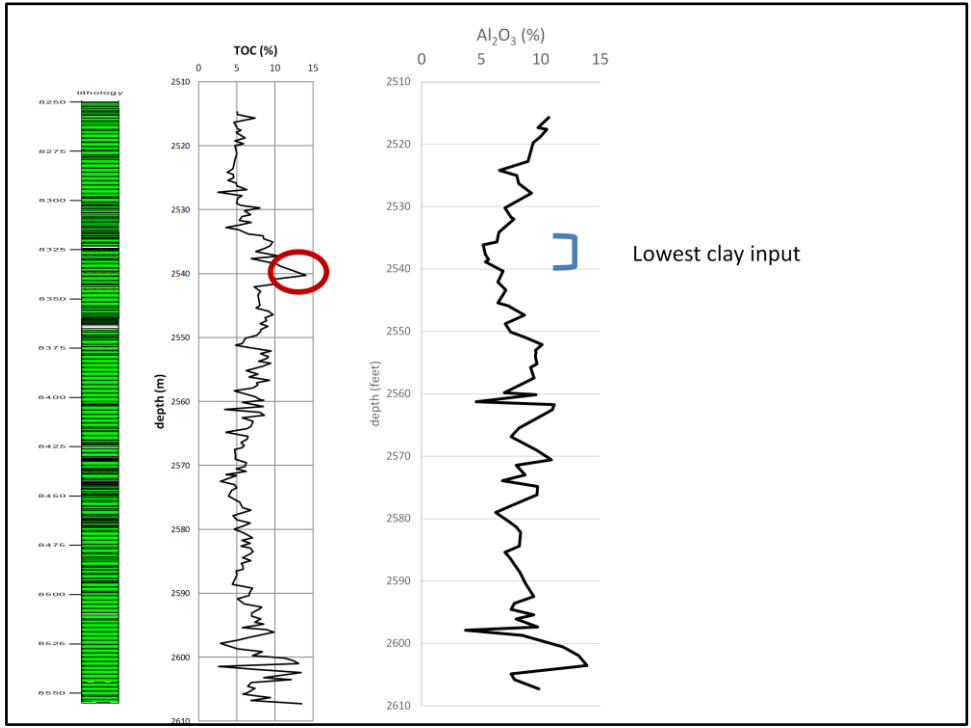
Framboids that average 7 µm are typical of dysoxic conditions. If 5 µm or less → euxinia (Wilkin et al., 1996)

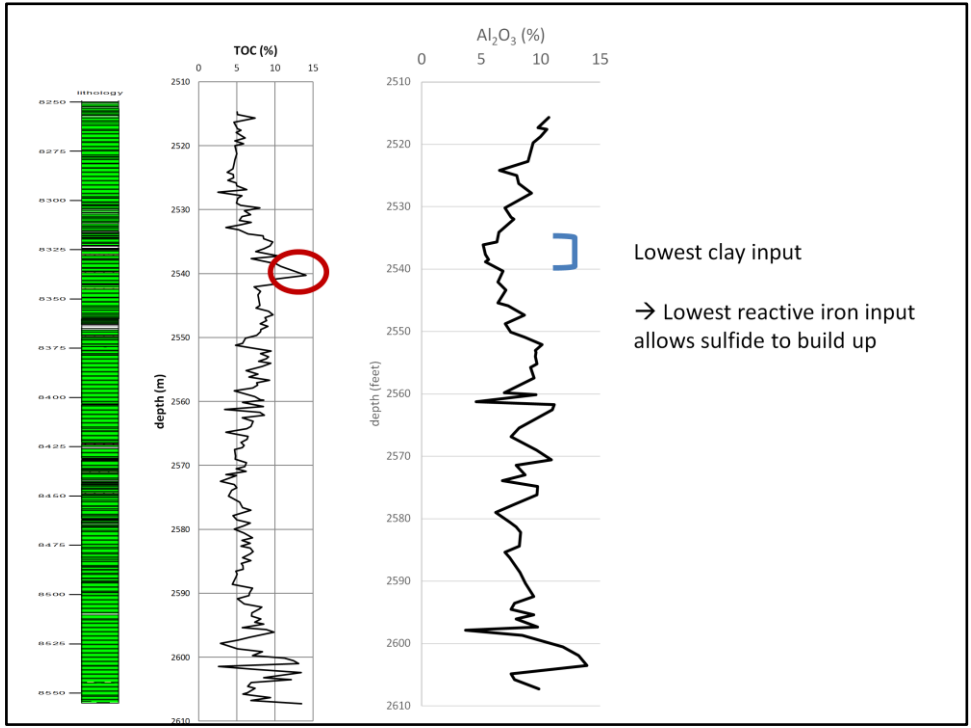
One period of water column euxinia is indicated at same stratigraphic level as in KCC 503 well.


TOC (%)
0
5
10
15
lithology
depth (m)
2510
2520
2530
2540
2550
2560
2570
2580
2590
2600
2610
KCC 503 well
Mo : U enrichment < seawater.
Anoxic but no clear evidence for euxinia
1000
100
10
1
Mo EF
1 X seawater
0.3 X seawater
0.1 X seawater
1
10
100
U EF




Why this one interval for development of euxinia?


lithology
8250
8275
8300
8325
8350
8375
8400
8425
8450
8475
8500
8525
8550
TOC (%)
0
5
10
15
depth (m)
2510
2520
2530
2540
2550
2560
2570
2580
2590
2600
2610
$Al_2O_3$ (%)
0
5
10
15
depth (feet)
2510
2520
2530
2540
2550
2560
2570
2580
2590
2600
2610
Lowest clay input


lithology
TOC (%)
0
5
10
15
depth (m)
2510
2520
2530
2540
2550
2560
2570
2580
2590
2600
2610
$Al_2O_3$ (%)
depth (feet)
Lowest clay input
→ Lowest reactive iron input allows sulfide to build up

## OBSERVATIONS

- In Woodford Shale, biomarker and pyrite framboid data indicate one brief period of water column euxenia that coincides with minimal clay input
- Mo-U enrichment factors permit interpretation of euxinia – if so, euxinic front at or just above sediment-water interface.

## IMPLICATIONS

- A persistent euxinic column should not be assumed even for very organic-rich black shale
- Connection to clay input suggests a different connection between sequence stratigraphy and OM accumulation
- Euxinia more likely in carbonate-rich than clastic-rich shales

## ACKNOWLEDGEMENTS

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