Vigorous Anaerobic Methane Oxidation in the Upper Devonian Succession, Western New York; Possible Evidence for Devonian Gas Hydrates*

Gary G. Lash[1] and Randy Blood[2]

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Abstract

Fine-grained organic-rich rocks that have accumulated under anoxic conditions can begin generating methane soon after deposition, sometimes at burial depths of several meters or so, as a consequence of microbially mediated degradation of organic matter. Biogenic methane migrates upward through the zone of methanogenesis to the sulfate-methane transition zone (SMTZ), where anaerobic methane oxidation (AMO) depletes interstitial water of seawater sulfate and methane to produce ^{13}C-depleted biocarbonate and ^{34}S-enriched sulfide. Methane flux is a principal control on the depth below the seafloor of the SMTZ. Specifically, high methane flux rates, such as those described from modern methane hydrates, result in the establishment of shallow (< 1 m) SMTZs. The Upper Devonian Rhinestreet-Angola-Pipe Creek-Hanover shale succession of western New York provides a record of non-steady state burial and related AMO. Evidence of the latter includes thin (10-30 cm) intervals moderately enriched in Fe and S, ^{13}C-depleted authigenic concretionary carbonate (δ^{13}C = -11 to -14‰ PDV), ^{34}S-enriched pyrite (δ^{34}S = 24 - 25% CDV) associated with the carbonate, and an interval of ^{34}S-enriched (δ^{34}S = 43% CDV) barite nodules. Differential compaction of host shale around concretions as well as the preservation of depositional clay grain microfabrics within concretions suggests that the latter formed as a consequence of passive carbonate precipitation at subseafloor depths of ~ 1 m. The organic-rich Rhinestreet Shale, then, appears to have been an especially active bioreactor that maintained a shallow SMTZ throughout the burial history of these deposits. Moreover, multiple concretion intervals from the lower Rhinestreet Shale through the overlying organic-lean Angola Shale reflect episodes of AMO induced by episodic reductions in sedimentation rate. Textural aspects of this succession, isotope data, and seemingly shallow SMTZ depths are consistent with a robust methane source, perhaps even a gas hydrate. Indeed, recent modeling suggests that gas hydrates could have formed beneath a warm, relatively shallow Middle to Late Devonian sea at burial depths of less than 300 m.

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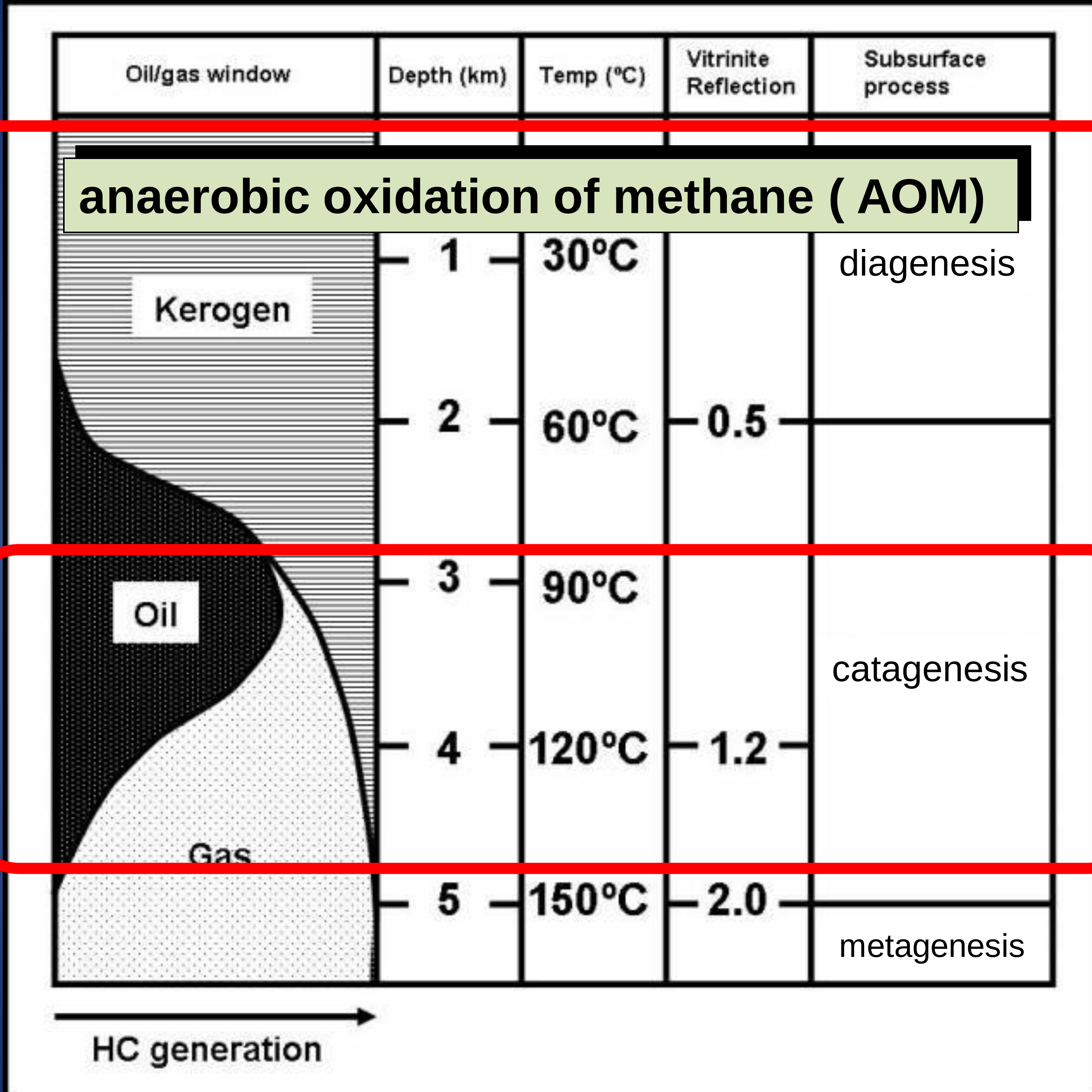
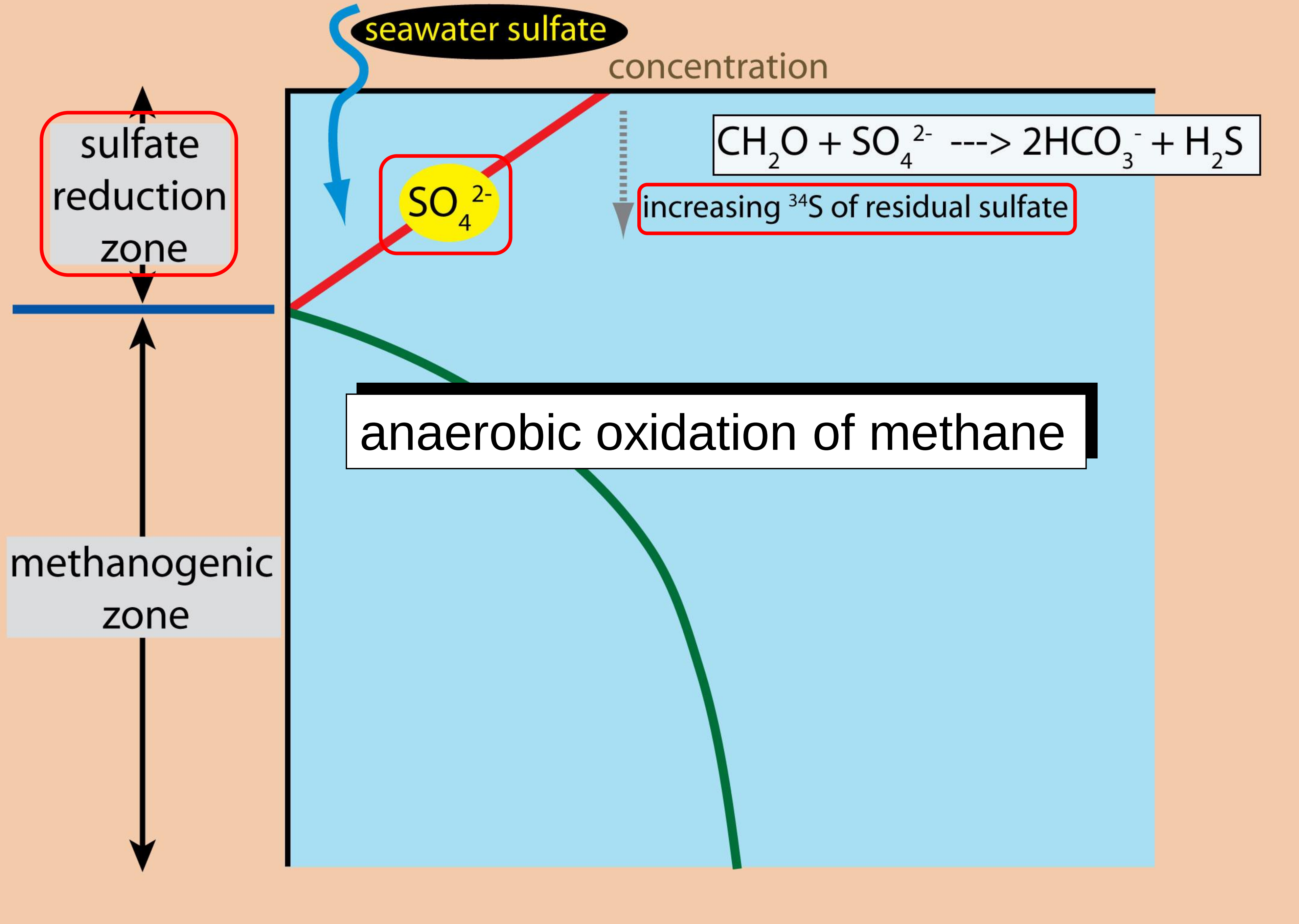
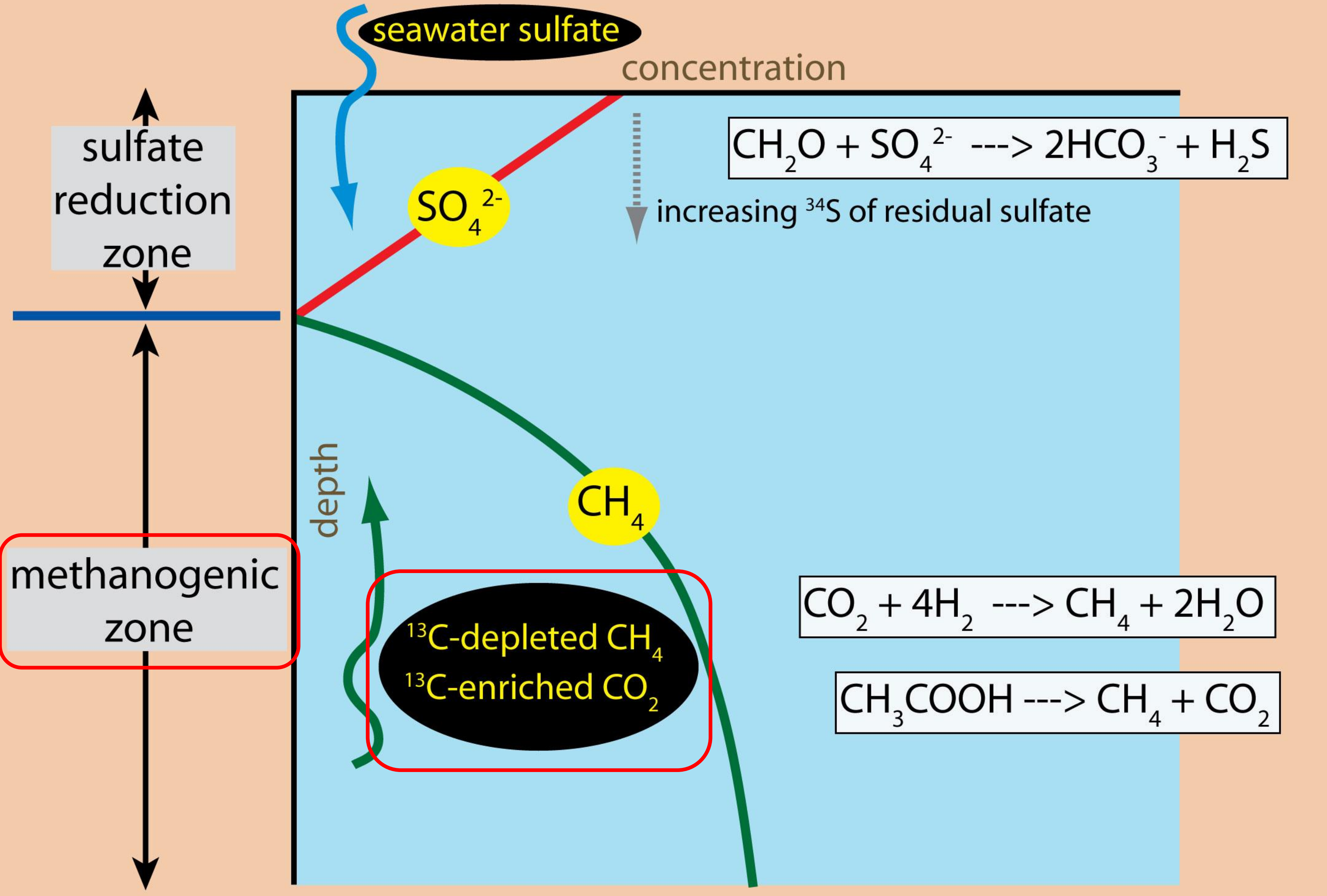
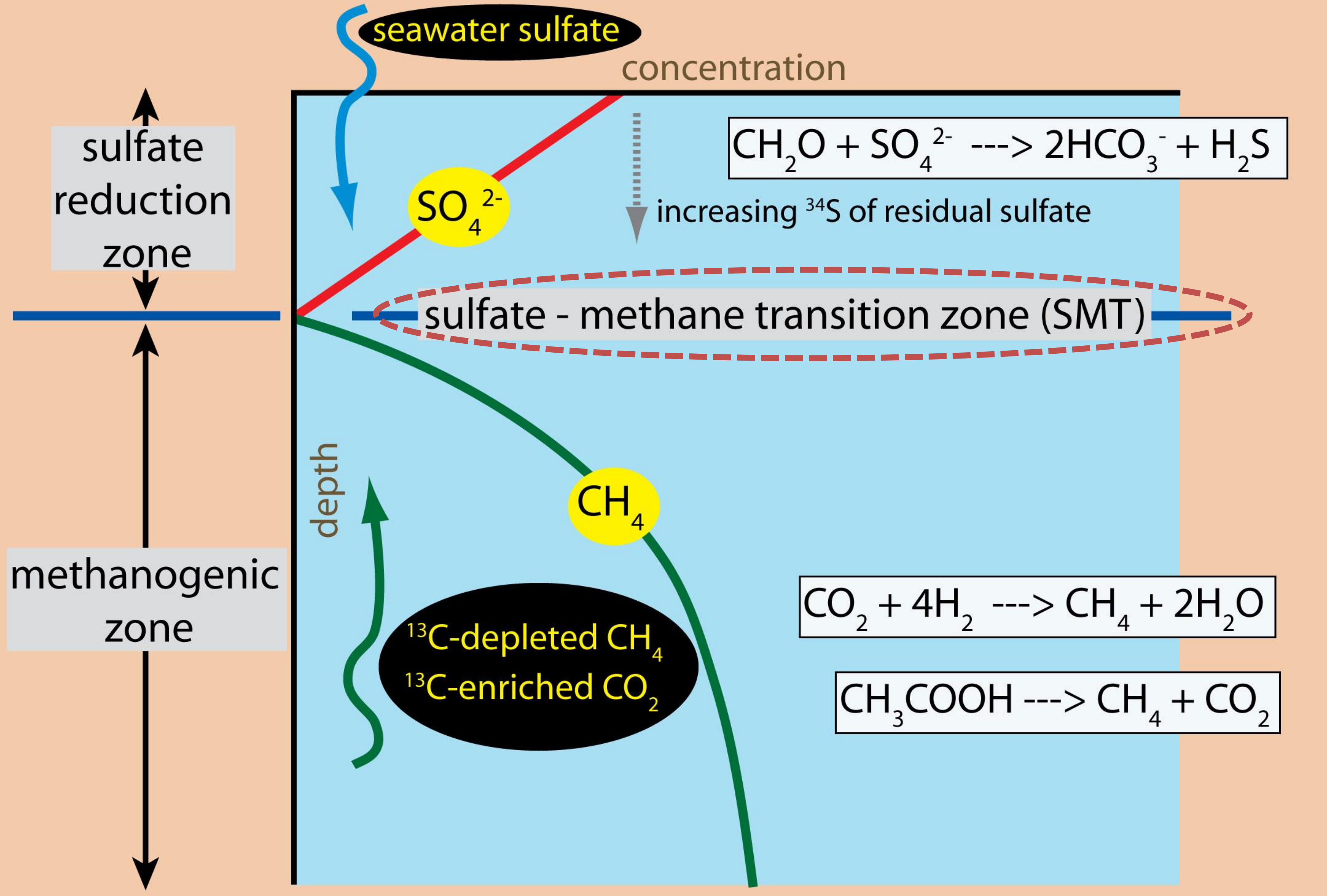
anaerobic oxidation of methane (AOM)



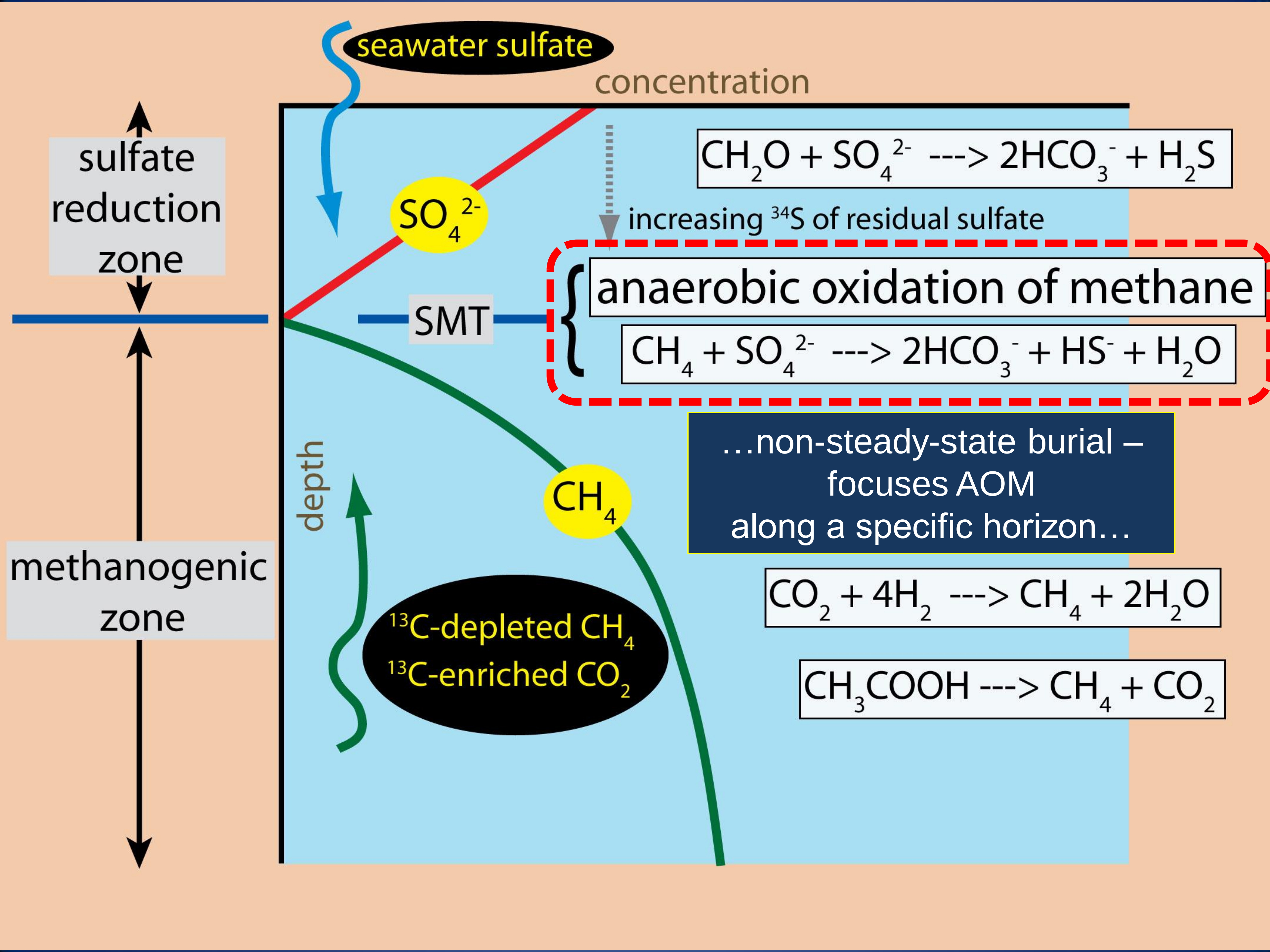

seawater sulfate
concentration
sulfate reduction zone
SO_4^{2-}
increasing ^{34}S of residual sulfate
$CH_2O + SO_4^{2-}$ ---> $2HCO_3^{-} + H_2S$
anaerobic oxidation of methane
methanogenic zone



seawater sulfate
concentration
sulfate reduction zone
SO_4^{2-}
$CH_2O + SO_4^{2-}$ ---> $2HCO_3^- + H_2S$
increasing ^{34}S of residual sulfate
depth
CH_4
methanogenic zone
^{13}C-depleted CH_4
^{13}C-enriched CO_2
$CO_2 + 4H_2$ ---> $CH_4 + 2H_2O$
CH_3COOH ---> $CH_4 + CO_2$

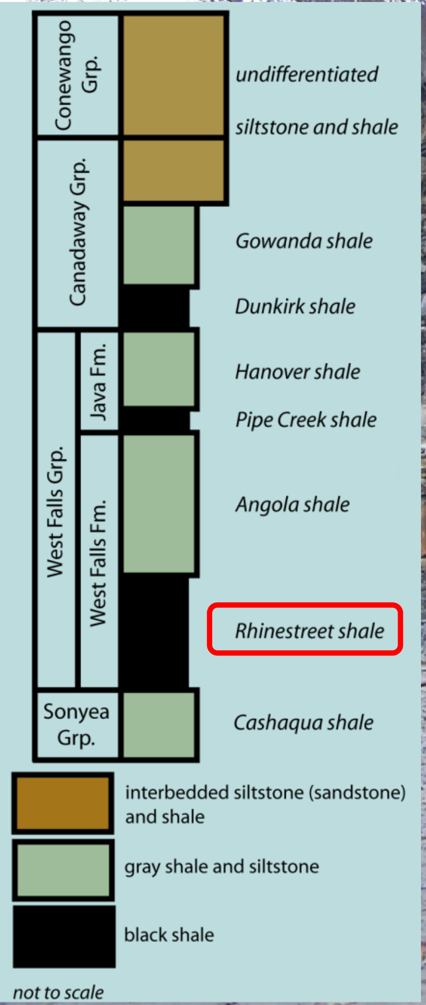


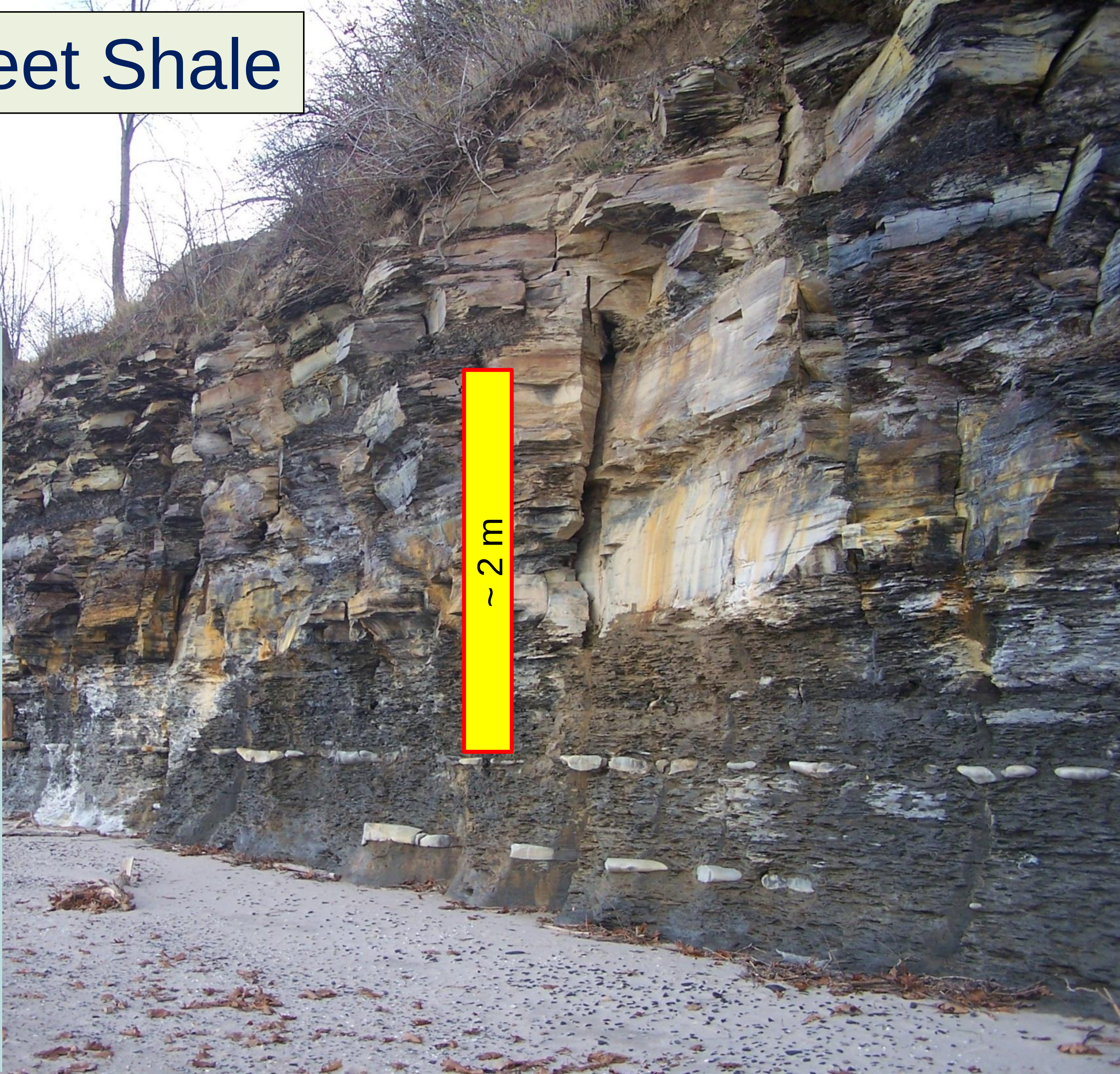
seawater sulfate
concentration
$CH_2O + SO_4^{2-}$ ---> $2HCO_3^- + H_2S$
sulfate reduction zone
SO_4^{2-}
increasing ^{34}S of residual sulfate
sulfate - methane transition zone (SMT)
depth
CH_4
methanogenic zone
^{13}C-depleted CH_4
^{13}C-enriched CO_2
$CO_2 + 4H_2$ ---> $CH_4 + 2H_2O$
CH_3COOH ---> $CH_4 + CO_2$

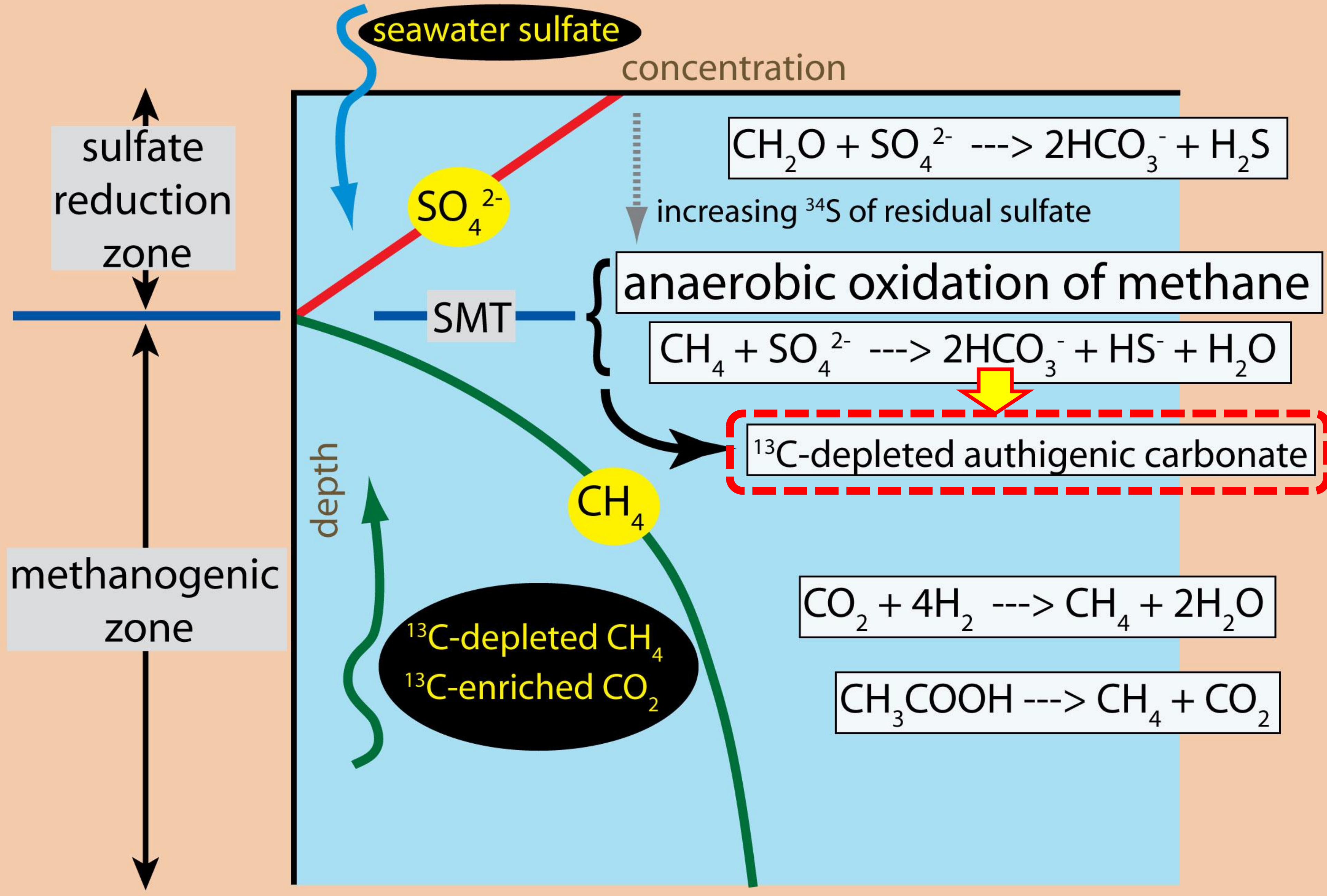


seawater sulfate
concentration
sulfate reduction zone
SO_4^{2-}
$CH_2O + SO_4^{2-}$ ---> $2HCO_3^- + H_2S$
increasing ^{34}S of residual sulfate
SMT
anaerobic oxidation of methane
$CH_4 + SO_4^{2-}$ ---> $2HCO_3^- + HS^- + H_2O$
…non-steady-state burial – focuses AOM along a specific horizon…
depth
CH_4
methanogenic zone
^{13}C-depleted CH_4
^{13}C-enriched CO_2
$CO_2 + 4H_2$ ---> $CH_4 + 2H_2O$
CH_3COOH ---> $CH_4 + CO_2$

Rhinestreet Shale



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$CH_2O + SO_4^{2-}$ ---> $2HCO_3^- + H_2S$
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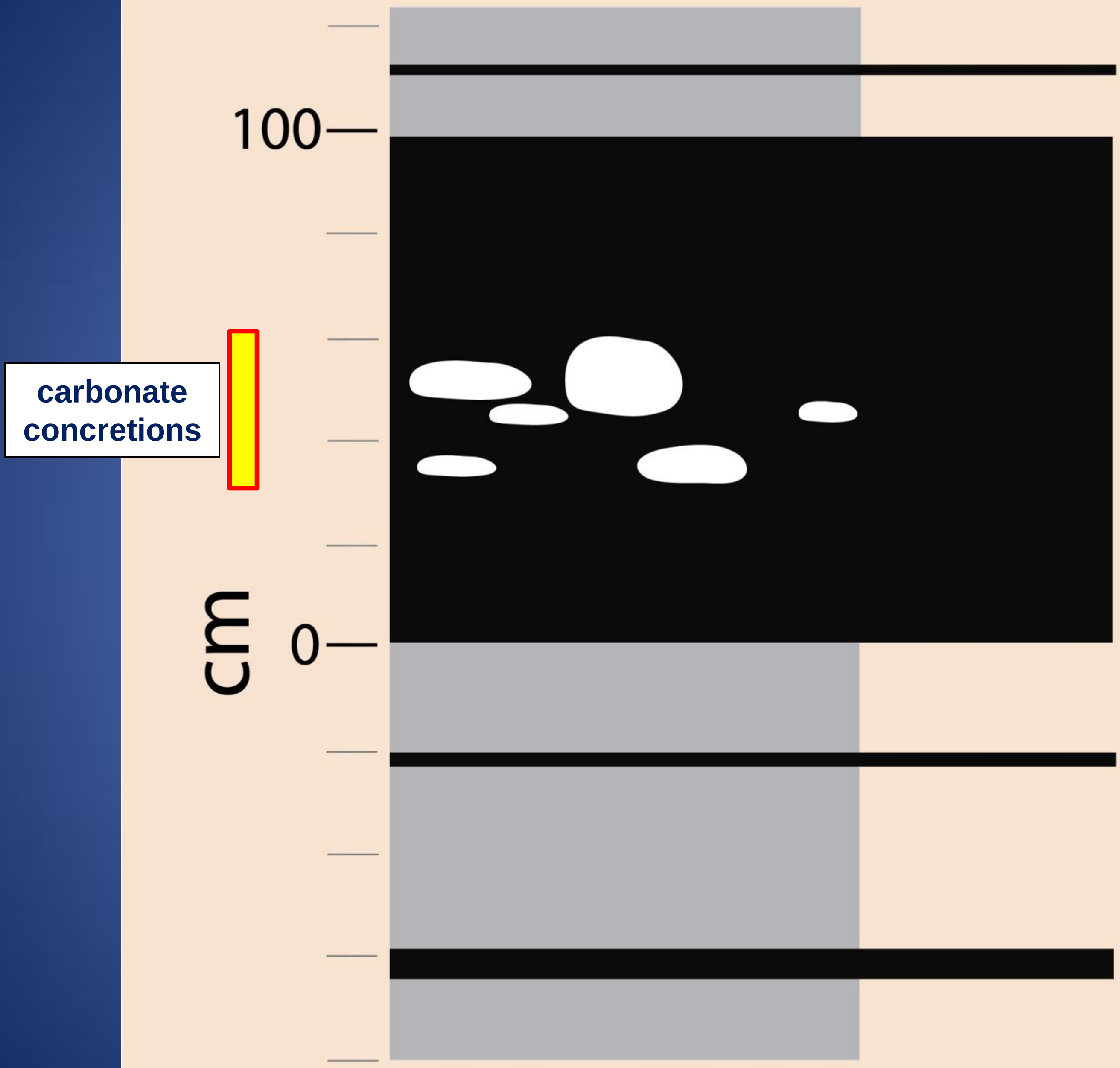
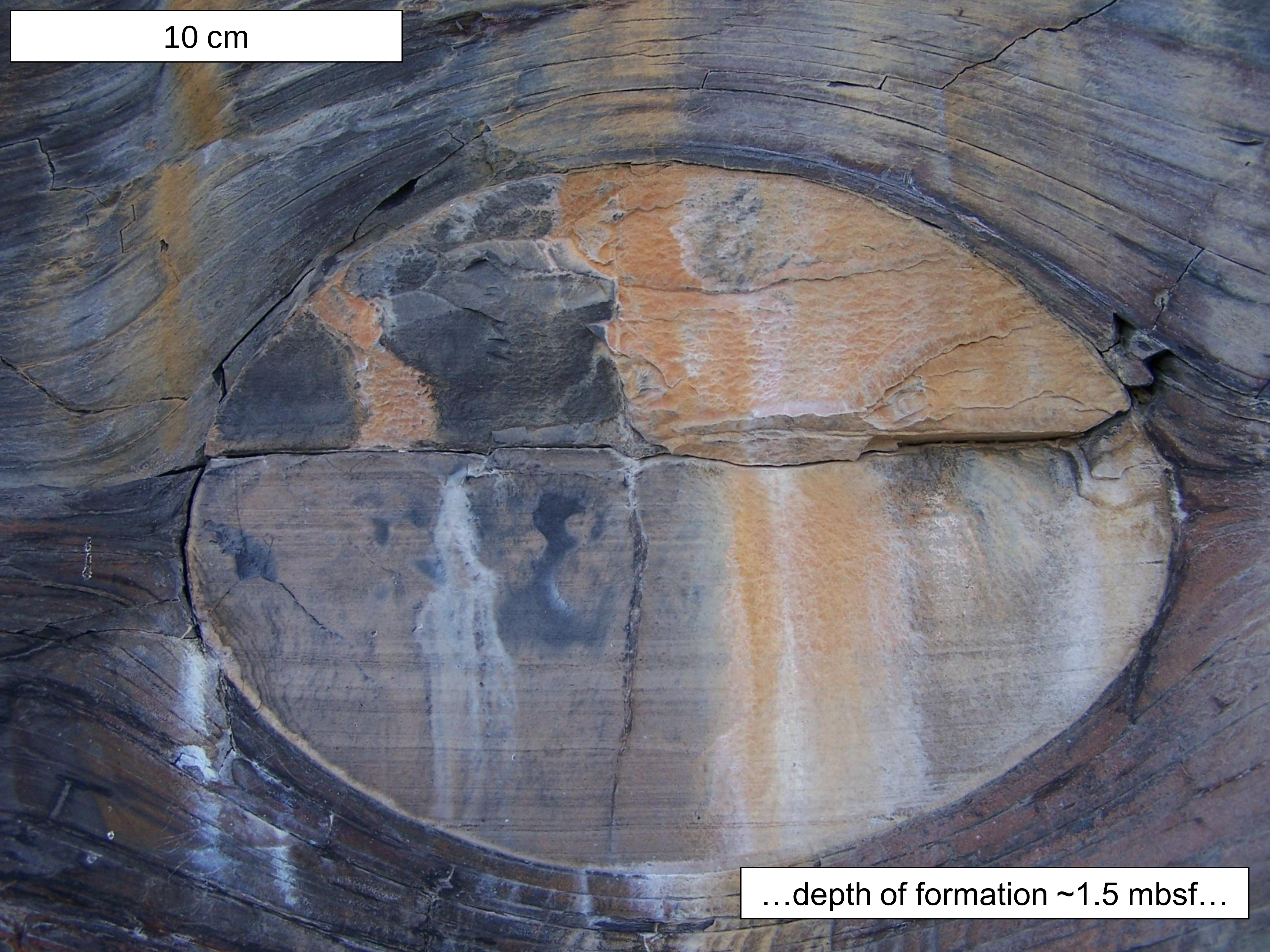
increasing ^{34}S of residual sulfate
SMT
anaerobic oxidation of methane
$CH_4 + SO_4^{2-}$ ---> $2HCO_3^- + HS^- + H_2O$
^{13}C-depleted authigenic carbonate
depth
CH_4
methanogenic zone
^{13}C-depleted CH_4
^{13}C-enriched CO_2
$CO_2 + 4H_2$ ---> $CH_4 + 2H_2O$
CH_3COOH ---> $CH_4 + CO_2$



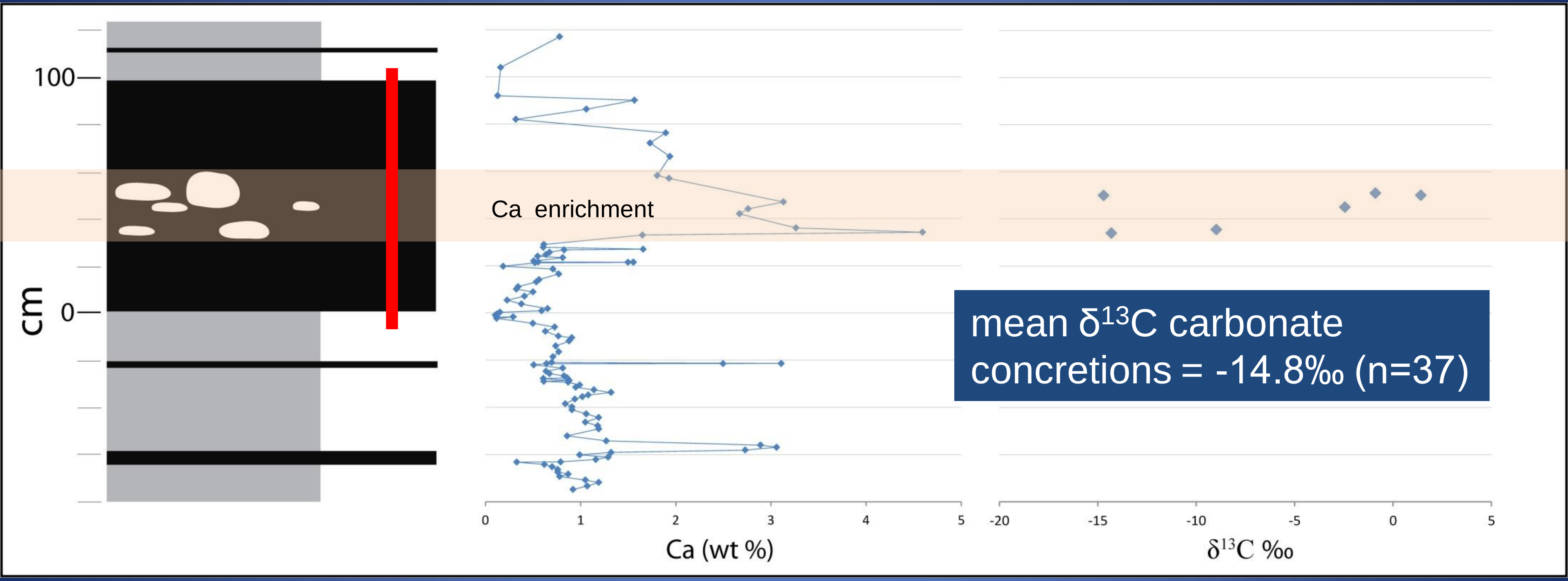
carbonate concretions
100
0
cm

carbonate concretion interval

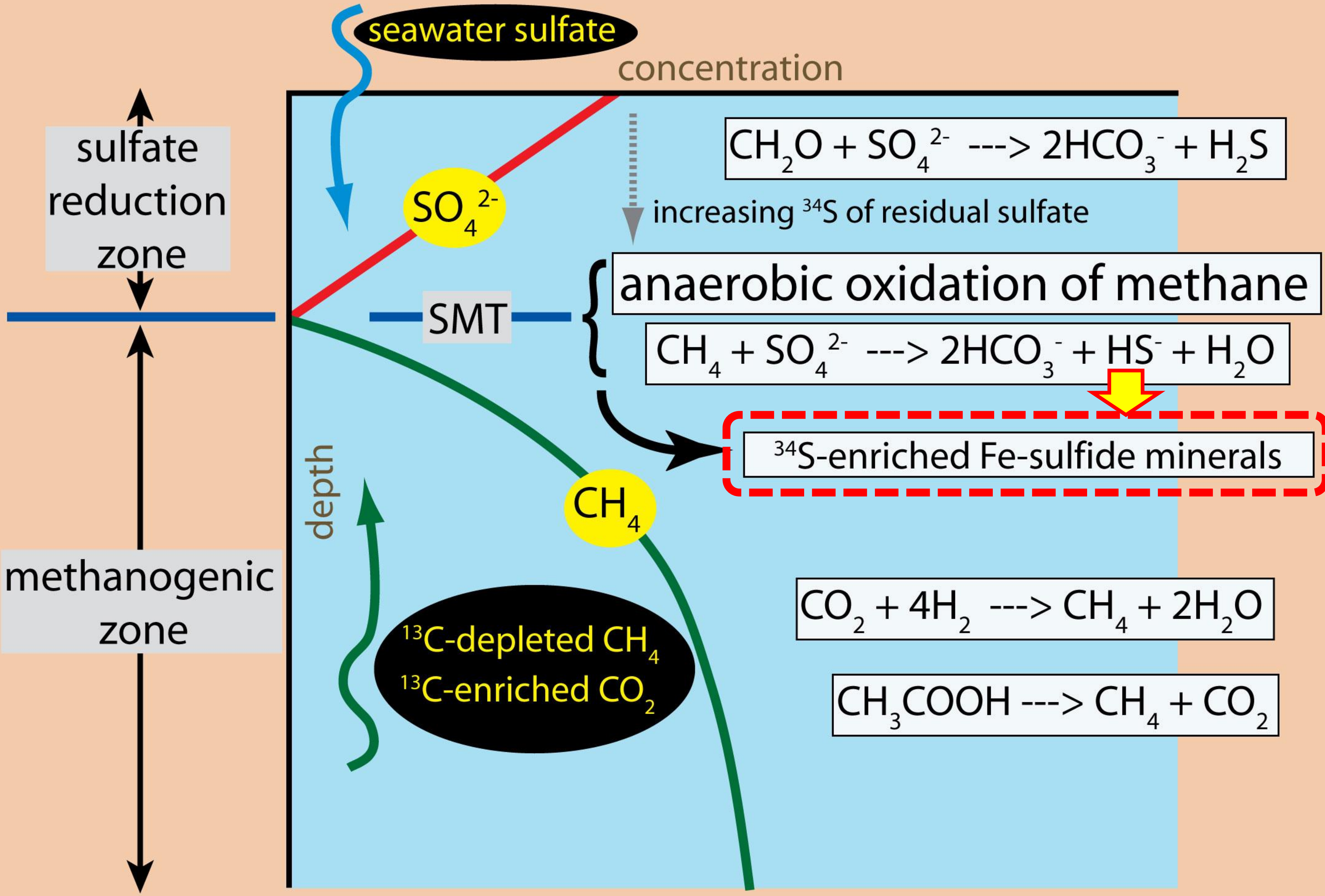

10 cm
…depth of formation ~1.5 mbsf…

matrix Ca (exclusive of concretions)

concretions generally depleted $\delta^{13}C$



mean $\delta^{13}C$ carbonate concretions = -14.8‰ (n=37)



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concentration
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increasing ^{34}S of residual sulfate
anaerobic oxidation of methane
SMT
$CH_4 + SO_4^{2-}$ ---> $2HCO_3^- + HS^- + H_2O$
^{34}S-enriched Fe-sulfide minerals
depth
CH_4
methanogenic zone
^{13}C-depleted CH_4
^{13}C-enriched CO_2
$CO_2 + 4H_2$ ---> $CH_4 + 2H_2O$
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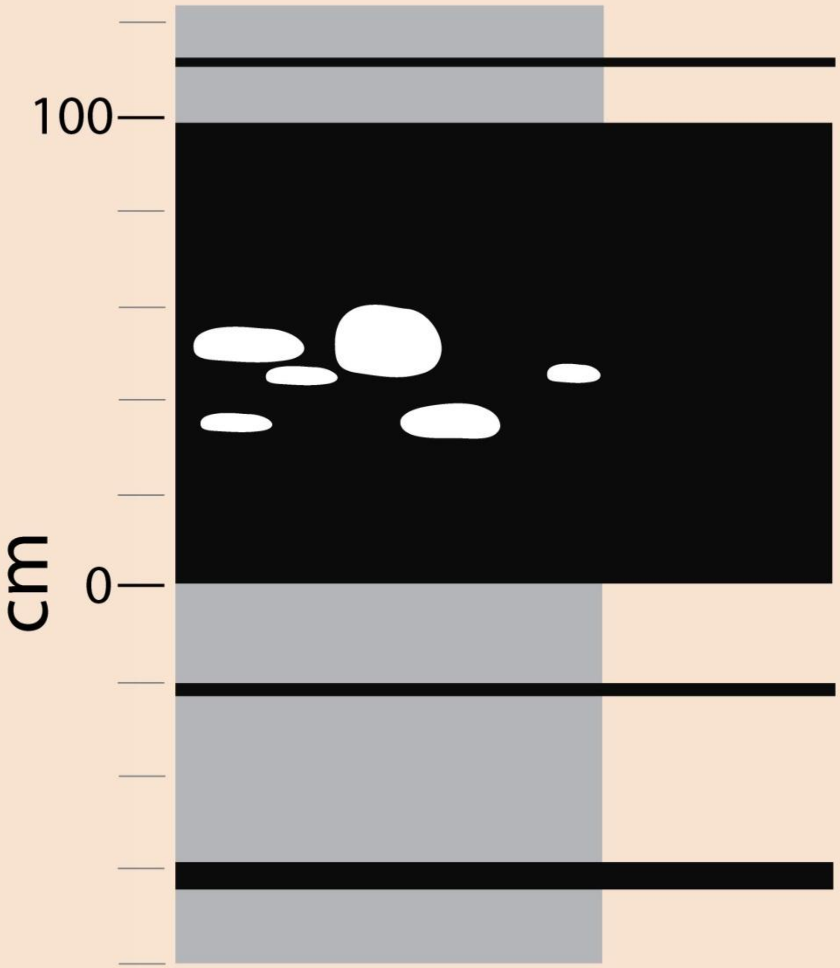
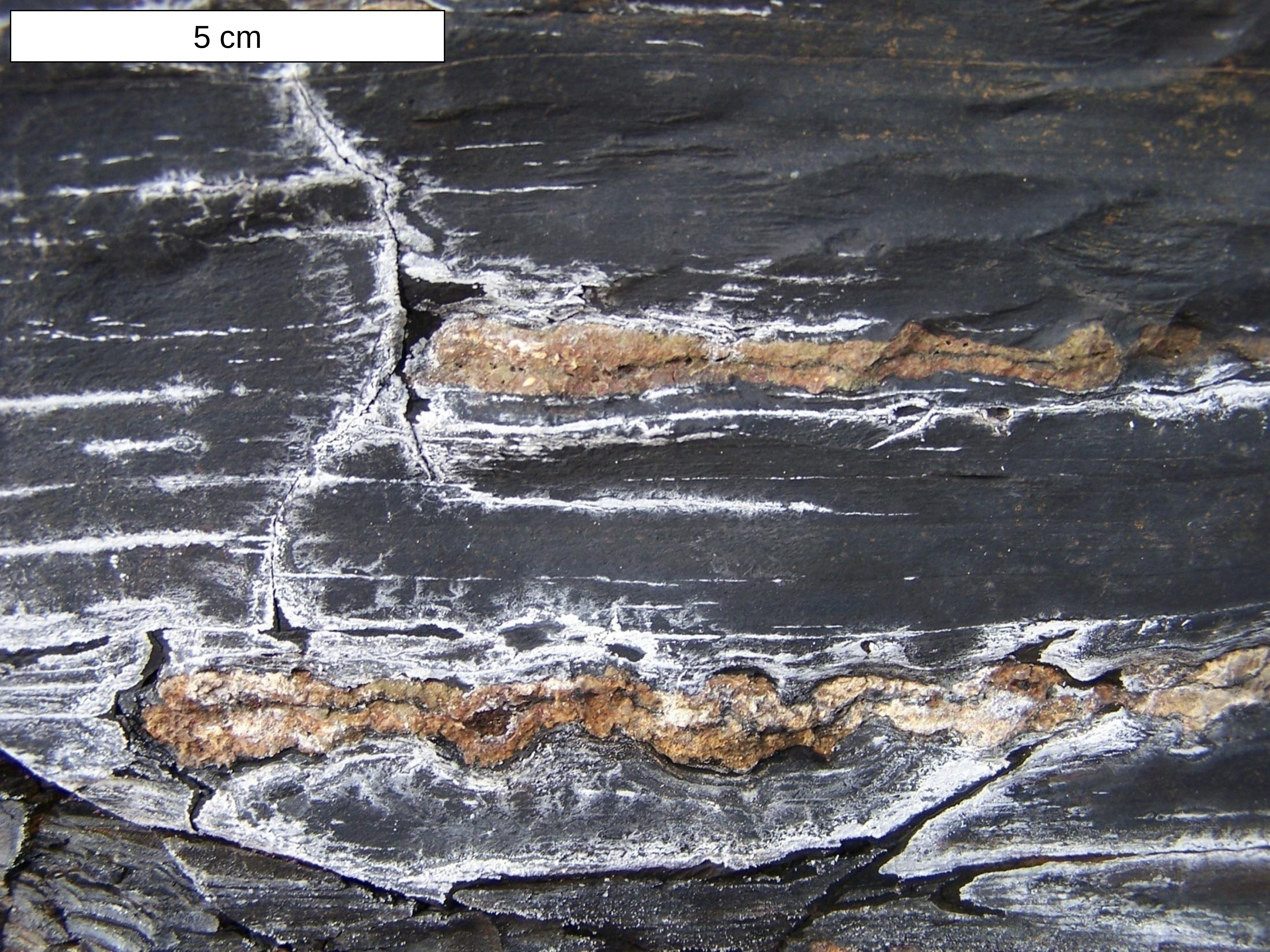
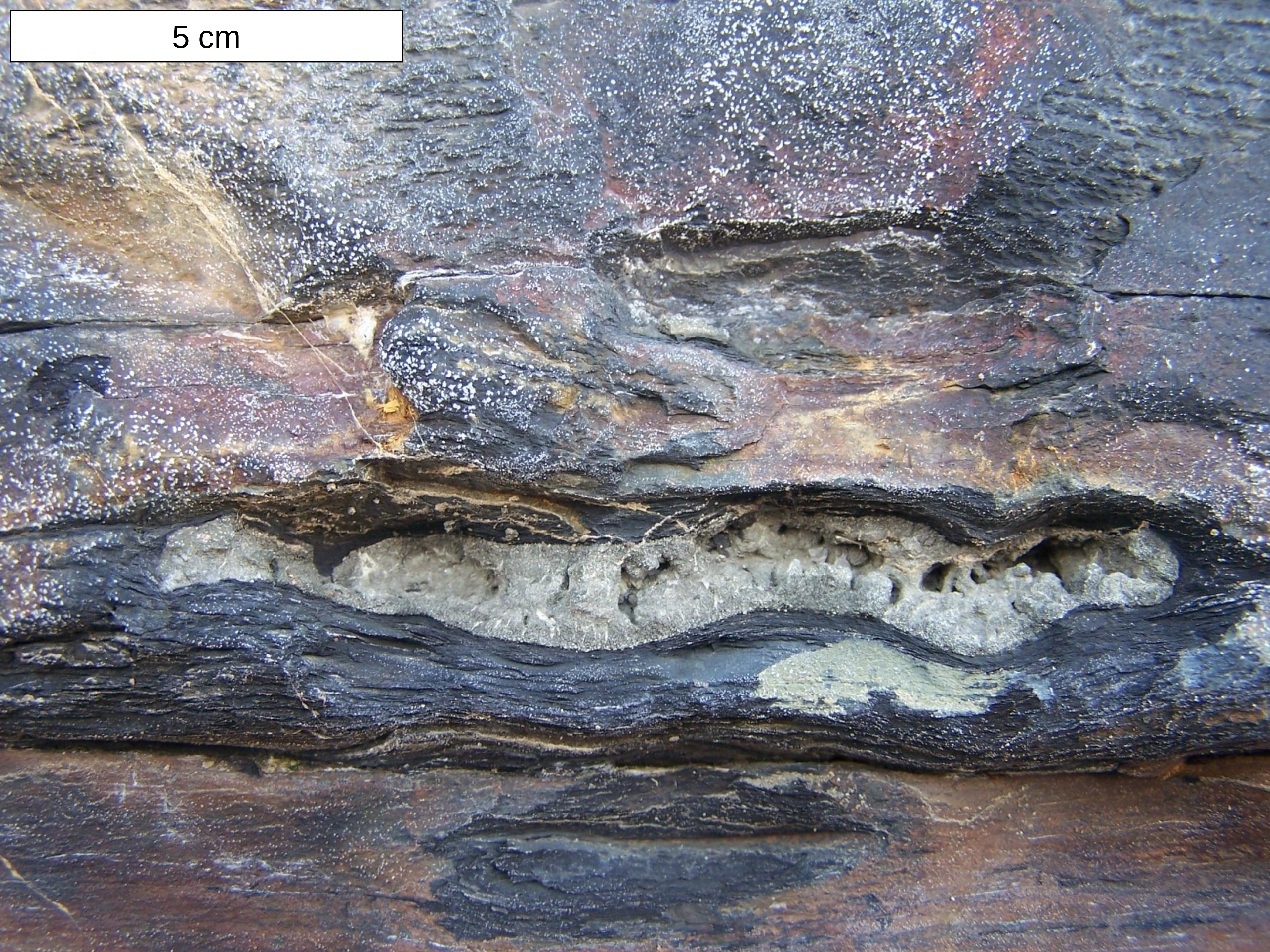
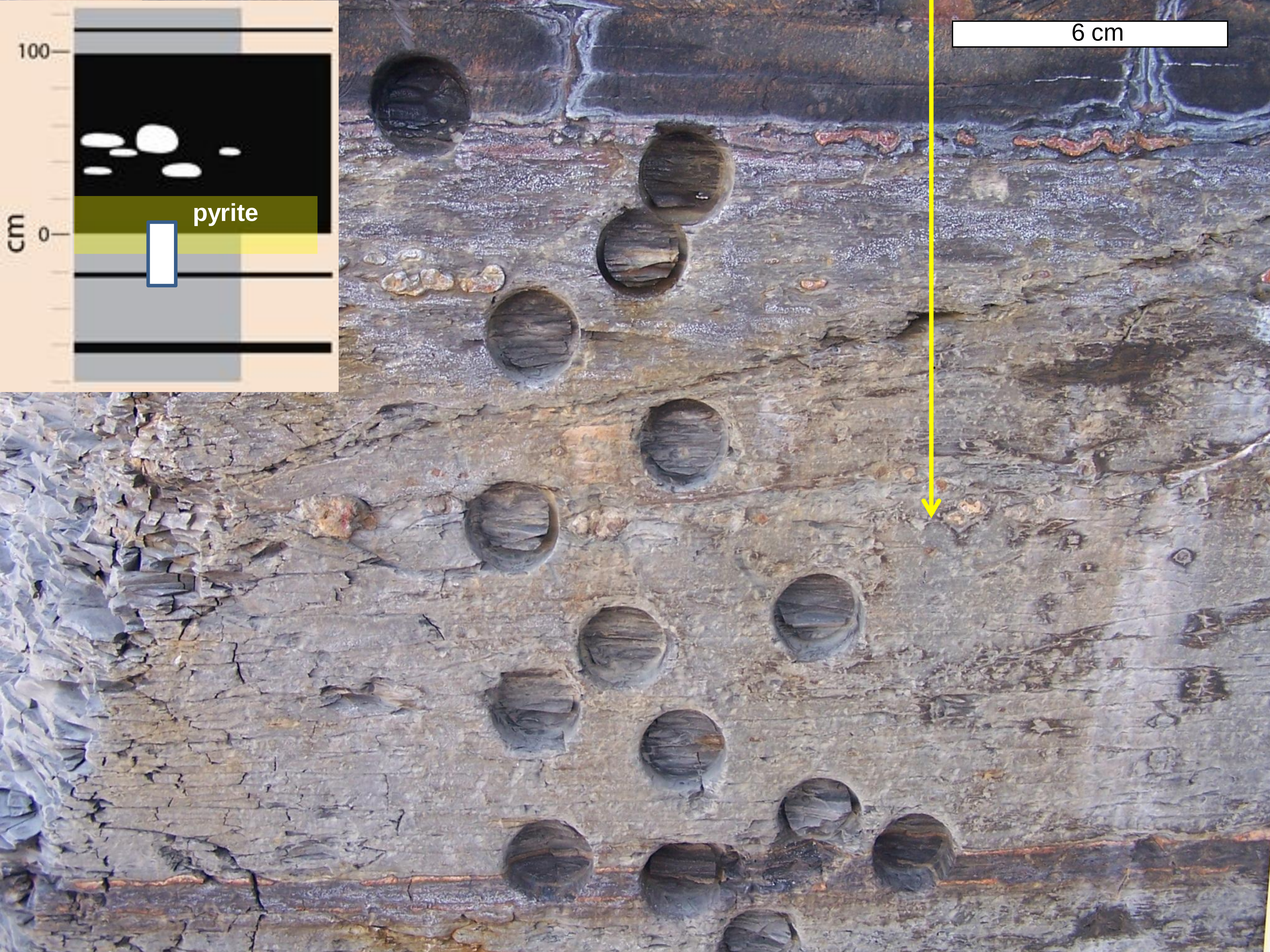
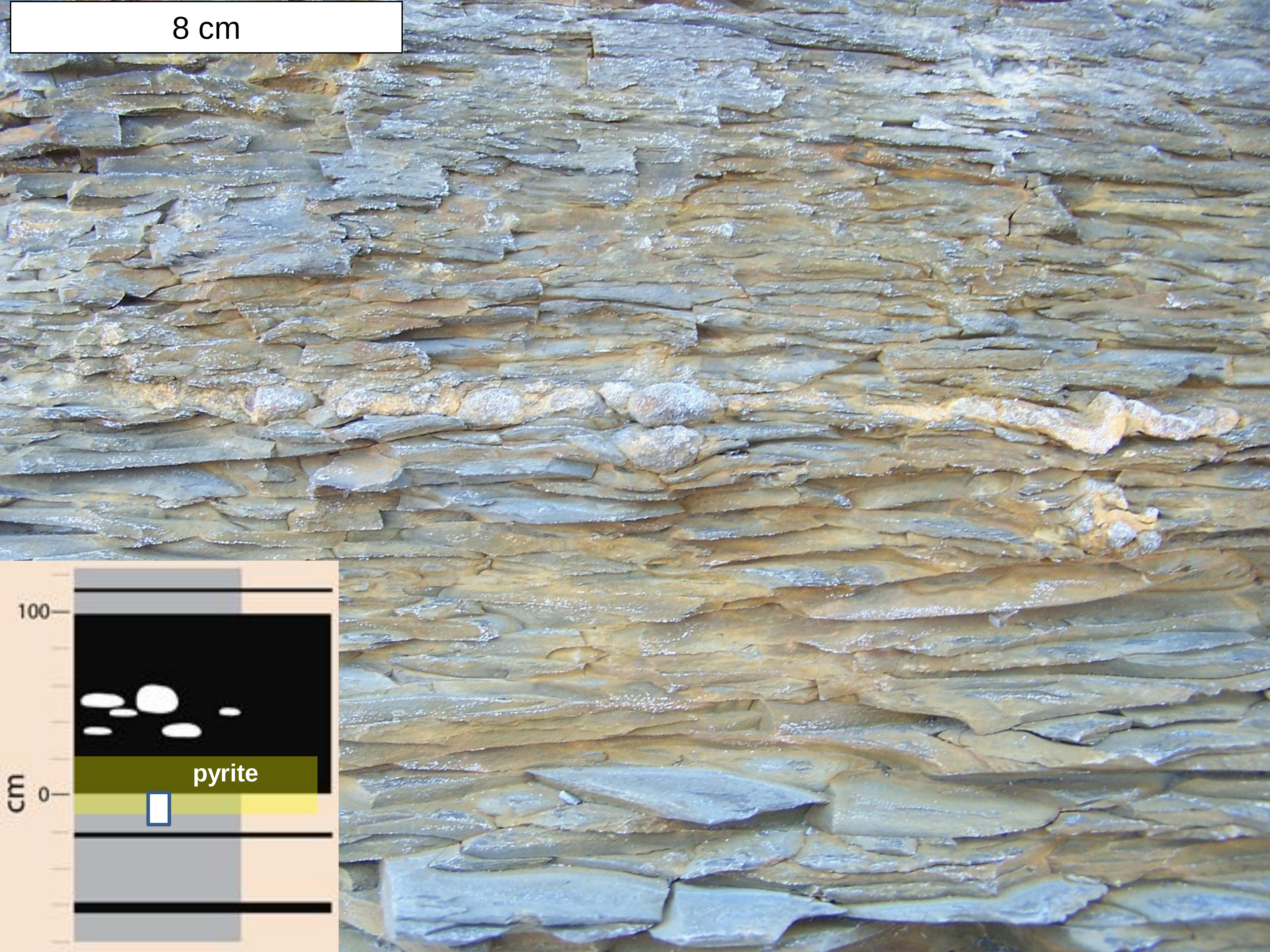


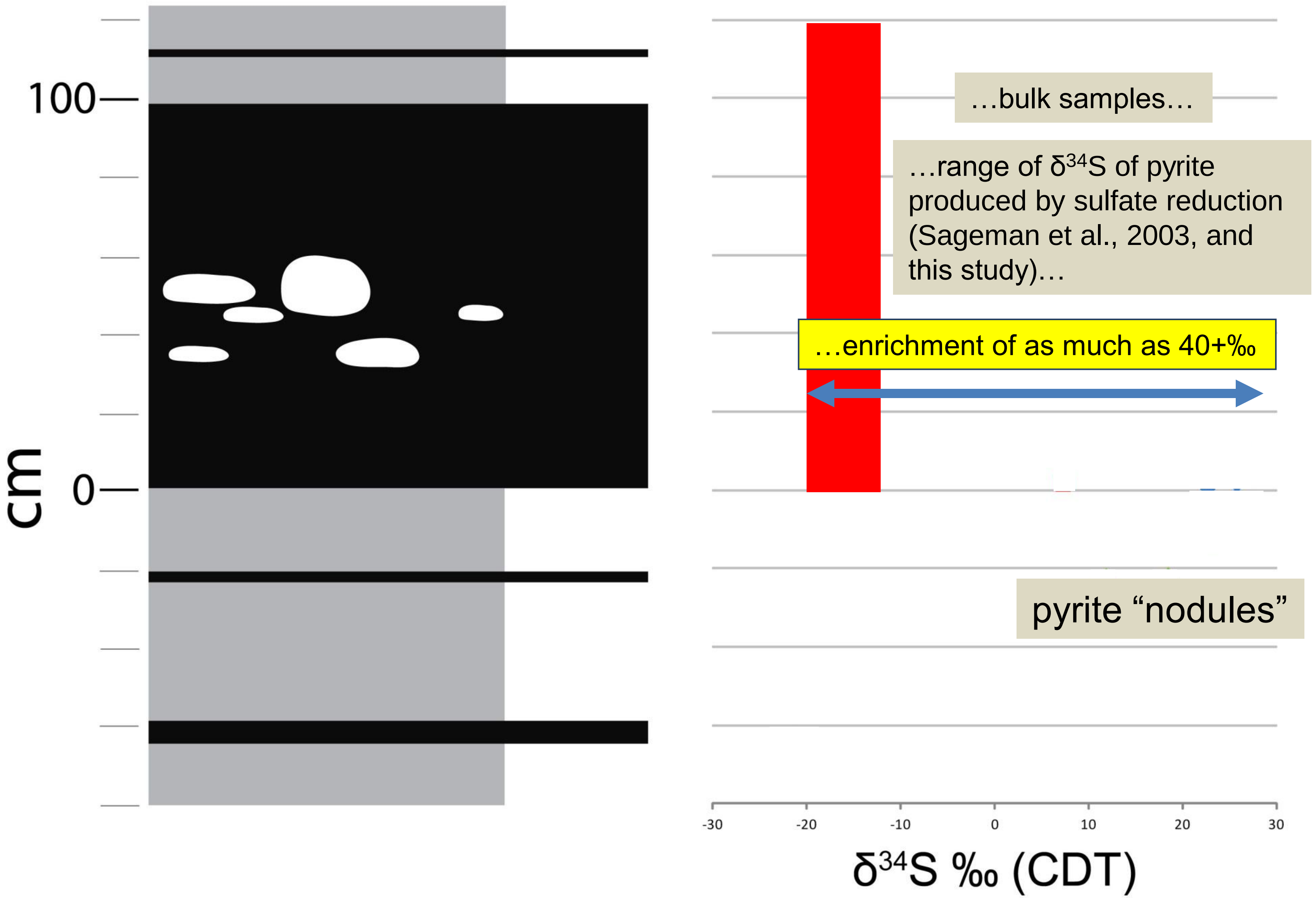
interval of
pyrite enrichment


5 cm

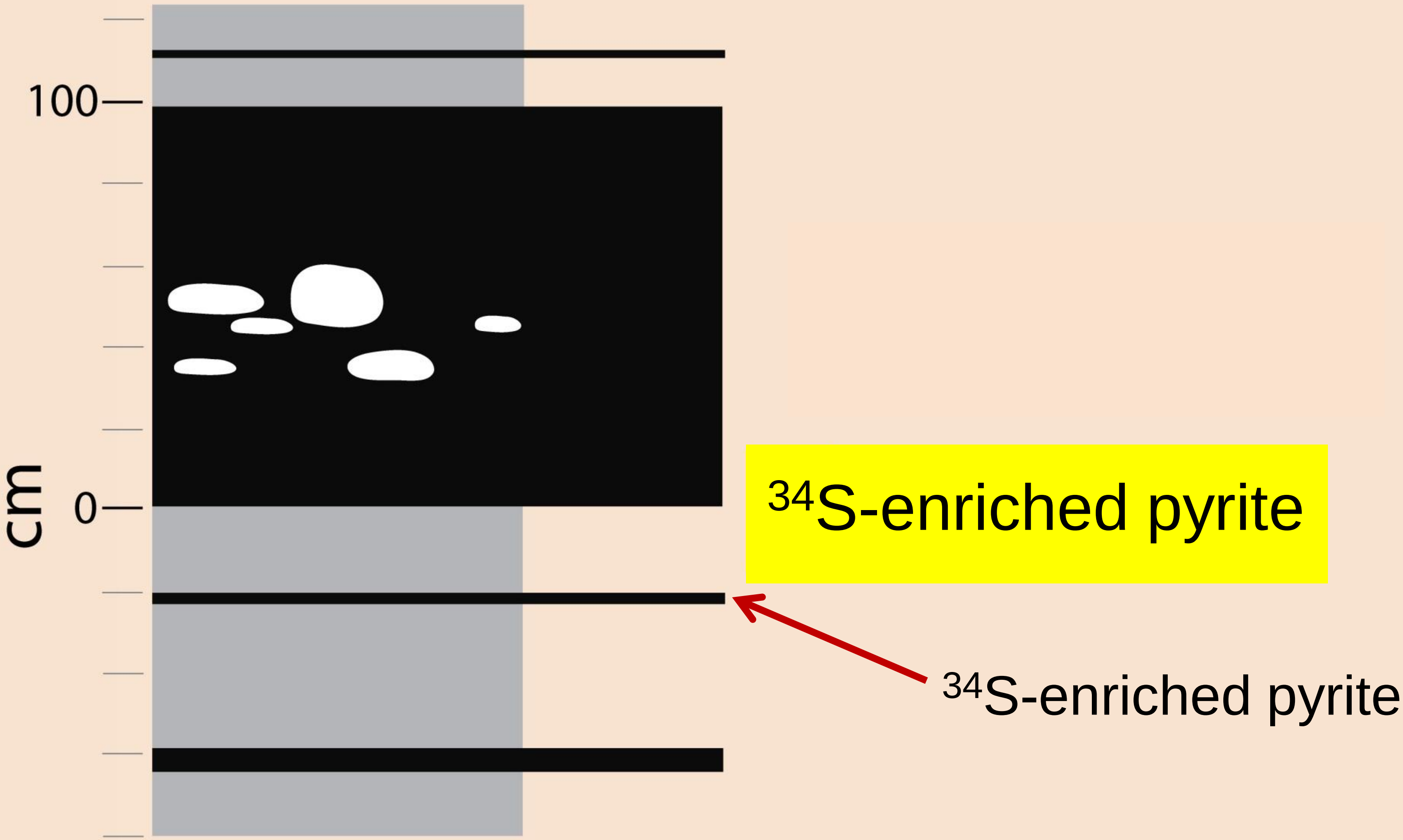

5 cm


100
0
cm
pyrite
6 cm


8 cm
100
pyrite
0
cm

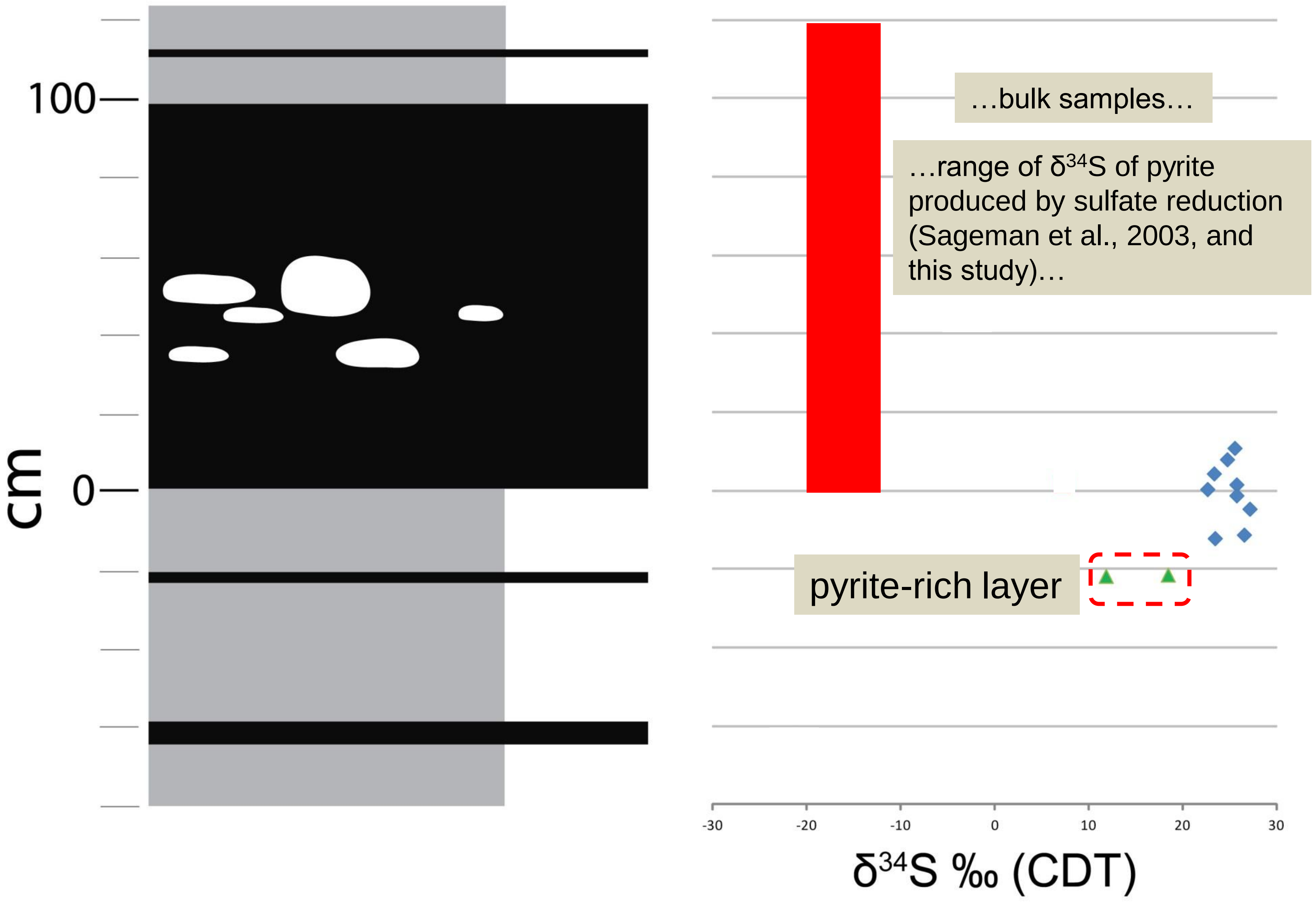


stable S isotopes



100
0
cm
^{34}S-enriched pyrite
^{34}S-enriched pyrite

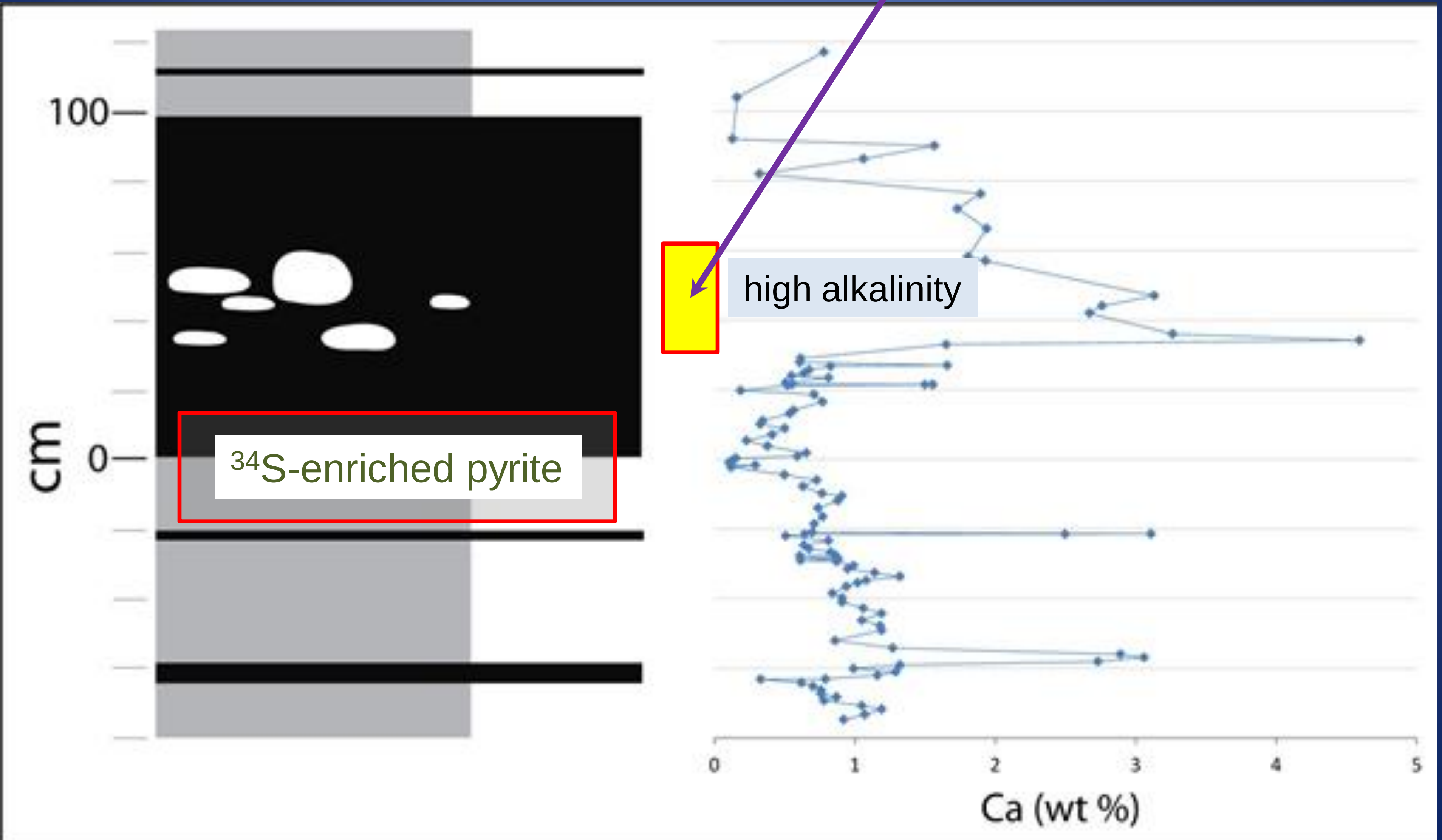

22 cm
100
0
cm



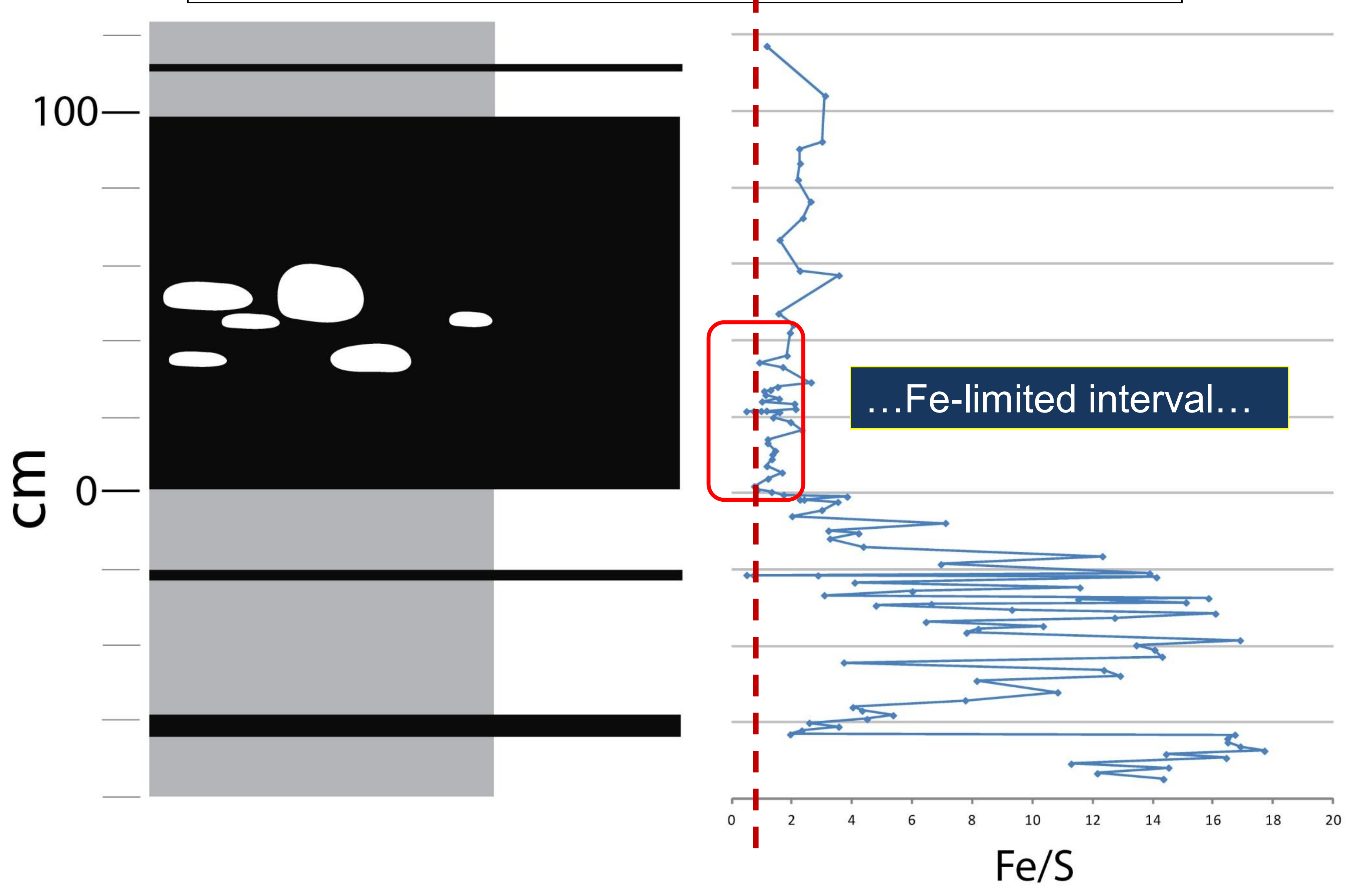
stable S isotopes

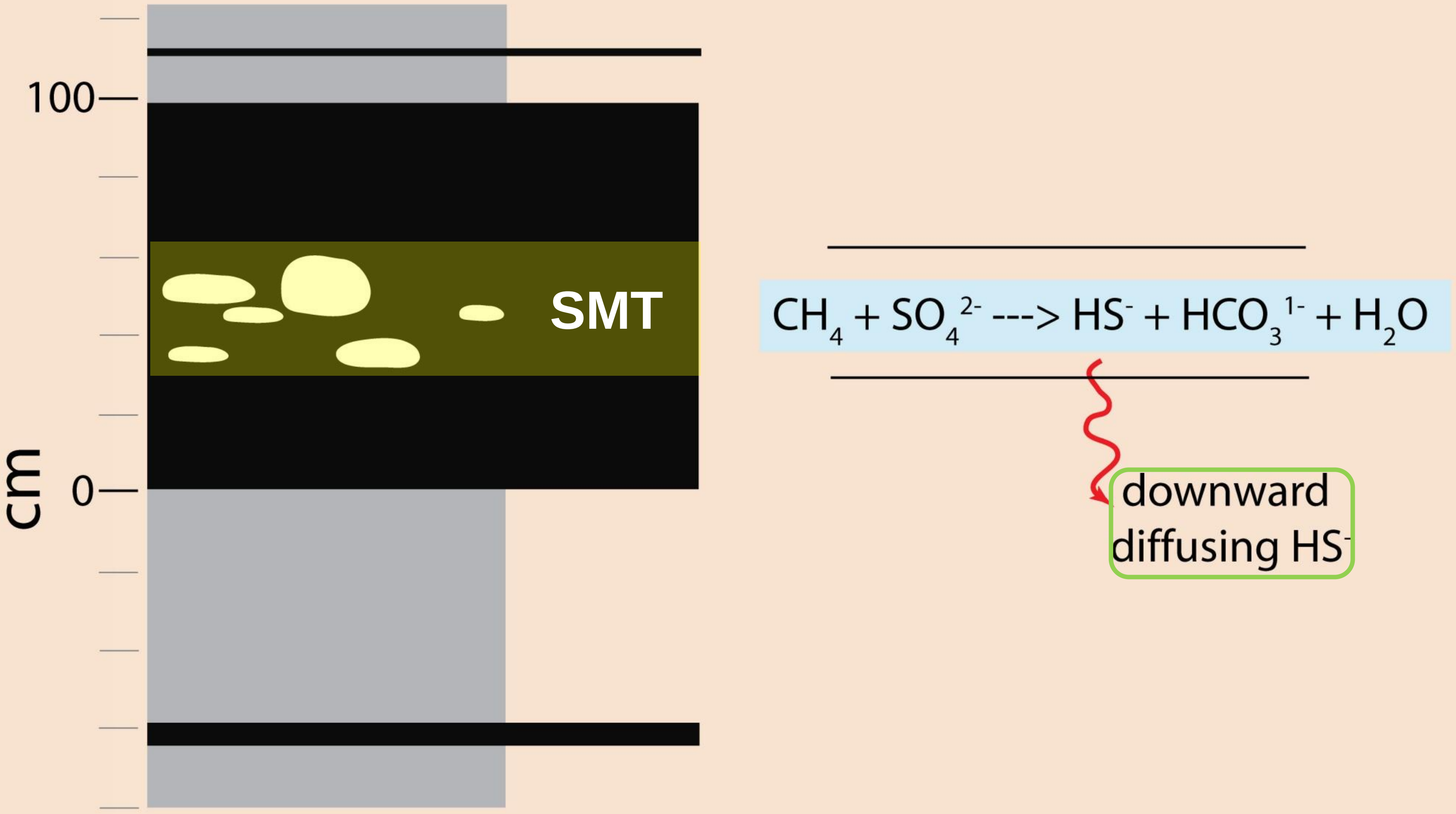
$CH_4 + SO_4^{2-} > HS^- + \mathbf{HCO_3^-} + H_2O$

$\mathbf{HCO_3^-} + Ca^{2+} > \mathbf{CaCO_3} + H^+$

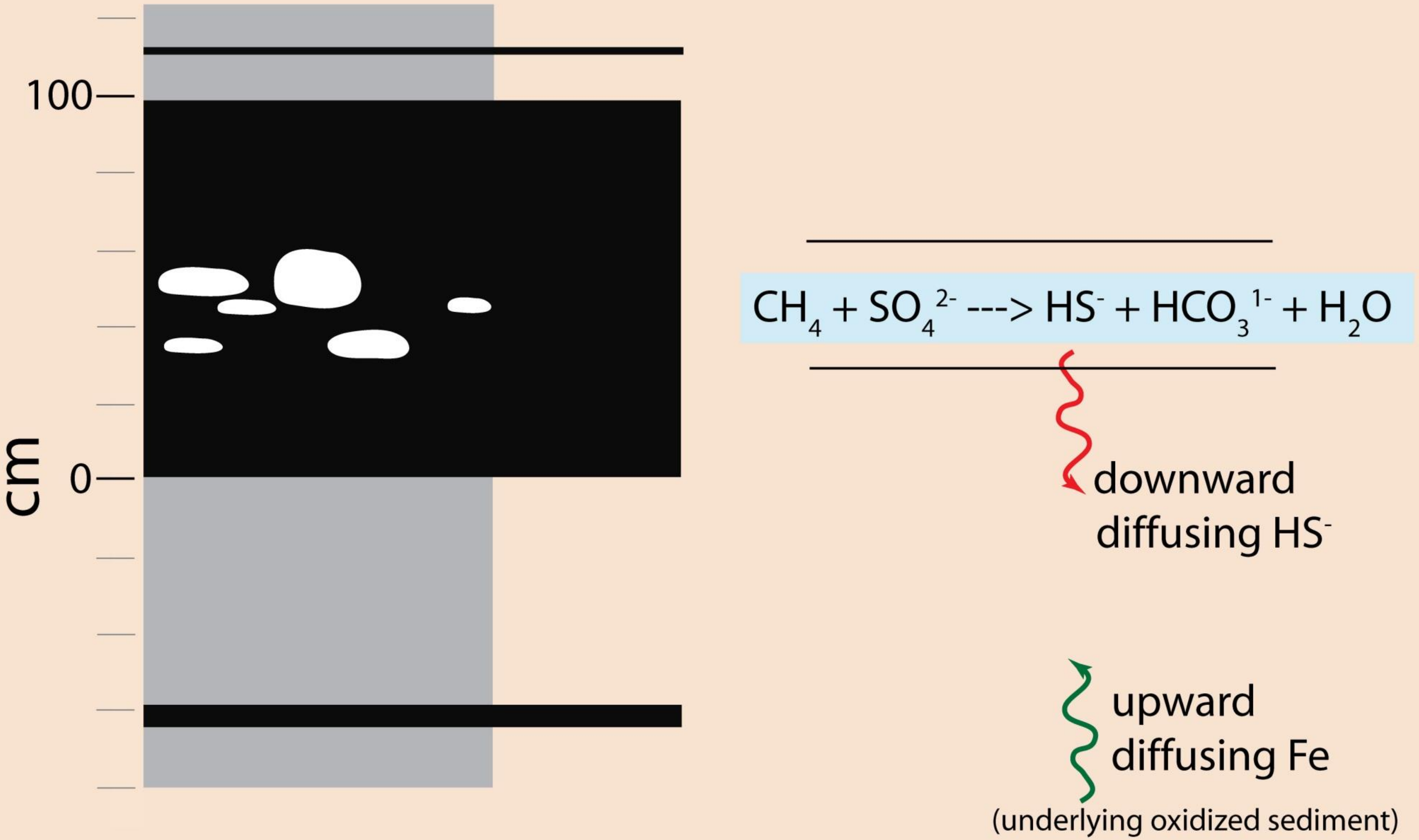


…Fe/S of stoichiometric pyrite = 0.87 (Gautier, 1987)…

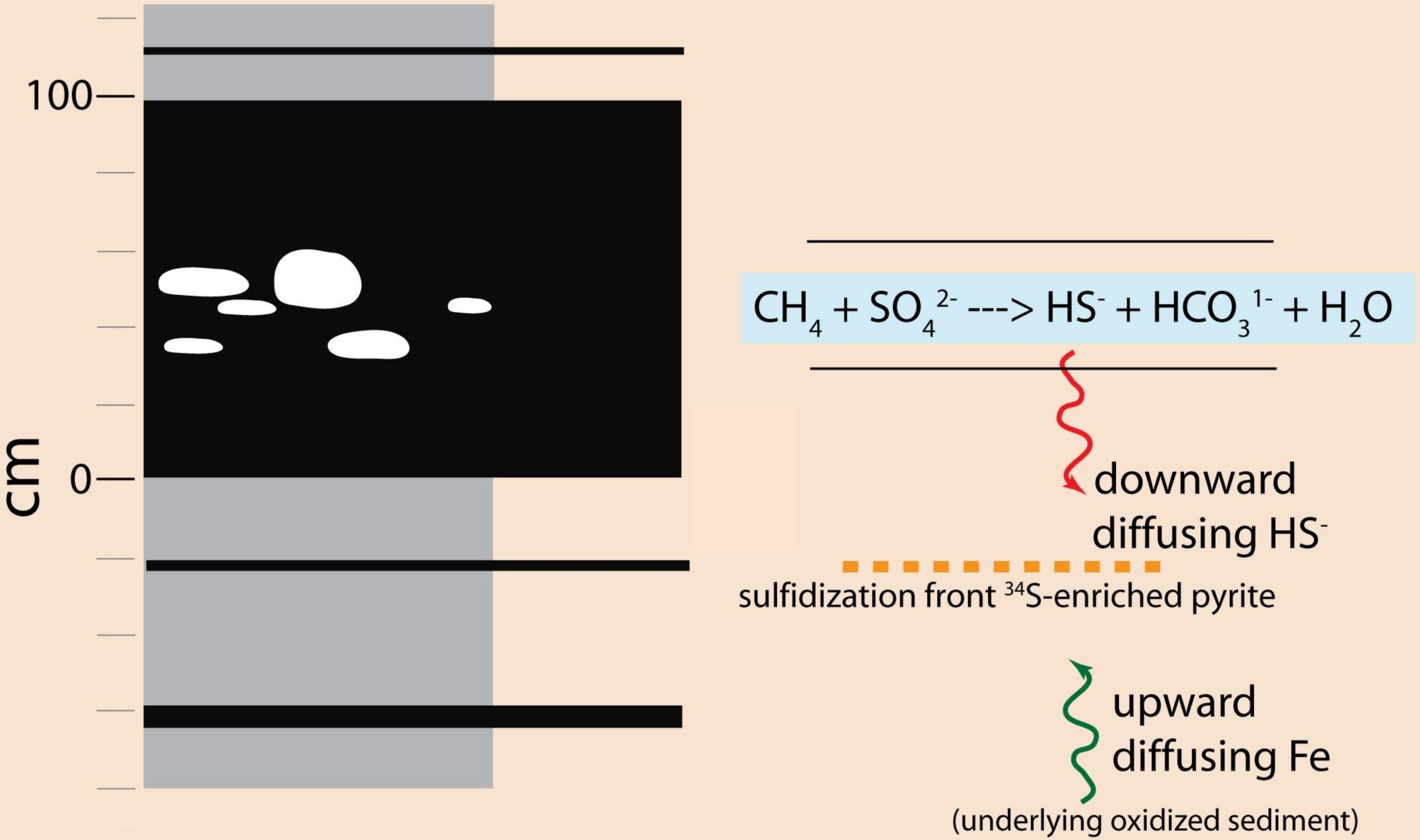


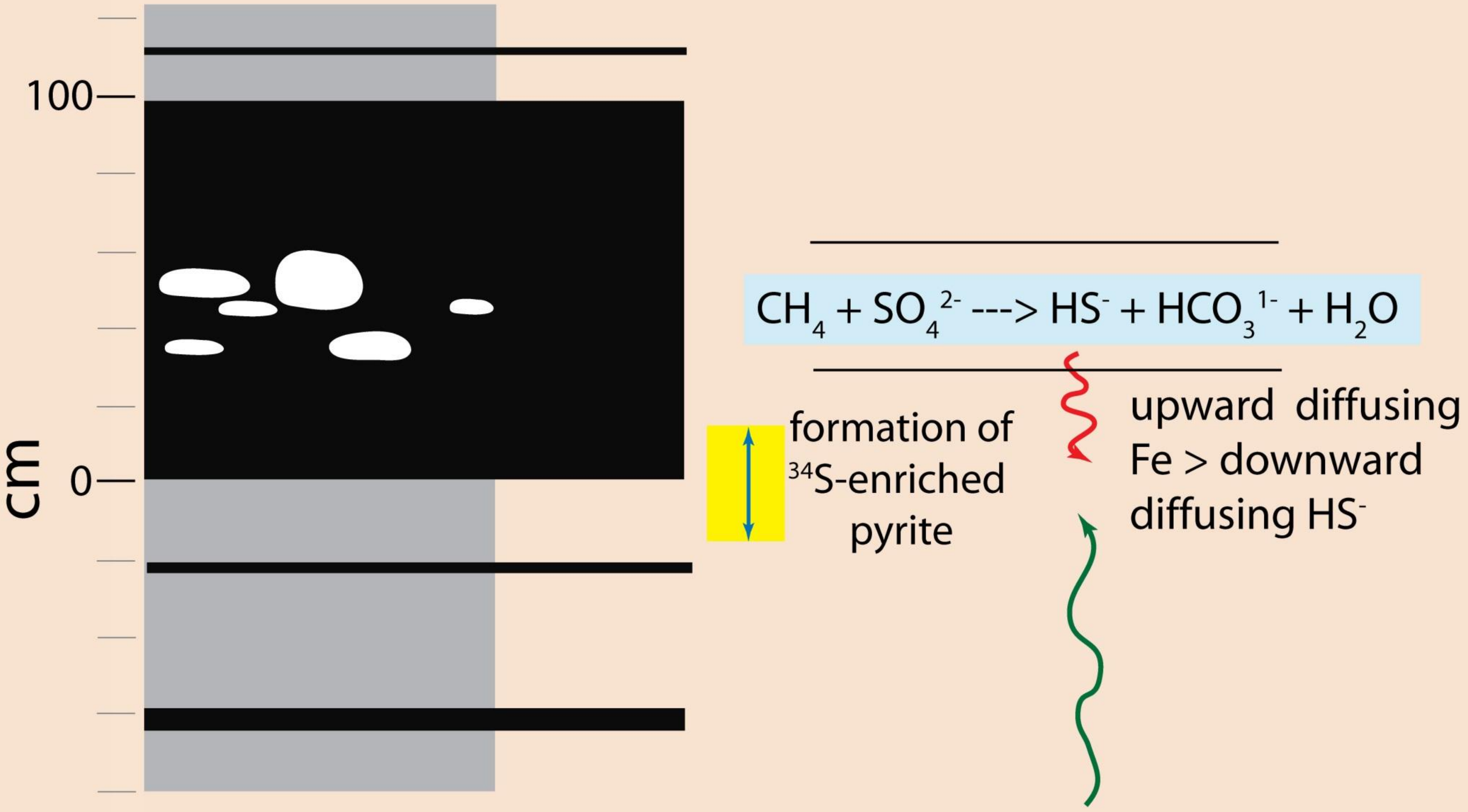


100
0
cm
SMT
CH4 + SO4 2- ---> HS- + HCO3 1- + H2O
downward diffusing HS-

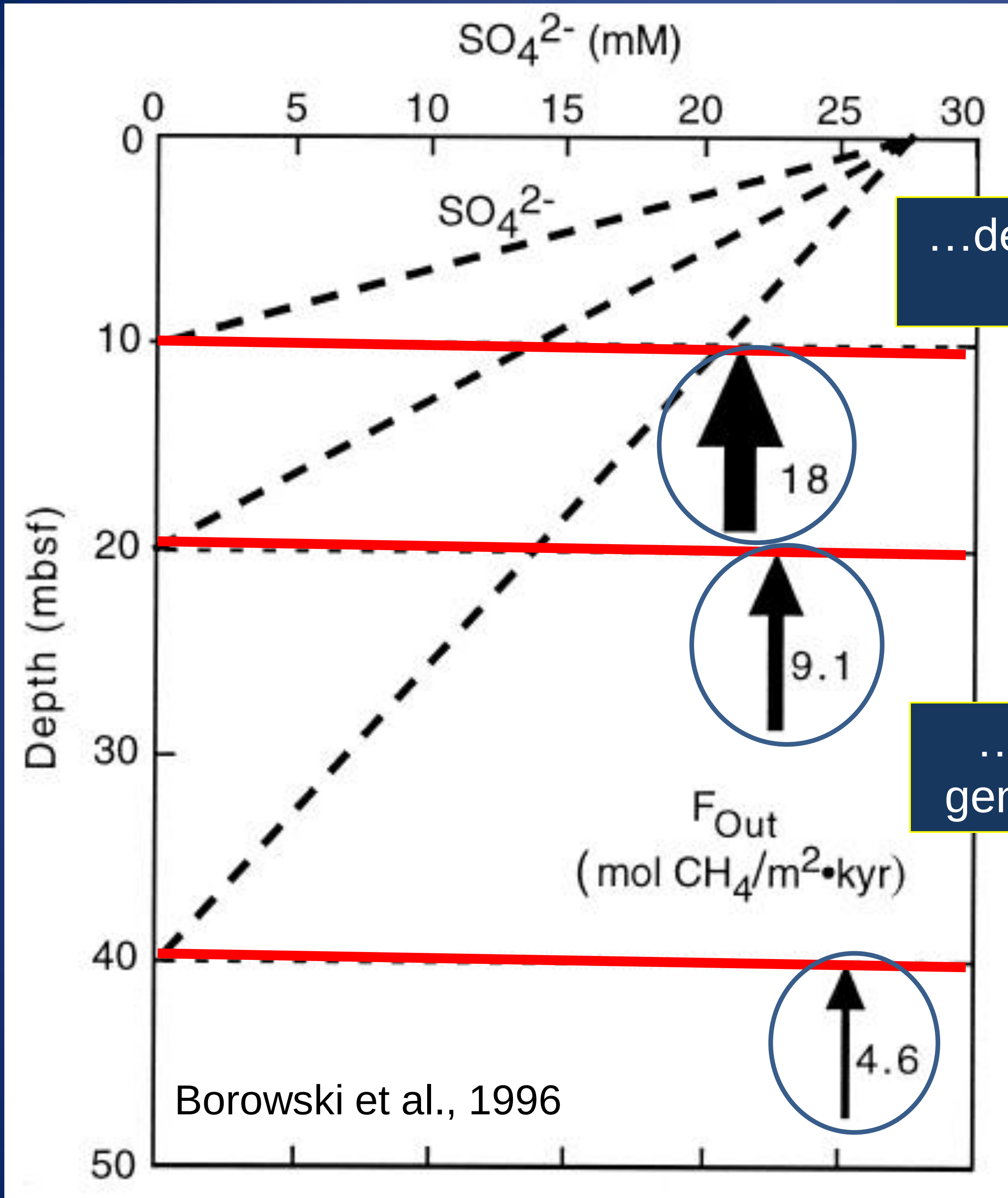


100
0
cm
$CH_4 + SO_4^{2-} \dashrightarrow HS^- + HCO_3^{1-} + H_2O$
downward diffusing HS^-
upward diffusing Fe
(underlying oxidized sediment)


100
0
cm
$CH_4 + SO_4^{2-}$ ---> $HS^- + HCO_3^{1-} + H_2O$
downward
diffusing HS^-
sulfidization front ^{34}S-enriched pyrite
upward
diffusing Fe
(underlying oxidized sediment)


100—
0—
cm
$CH_4 + SO_4^{2-}$ ---> $HS^- + HCO_3^{1-} + H_2O$
formation of ^{34}S-enriched pyrite
upward diffusing Fe > downward diffusing HS^-

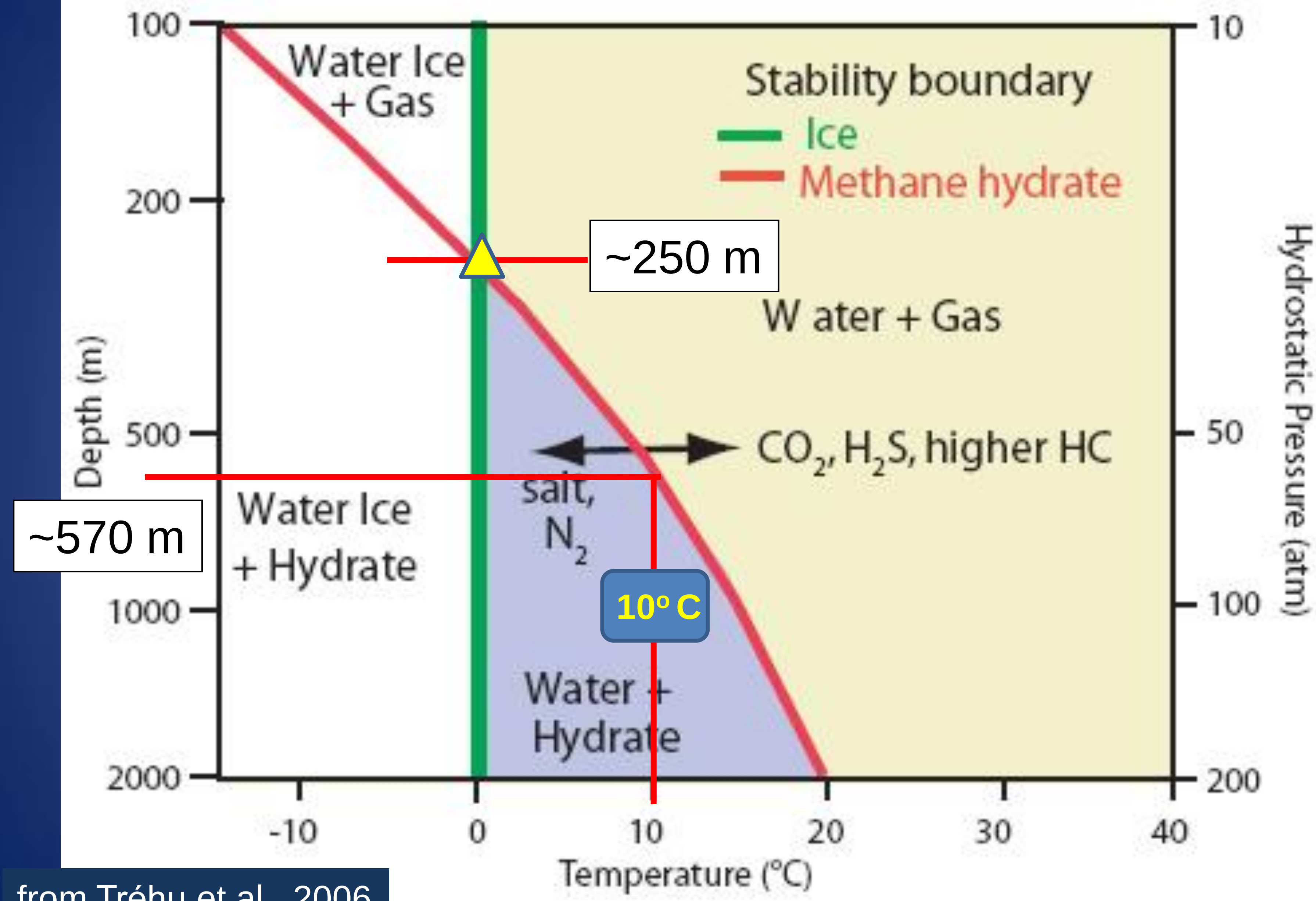

"fossil" SMT
…depth of SMT …~ 1.5 mbsf…



…depth of the SMT ≈ *ƒ* biogenic methane flux…

…voluminous biogenic CH_4 generation – gas hydrate (?)…

gas hydrate stability



from Tréhu et al., 2006

Conclusions

-the Rhinestreet Shale and overlying deposits preserves a record of the diagenetic effects of the anaerobic oxidation of methane (AOM) sustained by a robust flux of biogenic methane delivered from more deeply buried deposits;

-biogenic methane was probably sourced in the Rhinestreet itself, but it is more likely that the bulk of the methane originated in organic-rich intervals of the Marcellus Shale, ~ 125 m below the Rhinestreet in this region of the basin;

-modeling of the burial history of this region of the basin precludes the influence of a thermogenic methane imprint at this time (thanks to Nancy Rodriguez, Shell);

Conclusions

-non-steady-state sediment accumulation/burial focused AOM at particular sediment horizons for extended periods of time producing strong solid phase enrichment (^{13}C-depleted carbonate and ^{34}S-enriched sulfides) along those intervals;

-the voluminous biogenic methane flux (very shallow SMT) would have been favored by the abnormally warm oxygen-deficient nature of the shallow Late Devonian sea;

-would have ensured a greater abundance of metabolizable organic matter reaching the seafloor without oxidizing;

-elevated bottom temperatures of the Devonian ocean would have accelerated the rate of microbially induced methane generation.

Chesapeake ENERGY

Shell

Thermo SCIENTIFIC