Barite Mobilization in the Upper Devonian Succession of Western New York – Evidence for Anaerobic Methane Oxidation and Methanogenesis during Quasi-Steady State Burial*

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Abstract

The complexity of source rocks reflects the interrelationship among such factors as organic matter type, quantity, and quality, thermal maturity level, and diagenetic and burial history. Sulphate reduction reactions are among the first diagenetic modifications to a potential source rock. Subsequent reactions, notably anaerobic methane oxidation (AMO) and methanogenesis may result in concretionary growth. Small (cm-scale) barite nodules and rosettes concentrated in an ~ 3-m-thick interval at the bottom of the Upper Devonian Hanover Shale of western New York provide insight into what appears to be a quasi-steady state burial history of the Rhinestreet-Hanover shale succession. The nodules, composed principally of barium and sulfur, but also enriched in such trace metals as V, Au, Ni, and Co, formed later than associated carbonate concretions but during the same diagenetic event. Both barite nodules and carbonate concretions precipitated because of AMO at the sulphate-methane transition zone (SMTZ). Episodic reductions in burial rate stabilized the SMTZ enabling the growth of concretions and nodules. Renewal of burial, however, moved the newly formed concretionary horizon into the zone of methanogenesis causing dissolution of authigenic barite and subsequent upward diffusion of barium to the SMTZ where authigenic barite and carbonate formed again. Repeated dissolution-precipitation events, each one recorded by an interval of insoluble carbonate concretions, explains the observed elemental enrichment patterns of the nodules. Preservation of barite nodules at the bottom of the Hanover Shale may reflect the downward shift of the SMTZ induced by accumulation of organic-lean sediment of the middle Hanover Shale (reduced sulphate gradient) and/or the depletion of labile organic matter of the Rhinestreet Shale (reduced methane flux). Ongoing work has recognized similar barium-rich intervals in the upper part of the Marcellus Shale that probably reflect a comparable burial history.

References

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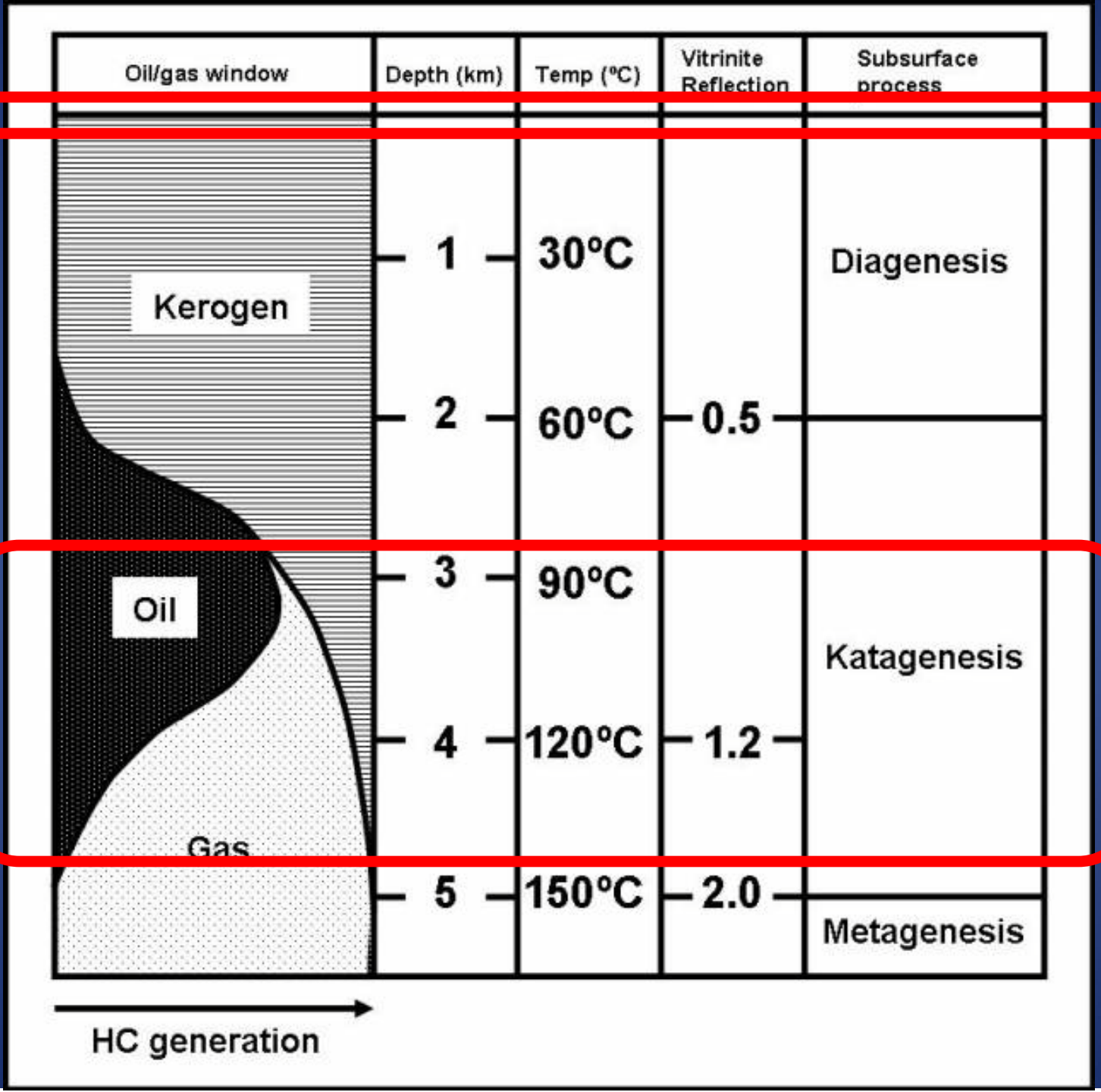
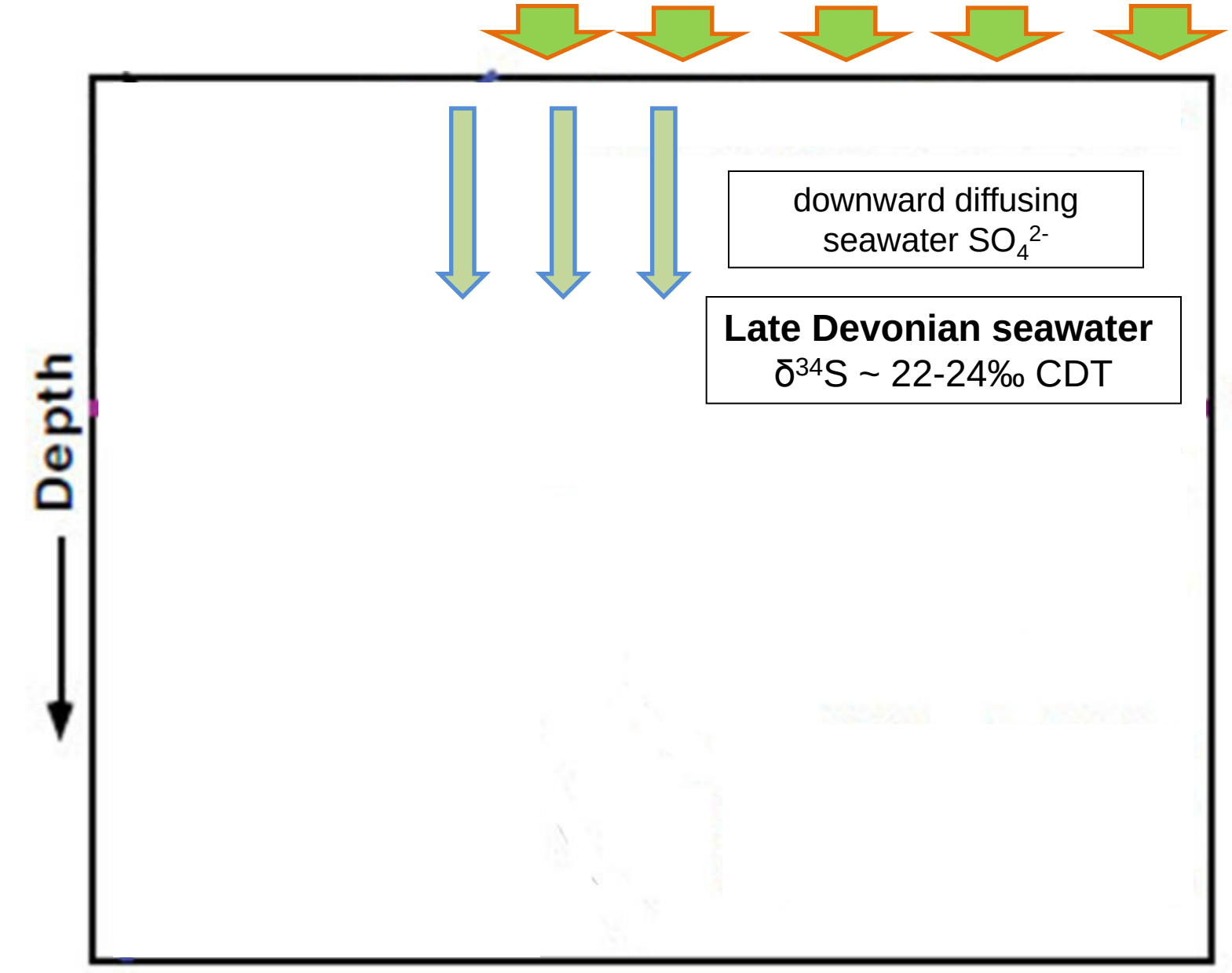
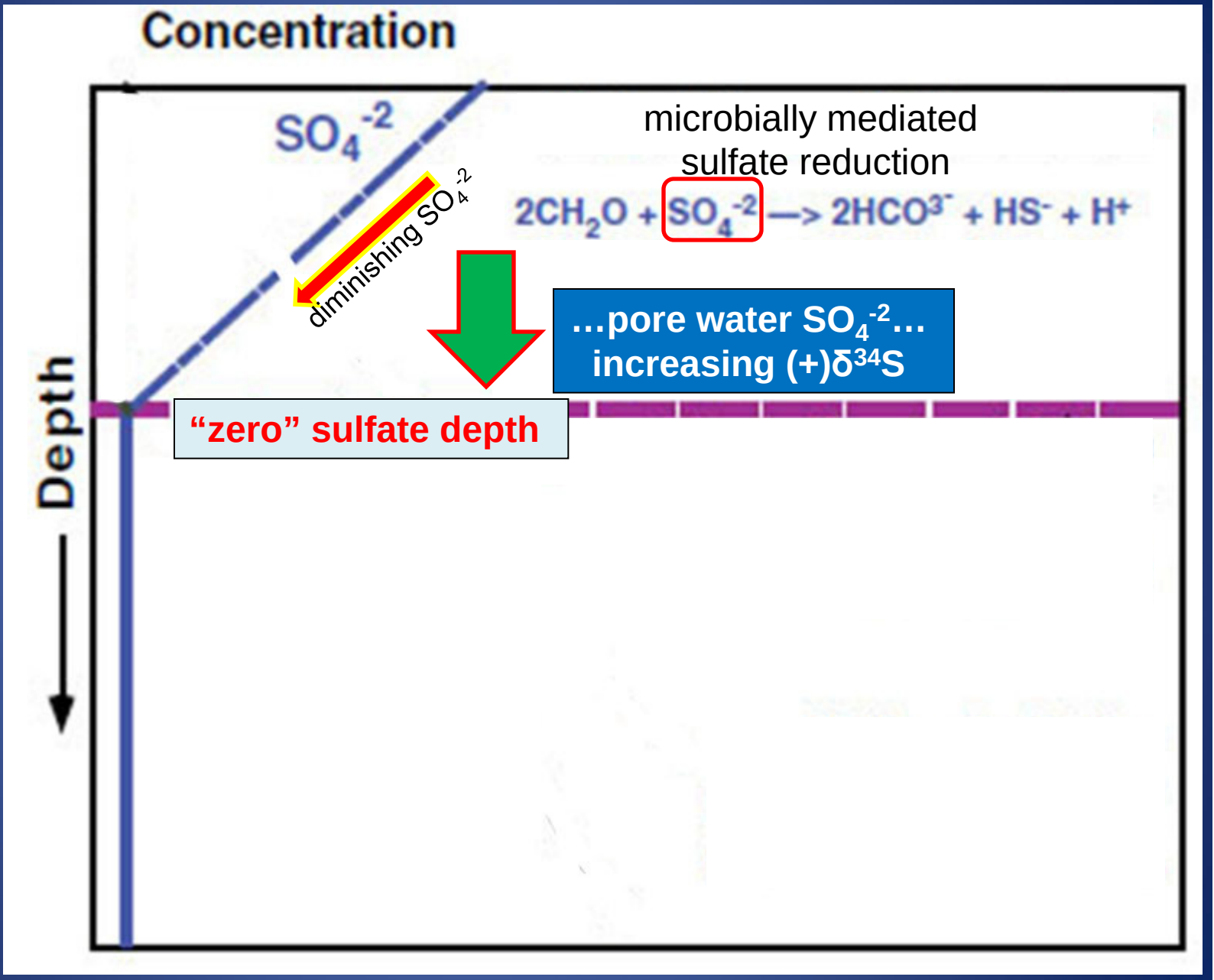

Oil/gas window
Depth (km)
Temp (°C)
Vitrinite Reflection
Subsurface process
Kerogen
Oil
Gas
1
30°C
Diagenesis
2
60°C
0.5
3
90°C
Katagenesis
4
120°C
1.2
5
150°C
2.0
Metagenesis
HC generation

accumulation of organic matter and biobarite



from Rodriguez et al., 2000

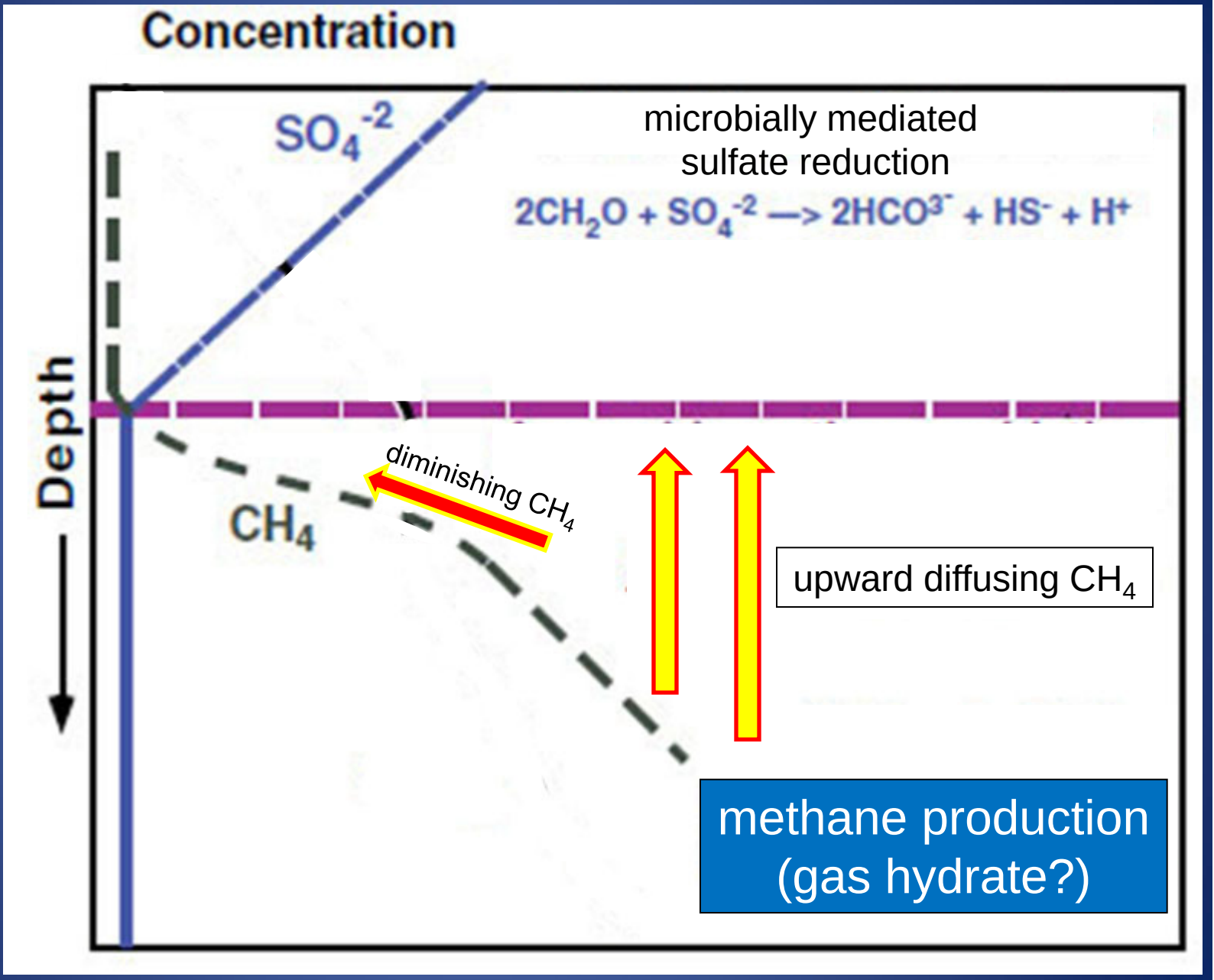
sulfate reduction zone



from Rodriguez et al., 2000

sulfate reduction zone

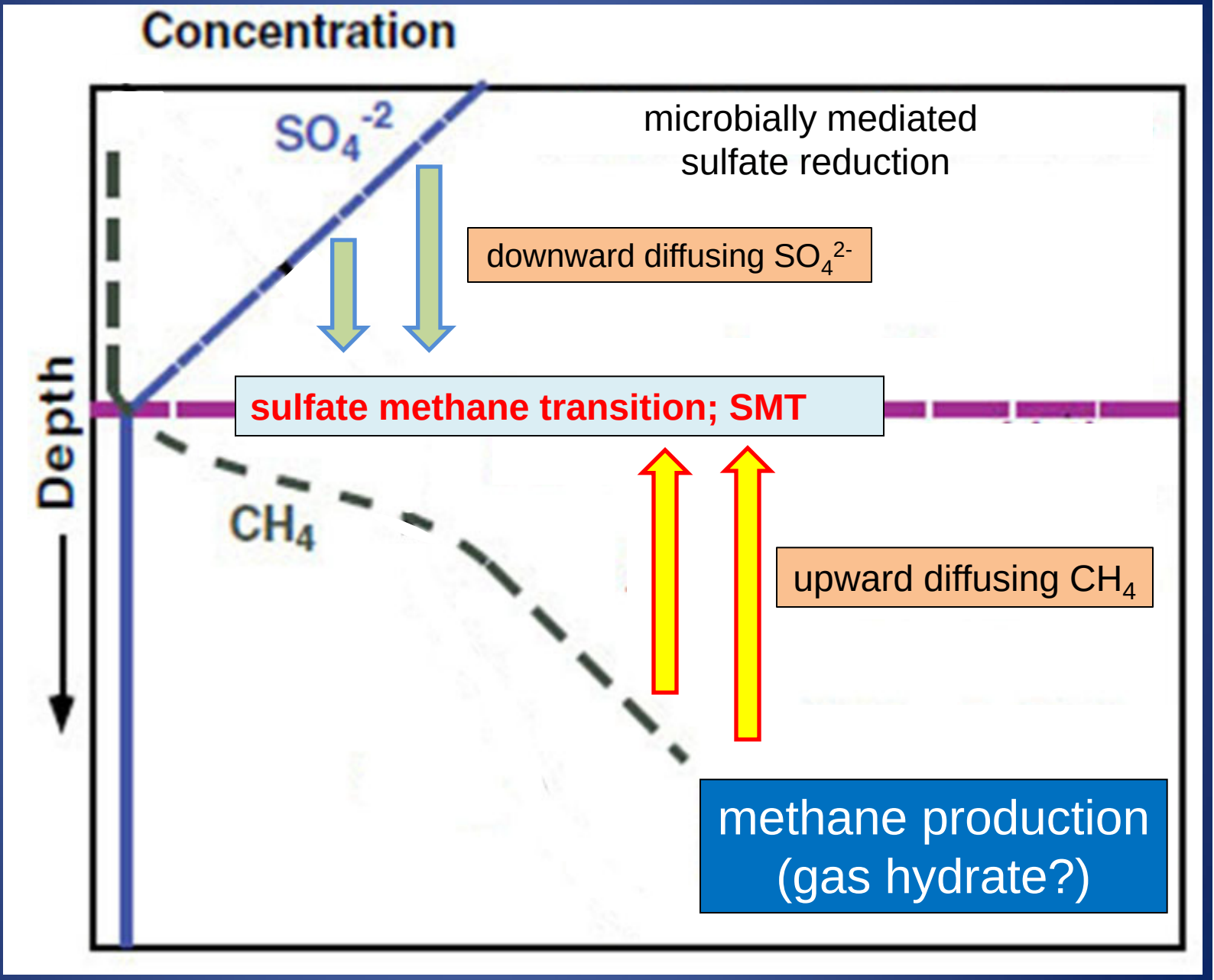
zone of methanogenesis



from Rodriguez et al., 2000

sulfate reduction zone

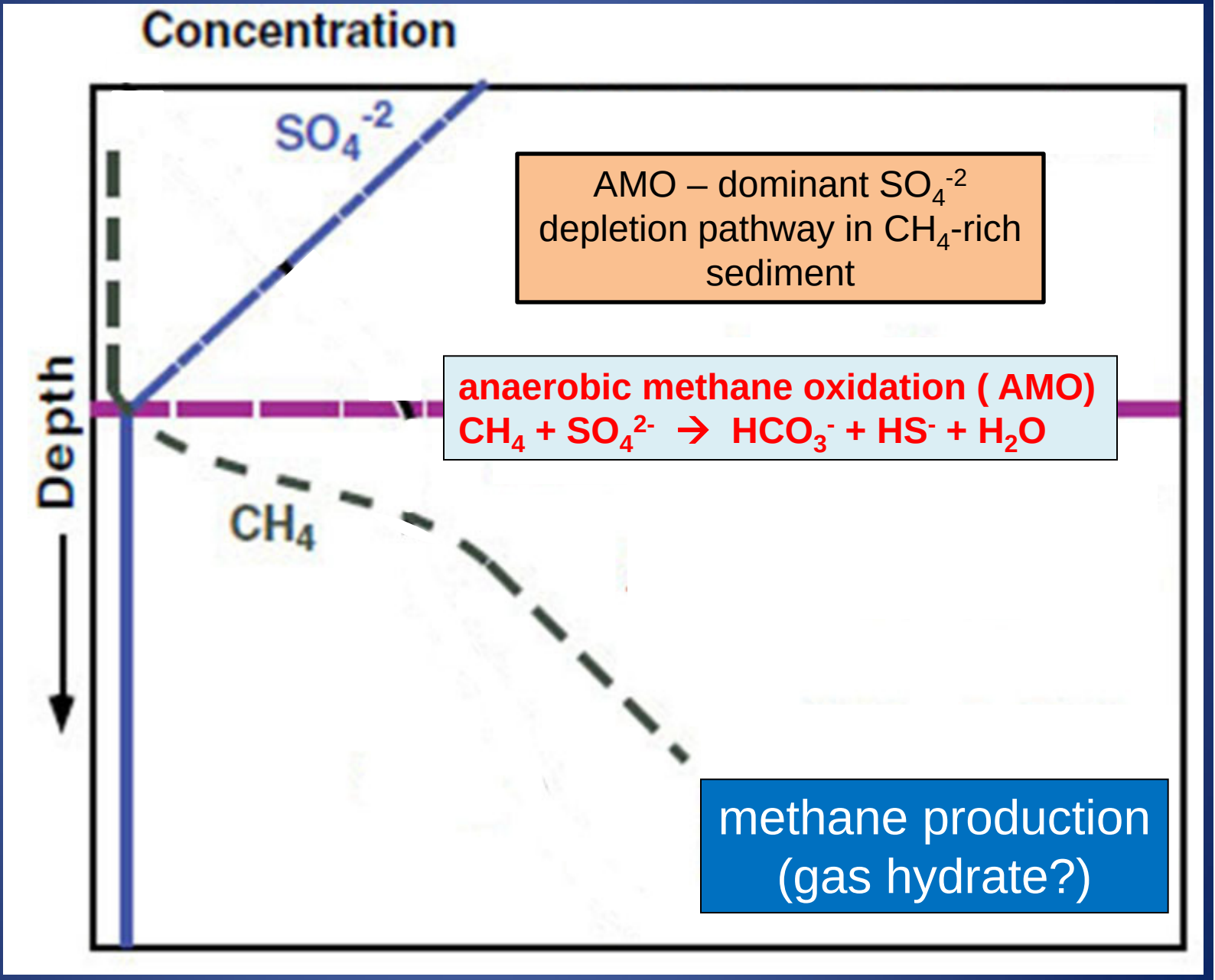
zone of methanogenesis



from Rodriguez et al., 2000

sulfate reduction zone

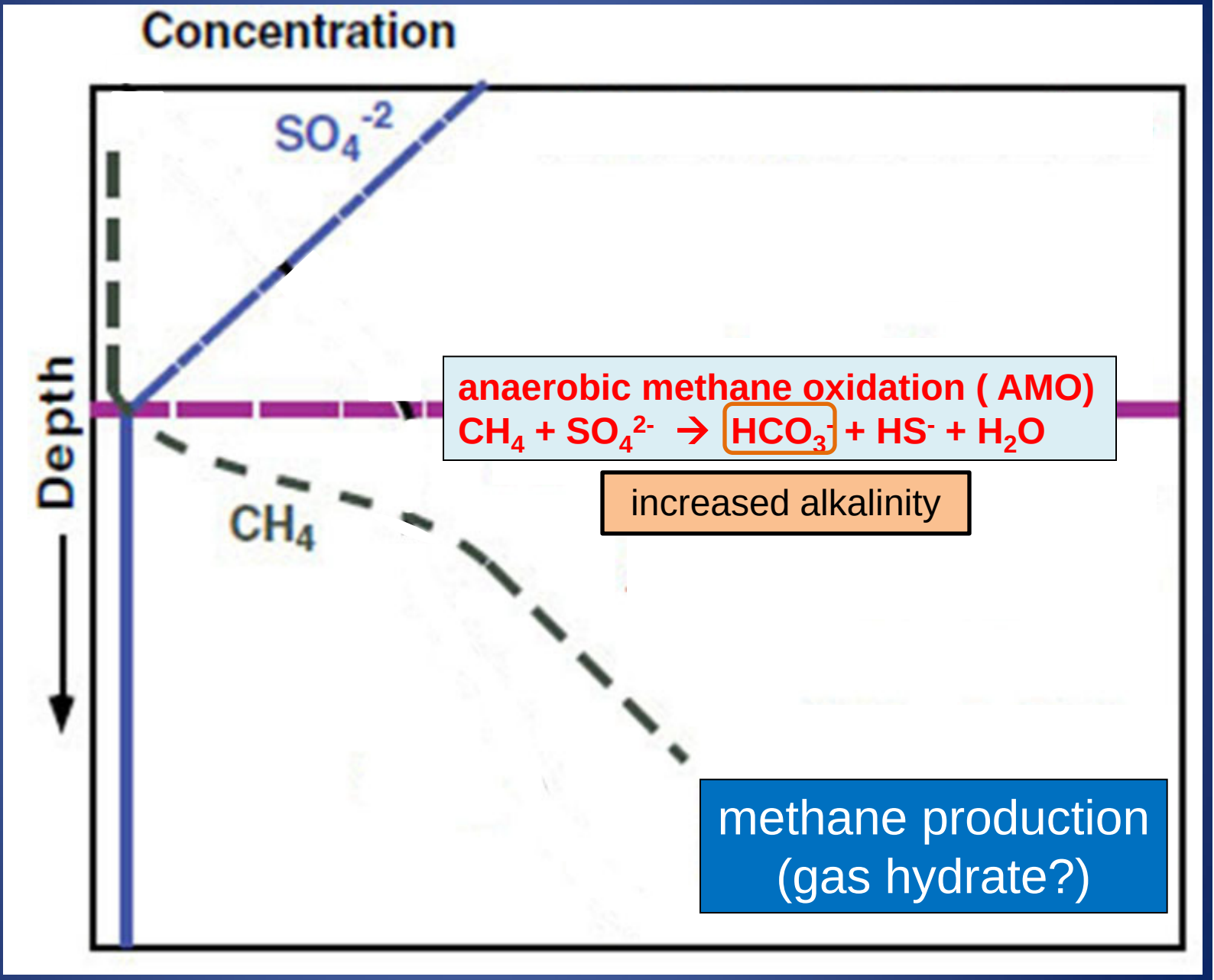
zone of methanogenesis



from Rodriguez et al., 2000

sulfate reduction zone

zone of methanogenesis



from Rodriguez et al., 2000

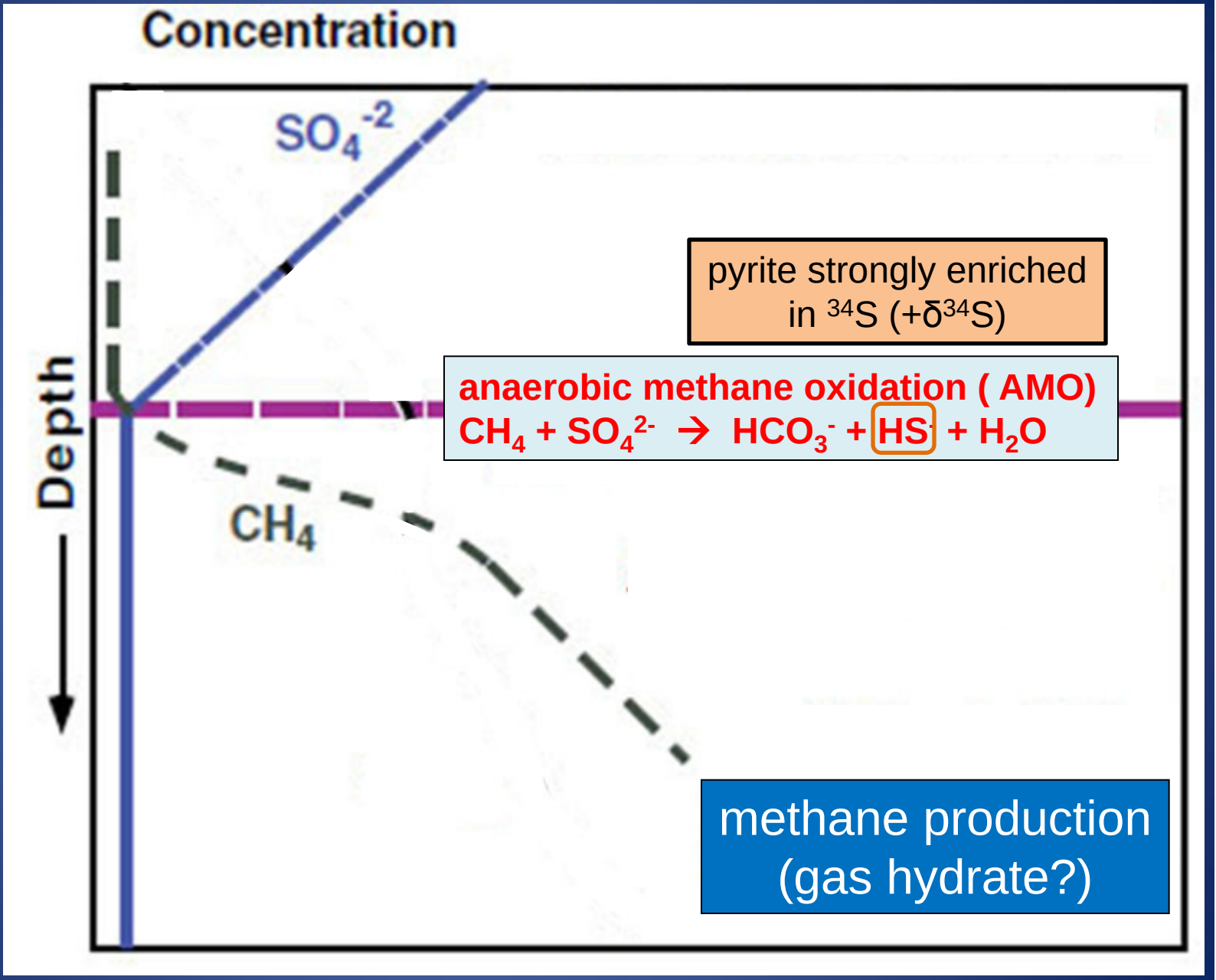
…carbonate concretion horizons…

Rhinestreet Shale

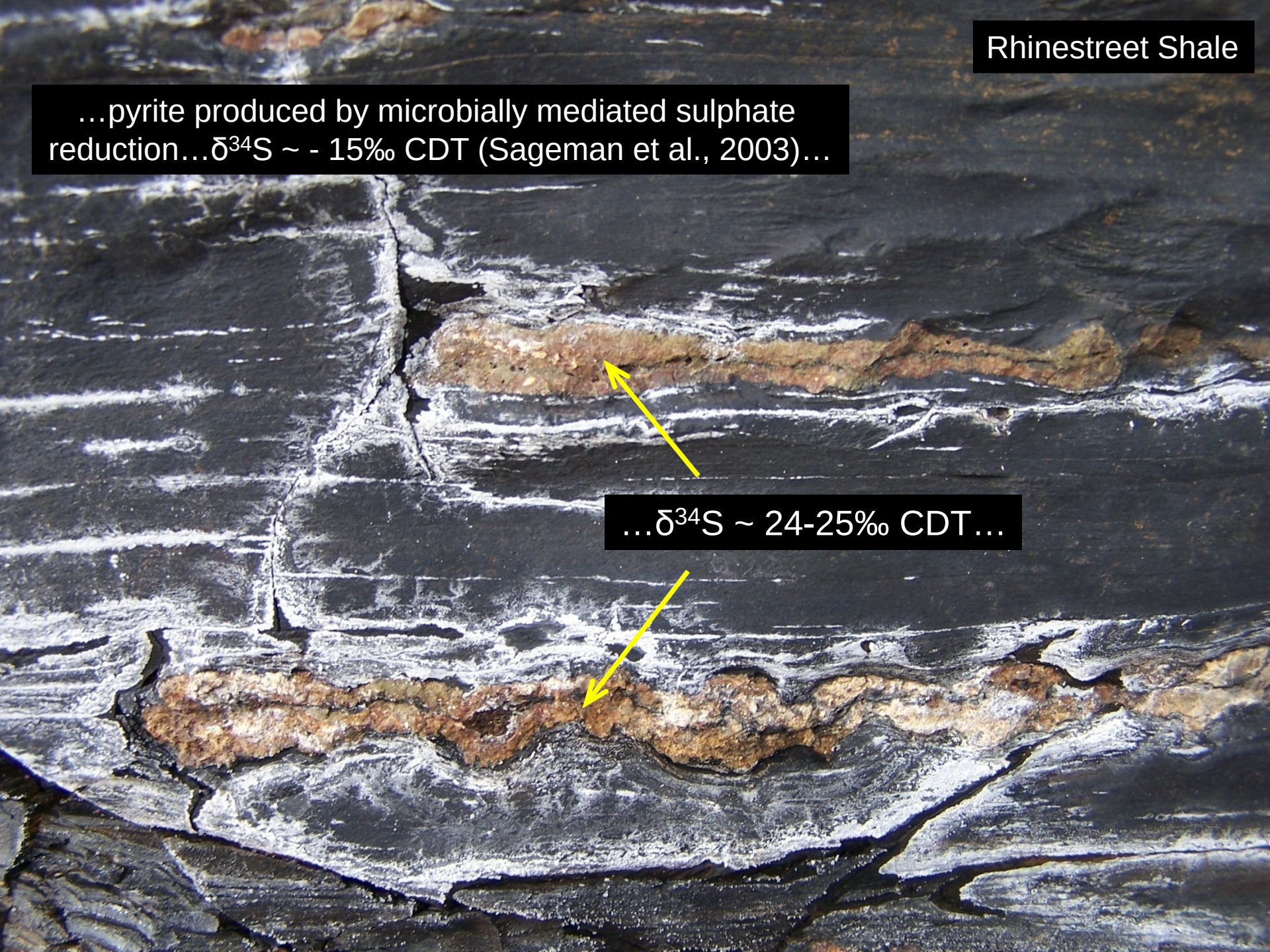
…$\delta^{13}C$ ~ -8 to -14‰…
indicative of AMO (Rodriguez et al., 2000)

sulfate reduction zone

zone of methanogenesis

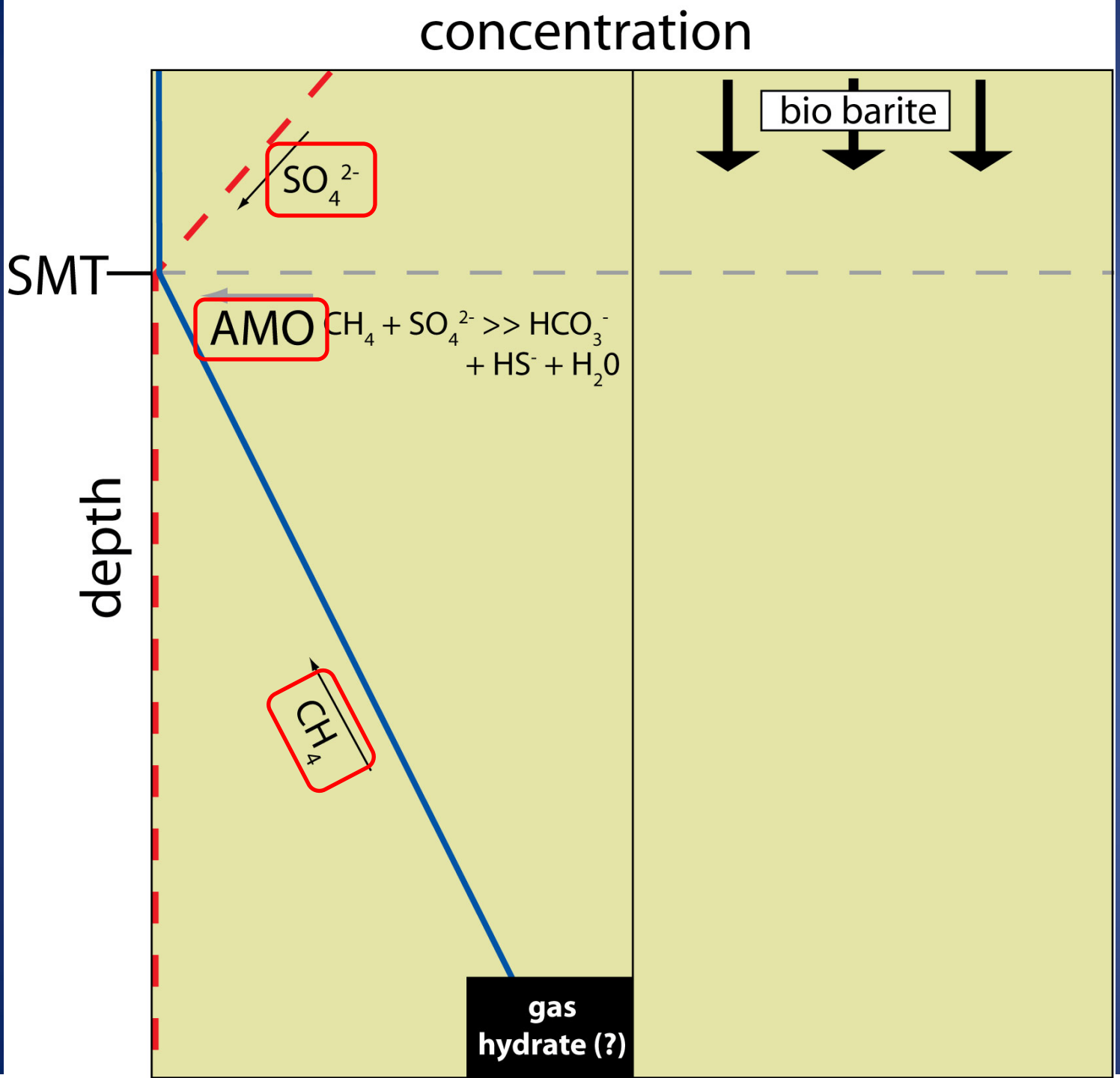


from Rodriguez et al., 2000

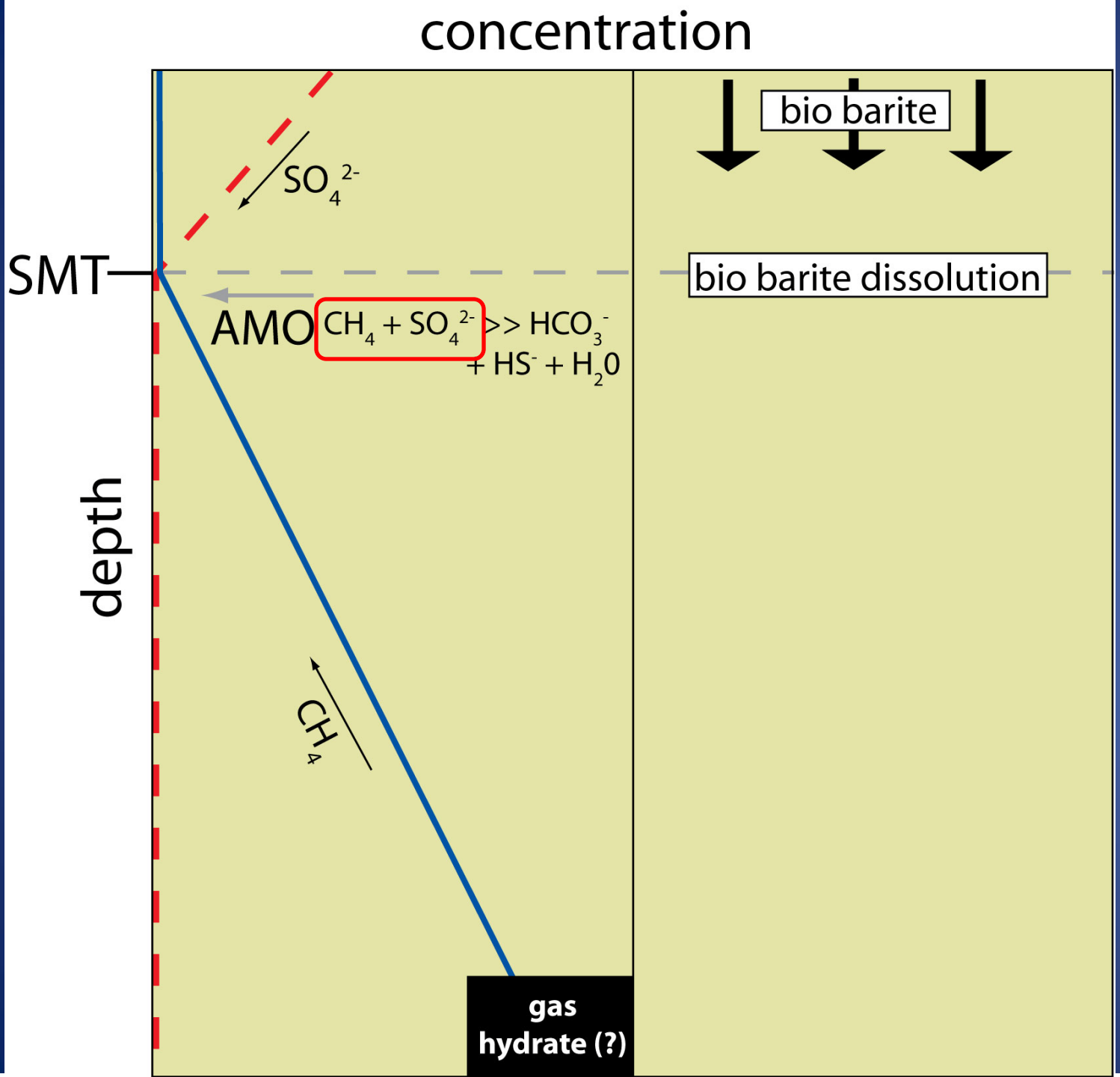

Rhinestreet Shale
…pyrite produced by microbially mediated sulphate reduction…δ34S ~ - 15‰ CDT (Sageman et al., 2003)…
…δ34S ~ 24-25‰ CDT…

…“fossil” sulfate-methane transition zone…

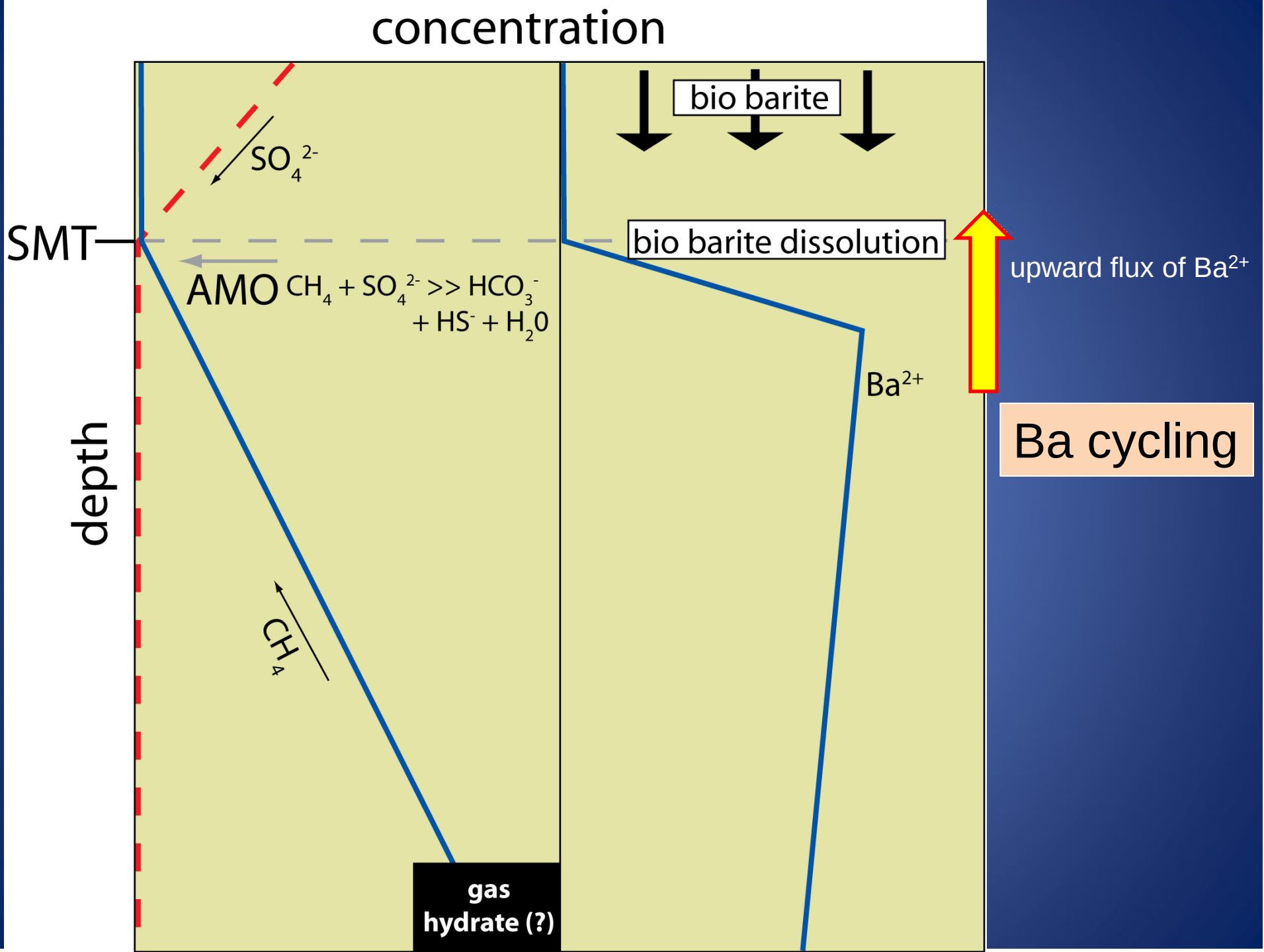
…evidence of AMO – methane-rich sediment (gas hydrate?)…

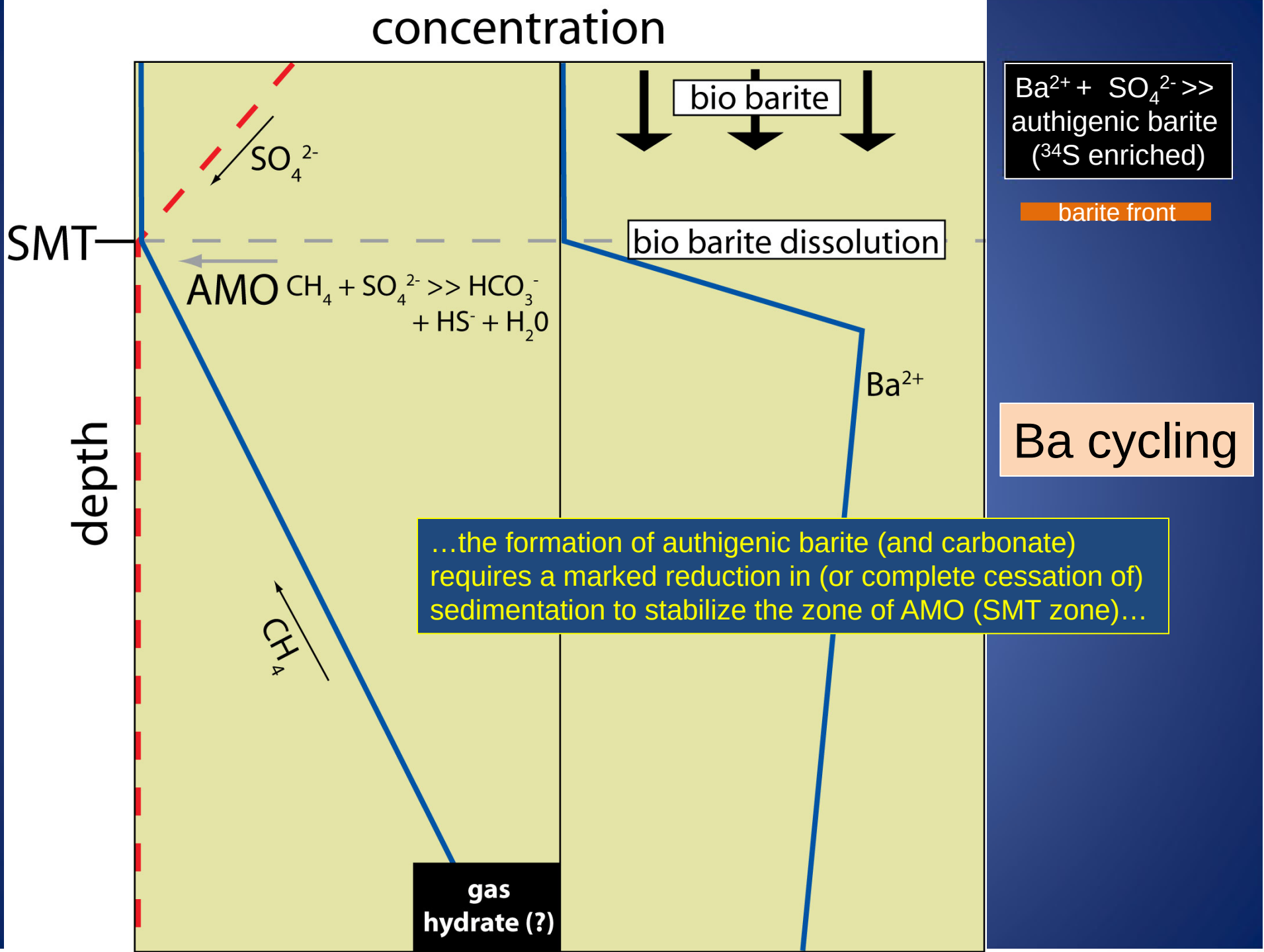

concentration
bio barite
SO_4^{2-}
SMT
AMO
$CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
depth
CH_4
gas hydrate (?)

Ba cycling

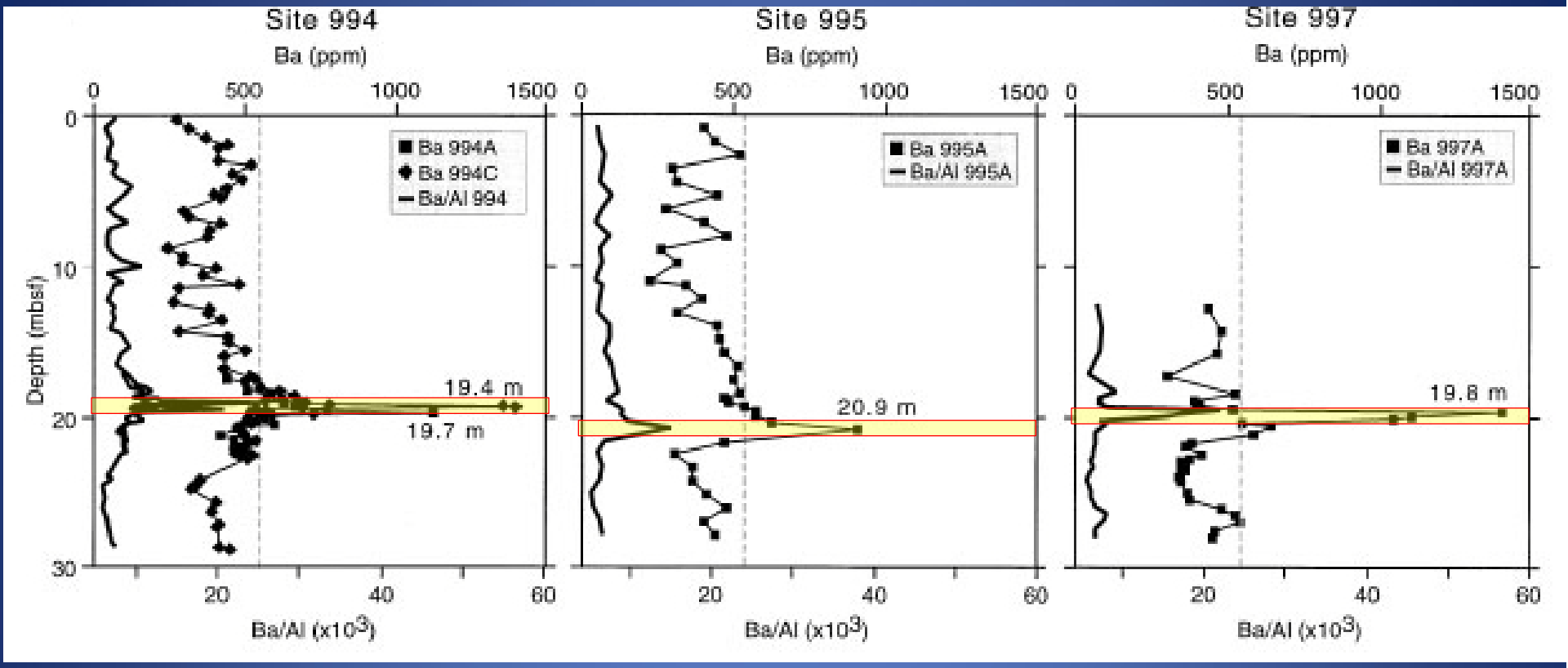

concentration
depth
SMT
SO_4^{2-}
bio barite
bio barite dissolution
AMO
$CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
CH_4
gas hydrate (?)

Ba cycling

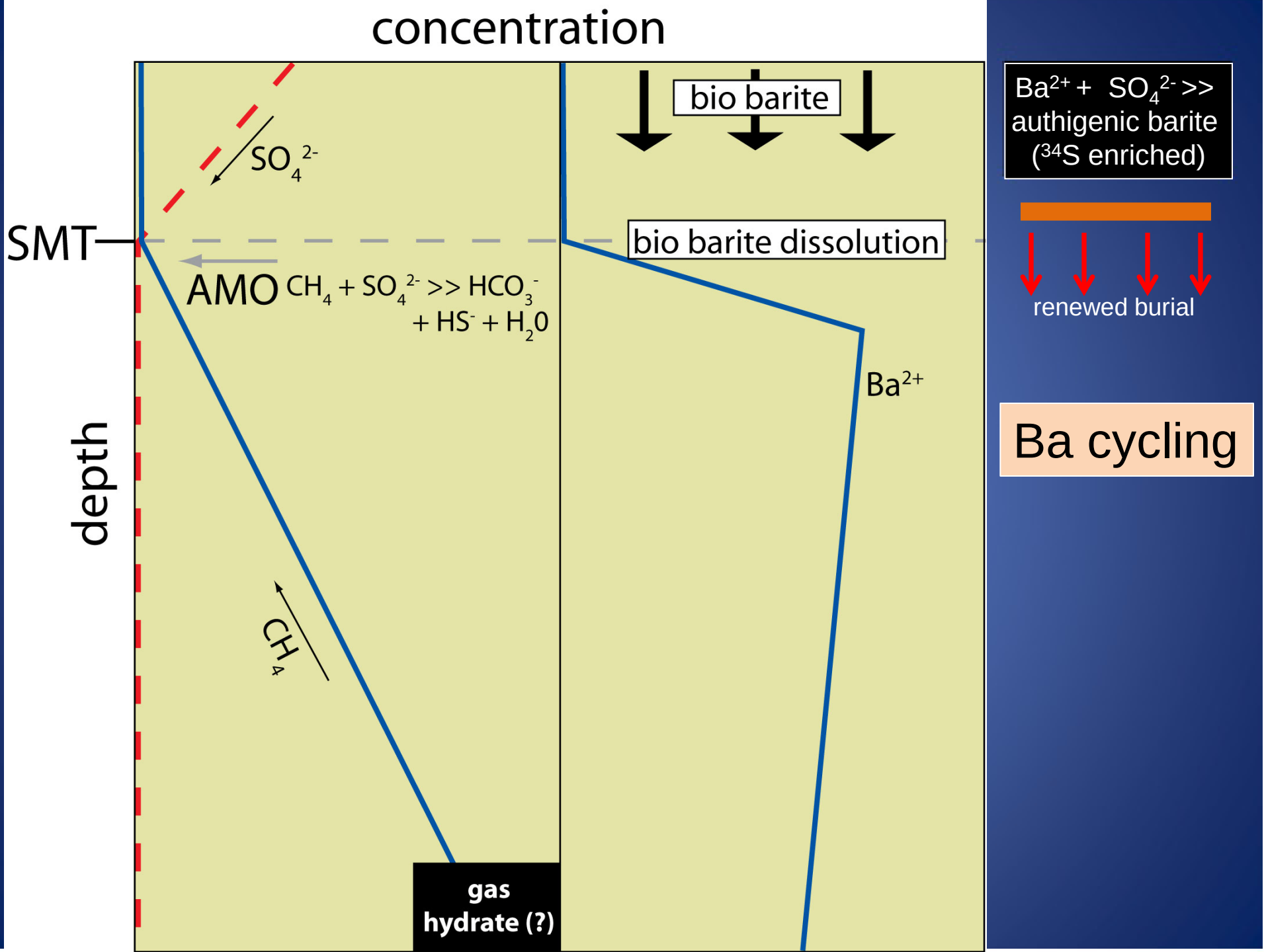

concentration
bio barite
SO_4^{2-}
SMT
bio barite dissolution
upward flux of Ba^{2+}
AMO $CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
Ba^{2+}
depth
Ba cycling
CH_4
gas hydrate (?)

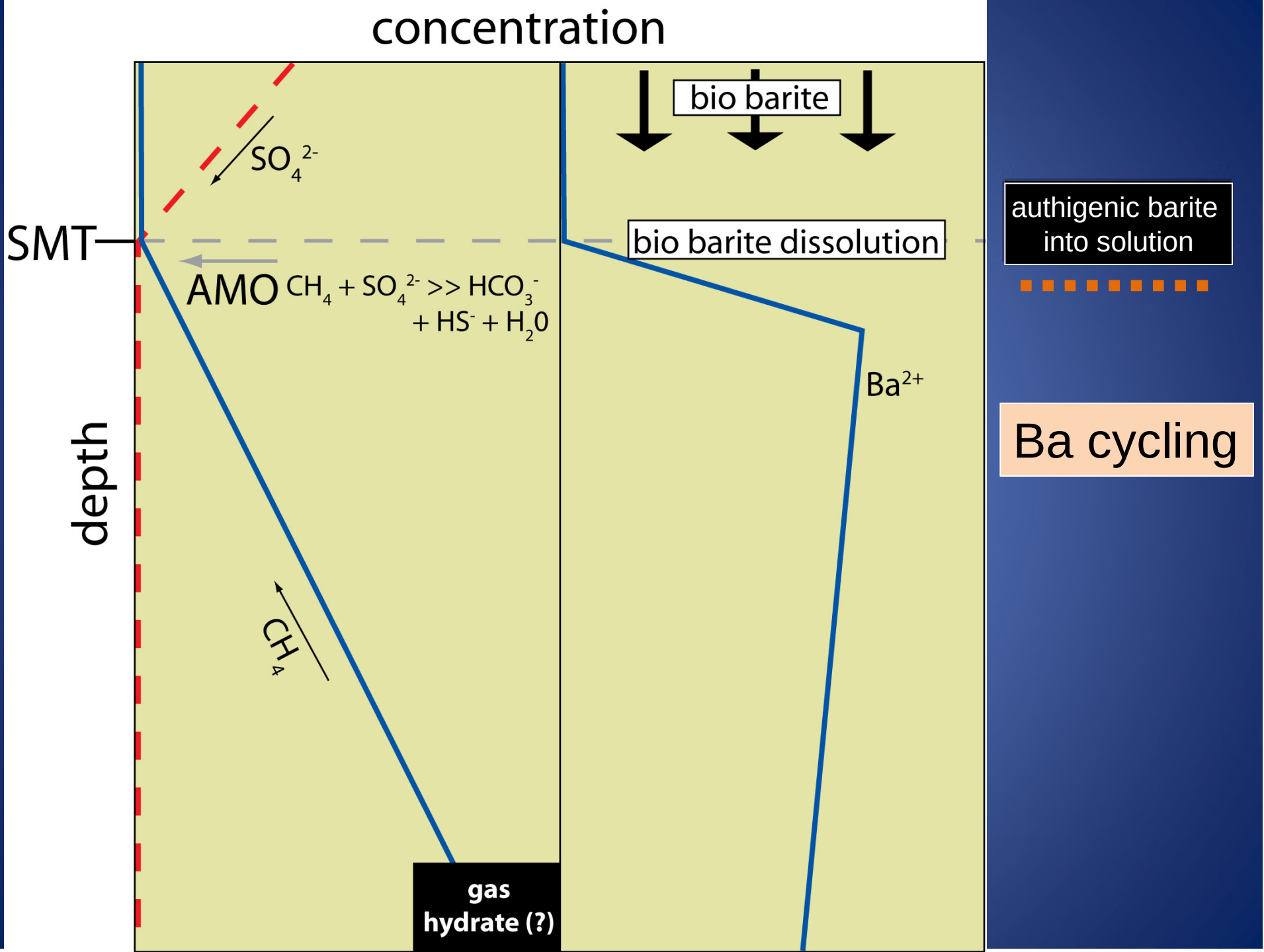

concentration
depth
SMT
SO_4^{2-}
bio barite
Ba^{2+} + SO_4^{2-} >> authigenic barite (^{34}S enriched)
barite front
bio barite dissolution
AMO $CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
Ba^{2+}
Ba cycling
…the formation of authigenic barite (and carbonate) requires a marked reduction in (or complete cessation of) sedimentation to stabilize the zone of AMO (SMT zone)…
CH_4
gas hydrate (?)

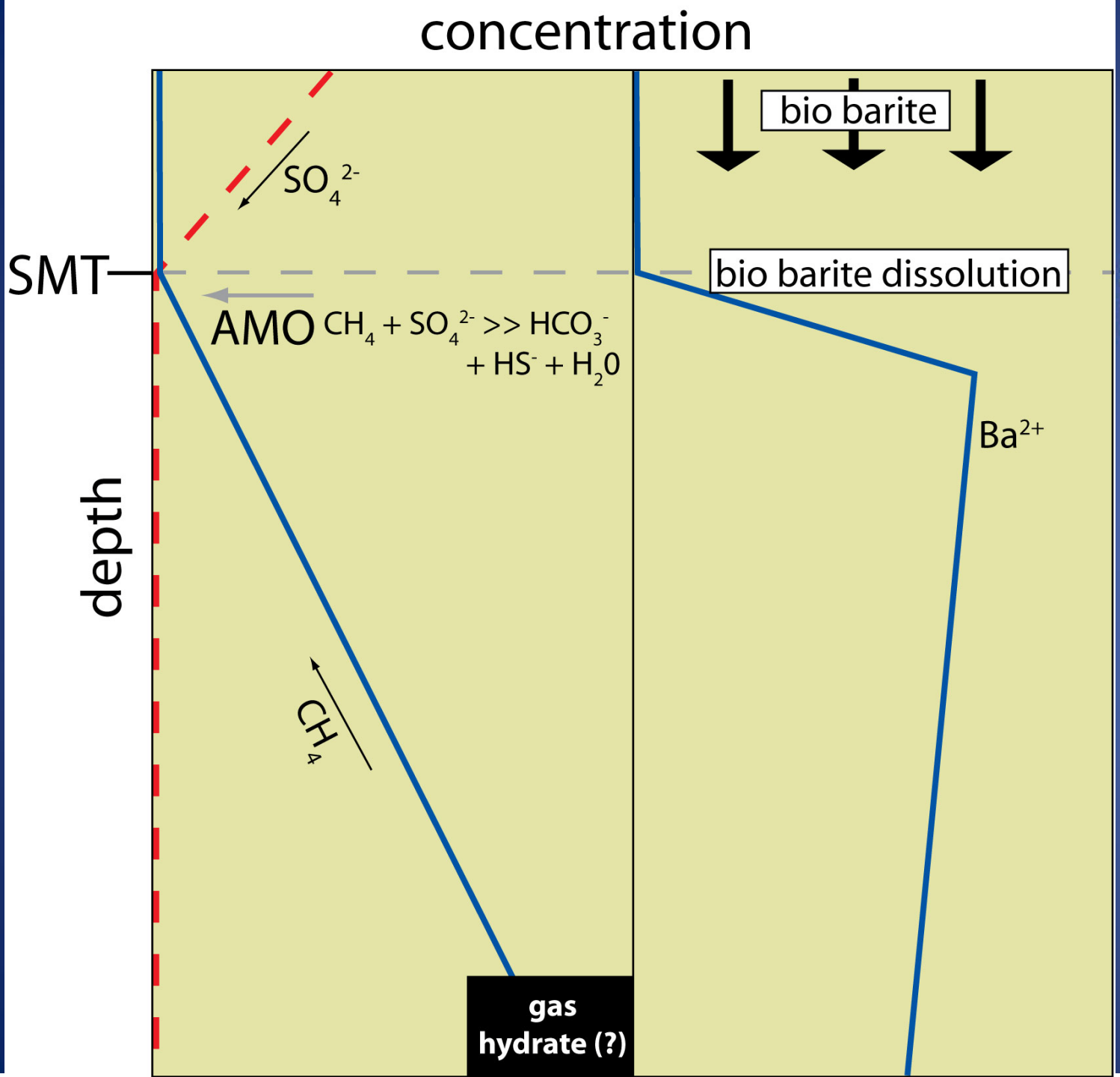
barite fronts; Blake Ridge

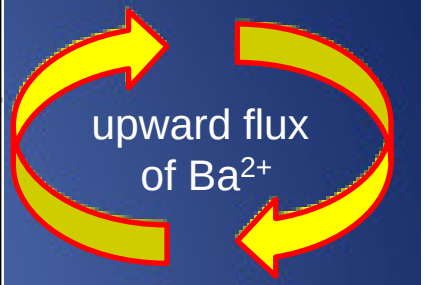


Dickens, 2001


concentration
depth
SMT
SO_4^{2-}
AMO $CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
CH_4
gas hydrate (?)
bio barite
bio barite dissolution
Ba^{2+}
$Ba^{2+} + SO_4^{2-} >>$ authigenic barite (^{34}S enriched)
renewed burial
Ba cycling

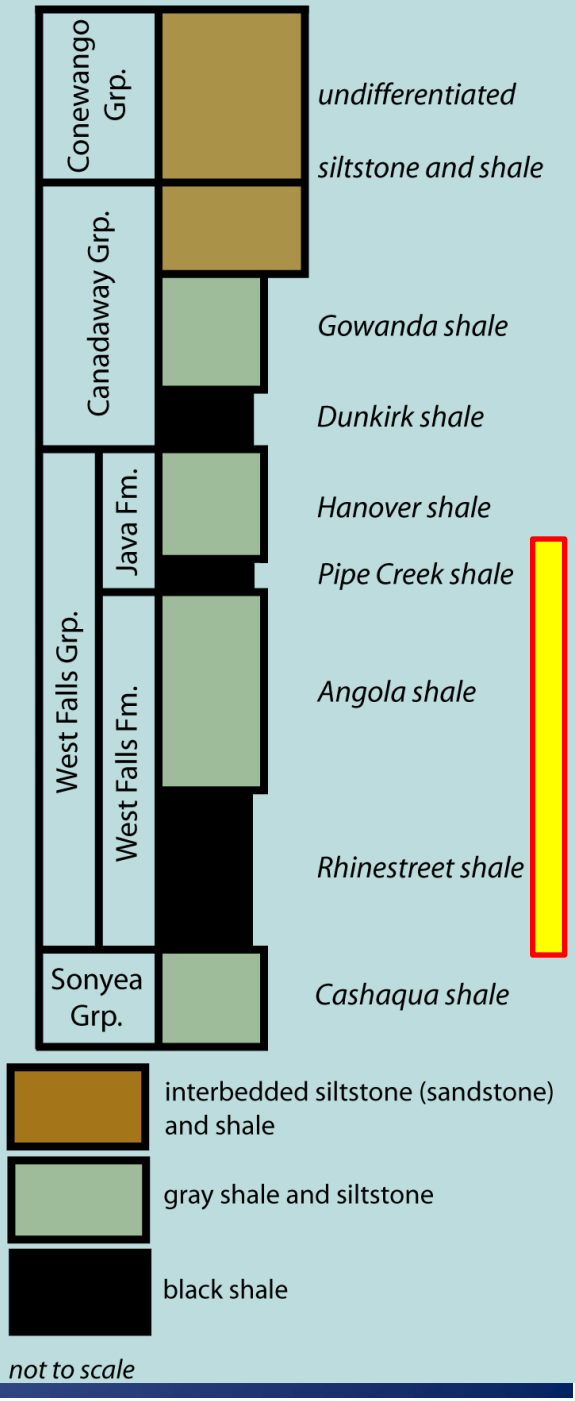

concentration
depth
SMT
SO_4^{2-}
AMO $CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
CH_4
bio barite
bio barite dissolution
Ba^{2+}
gas hydrate (?)
authigenic barite into solution
Ba cycling

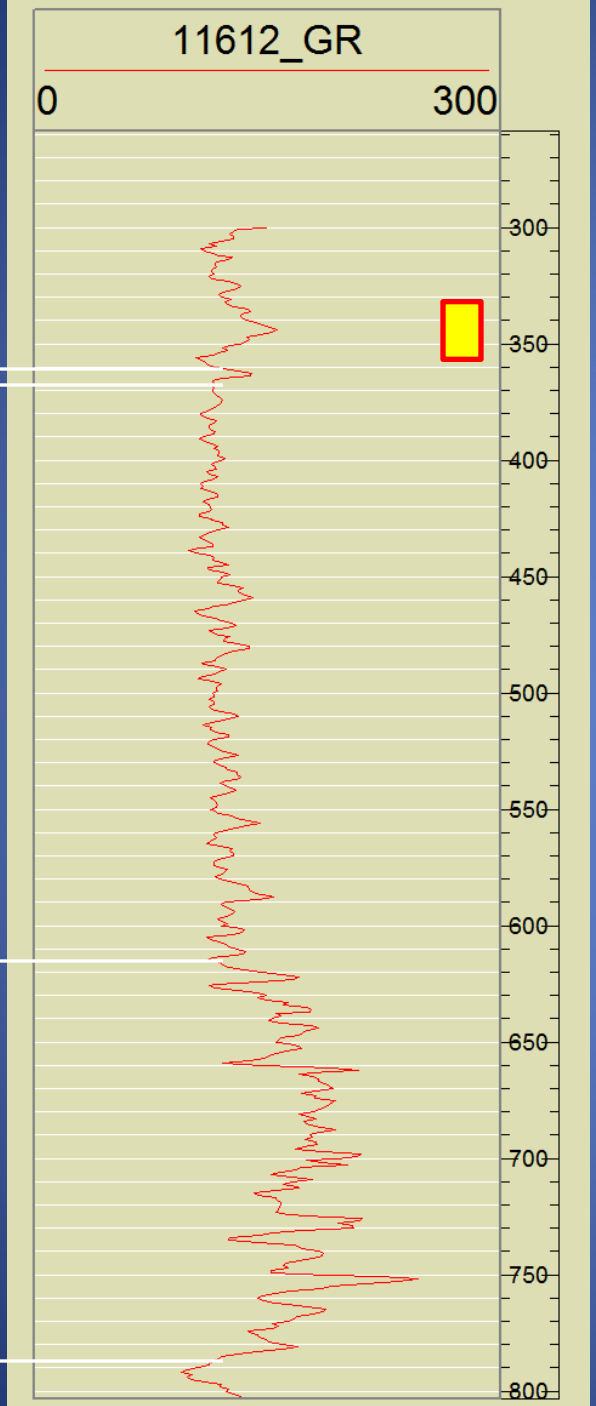

concentration
bio barite
SO_4^{2-}
SMT
bio barite dissolution
AMO $CH_4 + SO_4^{2-} >> HCO_3^- + HS^- + H_20$
Ba^{2+}
depth
CH_4
gas hydrate (?)


upward flux of Ba^{2+}

Ba cycling


New York State
44°
42°
78°
76°
74°
Lake
Erie
Sonyea Grp.
Cazenovia
Crk.
East
Aurora
Hamburg
West
Java Fm.
Silver Creek
Dunkirk
Silver
Crk.
Canadaway
Grp.
Walnut
Crk.
Cattaraugus
Crk.
Canadaway
Crk.
N
0
15
30 km
Conewango Grp.


Conewango Grp.
undifferentiated
siltstone and shale
Canadaway Grp.
Gowanda shale
Dunkirk shale
West Falls Grp.
Java Fm.
Hanover shale
Pipe Creek shale
West Falls Fm.
Angola shale
Rhinestreet shale
Sonyea Grp.
Cashaqua shale
interbedded siltstone (sandstone) and shale
gray shale and siltstone
black shale
not to scale



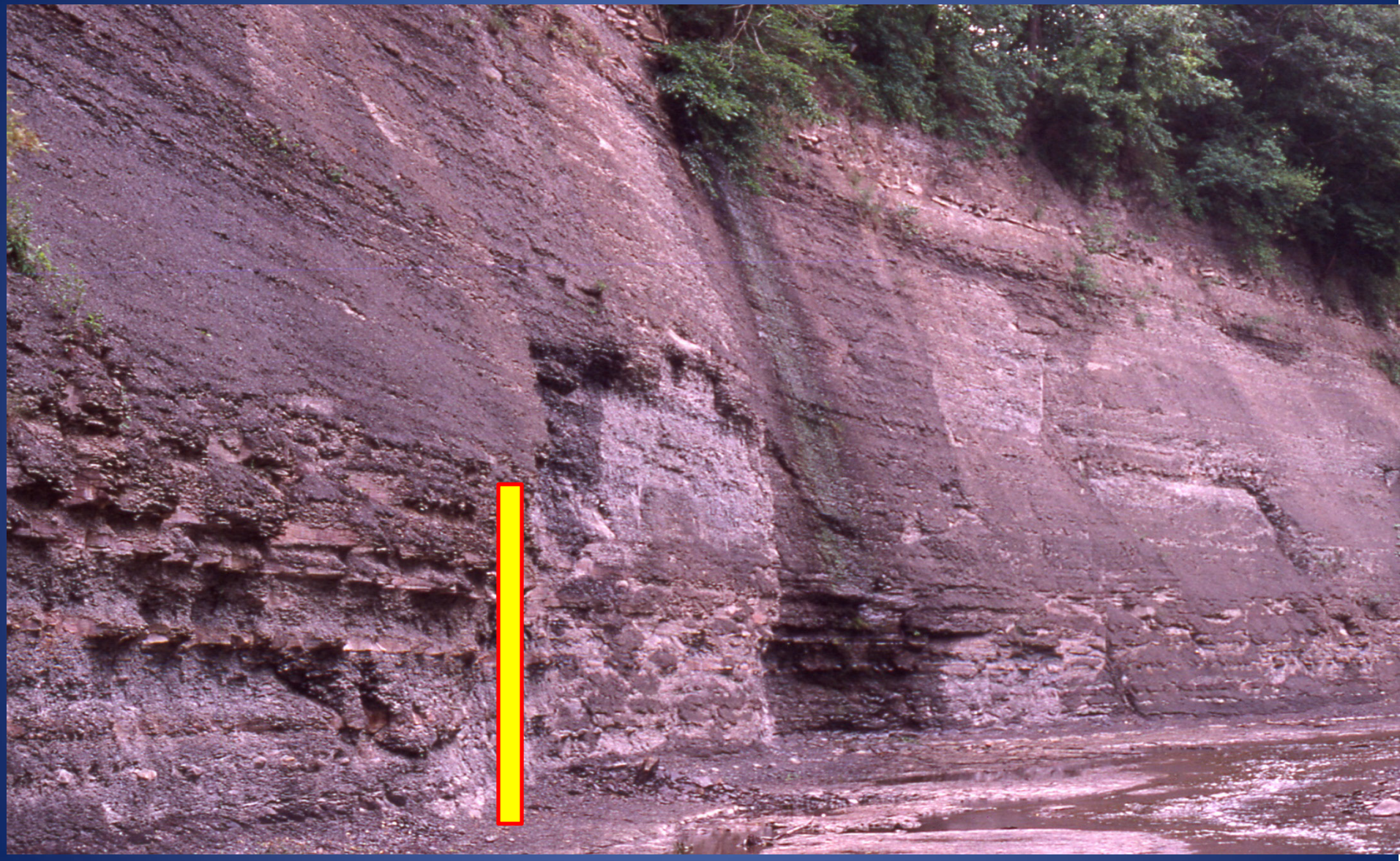
Hanover Shale

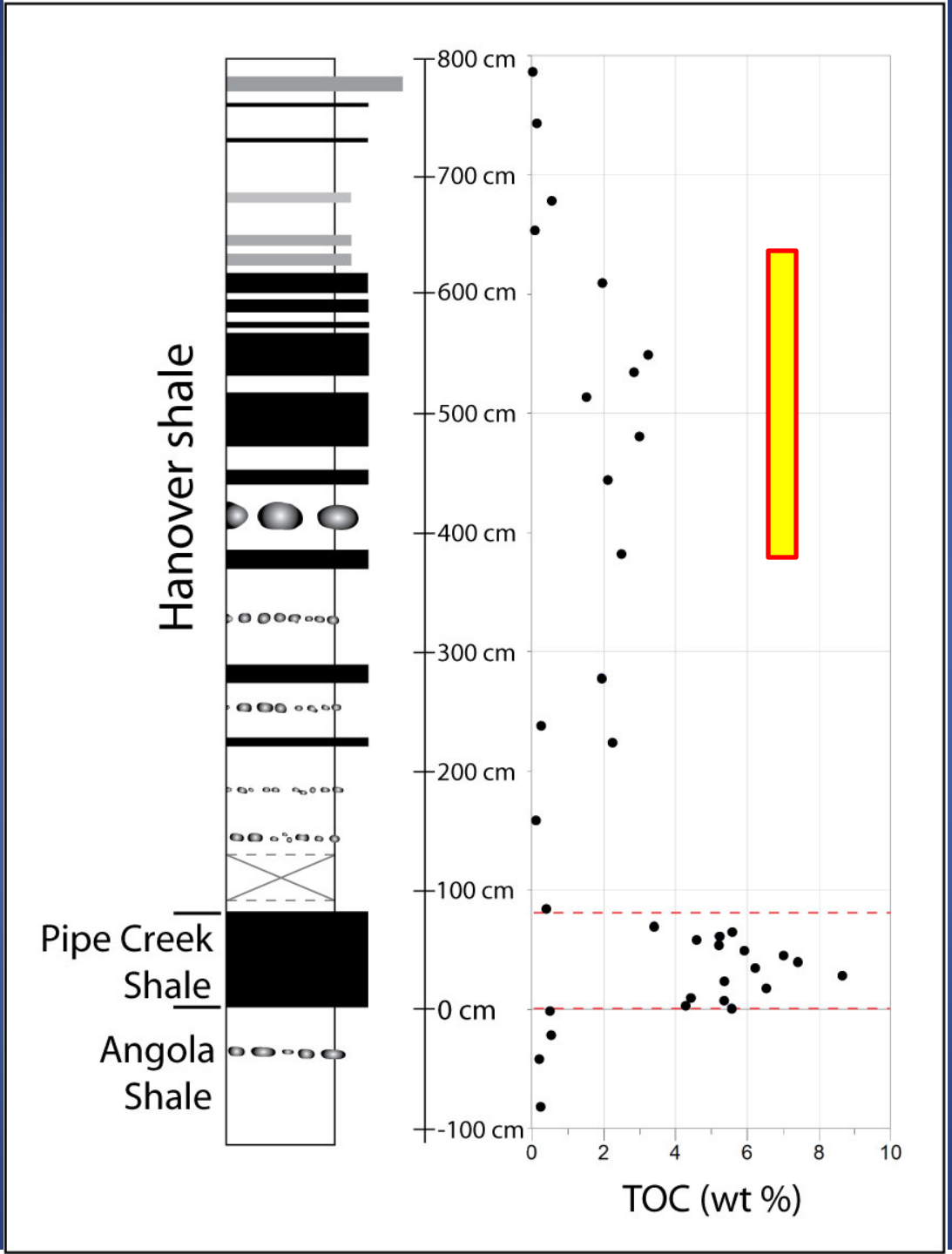
Pipe Creek Shale

Angola Shale

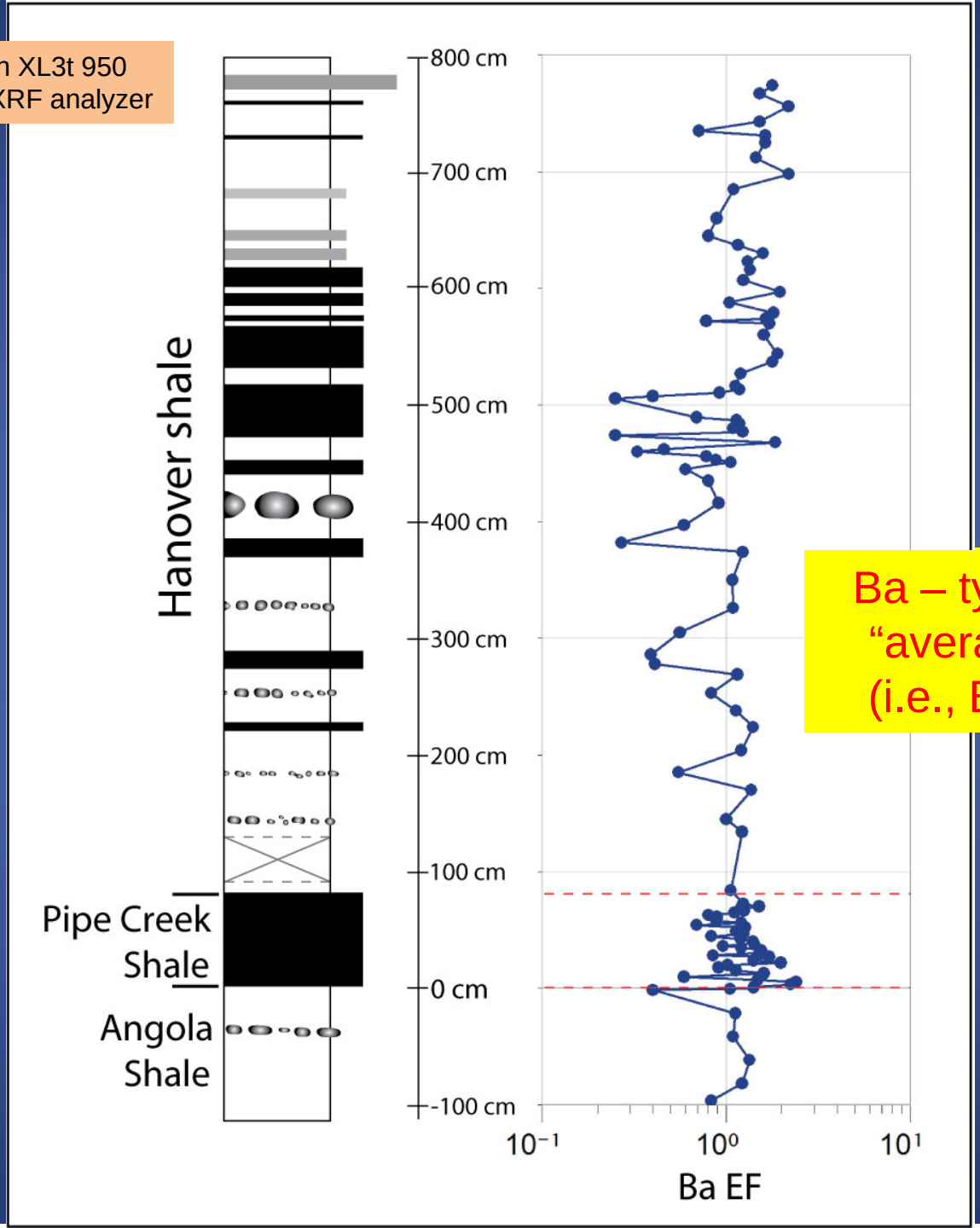
Rhinestreet Shale

barite nodule interval

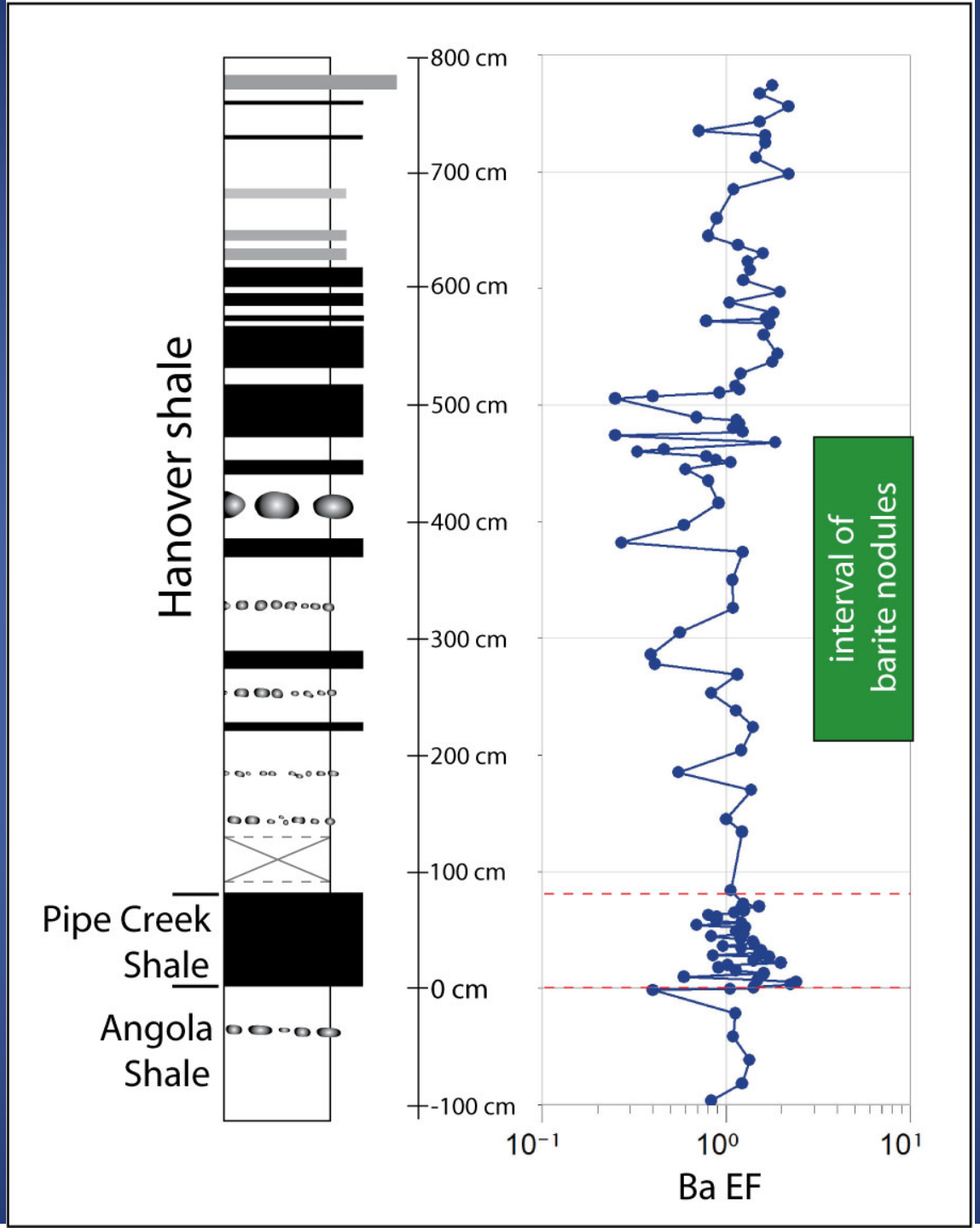



Hanover shale
Pipe Creek Shale
Angola Shale
800 cm
700 cm
600 cm
500 cm
400 cm
300 cm
200 cm
100 cm
0 cm
-100 cm
0
2
4
6
8
10
TOC (wt %)

Thermo Scientific Niton XL3t 950
GOLDD+…handheld XRF analyzer

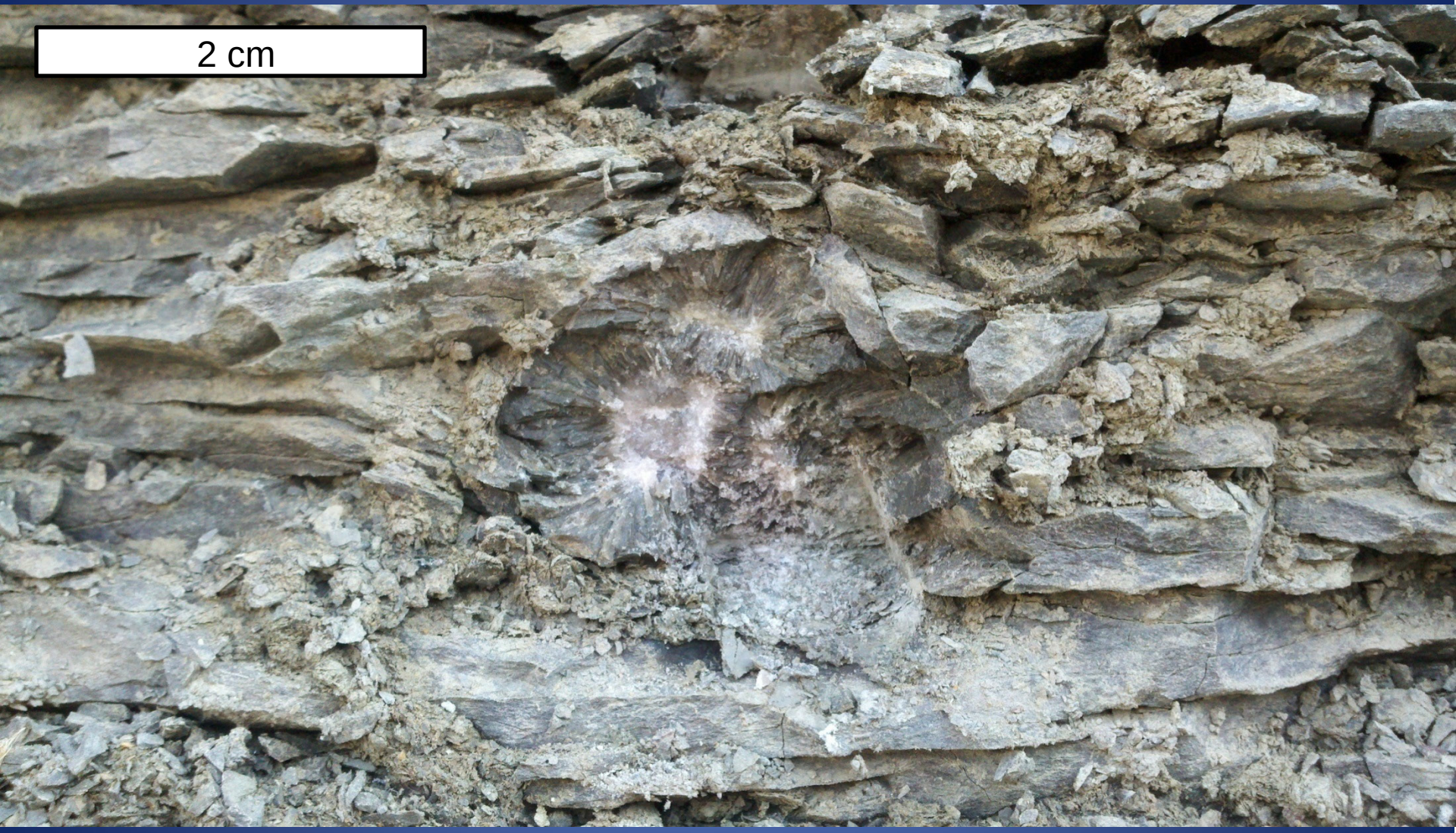


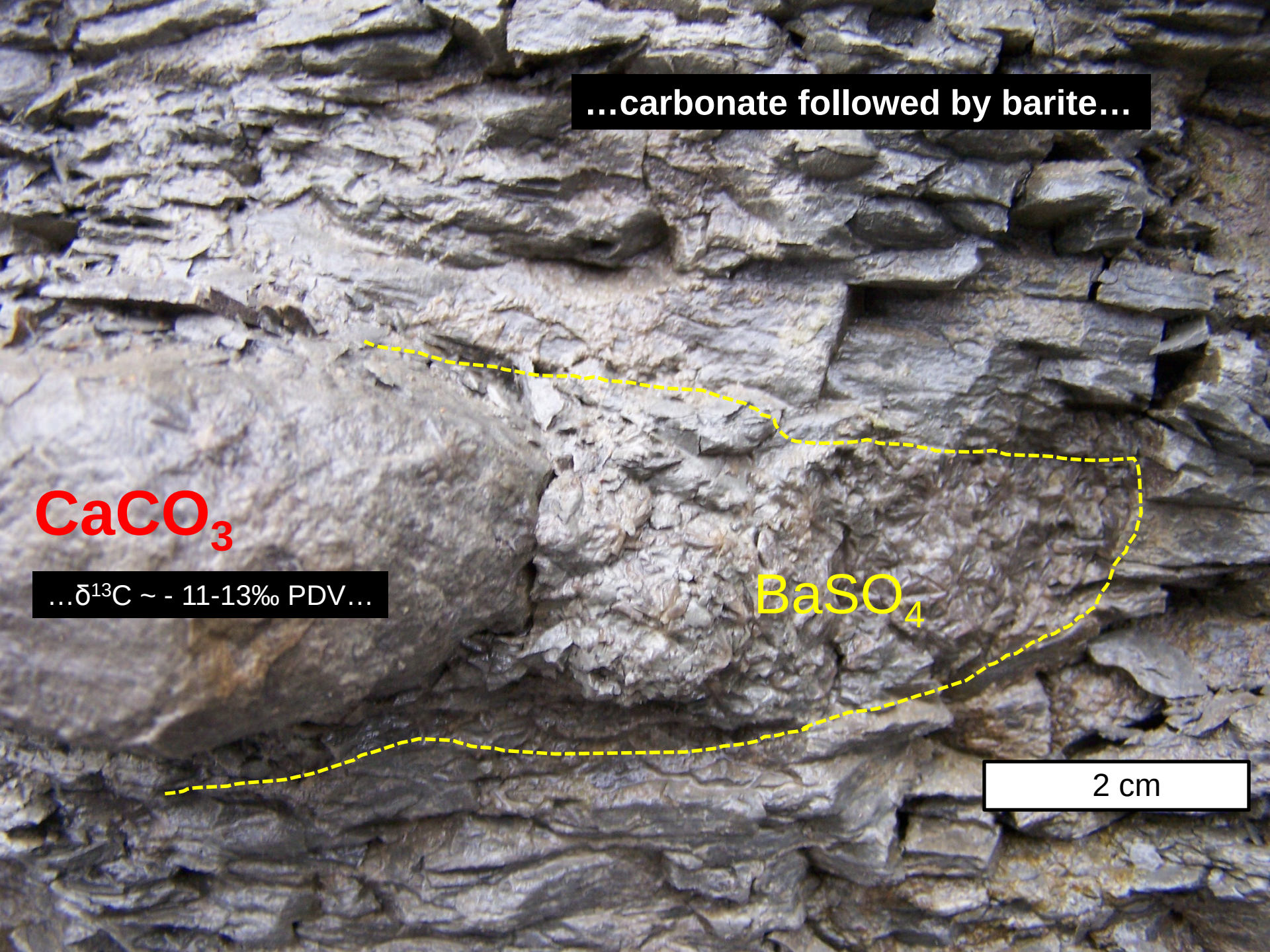
Ba – typical of an "average shale" (i.e., Ba EF ≈ 1)


Hanover shale
Pipe Creek Shale
Angola Shale
800 cm
700 cm
600 cm
500 cm
400 cm
300 cm
200 cm
100 cm
0 cm
-100 cm
interval of barite nodules
10^{-1}
10^{0}
10^{1}
Ba EF

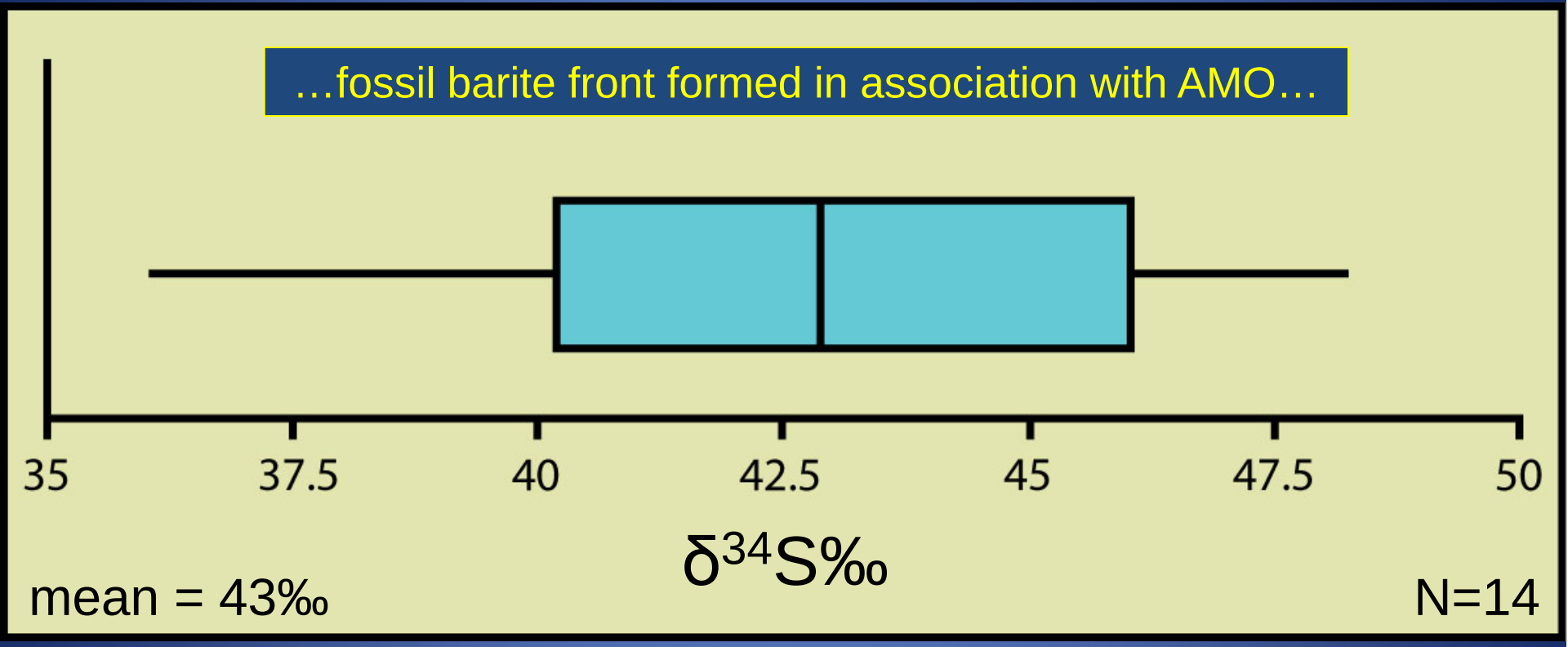

15 CM
UNIVERSITY
OF WYOMING


2 cm


2 cm

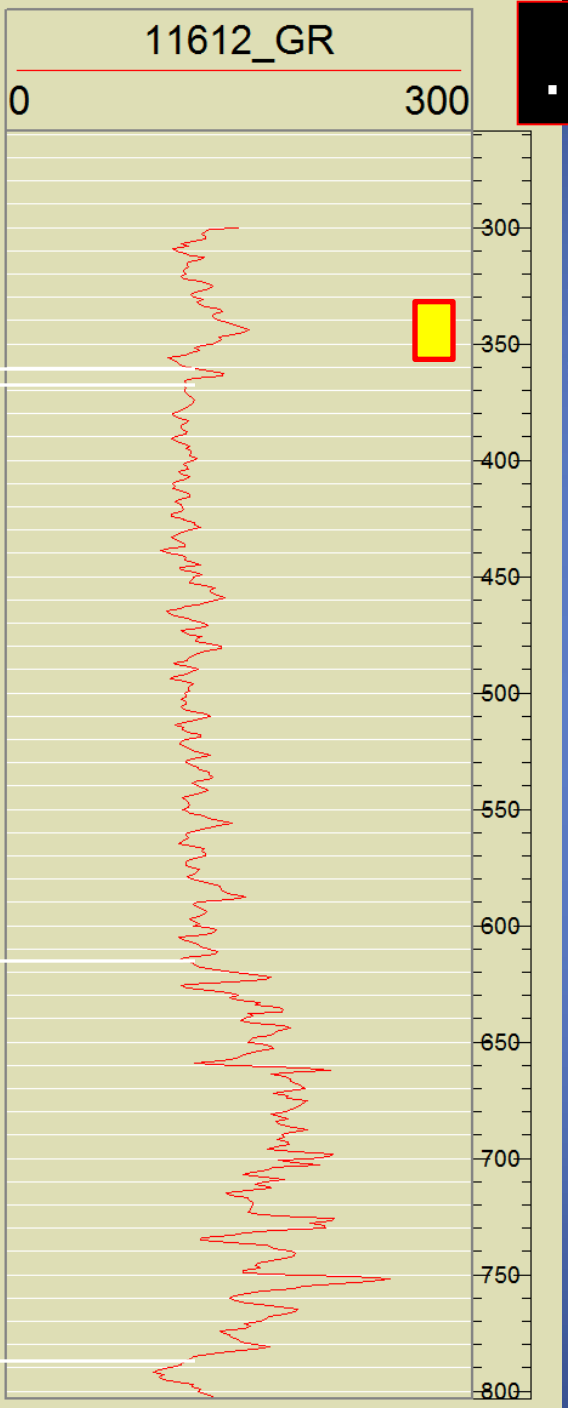

…carbonate followed by barite…
$CaCO_3$
…$\delta^{13}C$ ~ - 11-13‰ PDV…
$BaSO_4$
2 cm

$\delta^{34}S$ values - Hanover Shale (Upper Devonian) barite nodules…



Late Devonian seawater $\delta^{3}4S$ - ~22‰ (Claypool et al., 1980); 22-28‰ (Kampshulte and Strauss, 2004); 20-24‰ (Cecile et al., 1983);

…sources of methane…



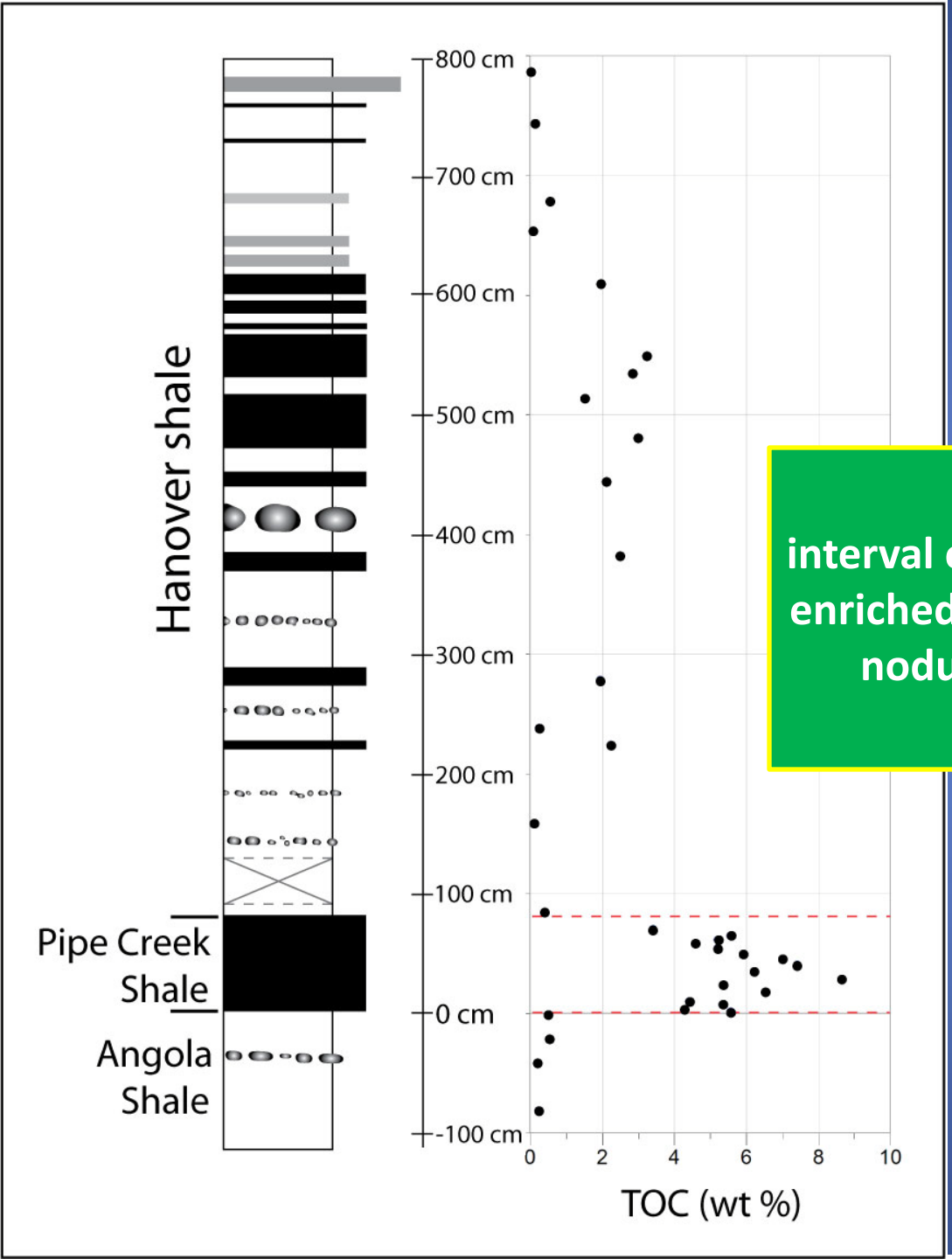
Hanover Shale

Pipe Creek Shale

barite nodule interval

Angola Shale

Rhinestreet Shale



?

sulfate reduction zone

diffusing SO_4^{2-}

increasing $\delta^{34}S$

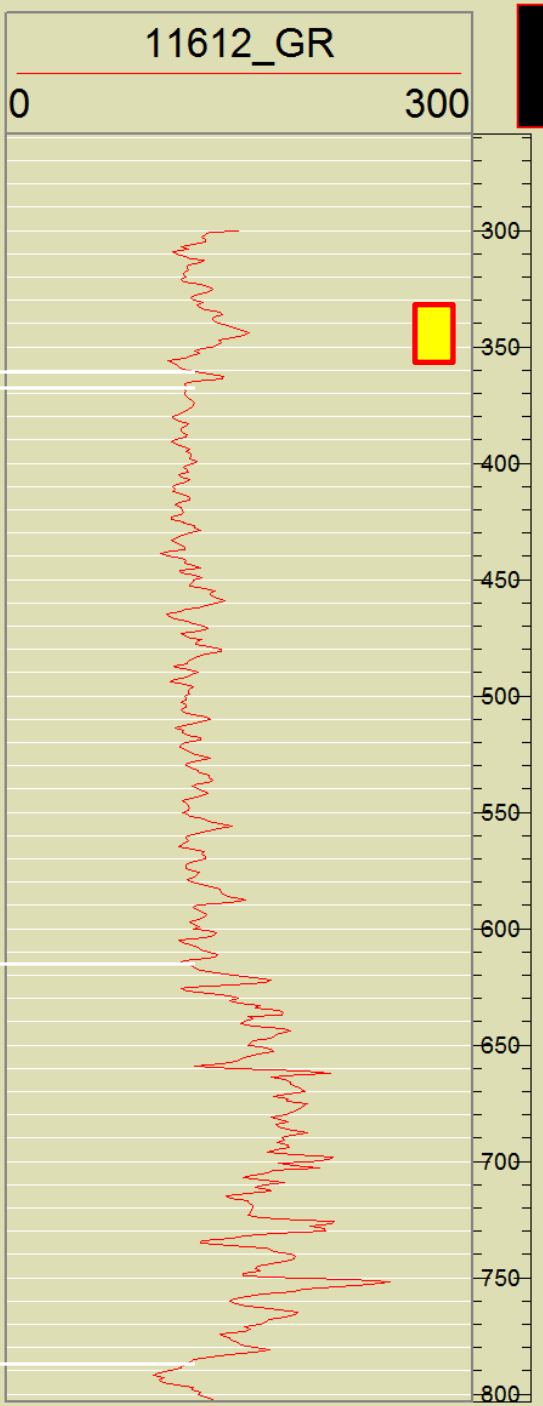
interval of $\delta^{34}S$-enriched barite nodules

anaerobic methane oxidation

diffusing methane and Ba^{2+}

methanogenesis

…sources of methane…



Hanover Shale

Pipe Creek Shale

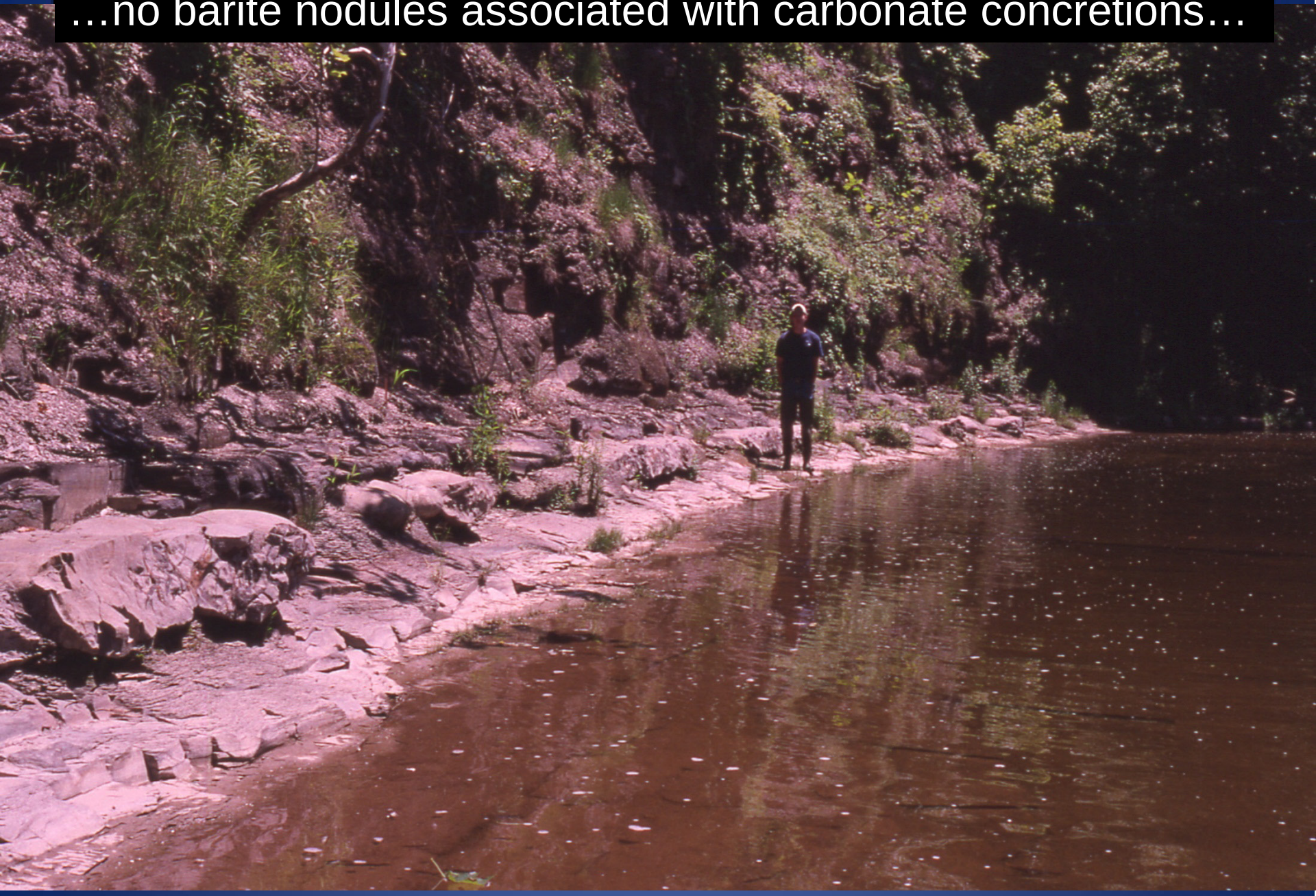
Angola Shale

Rhinestreet Shale

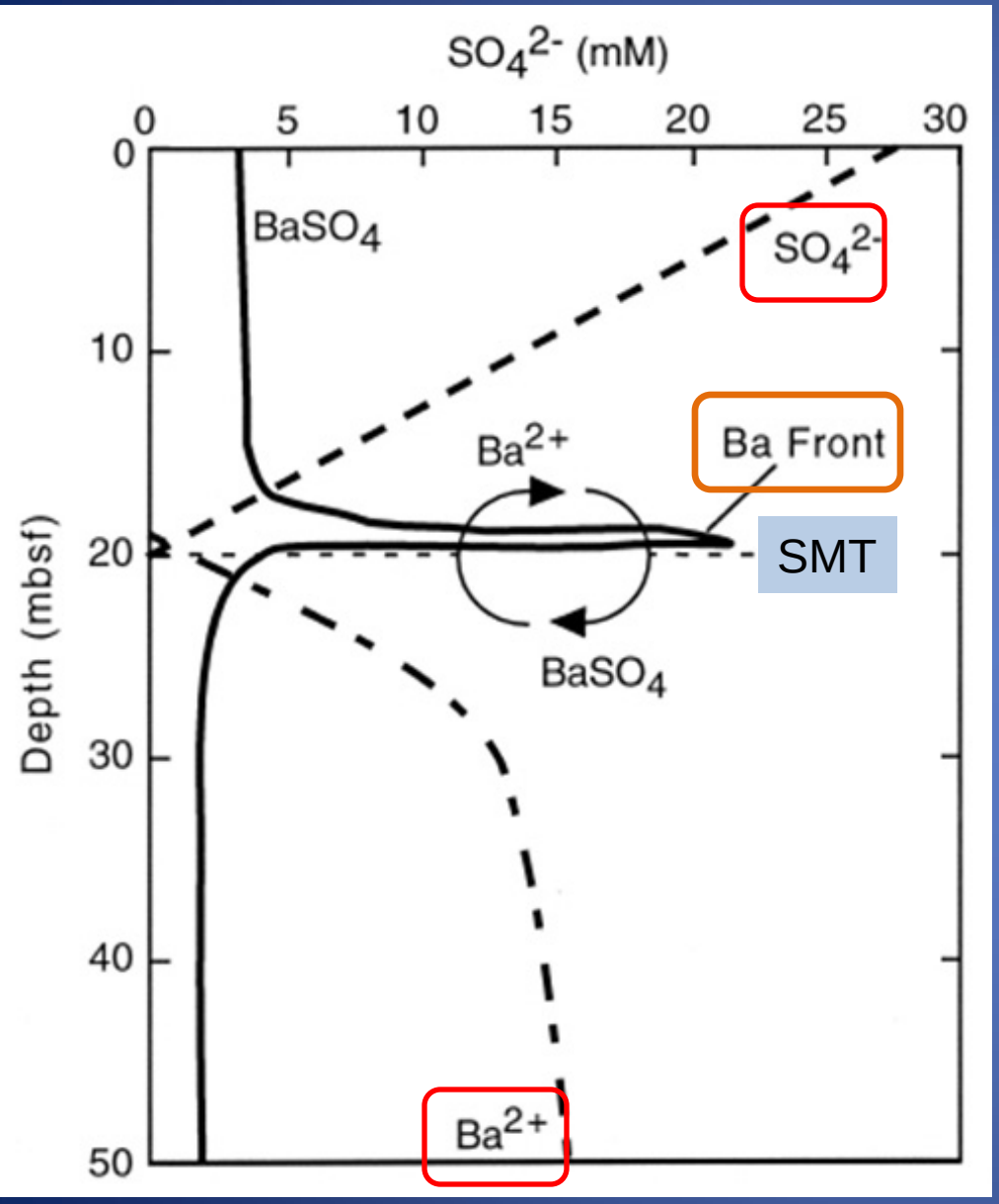
barite nodule interval

multiple concretionary carbonate horizons … *anaerobic methane oxidation*

…no barite nodules associated with carbonate concretions…

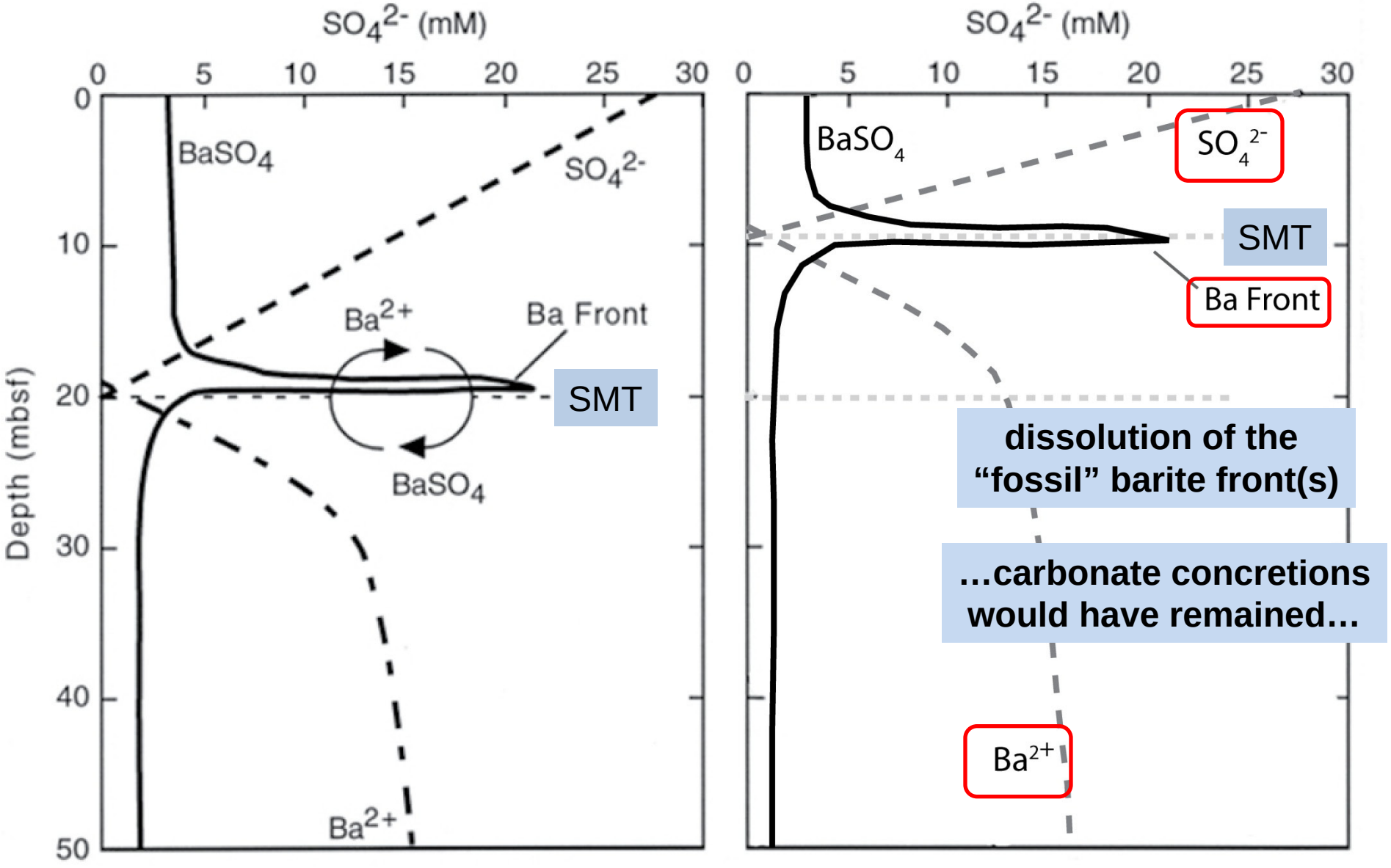


…loss of authigenic barite…



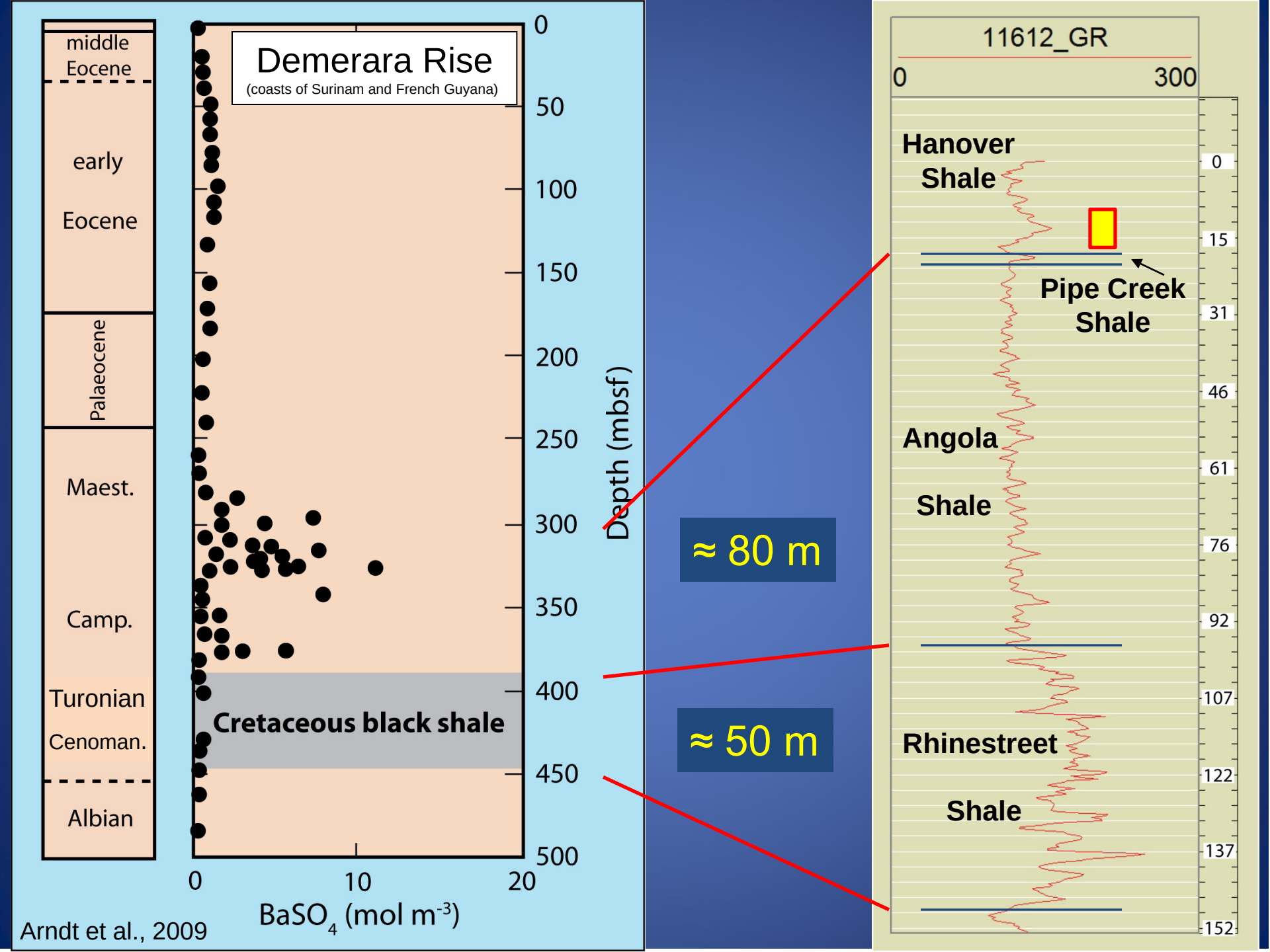
Dickens, 2001

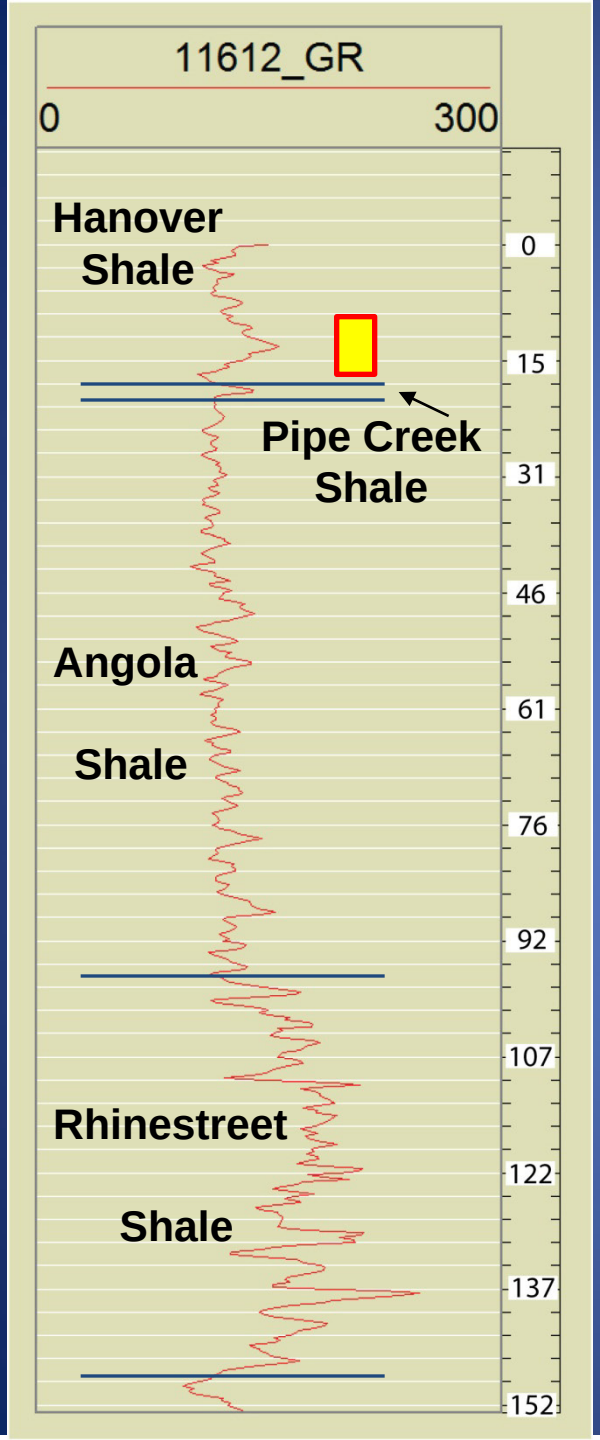
…loss of authigenic barite…

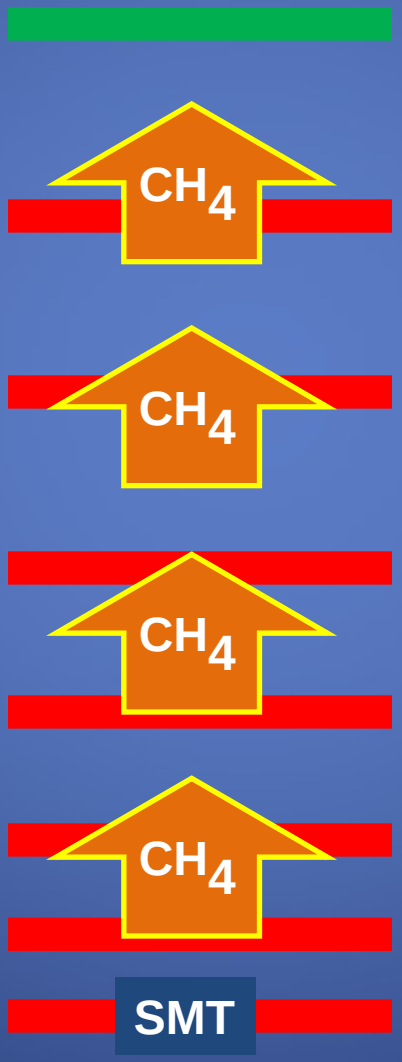


Dickens, 2001


fossil-SMT


middle Eocene
early Eocene
Palaeocene
Maest.
Camp.
Turonian
Cenoman.
Albian
Demerara Rise
(coasts of Surinam and French Guyana)
Cretaceous black shale
0
50
100
150
200
250
300
350
400
450
500
Depth (mbsf)
0
10
20
BaSO4 (mol m-3)
Arndt et al., 2009
≈ 80 m
≈ 50 m
11612_GR
0
300
Hanover Shale
Pipe Creek Shale
Angola Shale
Rhinestreet Shale
0
15
31
46
61
76
92
107
122
137
152



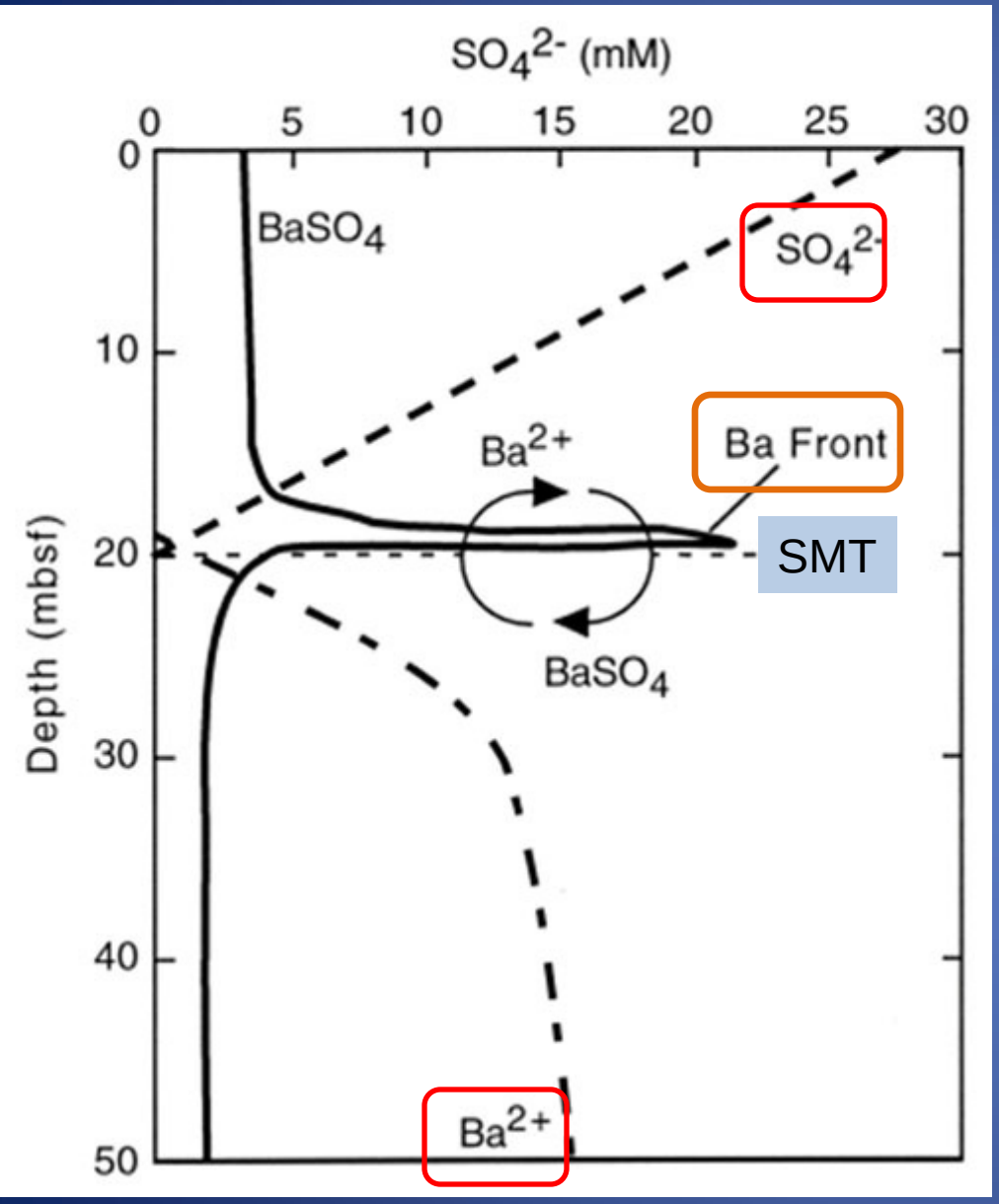


barite nodule interval
(a record of continuous Ba cycling)

upward migrating SMTs caused by non-steady state burial (marked reductions in sedimentation rate)

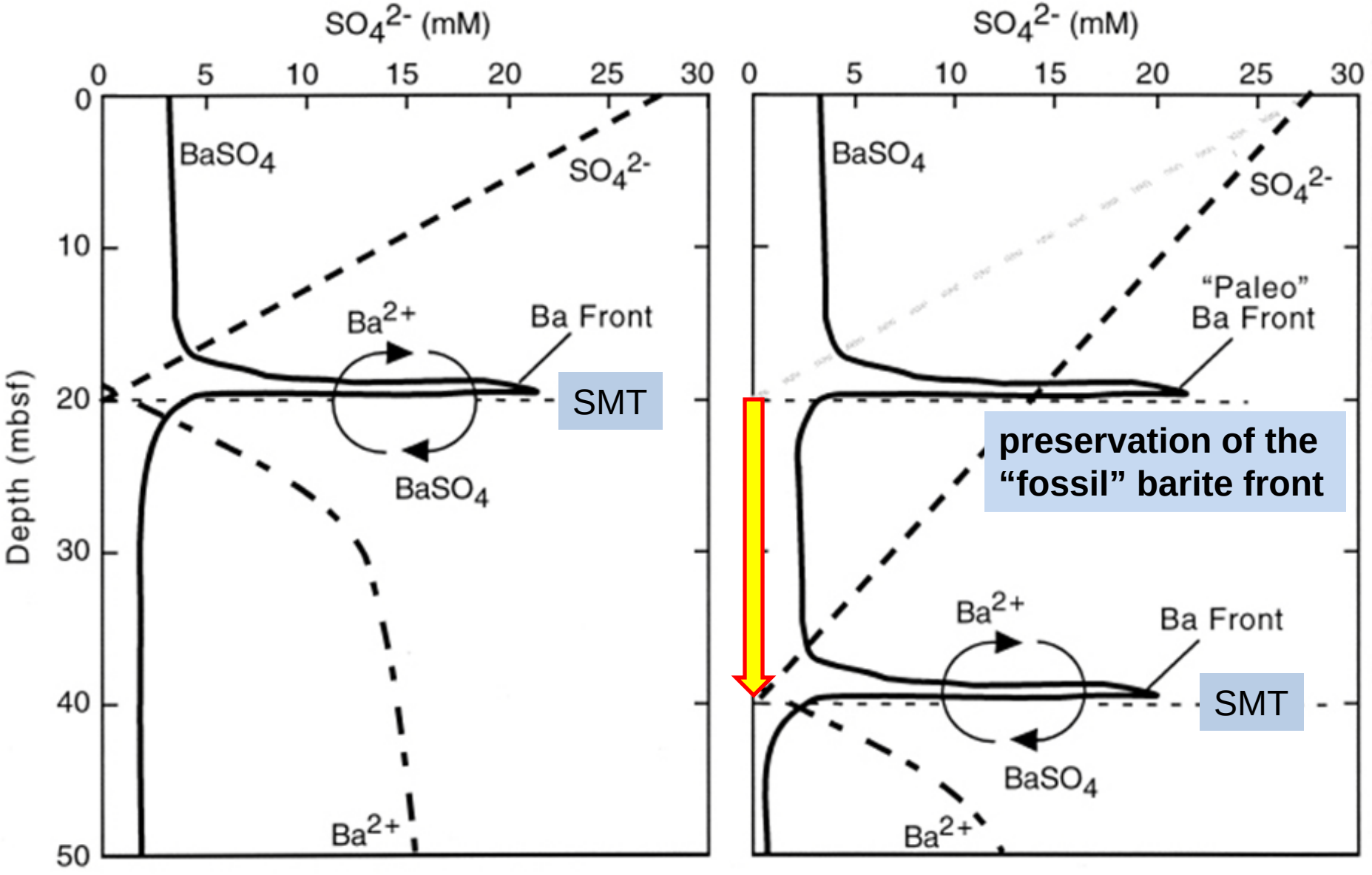
carbonate concretion horizons

…preservation of authigenic barite…

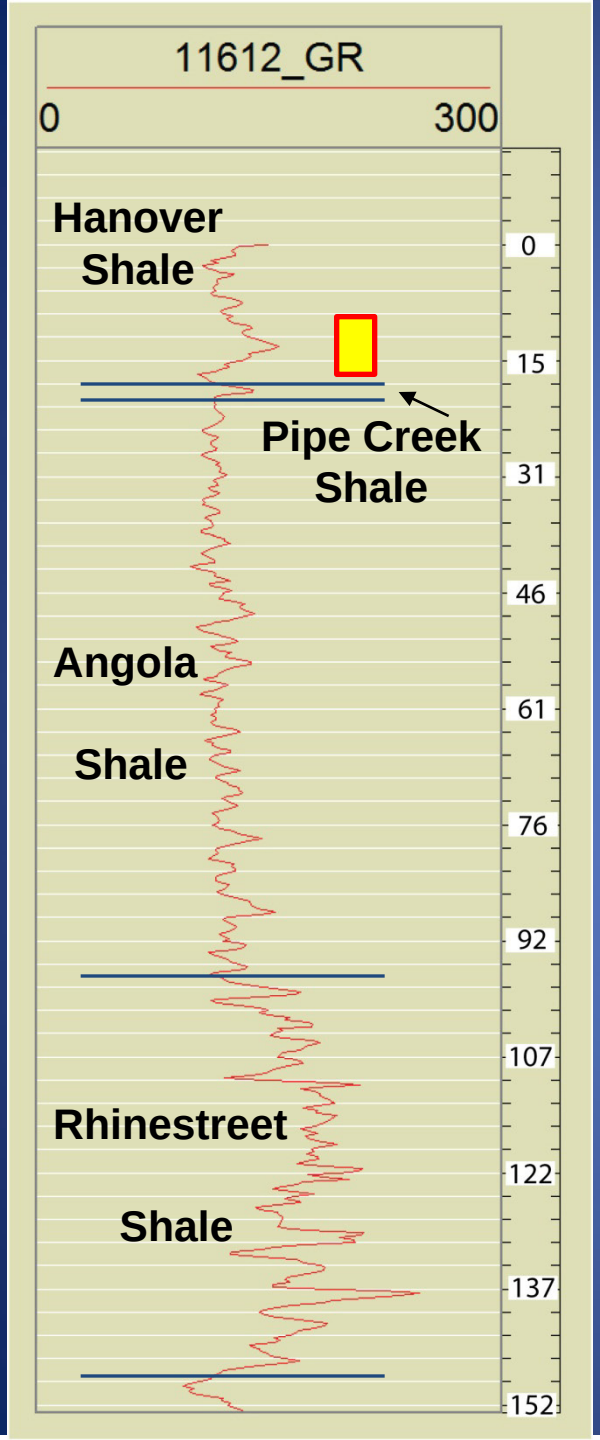


Dickens, 2001

…preservation of authigenic barite…



Dickens, 2001

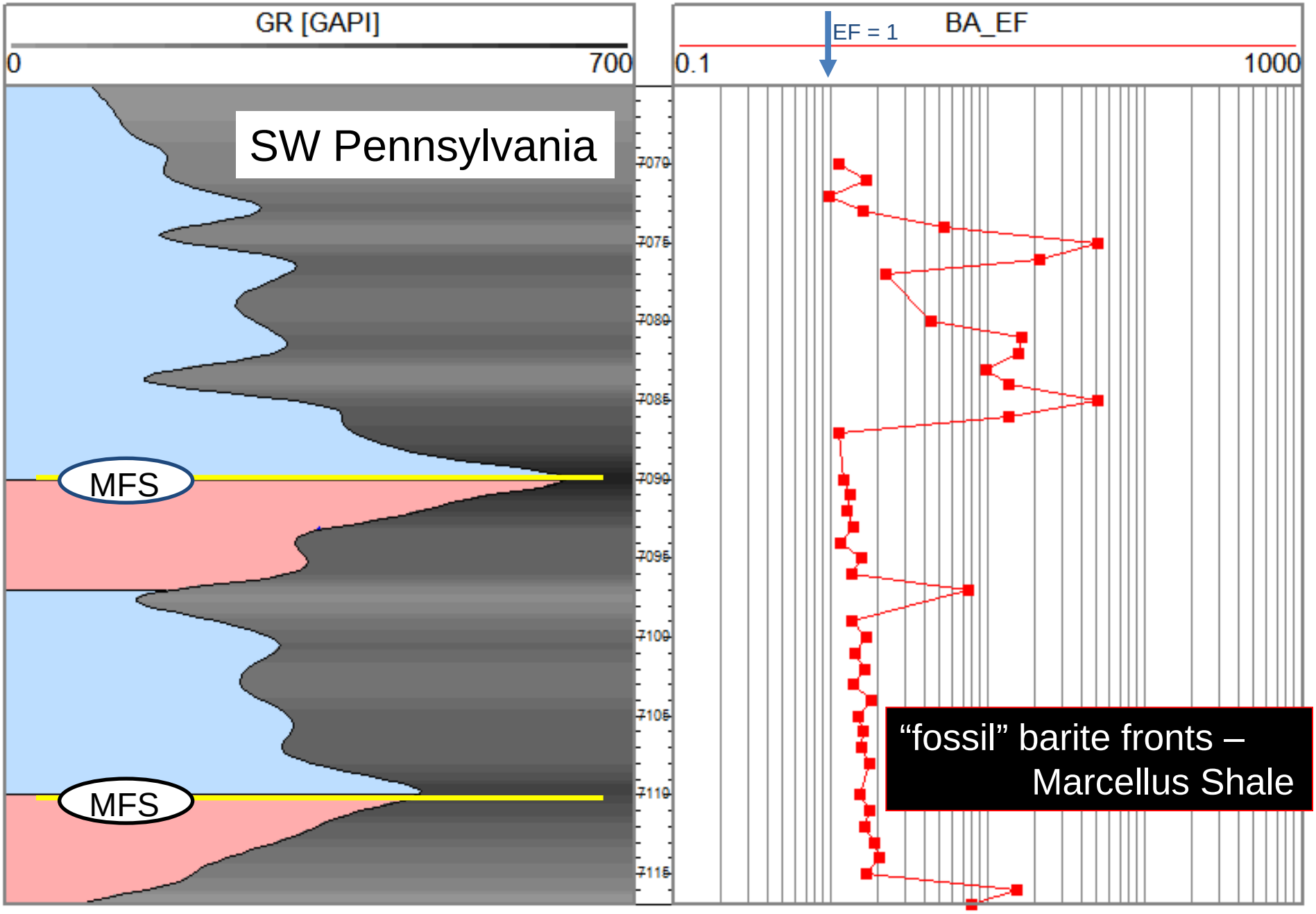


nature of the “event” that induced the sinking of the SMT and consequent preservation of the barite nodules?

barite nodule interval

…increased flux of organic-lean deposits of the upper Hanover Shale…

…increased diffusion distance of methane from the base of the Rhinestreet…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BA_EF
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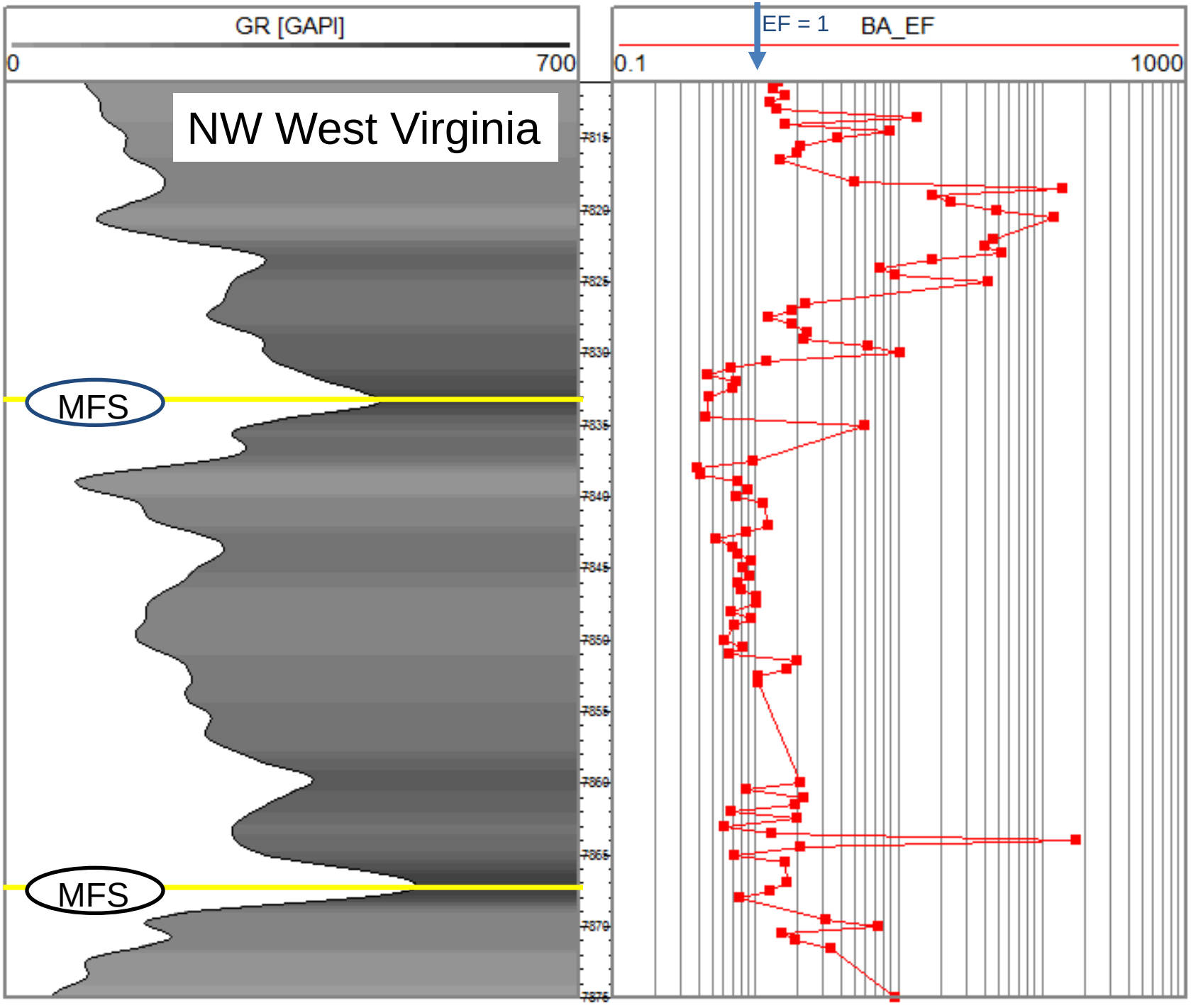
0.1
1000
SW Pennsylvania
MFS
MFS
7070
7075
7080
7085
7090
7095
7100
7105
7110
7115
"fossil" barite fronts –
Marcellus Shale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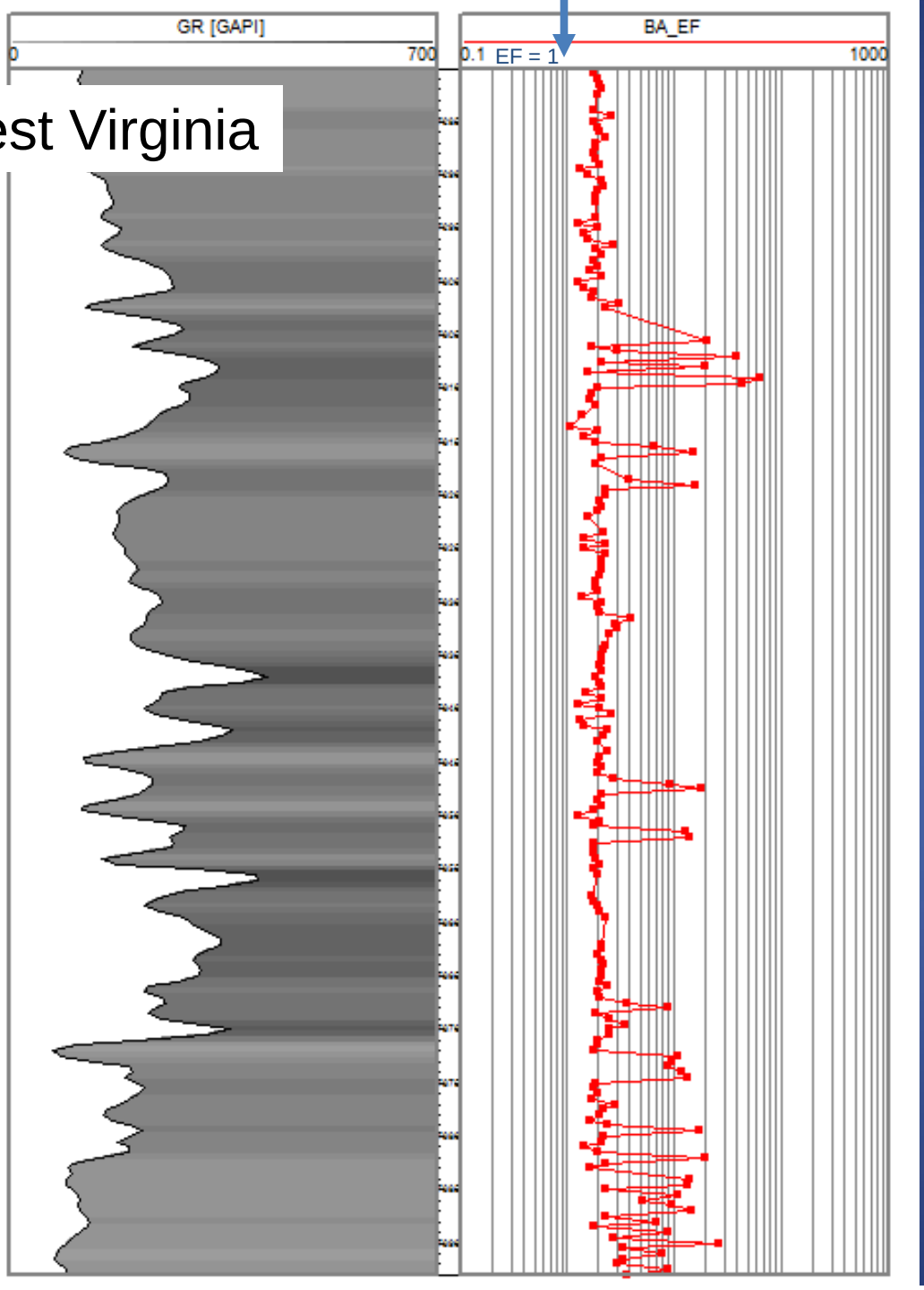
MFS
MFS

central West Virginia



Conclusions

-the Rhinestreet-Angola-Pipe Creek-Hanover sequence preserves a robust record of the diagenetic effects of anaerobic methane oxidation (AMO) resulting from the sustained delivery of biogenic methane from below;

-$\delta^{34}S$-enriched authigenic barite nodules – a proxy for the vertical migration of methane from either the Pipe Creek Shale or, more likely the Rhinestreet Shale;

-AMO in the Rhinestreet and overlying Angola Shale are reflected in the presence of numerous carbonate (^{13}C depleted) concretion horizons;

-the lack of barite in these horizons is a consequence of the progressive passage of these intervals through the SMT into the zone of methanogenesis resulting in the dissolution of the authigenic barite;

Conclusions

-the preservation of the barite nodules at the base of the Hanover Shale can only be explained by the subsidence of the SMT below the zone of AMO at least until the sediment became impermeable enough to resist the inward migration of sulfate-deficient interstitial pore fluid during continued subsidence;

-the linkage of ^{34}S-enriched sulfide minerals and possible existence of shallow gas hydrates during Middle and Late Devonian time…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