# Possible Sources of Dissolved Inorganic Carbon in the Formation of Middle and Upper Devonian Carbonate Concretions, Appalachian Basin*

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## Abstract

Calcium carbonate concretions are common to the Middle and Upper Devonian shale succession of the Appalachian Basin. Geologic and microtextural evidence suggests that the authigenic carbonate formed at shallow burial depth, perhaps no more than a few tens of meters below the sediment-water interface, in a diagenetic environment resulting from the anaerobic oxidation of methane (AOM). Burial histories of the Middle Devonian Marcellus Shale and Upper Ordovician Utica Shale suggest that only the latter had generated a small amount of thermogenic methane by the time the Devonian shale succession started to accumulate. Thus, oxidized biogenic methane appears to have been the principal dissolved inorganic carbon source of the authigenic carbonate. However, modestly depleted δ13C values of concretions, from the Marcellus Shale upward through the Upper Devonian Dunkirk Shale, are well in excess of δ13C values of authigenic carbonate formed within a diagenetic environment induced by the anaerobic oxidation of biogenic methane. One explanation of this seemingly incongruent relationship entails a combination of the prolonged oxidation of shallow biogenic methane mixed with methanogenic $CO_2$, both of which were sourced at the bottom of the Marcellus Shale. Alternatively, some volume of the methane inventory consumed by AOM within the Devonian shale succession may have originated within the Upper Ordovician Utica Shale. It is plausible that "ancient" biogenic methane was released from the Utica Shale, either over an extended period of time or as a geologically rapid event, to the overlying sedimentary column. Residual biogenic methane that finally reached the accumulating Middle and Upper Devonian deposits would have been only modestly depleted in 13C due to a protracted oxidation history. The obvious shortcoming of a scenario involving the expulsion of methane from the Utica Shale into the Middle and Upper Devonian shale succession is the presence of such intervening units as the Silurian Lockport Dolomite and overlying Salina Formation salt

deposits. However, transport of methane from the Utica could have been enhanced by Acadian foreland basin dynamics, including salt removal, reactivated basement faults and the formation of Acadian faults and related fractures.

## Selected References


Irwin, H., C. Curtis, and M. Coleman, 1977, Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments: Nature, v. 269, p. 209-213.

Katz, B.J., 1995, Biogenic gas - its formation and economic significance: Indonesian Petroleum Association, 24th Annual Convention Proceedings v. 1, p. 461-474.

Scotchman, I.C., 1993, Diagenetic pore fluid evolution in the Kimmeridge Clay Formation: from concretions to sandstone cements, *in* D.A.C. Manning, P.L. Hall, and C.R. Hughes, eds., Geochemist of Clay-Pore Fluid Interactions, Chapman and Hall, London, p. 127-159.

Zeikus, J.G., and M.R. Winfrey, 1976, Temperature limitation of methanogenesis in aquatic sediments: Applied and Environmental Microbiology, v. 31/1, p. 99-107.

# Possible sources of dissolved inorganic carbon in the formation of Middle and Upper Devonian carbonate concretions, Appalachian Basin

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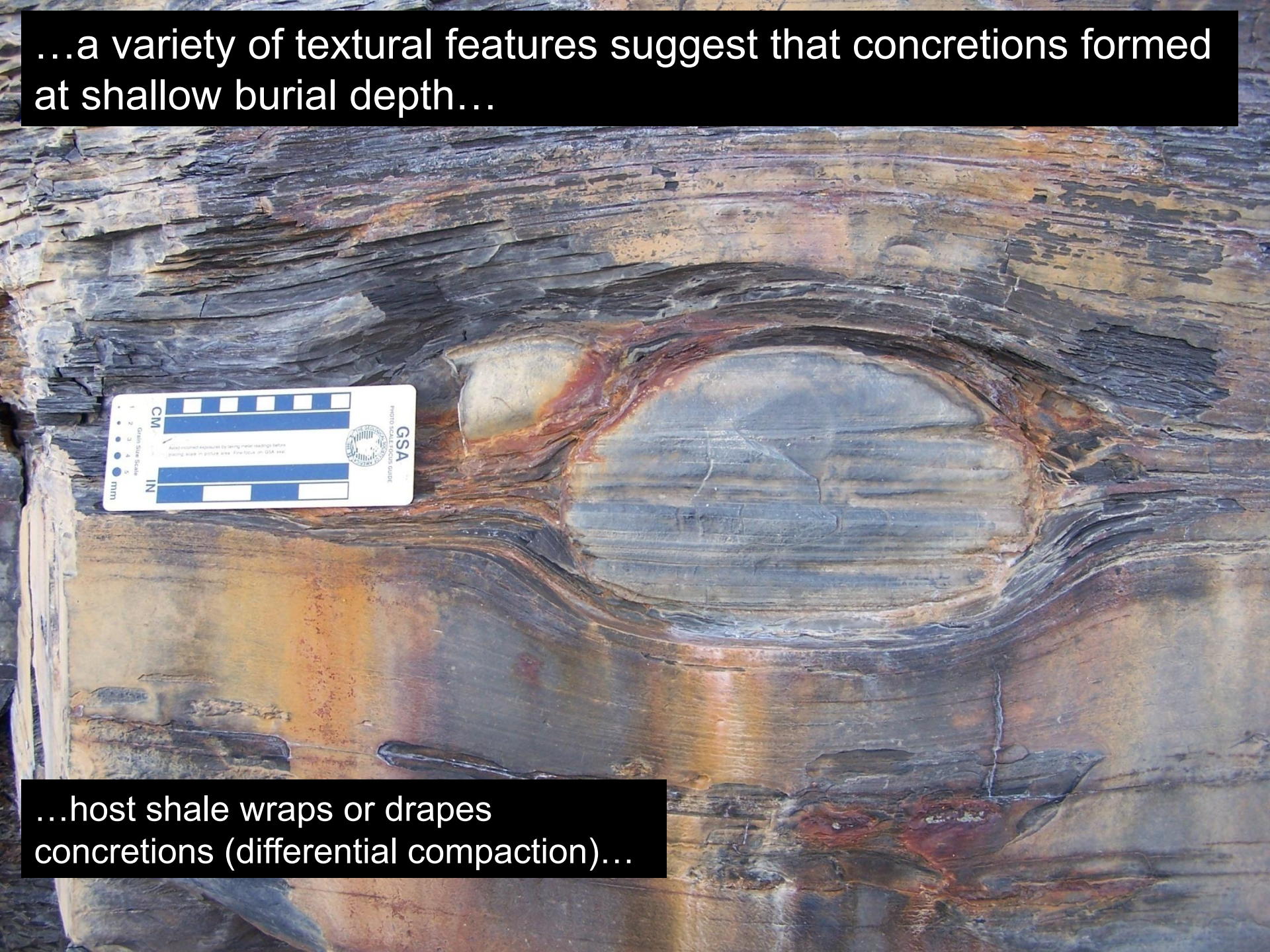
…source rock quality and reservoir integrity –strongly influenced by diagenetic reactions and consequent cementation that occurs at shallow burial depth …

…stable C isotopes – reveals much regarding the diagenetic history of the host shale, including sources of dissolved inorganic carbon …

…carbonate concretions – common throughout the Middle and Upper Devonian succession of the Appalachian Basin of western New York…

…hosted by organic-rich black shale…

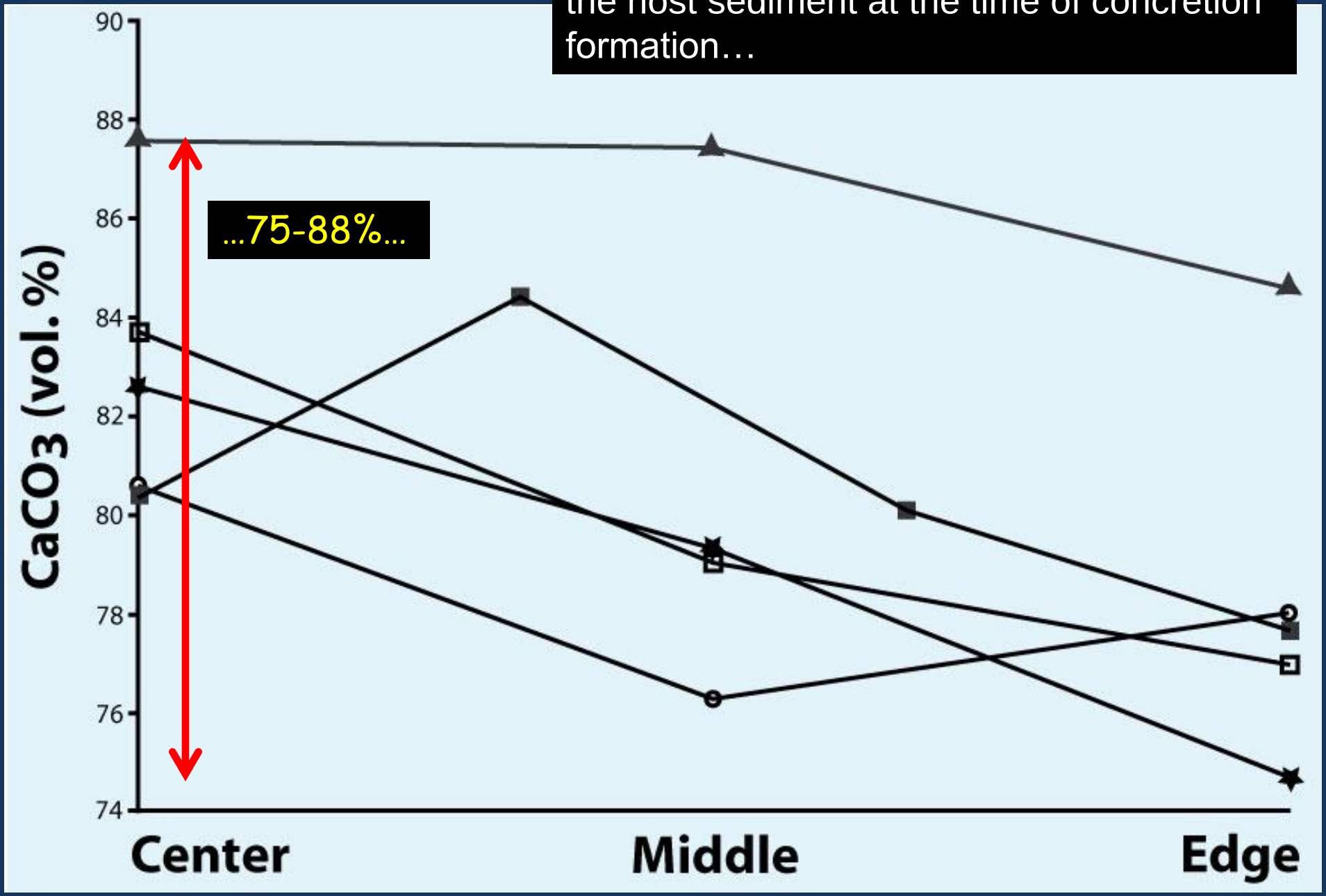

…and organic-lean gray shale…

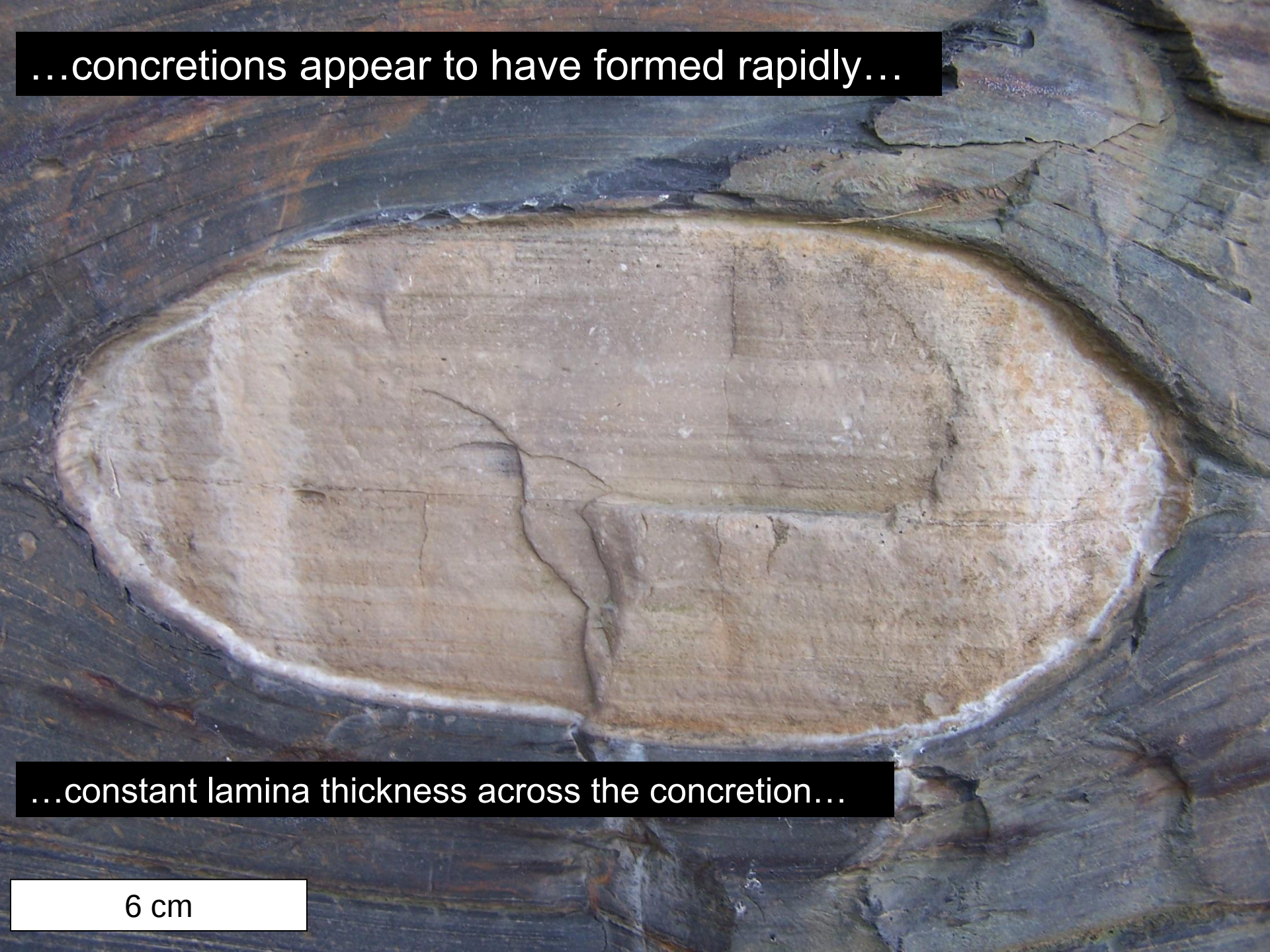

…a variety of textural features suggest that concretions formed at shallow burial depth…
GSA
PHOTO SCALE FOCUS GUIDE
CM
IN
Grain Size Scale
mm
…host shale wraps or drapes concretions (differential compaction)…


…preservation of depositional clay-grain micro-fabrics by carbonate cementation…
6μm 4500X

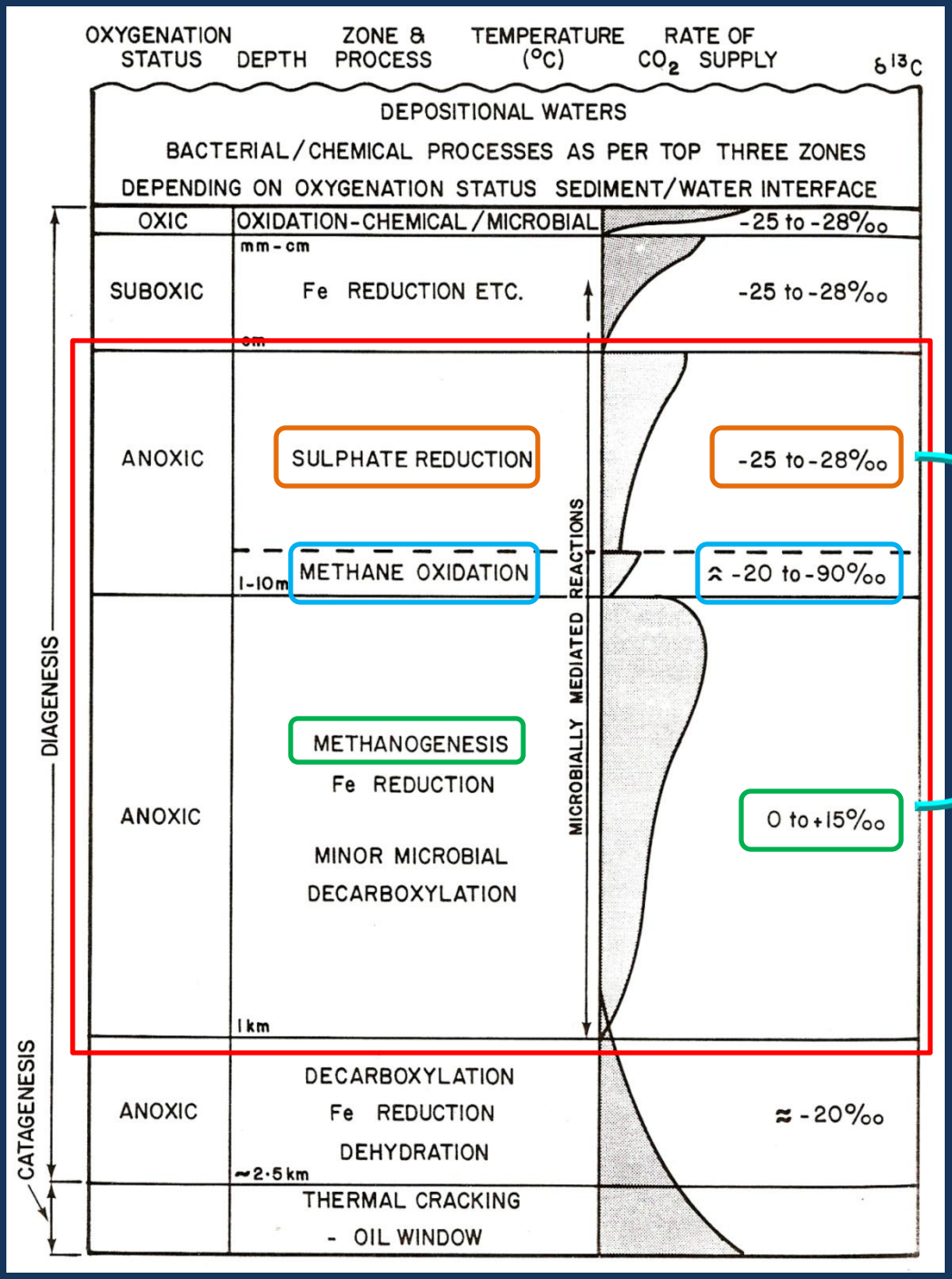
…carbonate content…

…can be used to estimate the porosity of the host sediment at the time of concretion formation…




…concretions appear to have formed rapidly…
…constant lamina thickness across the concretion…
6 cm

…most carbonate concretion are concentrated along specific stratigraphic horizons…




…$\delta^{13}C$ values of the cements can be used to assess the contributions of $CO_2$ produced within various diagenetic reaction zones related to the degradation of organic matter…

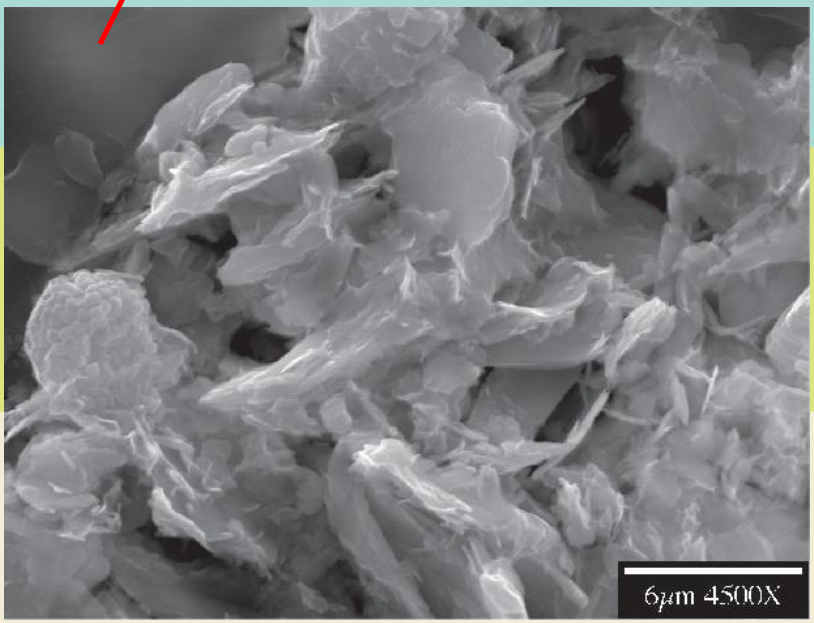
…note possible spread of $\delta^{13}C$ values over a relatively narrow depth range…

Irwin et al, 1977; Scotchman, 1993

$\delta^{13}C$

-20 -10 0 10

…masses (few wt. % $CaCO_3$) of porous compaction-resistant carbonate…




…strong concentration of $CaCO_3$ along preferential formation along stratal horizons…

…no depth implied…

sulfate reduction

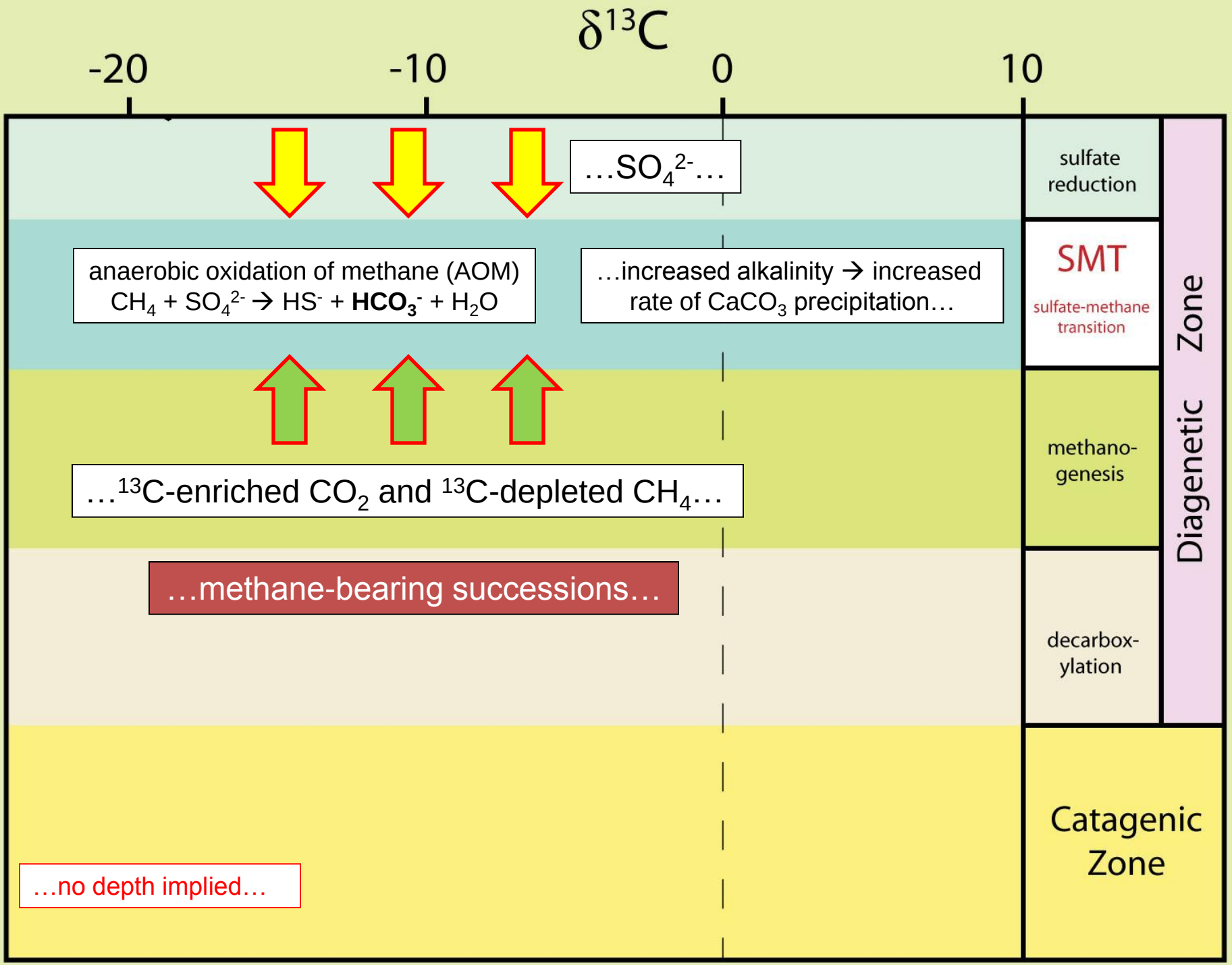
sulfate reduction-methanogenesis transition

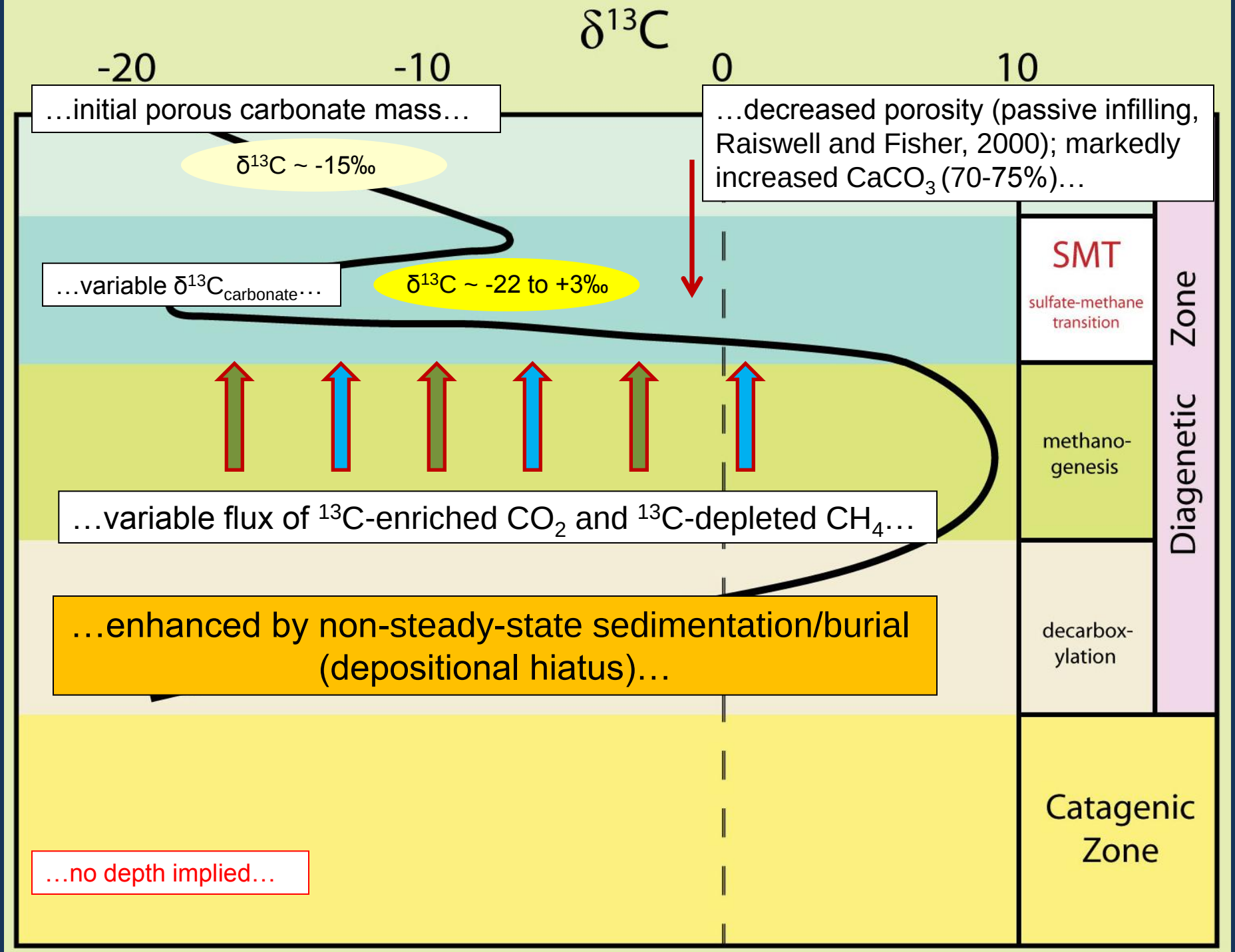
methano-genesis

decarbox-ylation

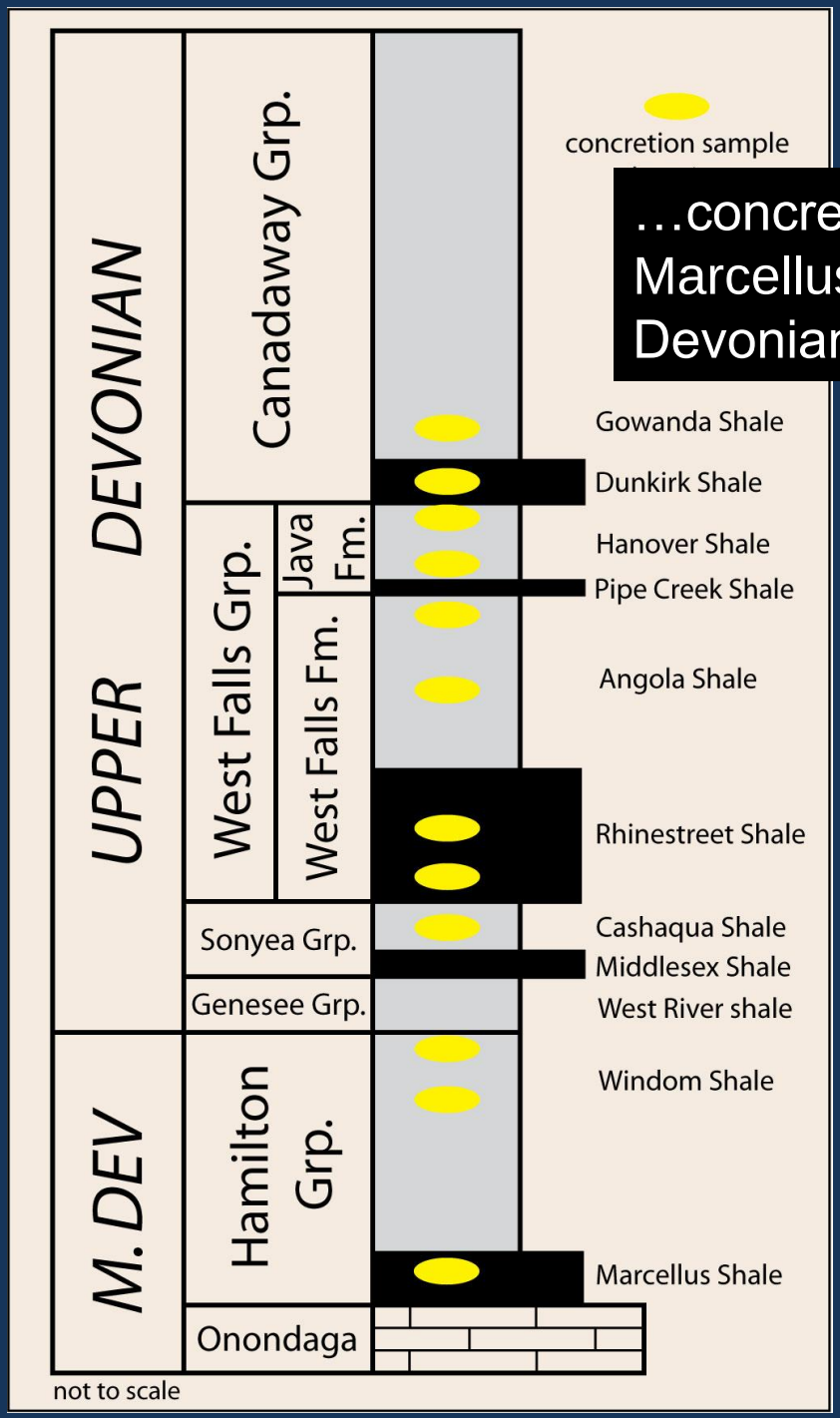
Diagenetic Zone

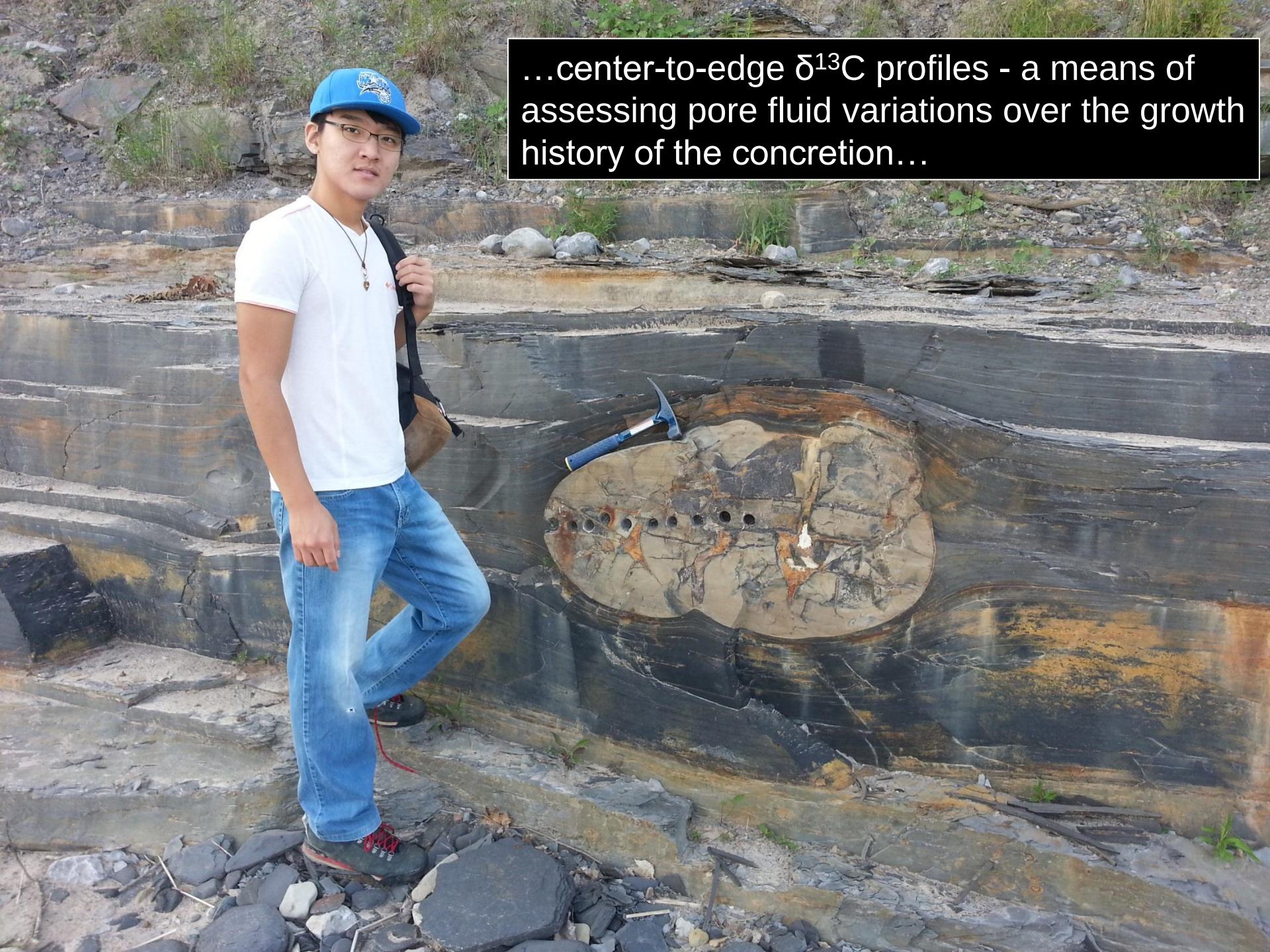
Catagenic Zone


δ13C
-20
-10
0
10
…SO4 2-…
anaerobic oxidation of methane (AOM)
CH4 + SO4 2- → HS- + HCO3- + H2O
…increased alkalinity → increased rate of CaCO3 precipitation…
…13C-enriched CO2 and 13C-depleted CH4…
…methane-bearing successions…
…no depth implied…
sulfate reduction
SMT
sulfate-methane transition
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone


δ13C
-20
-10
0
10
…initial porous carbonate mass…
δ13C ~ -15‰
…decreased porosity (passive infilling, Raiswell and Fisher, 2000); markedly increased CaCO3 (70-75%)…
…variable δ13Ccarbonate…
δ13C ~ -22 to +3‰
SMT
sulfate-methane transition
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone
…variable flux of 13C-enriched CO2 and 13C-depleted CH4…
…enhanced by non-steady-state sedimentation/burial (depositional hiatus)…
…no depth implied…

…concretions from the Middle Devonian Marcellus Shale upward through the Upper Devonian Gowanda Shale were sampled…



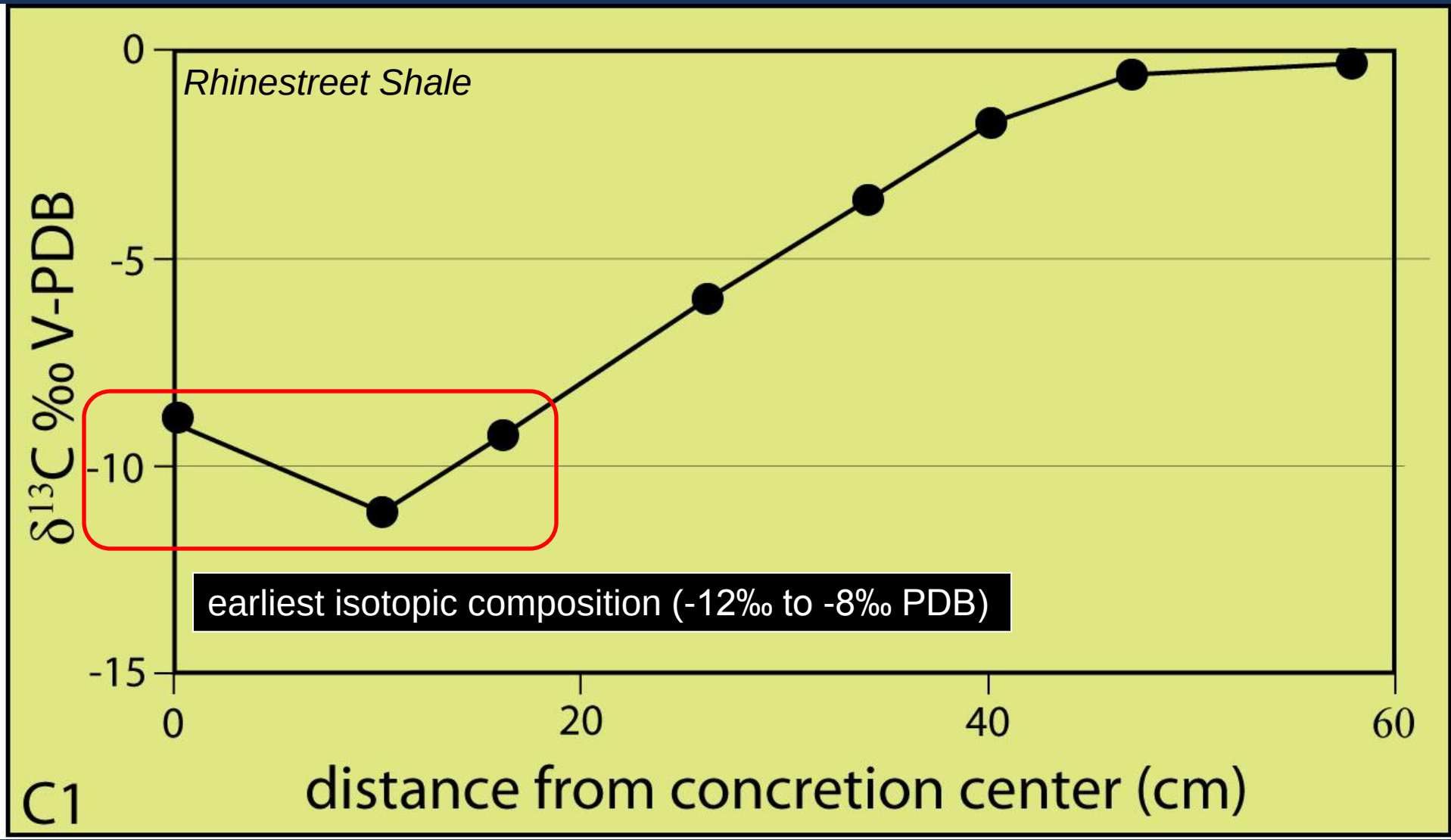

…center-to-edge δ13C profiles - a means of assessing pore fluid variations over the growth history of the concretion…

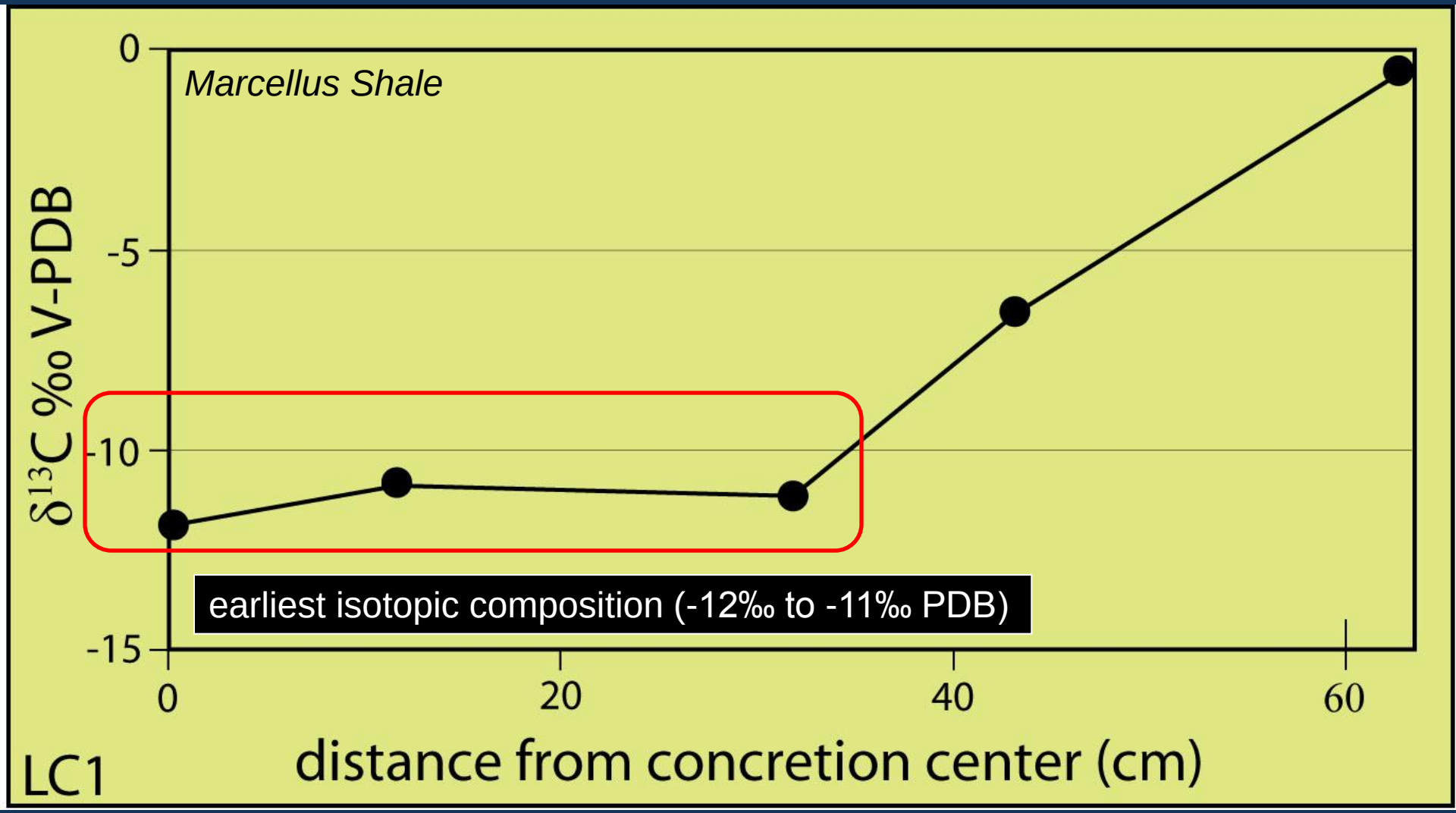
…absolute $\delta^{13}C$ values -secondary to the general trend of center-to-edge profiles…

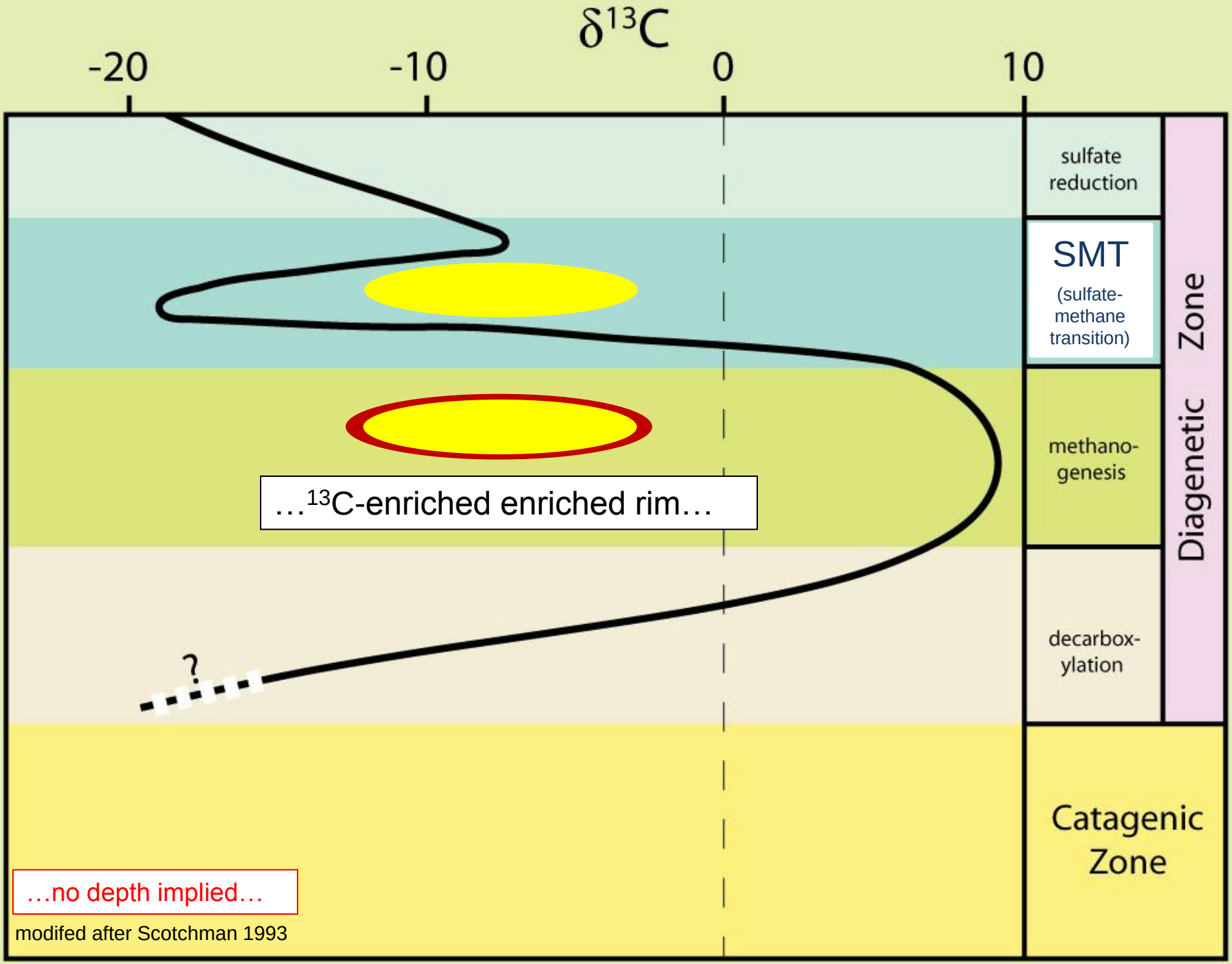
…absolute $\delta^{13}C$ values reflect:

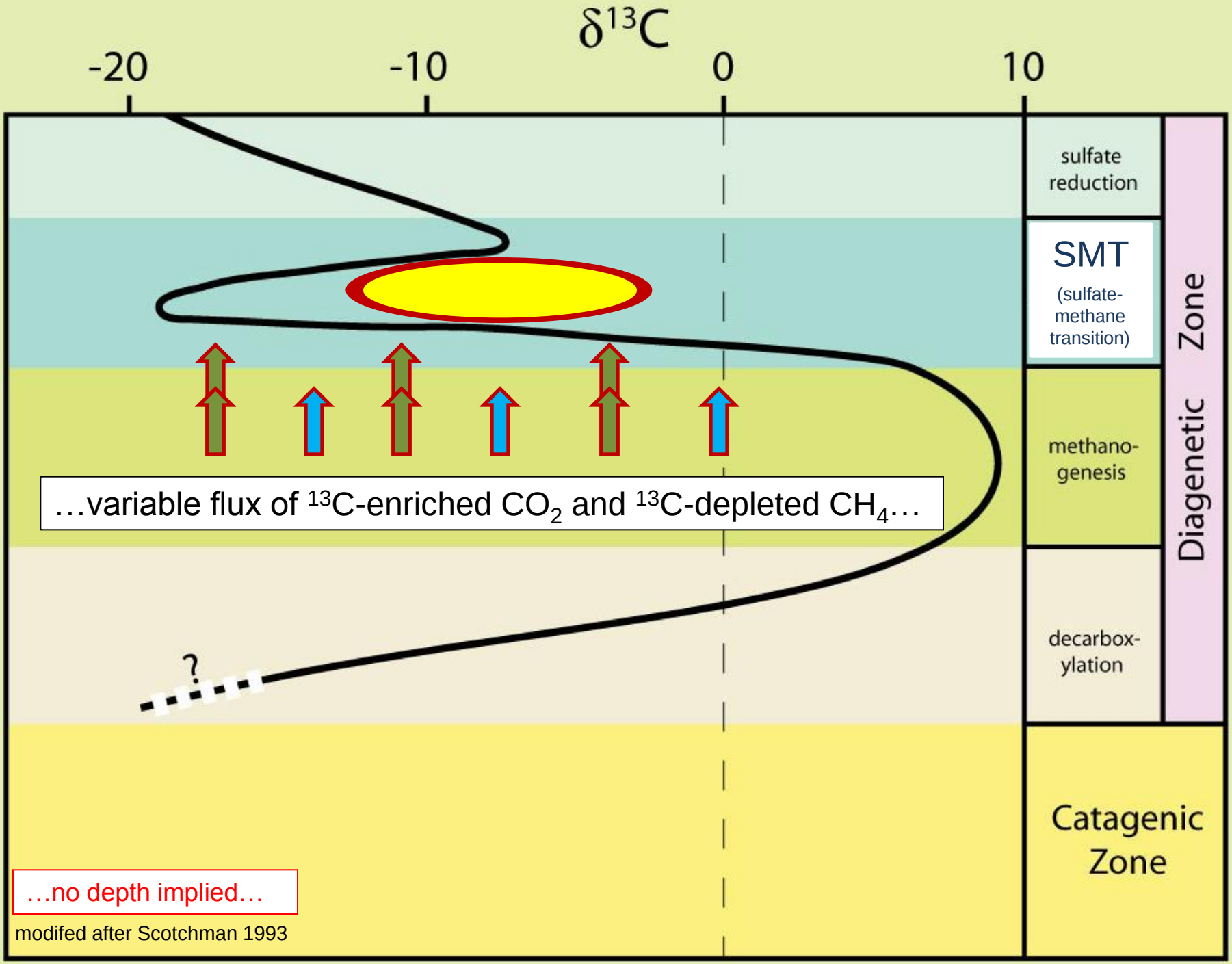
- -variable diffusional flux rates of methanogenic $CO_2$ and $CH_4$;
- -contribution of thermogenic $CH_4$;
- -extended oxidation history of upward diffusing $CH_4$;

…most common center-to-edge $\delta^{13}C$ profile of the studied Devonian carbonate concretions …increasing $\delta^{13}C$ …

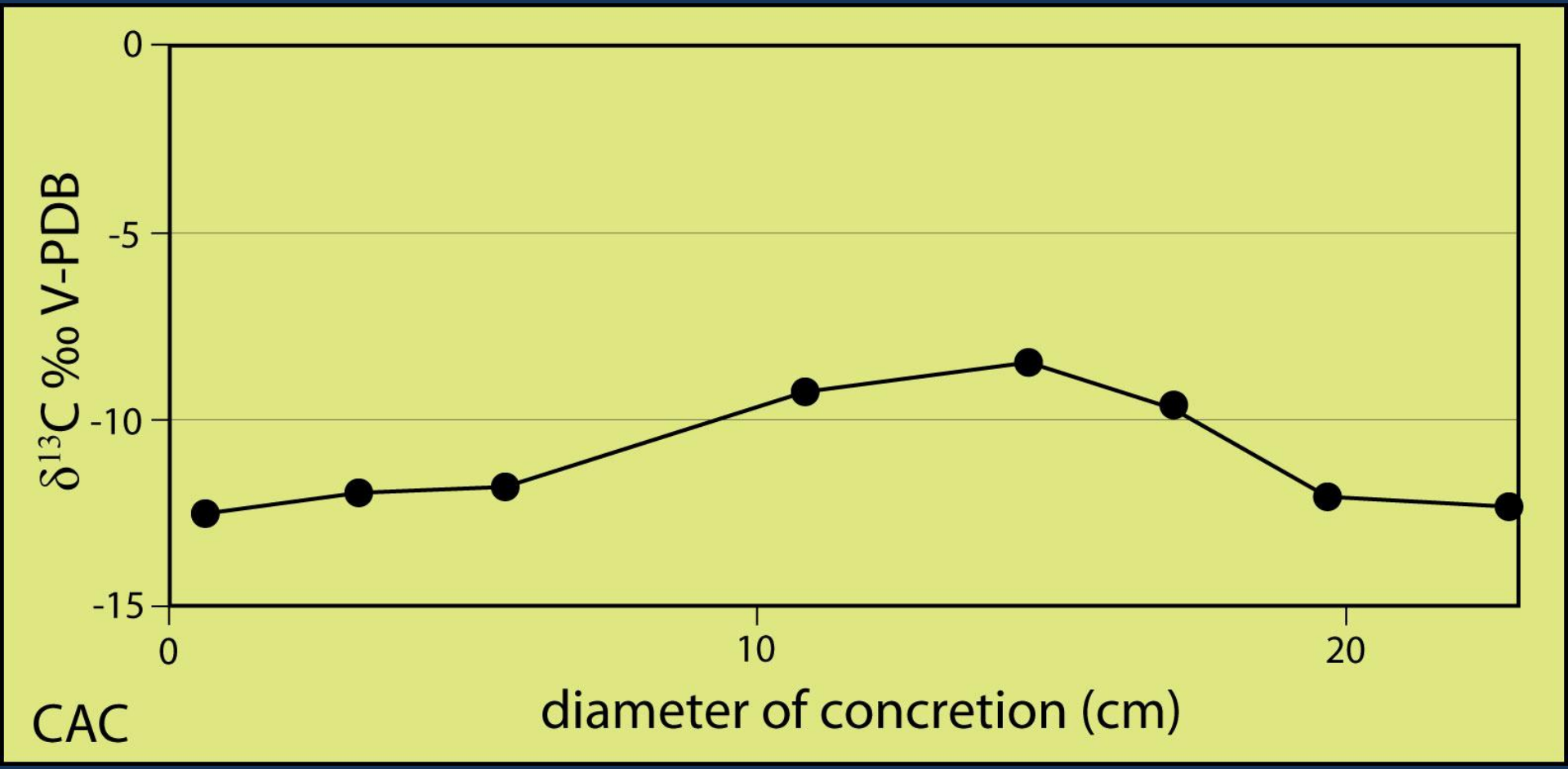


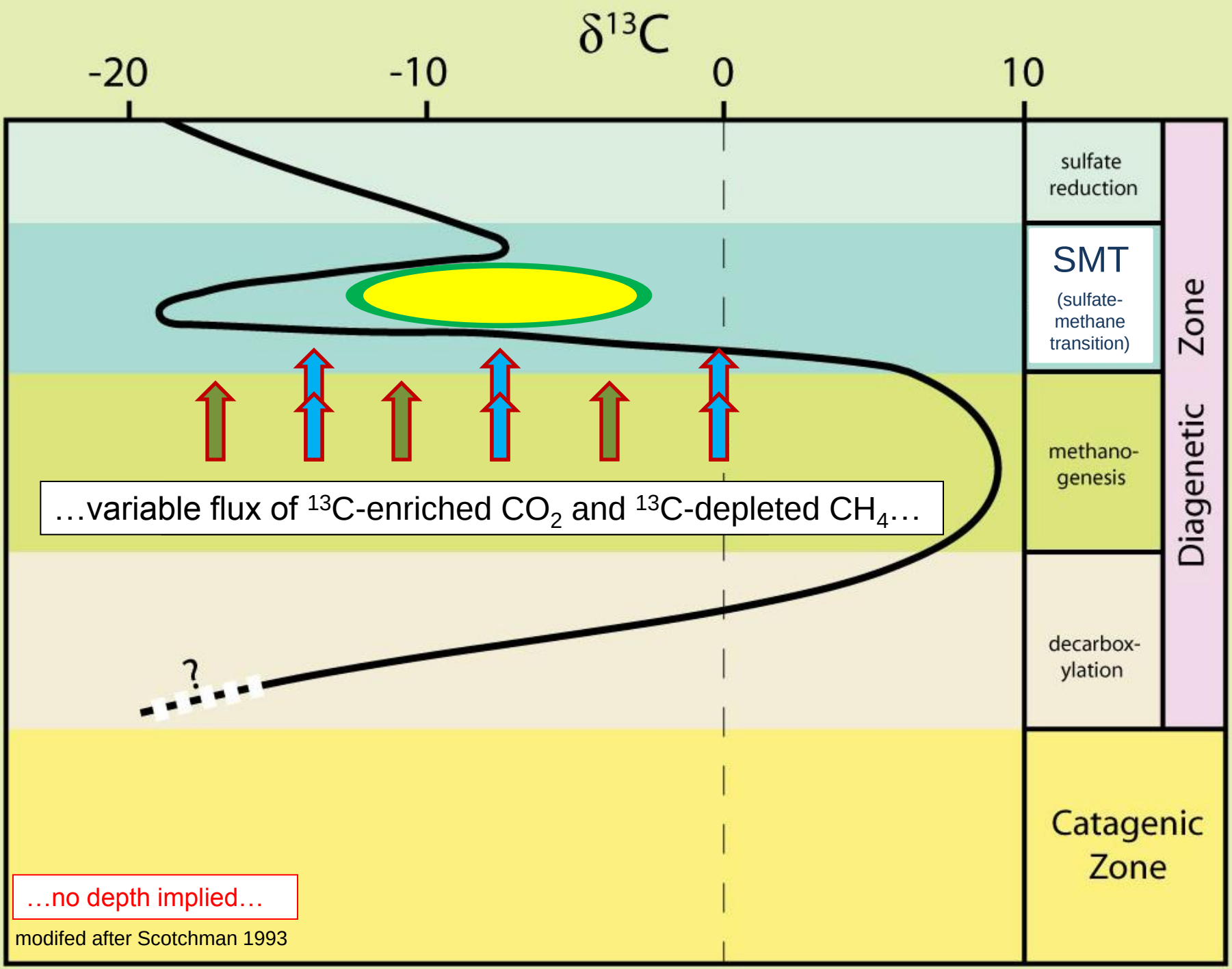

Marcellus Shale
0
-5
-10
-15
δ13C ‰ V-PDB
earliest isotopic composition (-12‰ to -11‰ PDB)
0
20
40
60
distance from concretion center (cm)
LC1


δ13C
-20
-10
0
10
sulfate reduction
SMT
(sulfate-methane transition)
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone
…13C-enriched enriched rim…
?
…no depth implied…
modifed after Scotchman 1993

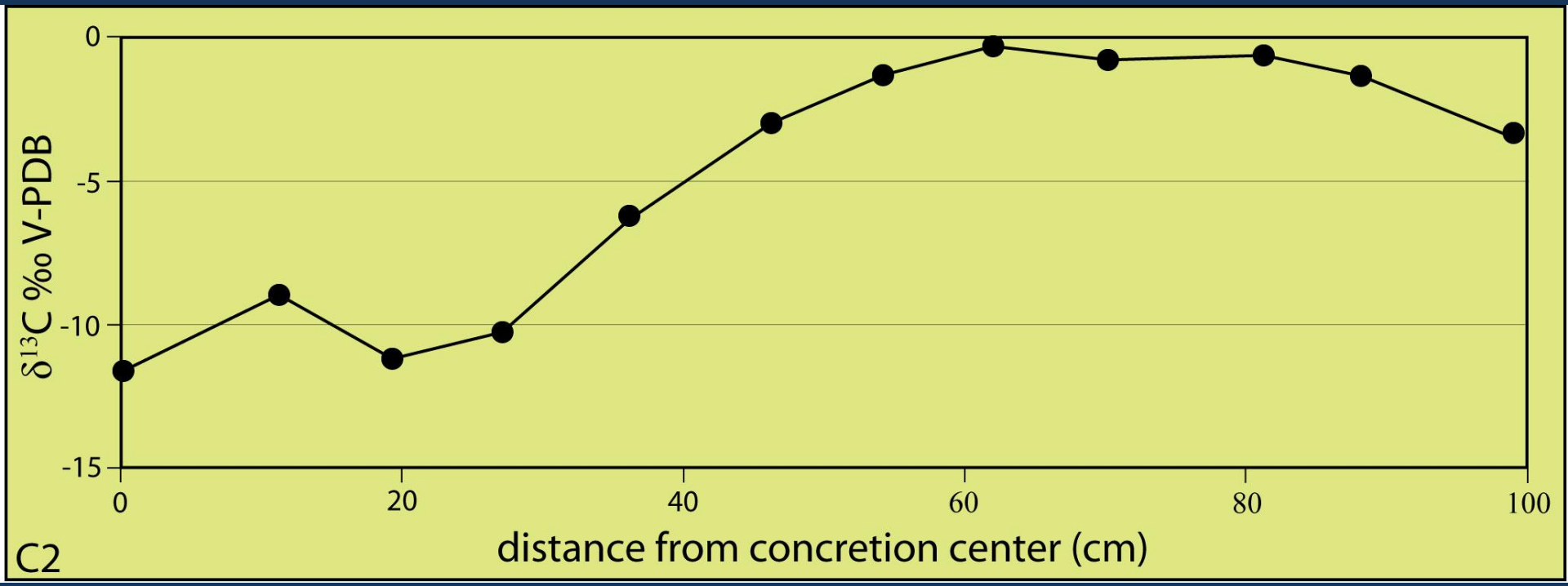

δ13C
-20
-10
0
10
sulfate reduction
SMT
(sulfate-methane transition)
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone
…variable flux of 13C-enriched CO2 and 13C-depleted CH4…
?
…no depth implied…
modifed after Scotchman 1993

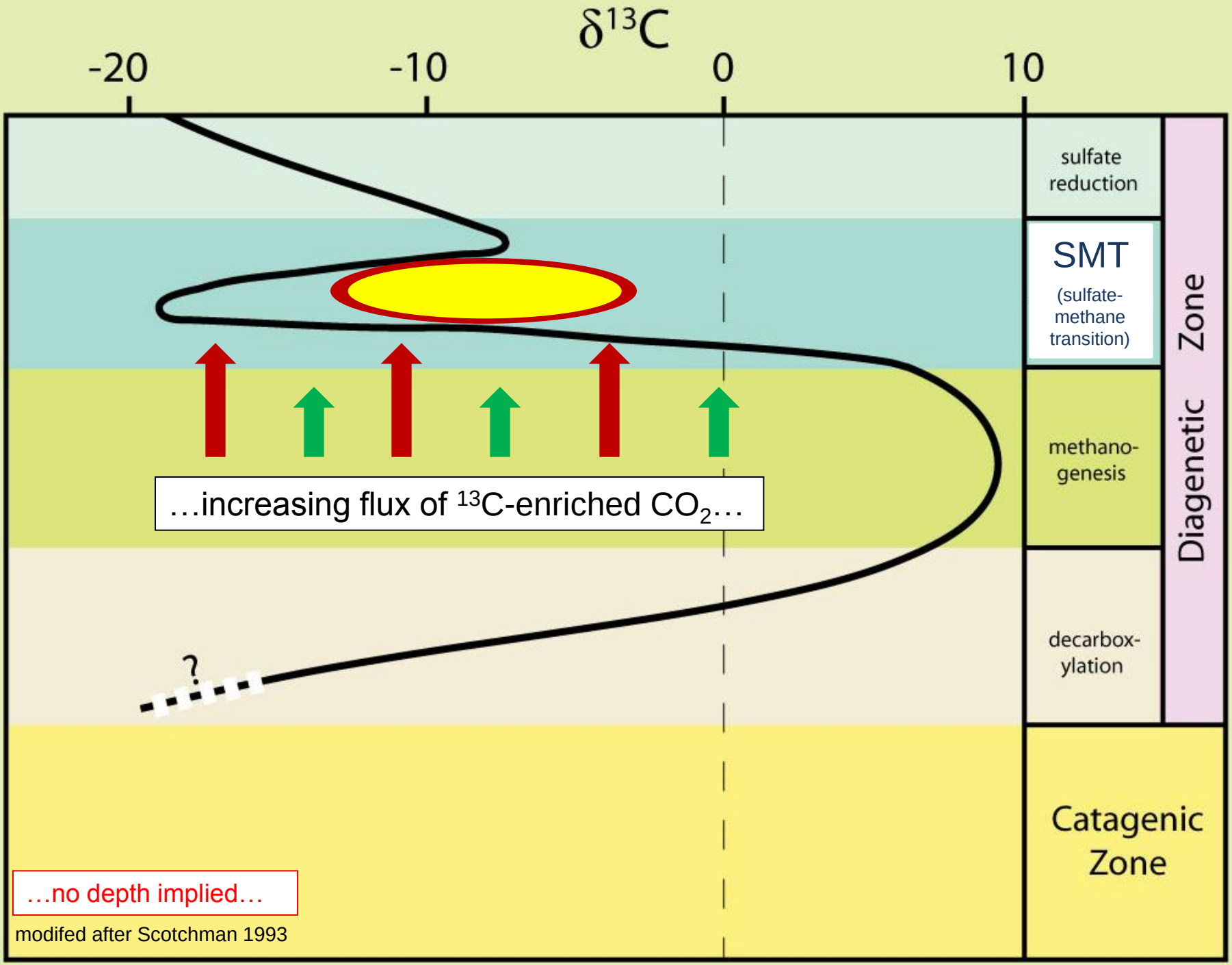
…outward decreasing $\delta^{13}C$ …

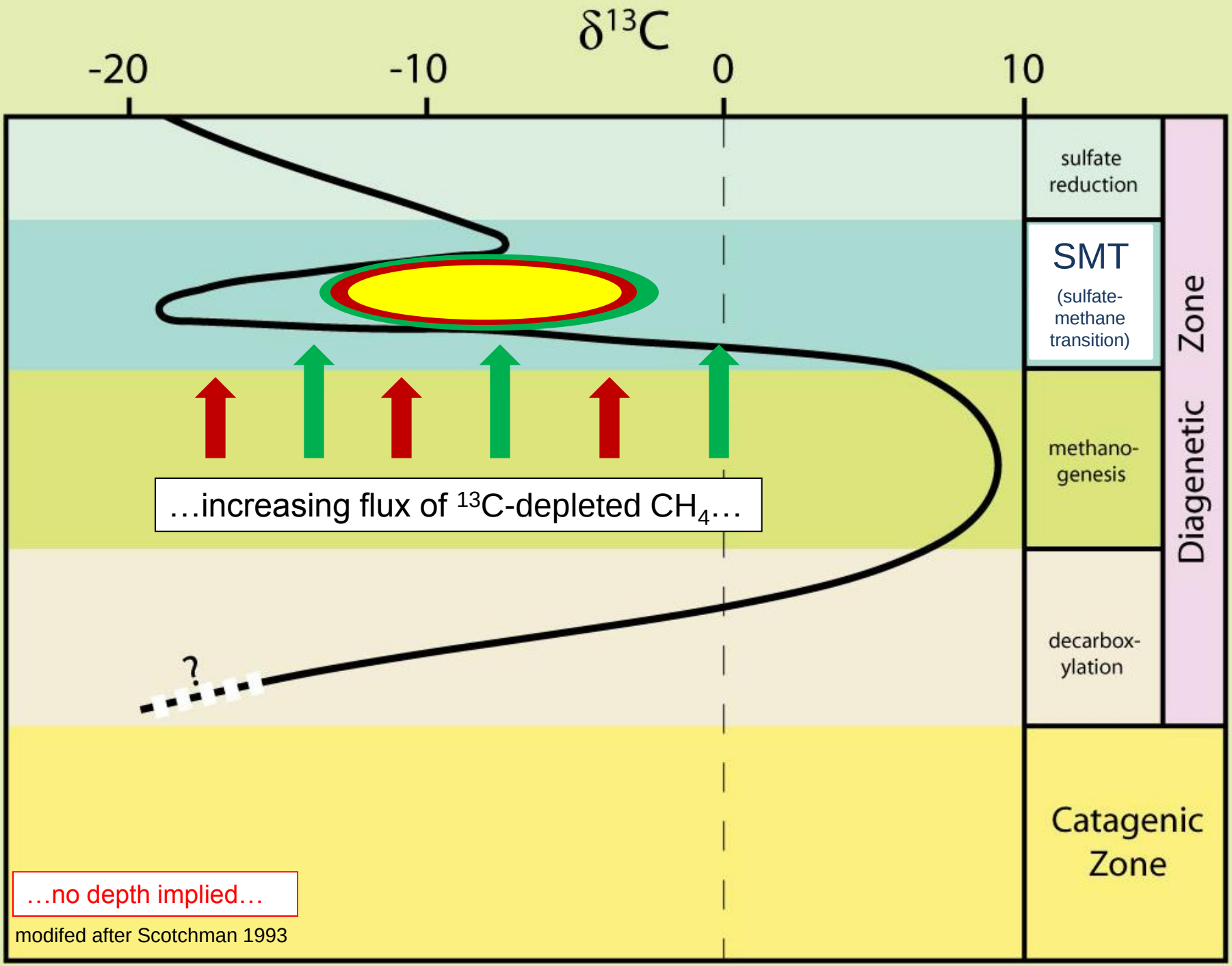



δ13C
-20
-10
0
10
sulfate reduction
SMT
(sulfate-methane transition)
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone
…variable flux of 13C-enriched CO2 and 13C-depleted CH4…
?
…no depth implied…
modifed after Scotchman 1993

…outward increase of $\delta^{13}C$ followed by decreasing $\delta^{13}C$…




δ13C
-20
-10
0
10
sulfate reduction
SMT
(sulfate-methane transition)
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone
…increasing flux of 13C-enriched CO2…
?
…no depth implied…
modifed after Scotchman 1993


δ13C
-20
-10
0
10
sulfate reduction
SMT
(sulfate-methane transition)
methano-genesis
decarbox-ylation
Diagenetic Zone
Catagenic Zone
…increasing flux of 13C-depleted CH4…
?
…no depth implied…
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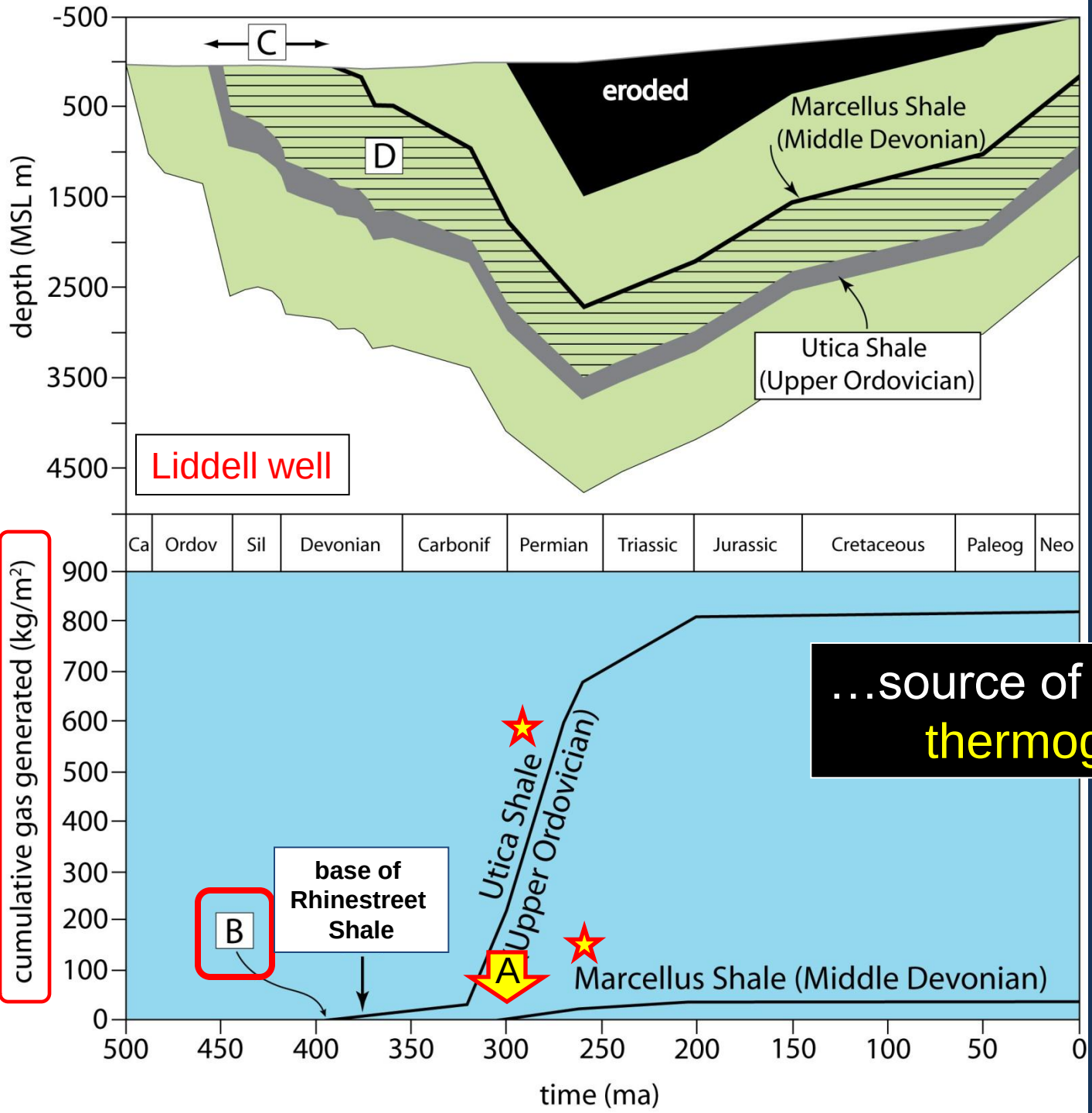
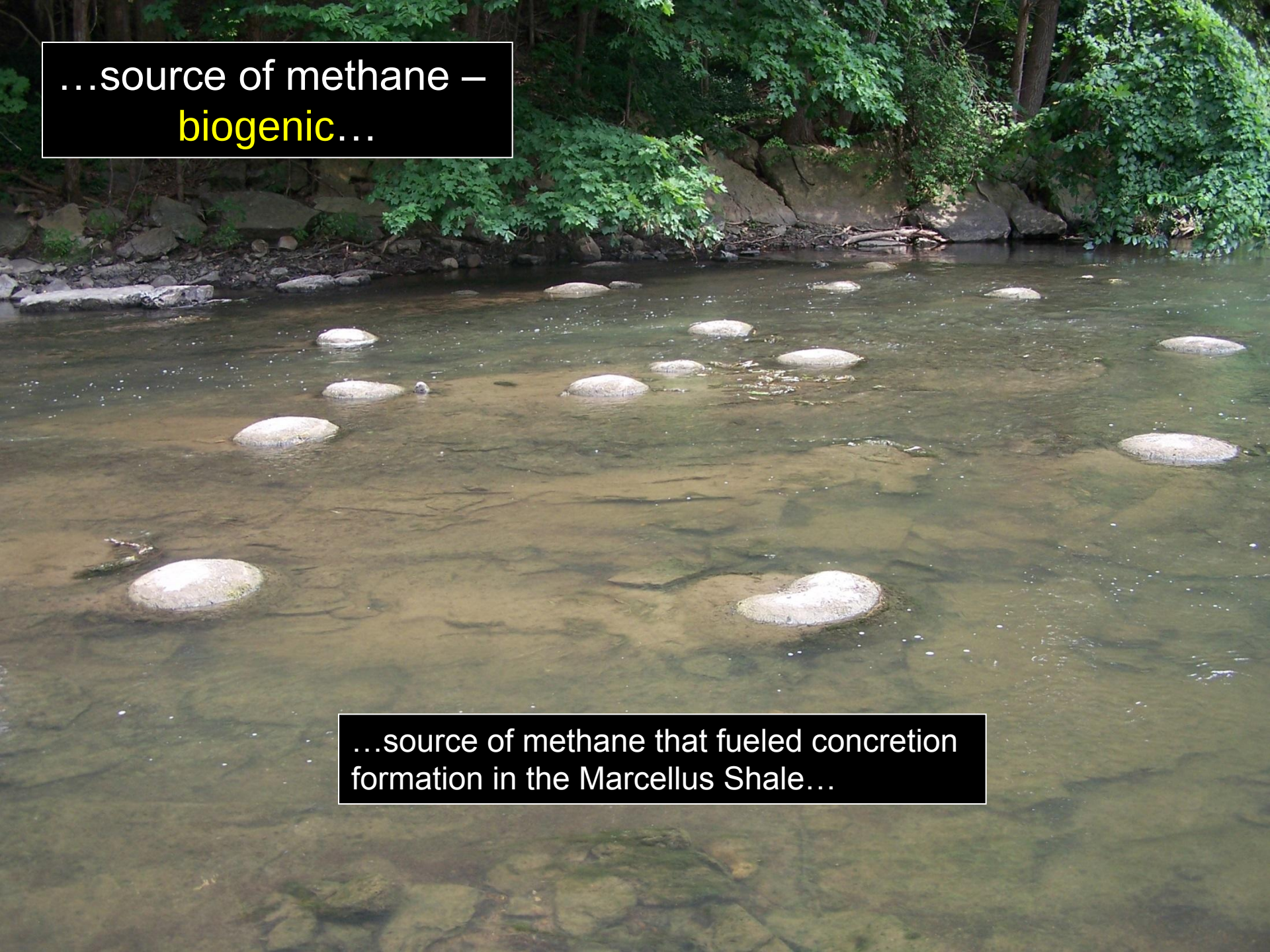



A - onset of thermogenic generation in the Marcellus Shale – post-dates deposition of the Rhinestreet Shale

B - onset of thermogenic generation – Utica Shale; shortly before accumulation of the Rhinestreet Shale

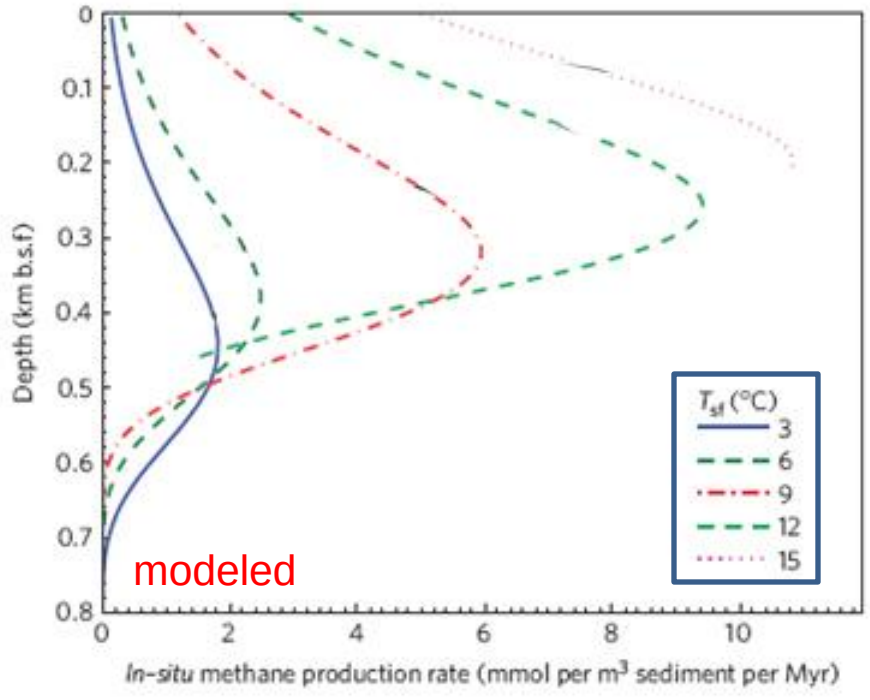
…source of methane – thermogenic…

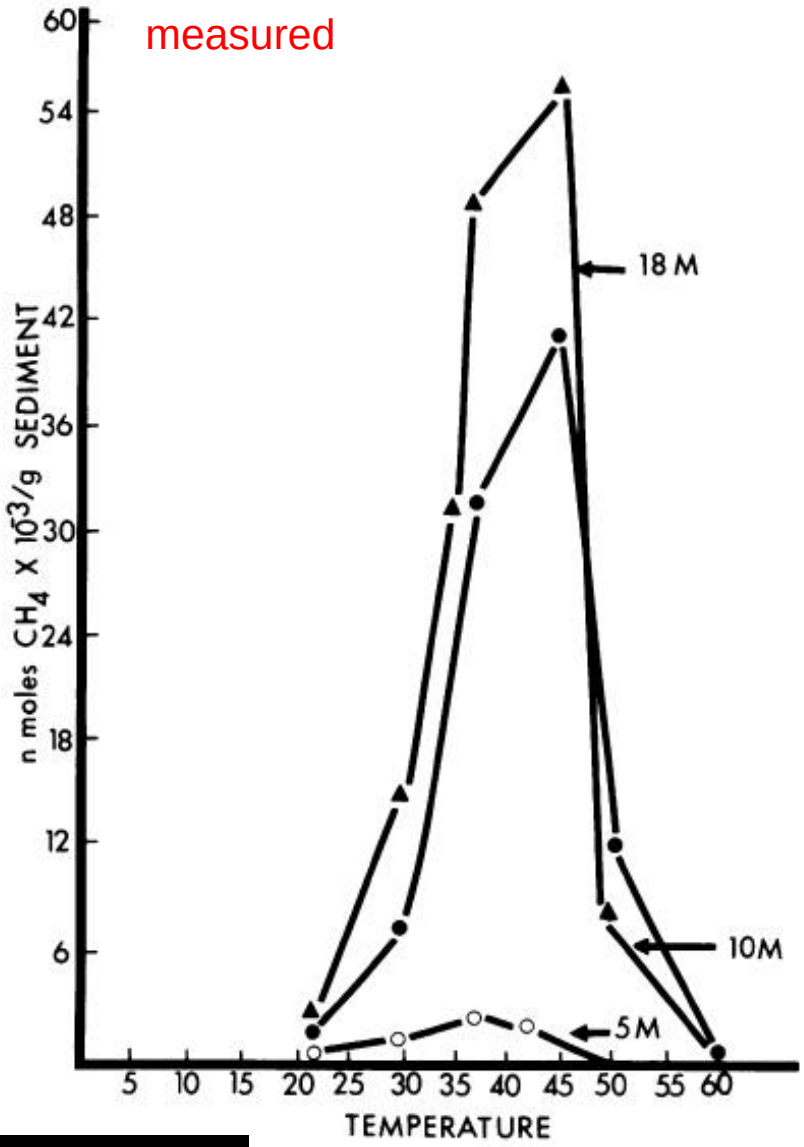

…source of methane – biogenic…
…source of methane that fueled concretion formation in the Marcellus Shale…

…methanogenesis increases exponentially with increasing temperature (burial depth)…

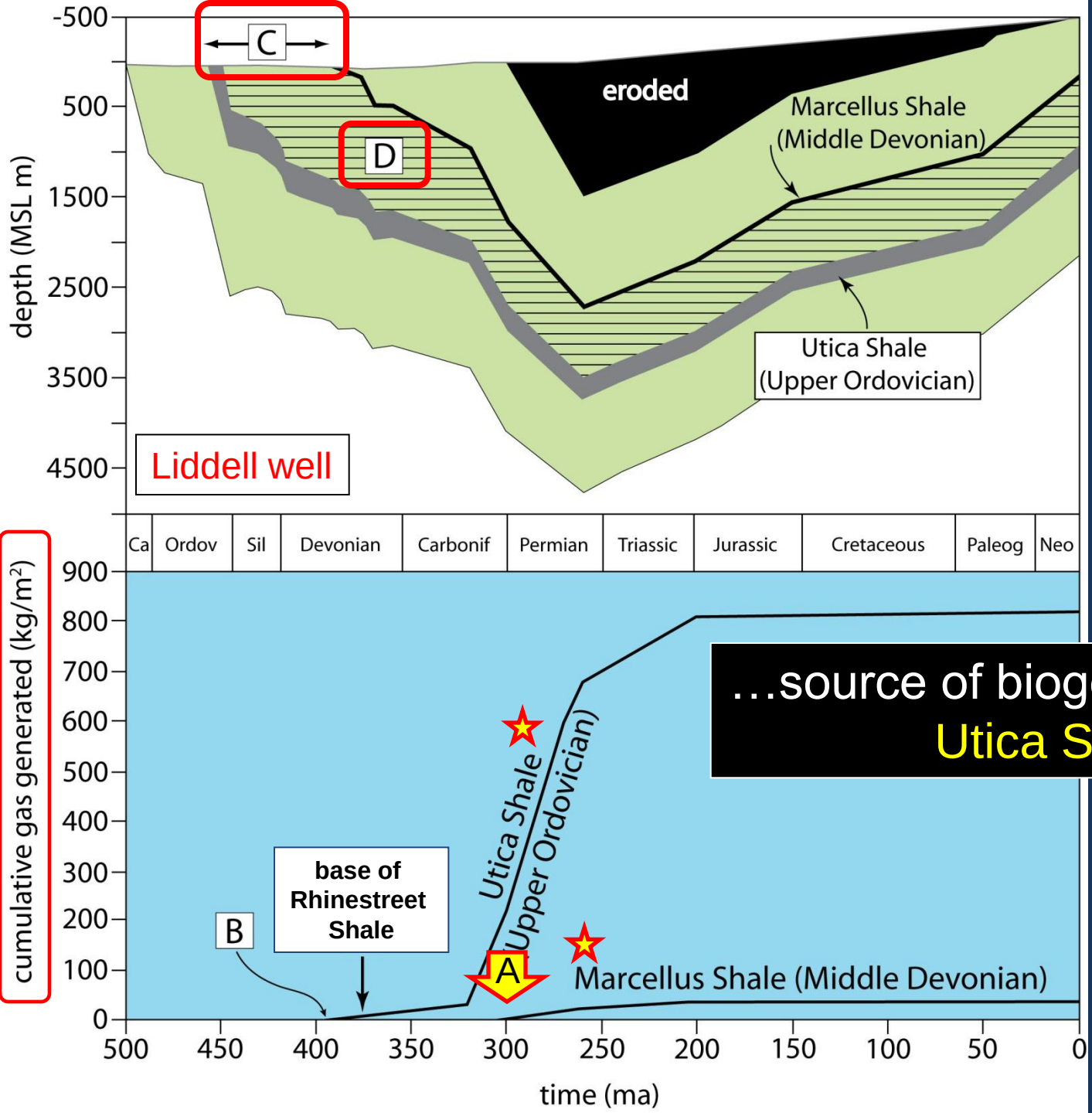
…likely that the $CH_4$ that fueled Marcellus concretions did not originate within the Marcellus…

…biogenic $CH_4$ production as a function of seafloor temperature ($T_{sf}$) …




(Zeikus and Winfrey, 1976; Katz, 1995; Mikucki et al.,2003; Gu et al., 2011)




C - duration of biogenic methane production in the Utica Shale (at least 50 MY)

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

…source of biogenic methane – Utica Shale…

# Conclusions

-the Middle and Upper Devonian shale succession was methane – charged (likely biogenic methane) early in its burial history;

-non-steady-state sedimentation/burial focused AOM and consequent enhanced alkalinity along specific stratal horizons giving rise to the precipitation of authigenic carbonate;

-center-to-edge $\delta^{13}C$ profiles of carbonate concretions generally reflect an increasing influence of methanogenic $CO_2$ that may preserve a record of the enhanced diffusion of $CO_2$ relative to $CH_4$;

-variable flux of $CO_2$ and $CH_4$ provides a record of varying intensities of biogenic methane generation;

-could the Utica Shale have contributed biogenic (and minor thermogenic) methane?

…acknowledgements to former students Randy Blood, Steve Saboda, and Junhee Choi…