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 $^{13}$C-depleted calcium carbonate concretions and $^{34}$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 $^{34}$S enrichment and high $\delta^{34}$S/$\delta^{18}$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 CH$_4$/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 $^{13}$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


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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)...

\[ CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \]

...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$_4$/year of which > 90% is consumed by AOM...
...AOM occurs at the sulfate-methane transition zone (SMT)...

\[ \text{biogenic or thermogenic CH}_4 \text{ and SO}_4^{2-} \text{ consumed at the SMT;} \]

\[ \text{depth of SMT is a function of CH}_4 \text{ flux} \]
...AOM occurs at the sulfate-methane transition zone (SMT)...

CH$_4$ + SO$_4^{2-}$ → HCO$_3^-$ + HS$^-$ + H$_2$O

BaSO$_4$ dissolved at the SMT to provide SO$_4^{2-}$ for AOM...

aqueous Ba (Ba$^{2+}$)

(bio)barite

Ba cycling

bacterial sulfate reduction

methanogenesis

sulfate-methane transition zone

increasing $\delta^{34}$S

CH$_4$ and SO$_4^{2-}$

Ba$^{2+}$ (aqueous)
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

9 cm
δ³⁴S = 36.0‰ to 48.24‰ V-CDT (mean = 42.91 ‰ V-CDT)

Late Devonian seawater δ³⁴S - ~22‰ (Claypool et al., 1980);
acicular barite crystals
...extremely high $\text{Ba}^{2+}$ concentration...
$\delta^{13}\text{C} = -11.49$ to $-4.27\%_\text{o}$ V-PDB (mean = $-7.70\%_\text{o}$ V-PDB)

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

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

…source of the methane…
...gas hydrate...
...source of the methane...

...thermogenic methane; $\delta^{13}C = -50$ to $-20 \%_{oo}$ 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

...thermogenic methane sources...
...source of the methane...

...microbial methane (very low $\delta^{13}C$; -110 to -50 ‰ V-PDB; Whiticar, 1999)...
\[ \delta^{13}C = -11.49 \text{ to } -4.27\% \text{ V-PDB (mean = } -7.70\% \text{ V-PDB)} \]

(1) extensive oxidation (AOM) of \(^{13}\)C-depleted biogenic methane and (2) incorporation of \(^{13}\)C-enriched CO\(_2\) produced as a consequence of methanogenesis.
...association of authigenic barite and calcium carbonate...
...barite formed *after* carbonate and within the same stratigraphic interval...
...the barite “front” forms at the *top* of the SMT (where authigenic carbonate forms) or immediately above it...
…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 CH$_4$ flux...
...diminished methane flux...

...diminished CH₄ 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)
...diminished methane flux as a consequence of the burial of the Middle-Upper Devonian shale succession...
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…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?
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