

# **Authigenic Barite Nodules and Carbonate Concretions in the Upper Devonian Shale Succession of Western New York – a Record of Variable Biogenic Methane Flux During Burial\***

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## **Abstract**

Authigenic barite nodules associated with <sup>13</sup>C-depleted calcium carbonate concretions and <sup>34</sup>S-enriched pyrite within a 2.8-m-thick interval at the bottom of the Upper Devonian Hanover Shale of western New York provide evidence of sulfate reduction fueled by upward-diffusing biogenic methane, perhaps sourced within the Middle Devonian Marcellus Shale. Strong <sup>34</sup>S enrichment and high  $\delta^{34}\text{S}/\delta^{18}\text{O}$  values of the barite nodules reflect (1) a high rate of kinetic fractionation induced by microbial sulfate reduction in a semi-enclosed system and (2) a slow seepage rate of the upward-diffusing Ba- and methane-bearing fluid. However, the association of authigenic calcium carbonate and barite in the same stratigraphic interval, especially the presence of barite overgrowths on carbonate concretions, is not entirely consistent with what is known of mineralization induced by anaerobic oxidation of methane focused at the sulfate-methane transition (SMT). The observed relations may reflect a reduced  $\text{CH}_4/\text{Ba}^{2+}$  ratio of pore fluids ascending the sediment column induced by a diminished rate of methanogenesis. The tempered methane flux caused the SMT to descend the sediment column enabling barite to form within the same interval <sup>13</sup>C-depleted calcium carbonate had most recently precipitated. Diminished methane flux may have been caused by burial-related passage of the organic-rich Marcellus below the biogenic methane window and its replacement in that depth interval by overlying organic-lean deposits of the Hamilton Group. Subsidence of the SMT would have increased the preservation potential of labile authigenic barite by enabling the compacting host shale to buffer the nodules. Thus, the barite would be protected from sulfate-deficient interstitial fluids produced when burial eventually carried the organic-rich Upper Devonian Rhinestreet Shale into the biogenic methane window inducing an upward shift of the SMT through the sediment column.

## **References Cited**

Gu, J., H. Cai, S-L Yu, R. Qu, B. Yin, Y-F Guo, 2007, *Marinobacter gudaonensis* sp. nov., isolated from an oil-polluted saline soil in a Chinese oilfield: International Journal of Systematic and Evolutionary Microbiology, v. 57, p. 250–254.

Wedepohl, K.H., 1971, Environmental influences on the chemical composition of shales and clays: in L.H. Ahrens, F. Press, S.K. Runcorn, and H.C. Urey, (eds.), *Physics and Chemistry of the Earth*, Pergamon Press, p. 307-333.

Whiticar, M.J., 1999, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane: Chemical Geology, v. 161/1-3, p. 291-314.

# Authigenic barite nodules and carbonate concretions in the Upper Devonian shale succession of western New York – a record of variable biogenic methane flux during burial

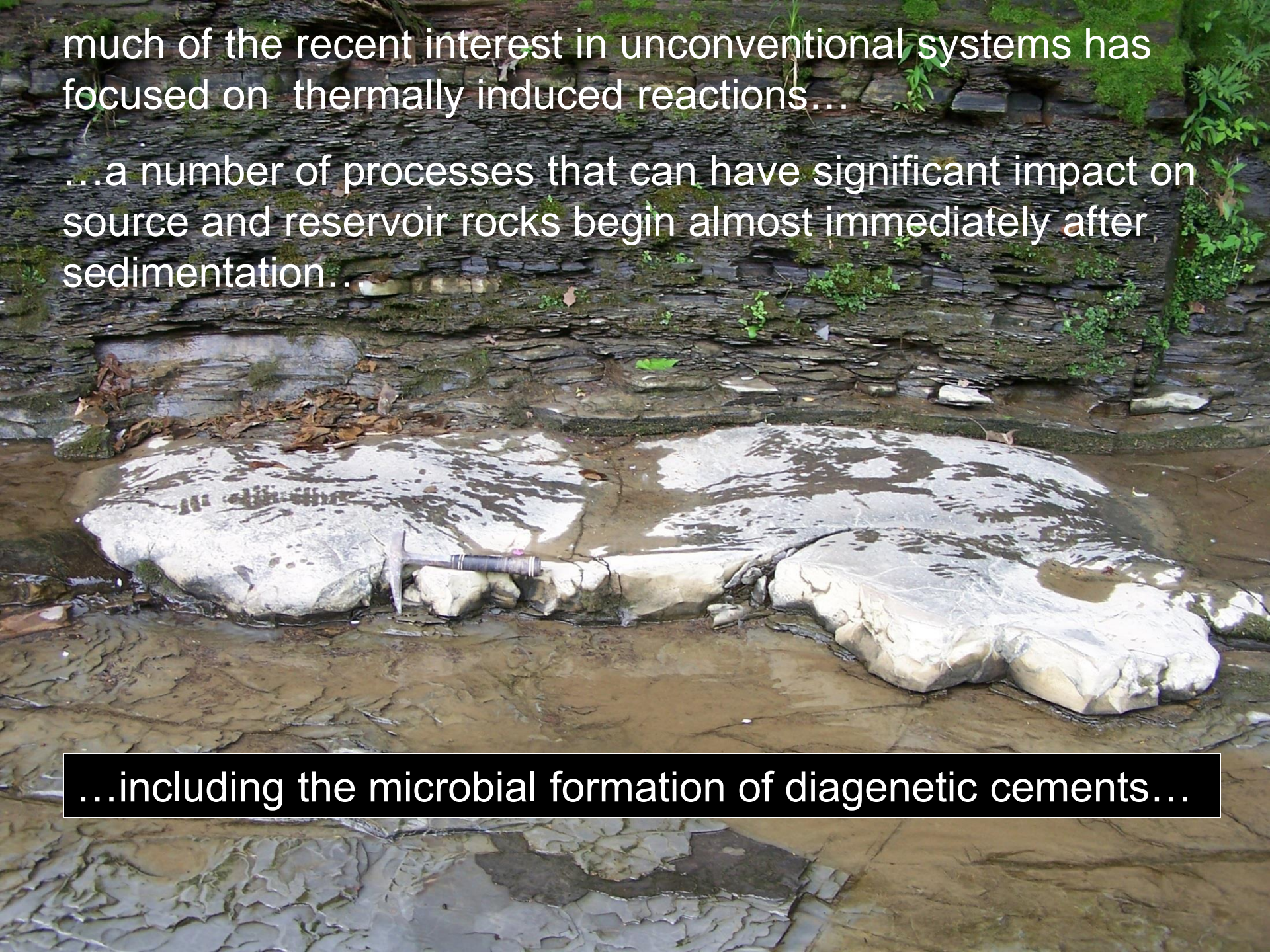
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Fredonia, NY, 14063



much of the recent interest in unconventional systems has focused on thermally induced reactions...

...a number of processes that can have significant impact on source and reservoir rocks begin almost immediately after sedimentation...

...including the microbial formation of diagenetic cements...





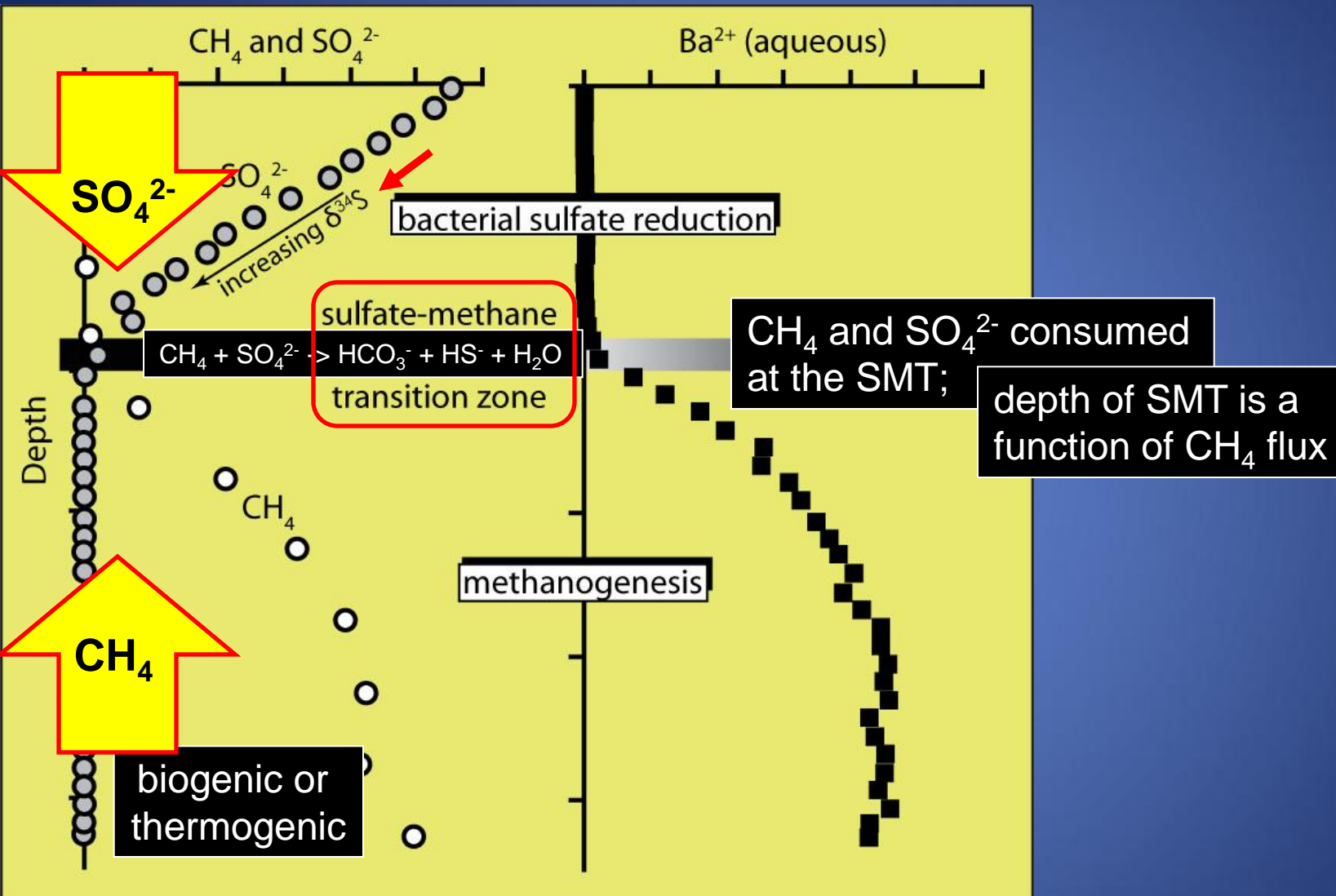
## ... anaerobic oxidation of methane (AOM)...



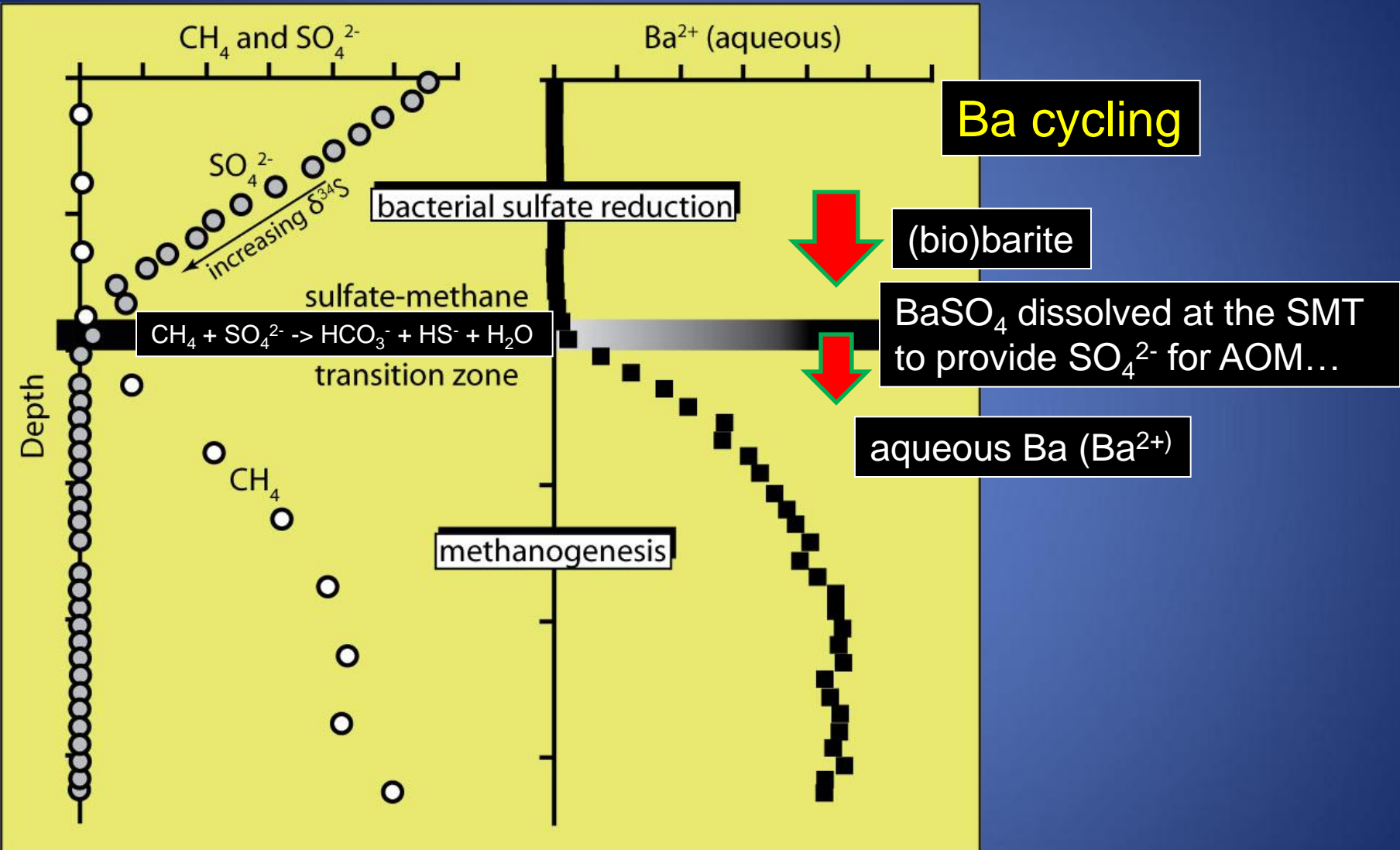
...efficiently controls (consumes) the oceanic methane flux along continental margins (gas hydrate systems)...

...rate of methanogenesis in oceans is estimated to be ~ 85-300 Tg CH<sub>4</sub>/year of which > 90% is consumed by AOM...

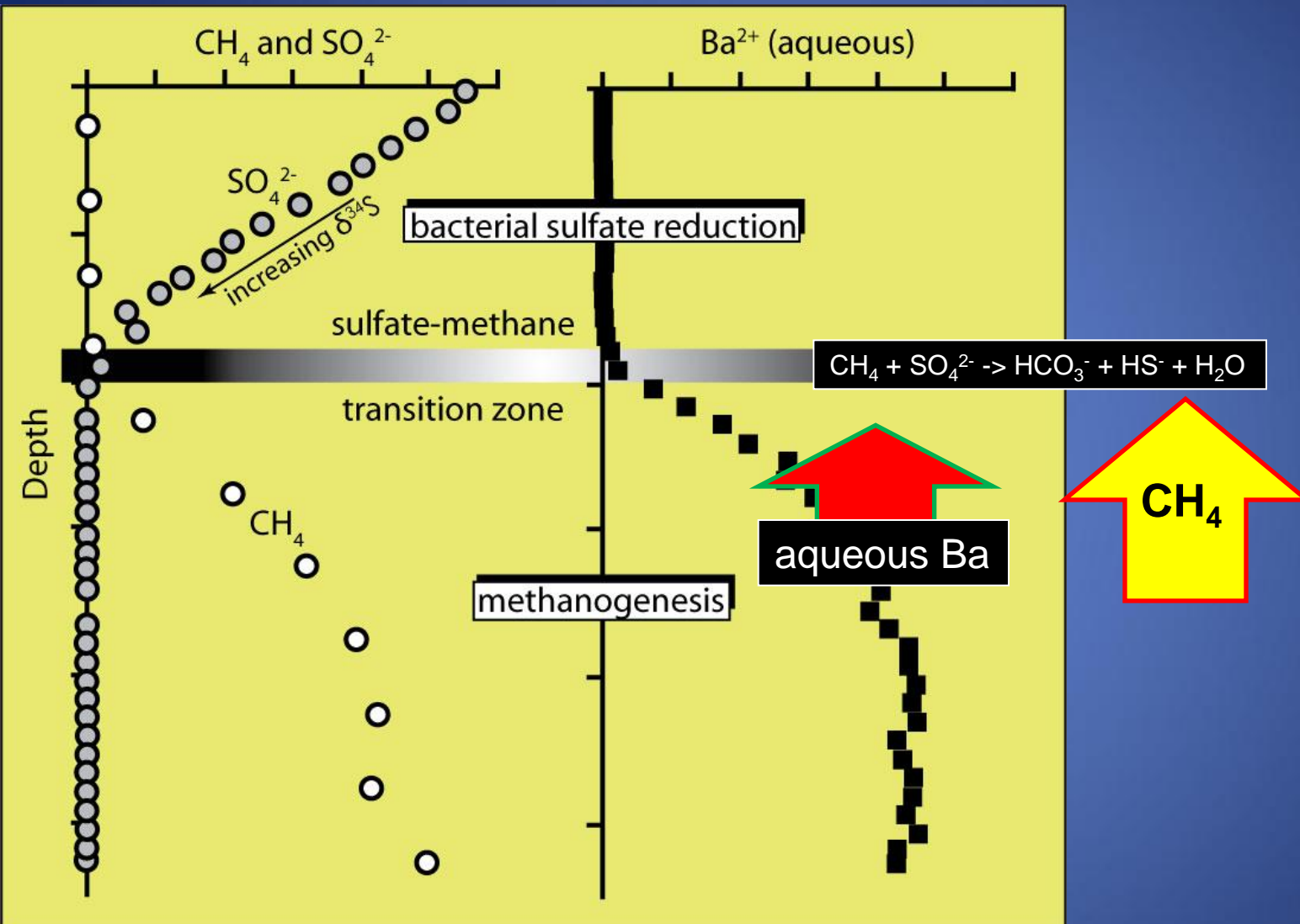
...AOM occurs at the sulfate-methane transition zone (SMT)...



...AOM occurs at the sulfate-methane transition zone (SMT)...

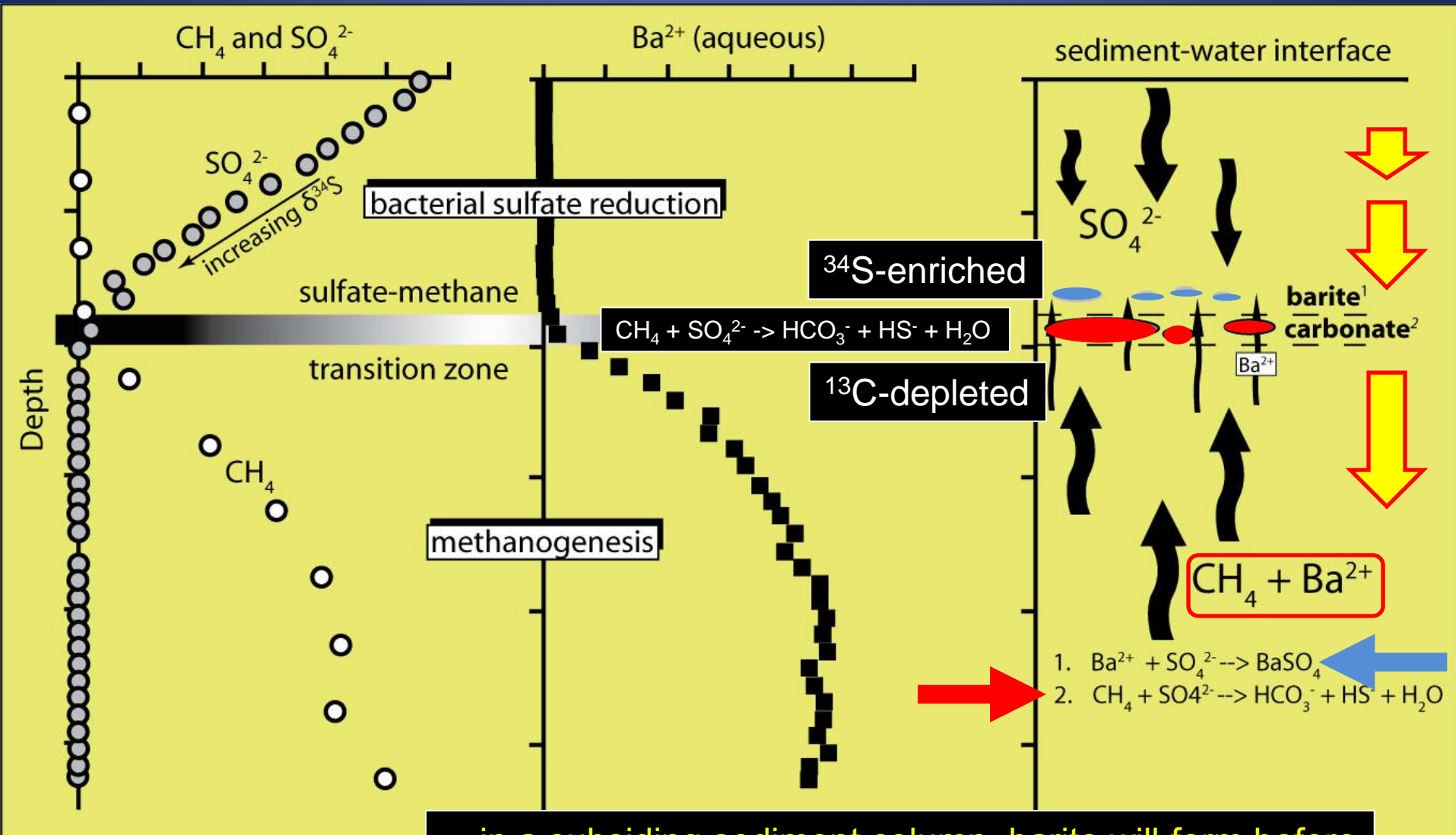


...AOM occurs at the sulfate-methane transition zone (SMT)...

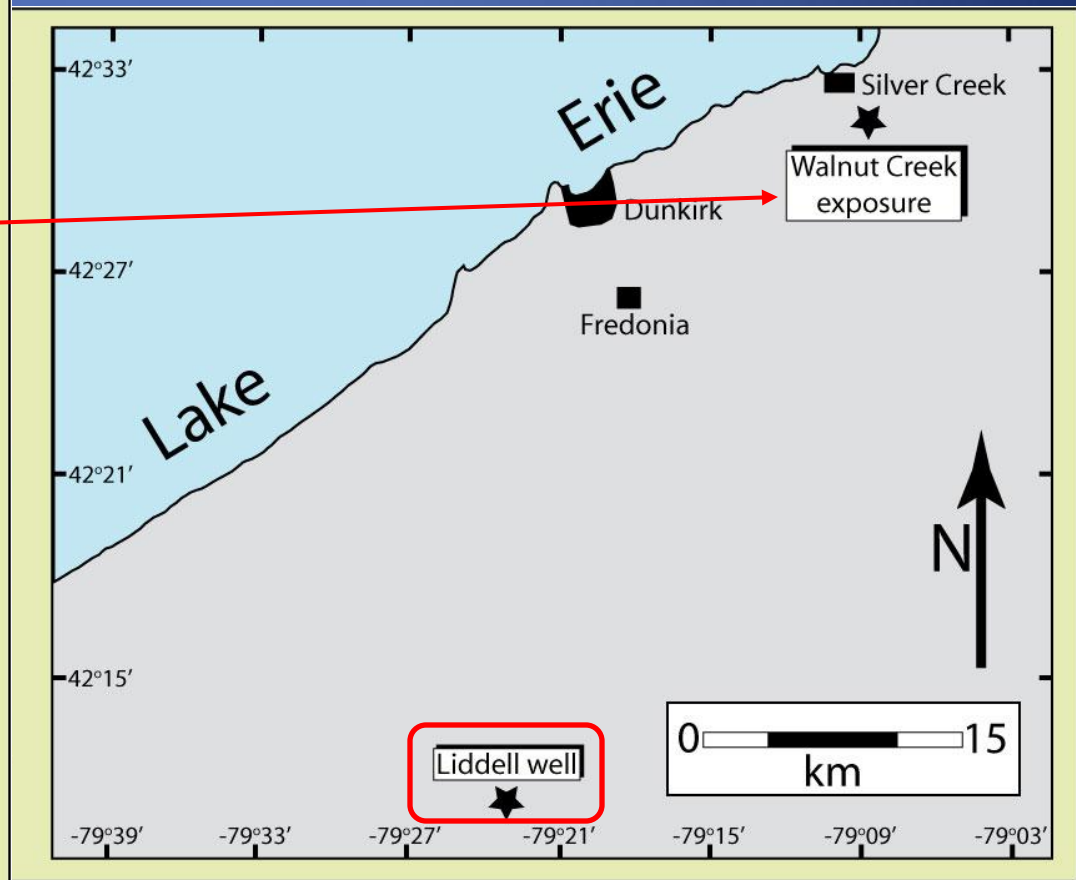
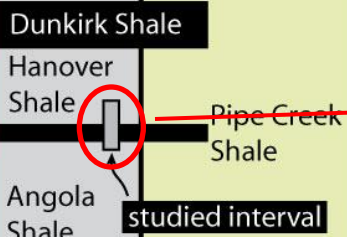
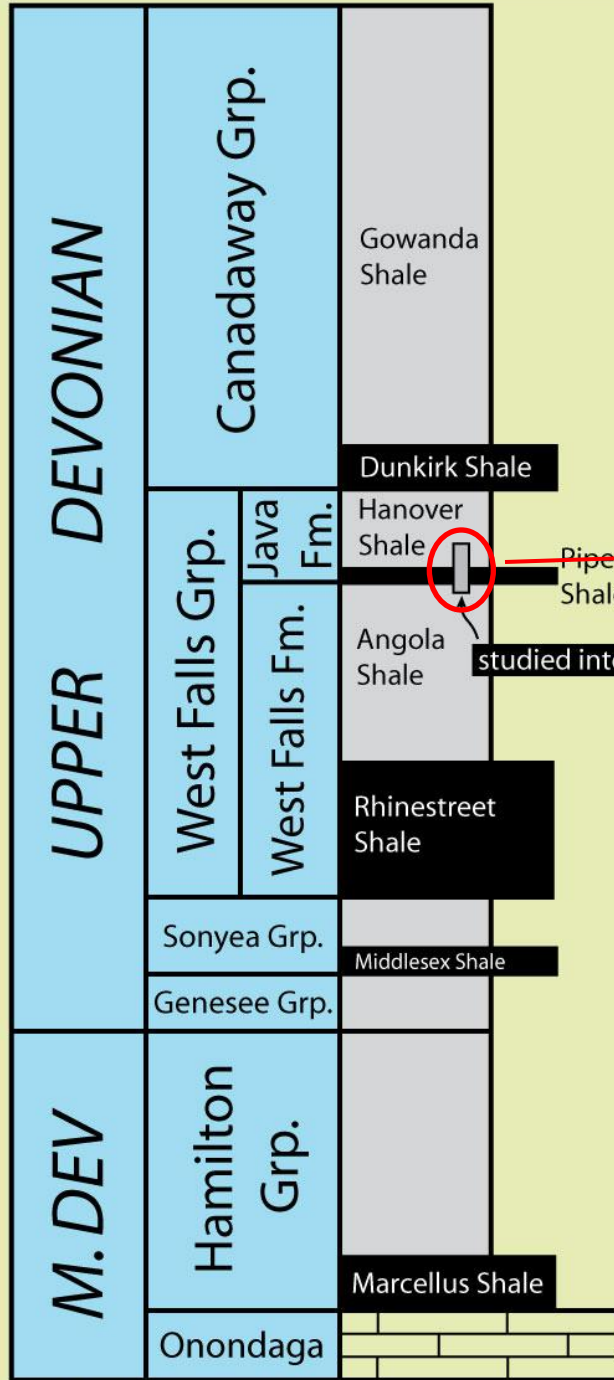




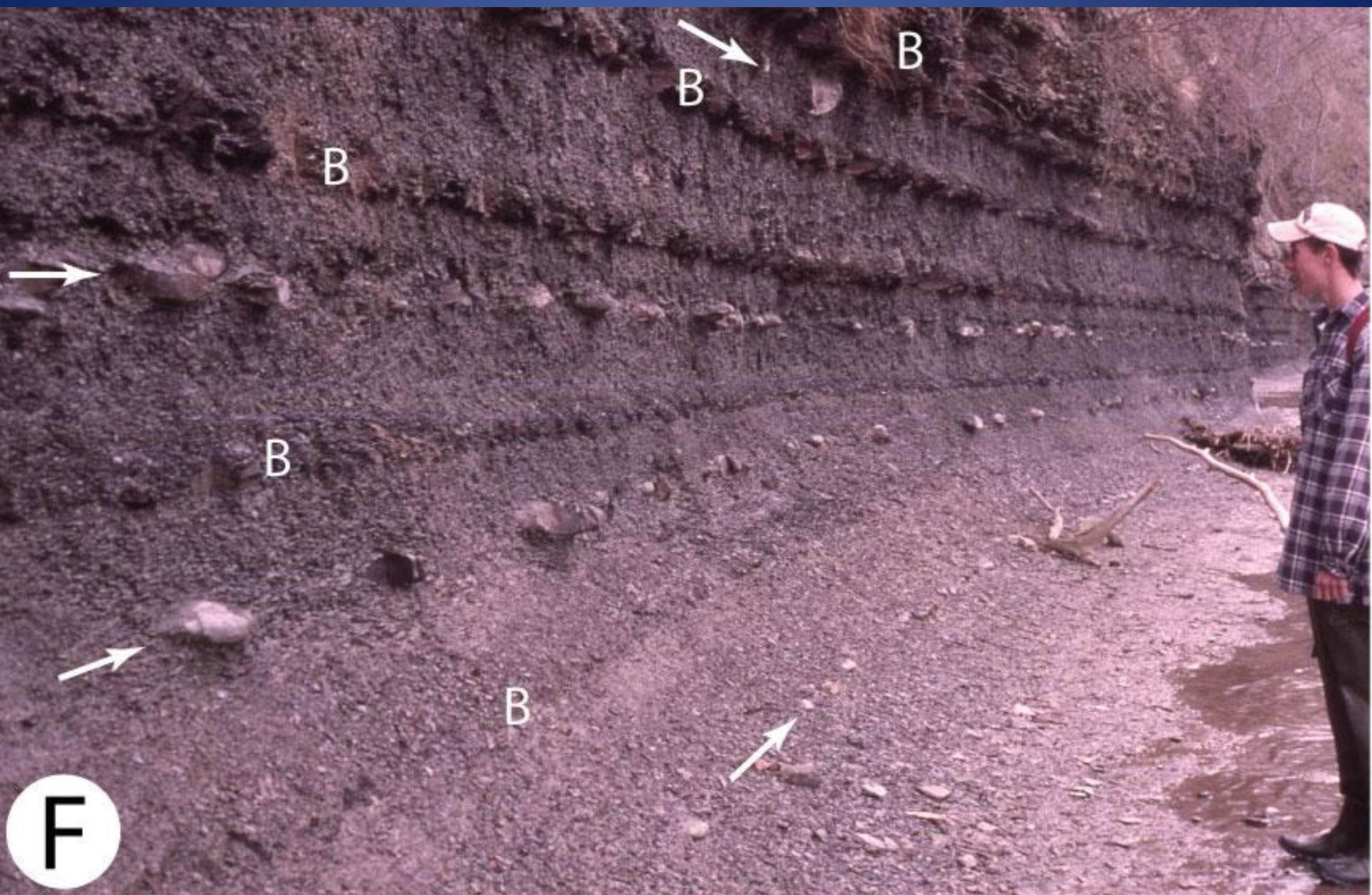
...AOM occurs at the sulfate-methane transition zone (SMT)...

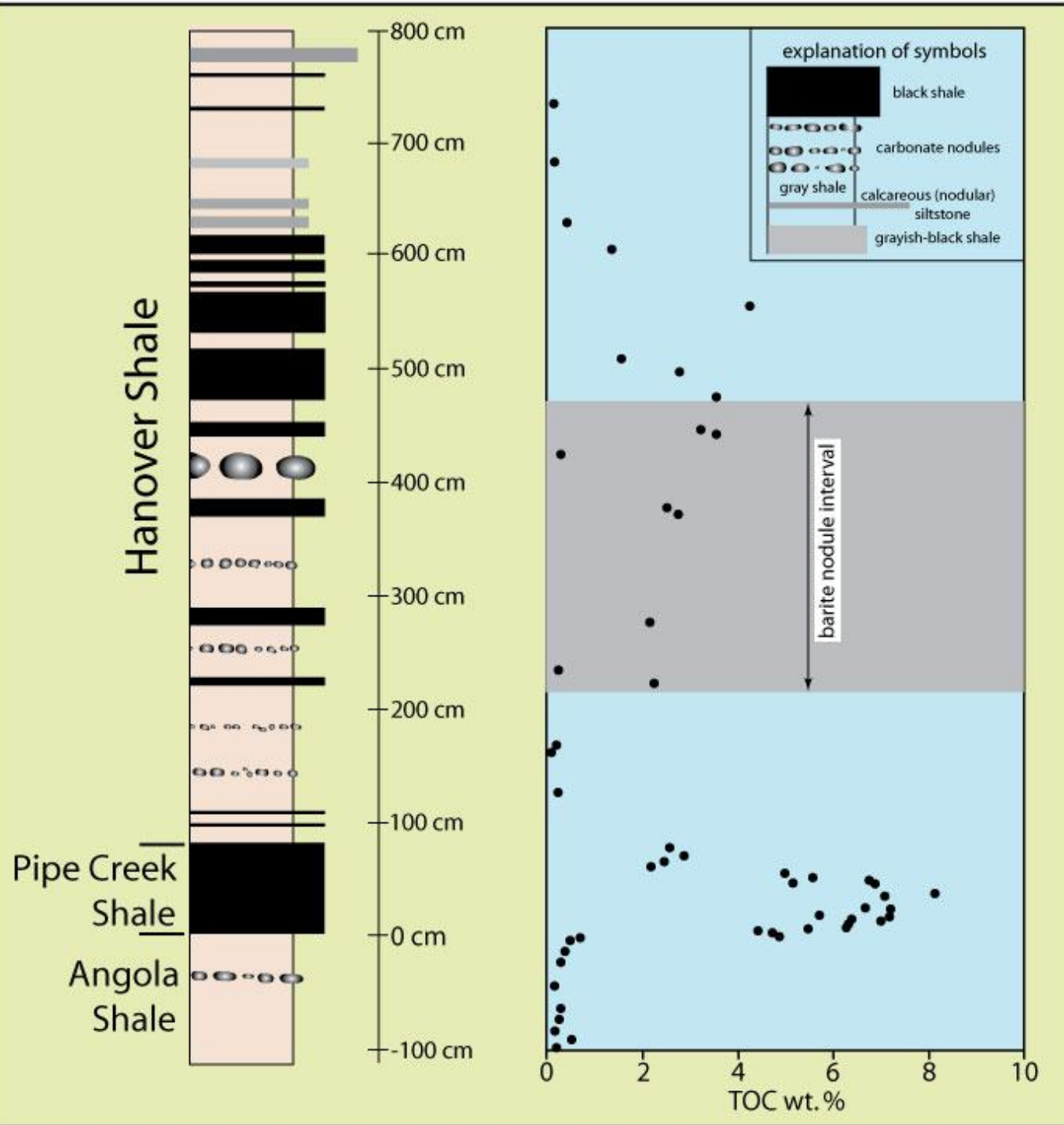


...in a subsiding sediment column, barite will form before calcium carbonate...



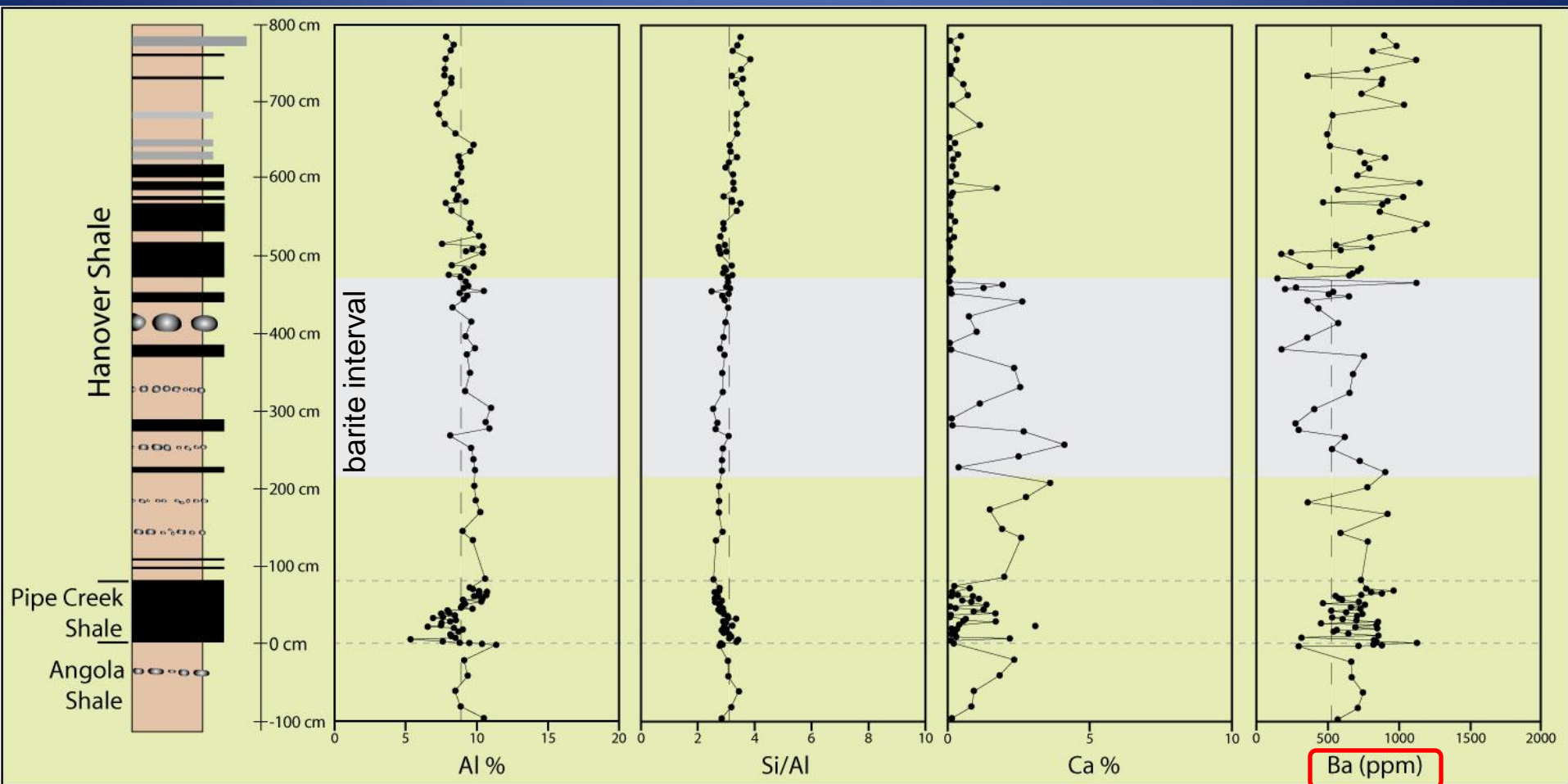








# ...host shale geochemistry...



dashed vertical lines = average shale of Wedepohl (1971)

# barite nodules

associated with carbonate concretions





$\delta^{34}\text{S} = 36.0\text{‰}$  to  $48.24\text{‰}$  V-CDT (mean =  $42.91\text{‰}$  V-CDT)

Late Devonian seawater  $\delta^{34}\text{S}$  -  $\sim 22\text{‰}$  (Claypool et al., 1980);







acicular barite crystals

B

4 cm





2 mm 31x 8.19 mm NavCam GL13\_LM#6



200 μm 340x 792 μm 15kV -Point BSD Full GL13\_LM#6



...extremely high  $\text{Ba}^{2+}$  concentration...



200  $\mu\text{m}$

340x  
798  $\mu\text{m}$

15kV -Point  
BSD Full

GL13\_LM#6

$\delta^{13}\text{C} = -11.49$  to  $-4.27\text{‰}$  V-PDB (mean =  $-7.70\text{‰}$  V-PDB)



pyrite  $\delta^{34}\text{S} = 48.44\text{‰}$  V-CDT (n=3)

carbonate concretion

4 cm



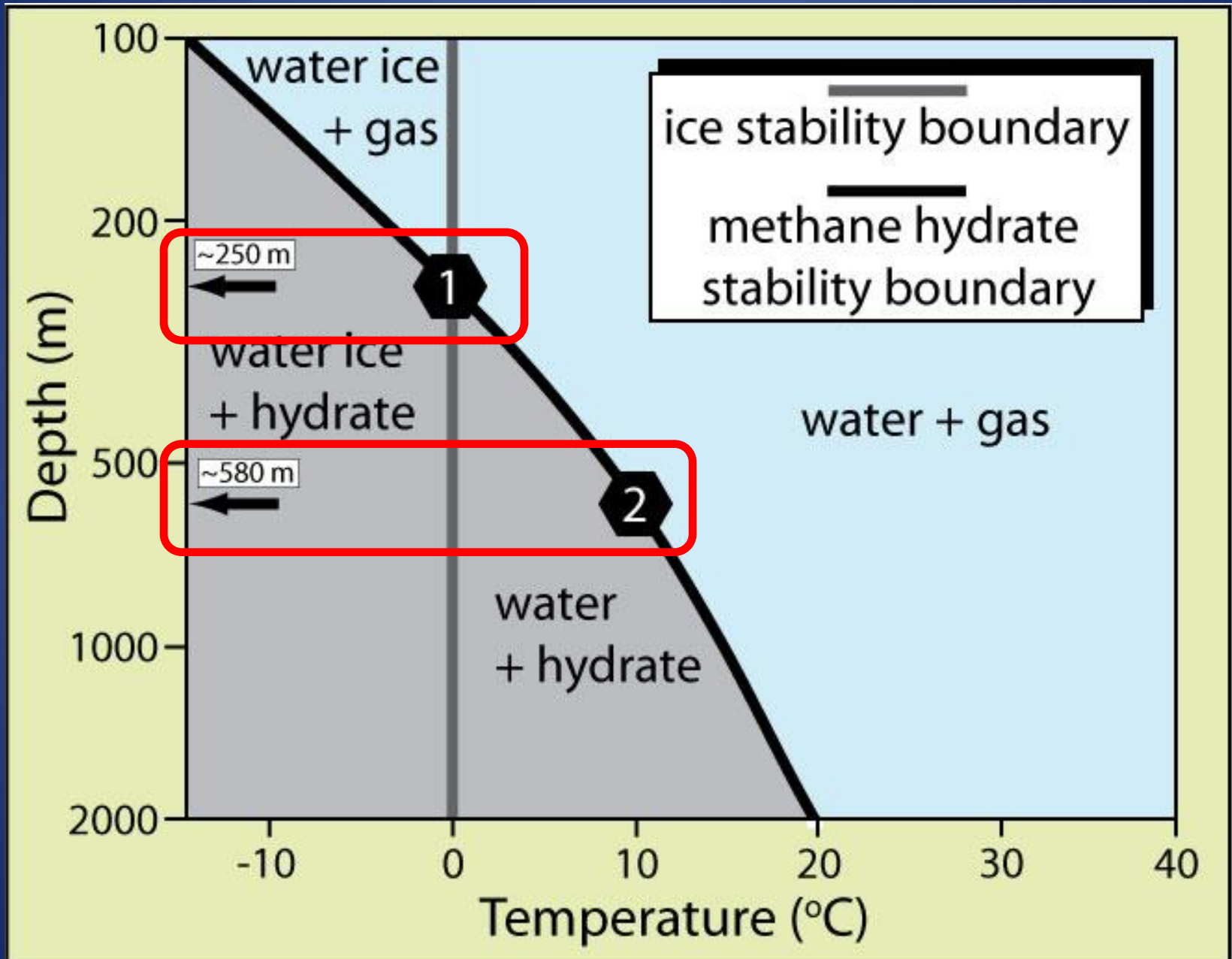
...close association of  $^{13}\text{C}$ -depleted carbonate concretions,  $^{34}\text{S}$ -enriched pyrite, and  $^{34}\text{S}$ -enriched barite suggest AOM-related diagenesis...

...source of the methane...





# ...gas hydrate...



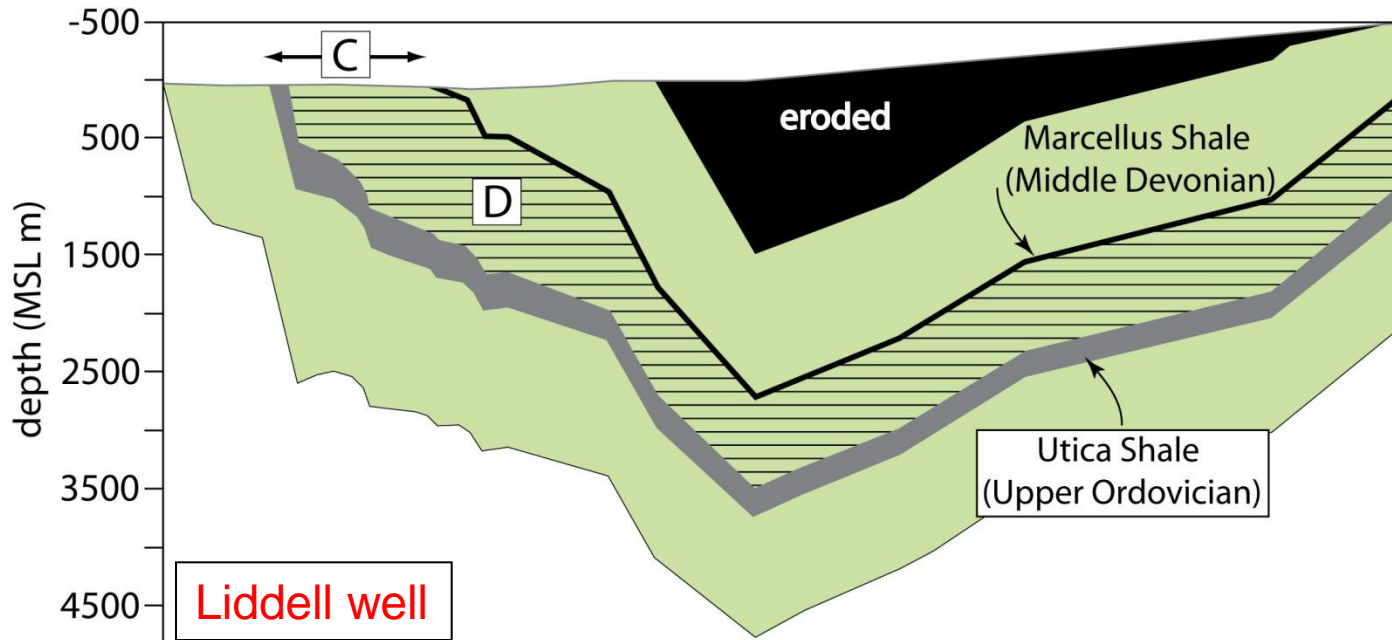


...source of the methane...

3.5 cm

...thermogenic methane;  $\delta^{13}\text{C} = -50$  to  $-20$  ‰ V-PDB;  
Whiticar, 1999)...



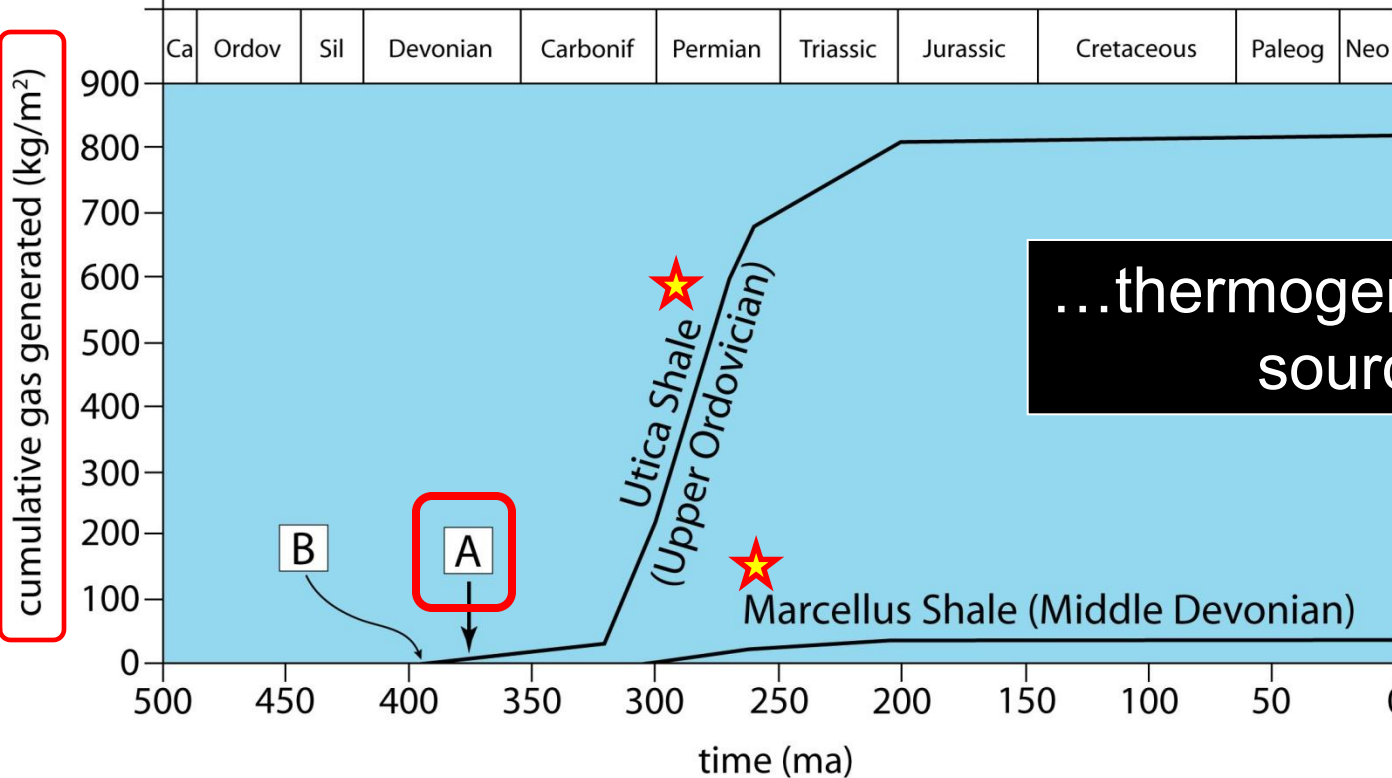


A - base of the Hanover Shale

B - onset of thermogenic generation

C - duration of biogenic methane production in the Utica Shale

D - deposits between base of the Marcellus and top of the Utica Shale





...source of the methane...

3.5 cm

...microbial methane (very low  $\delta^{13}\text{C}$ ;  
-110 to -50 ‰ V-PDB; Whiticar, 1999)...



...microbial methane = -110 to -50 ‰ V-PDB...

$\delta^{13}\text{C} = -11.49 \text{ to } -4.27\text{‰ V-PDB}$  (mean =  $-7.70\text{‰ V-PDB}$ )

3.5 cm

(1) extensive oxidation (AOM) of  $^{13}\text{C}$ -depleted biogenic methane and (2) incorporation of  $^{13}\text{C}$ -enriched  $\text{CO}_2$  produced as a consequence of methanogenesis



...association of authigenic barite and calcium carbonate...



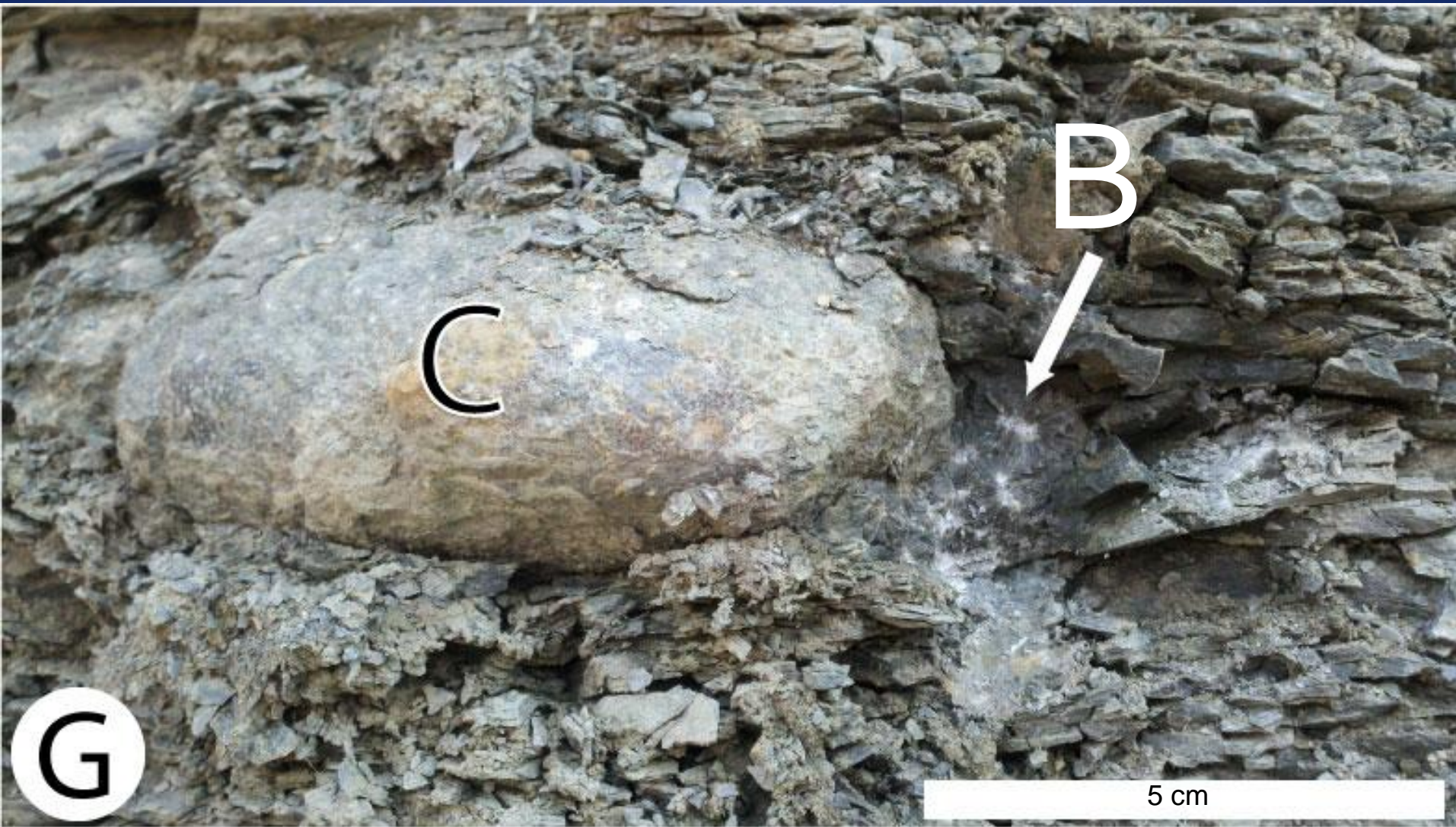


barite rim



4 cm







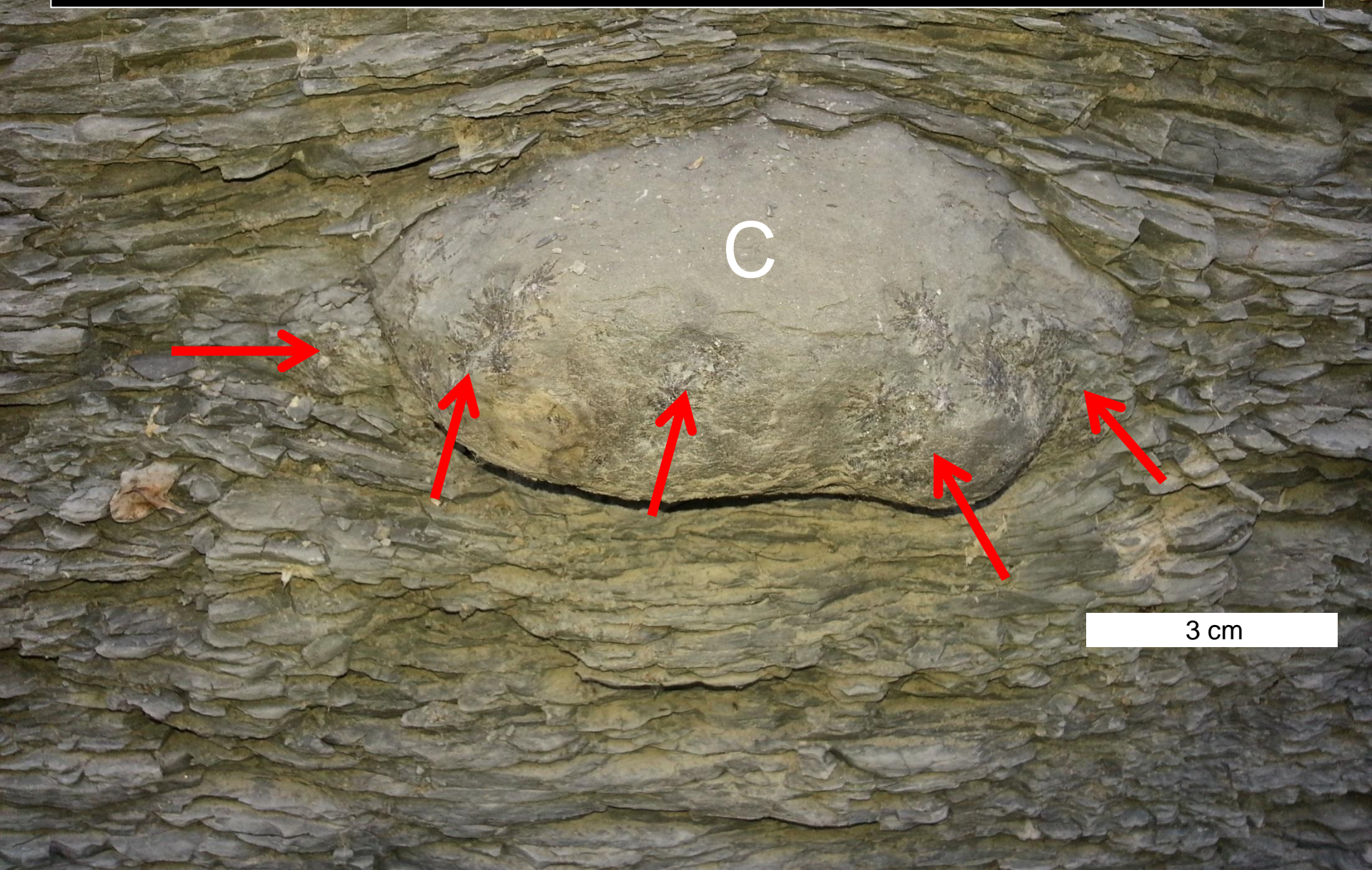


C

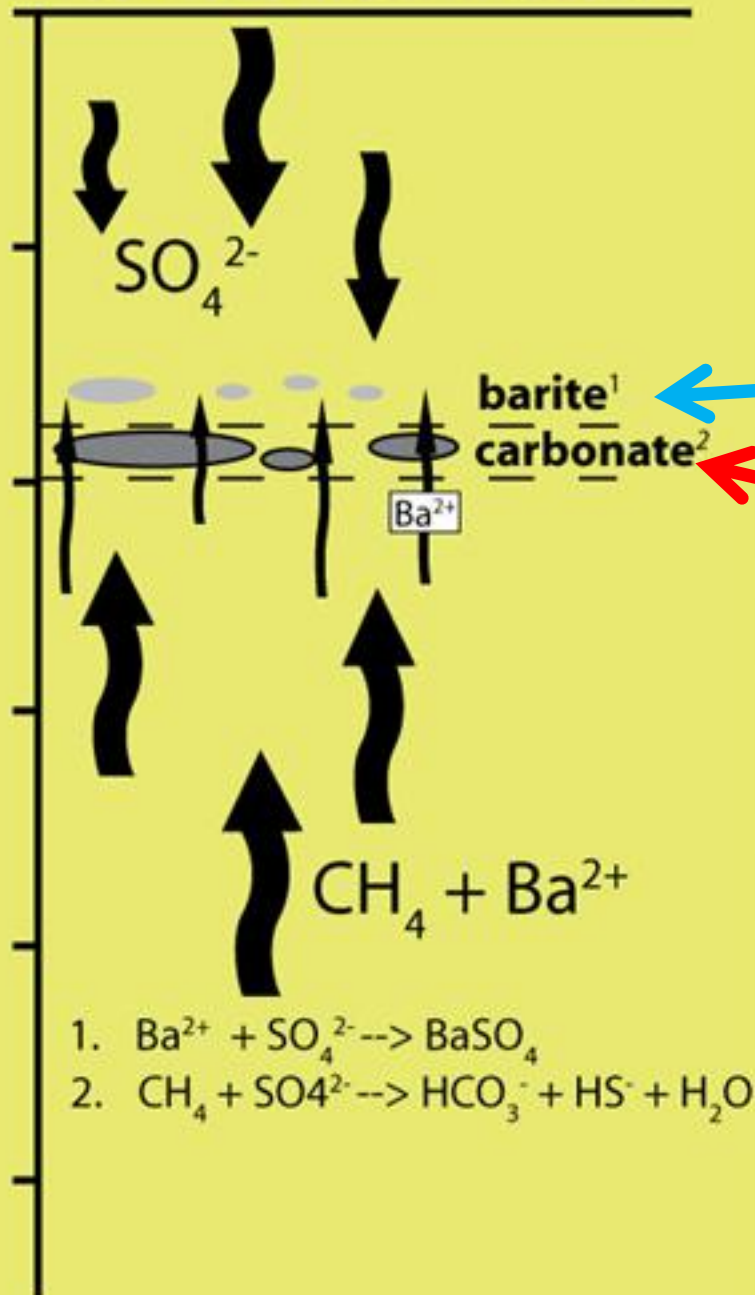
5 cm



...barite formed *after* carbonate and within the same stratigraphic interval...



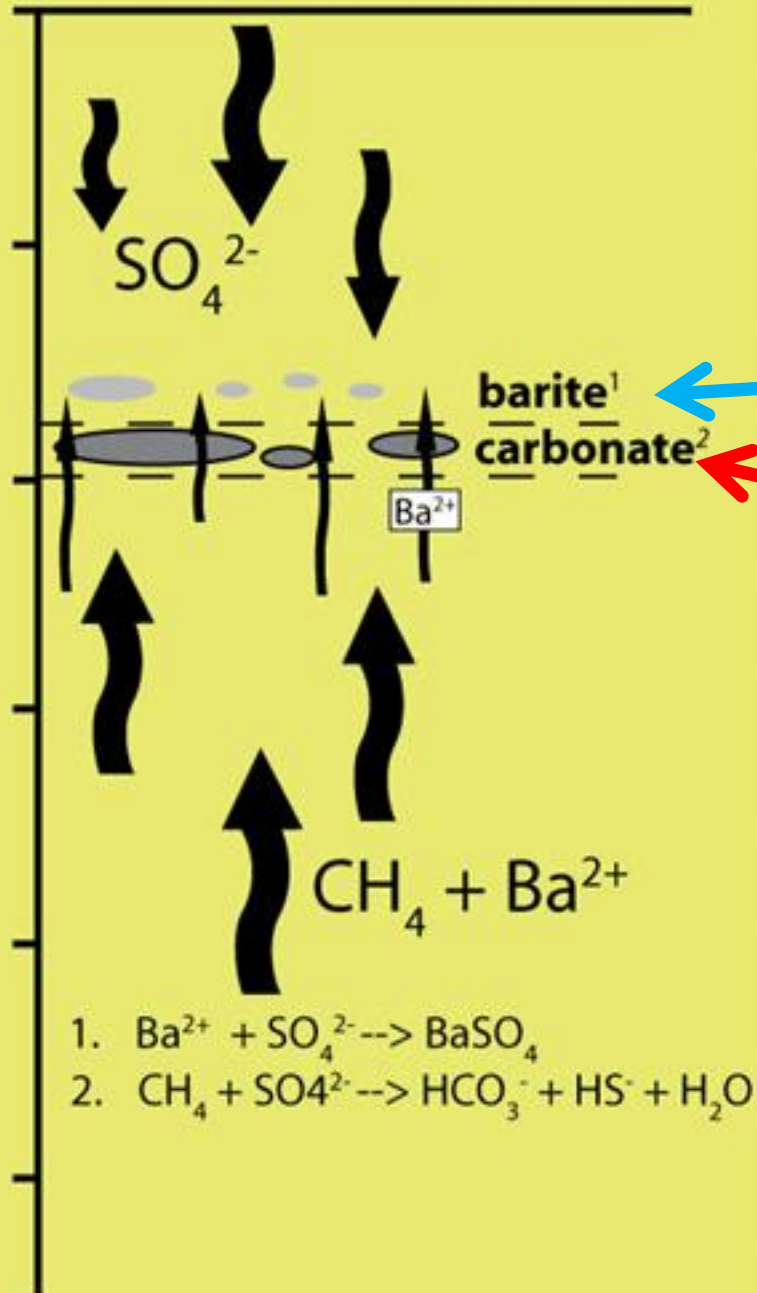
# sediment-water interface



...the barite “front” forms at the *top* of the SMT (where authigenic carbonate forms) or immediately above it...



# sediment-water interface

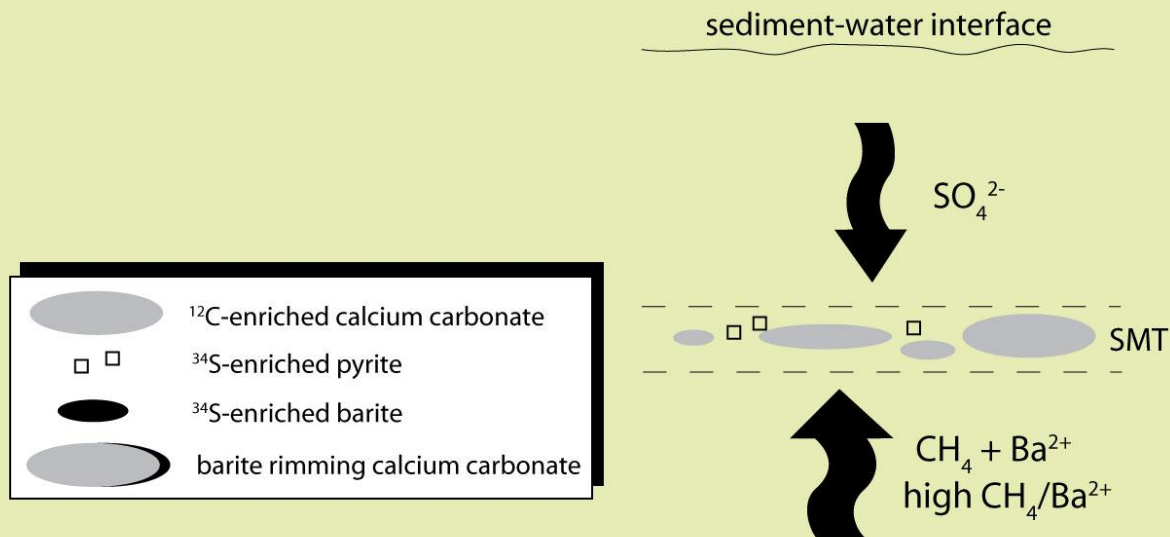


...the barite “front” forms at the *top* of the SMT (where authigenic carbonate forms) or immediately above it...

need to explain (1) the presence of barite and carbonate in same stratigraphic horizon and (2) the formation of barite **after** carbonate...

...the SMT migrated **down-section** resulting in the formation of barite in that interval where carbonate had most recently formed...

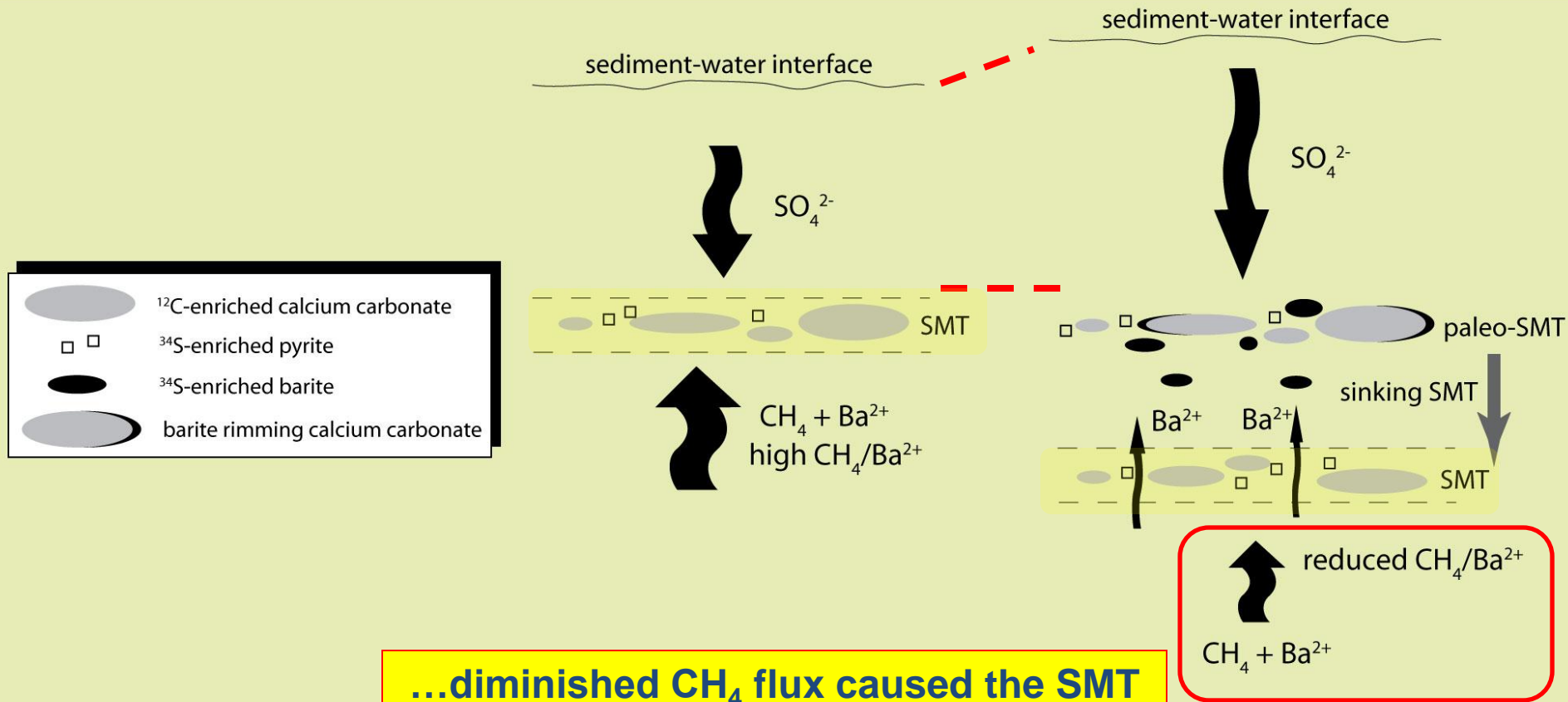
...diminished methane flux...



...depth of SMT ... a function of  $\text{CH}_4$  flux...

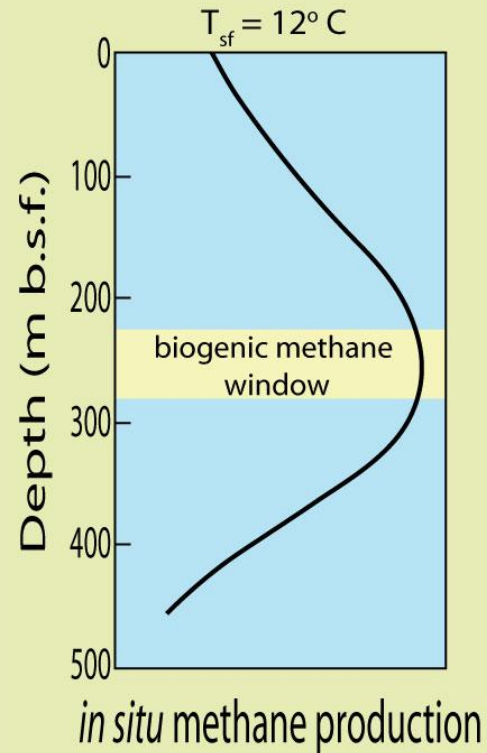


...diminished methane flux...



...diminished  $\text{CH}_4$  flux caused the SMT to sink resulting in the formation of barite along the paleo-SMT...

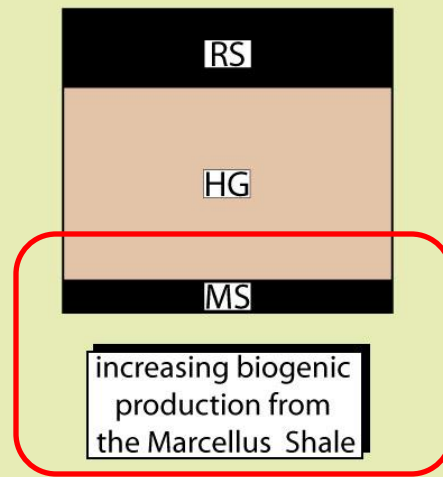
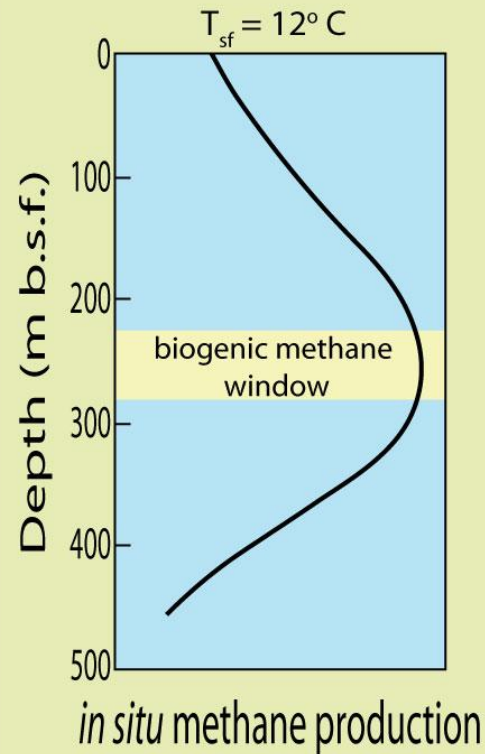
...diminished methane flux as a consequence of the burial of the Middle-Upper Devonian shale succession...



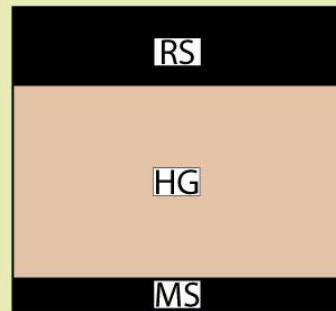
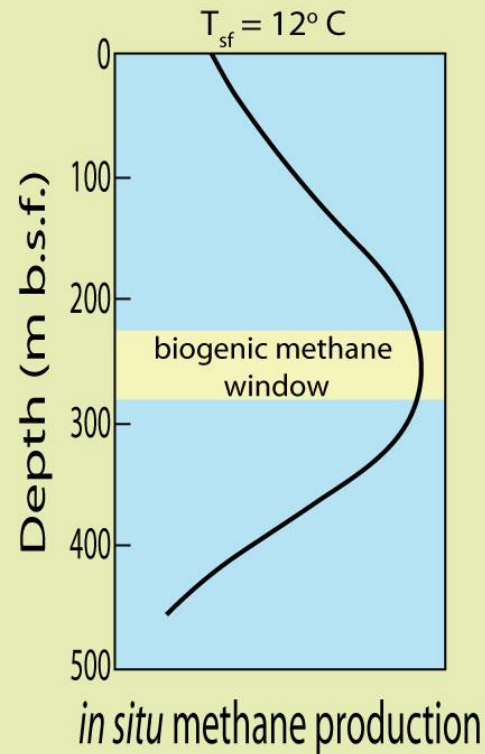
biogenic methanogenesis...largely a function of temperature (Gu et al., 2011, and many others)



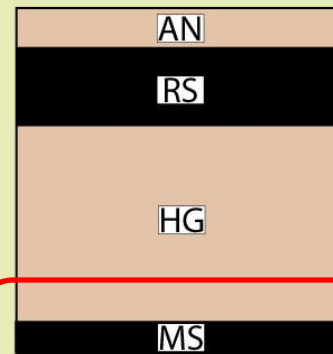
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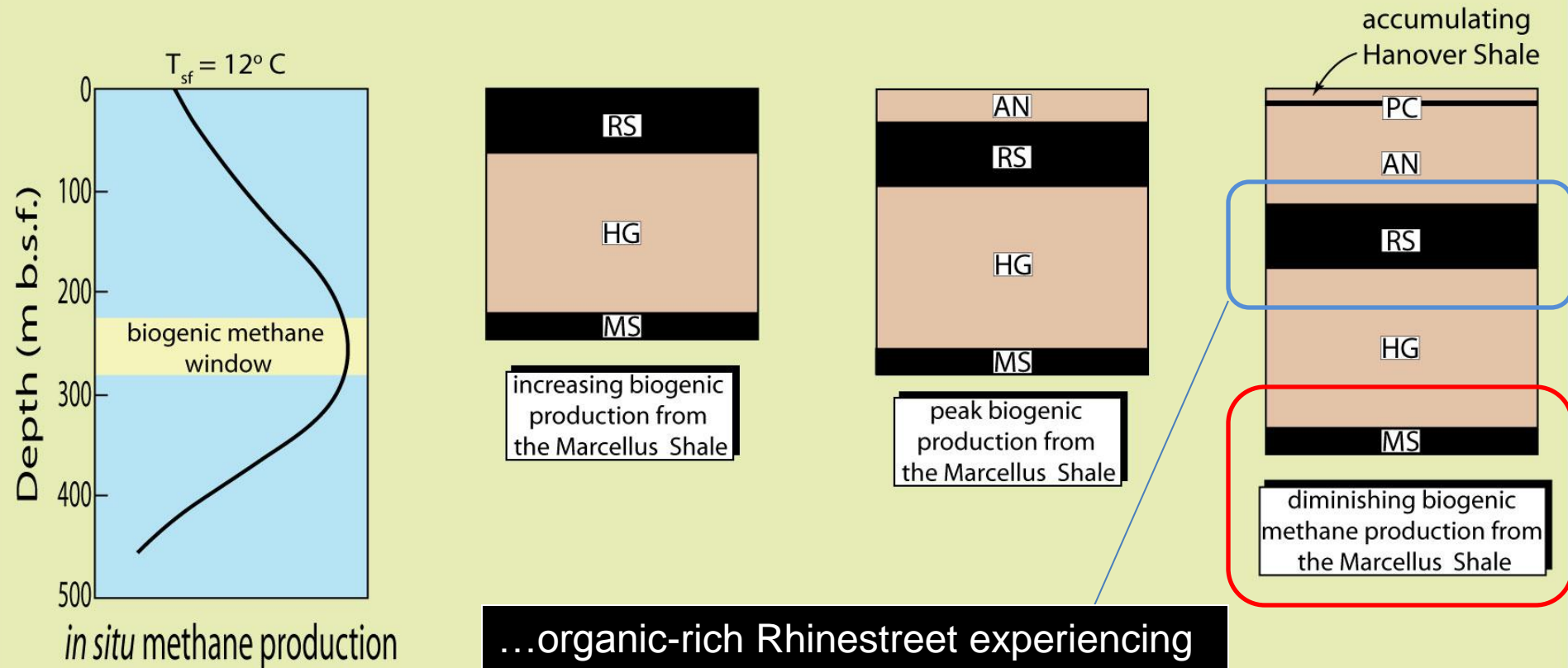
increasing biogenic  
production from  
the Marcellus Shale



peak biogenic  
production from  
the Marcellus Shale



...diminished methane flux as a consequence of the burial of the Middle-Upper Devonian shale succession...



...organic-rich Rhinestreet experiencing increased methanogenesis...

...eventually generated enough biogenic methane to fuel AOM in the Dunkirk Shale and overlying deposits...

# Conclusions

- the Middle and Upper Devonian shale succession was a prolific source of biogenic methane;
- upward migrating methane (mostly biogenic) fueled AOM in overlying deposits and consequent authigenic barite and carbonate precipitation;
- as methanogenesis in the Marcellus waned, the diminished methane flux caused the SMT to descend into the sediment column thereby preserving the authigenic barite;
- a subsequent increased methane flux due to increased methanogenesis of the Rhinestreet Shale caused the SMT to ascend the sediment column resulting in carbonate concretion growth in the Upper Devonian sequence;
- could the Utica Shale have contributed biogenic (and minor thermogenic) methane?



...acknowledgements to former students Randy Blood and Steve Saboda...

