



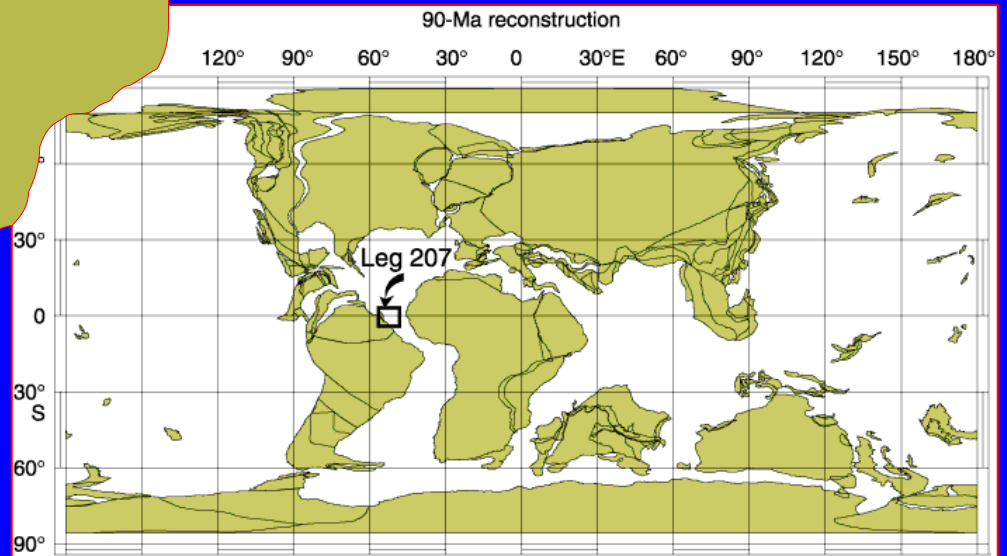
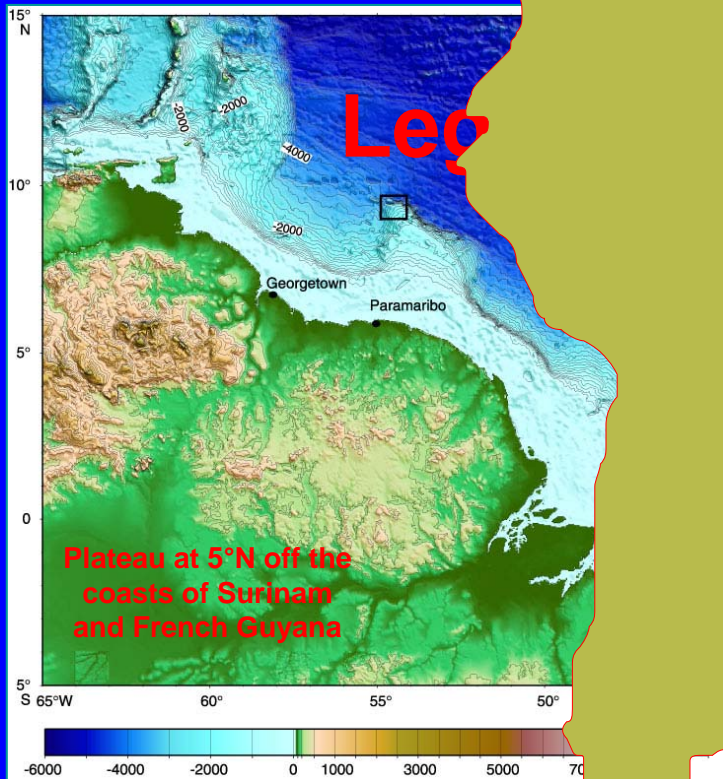
Isotope Biogeochemistry of Diagenesis caused by a Black Shale-fueled Deep Marine Biosphere (ODP Leg 207)

**Böttcher M.E. *, Brumsack H.-J.
Hetzel A., Schipper A. *, Gehre M. #,
Arndt S. & Wirtz K.**

* Max Planck Institute for Marine Microbiology, Bremen, Germany
ICBM, University of Oldenburg, Germany
UFZ Leipzig-Halle, Germany

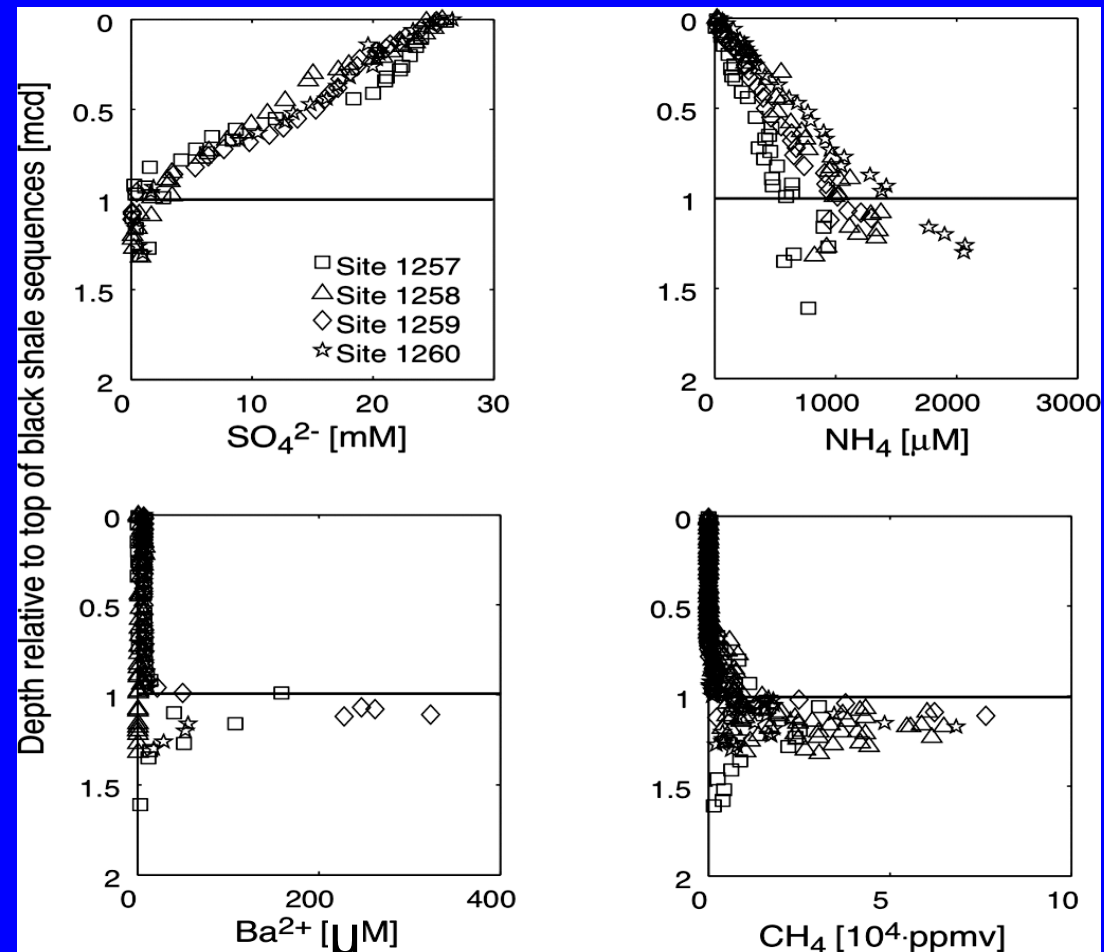
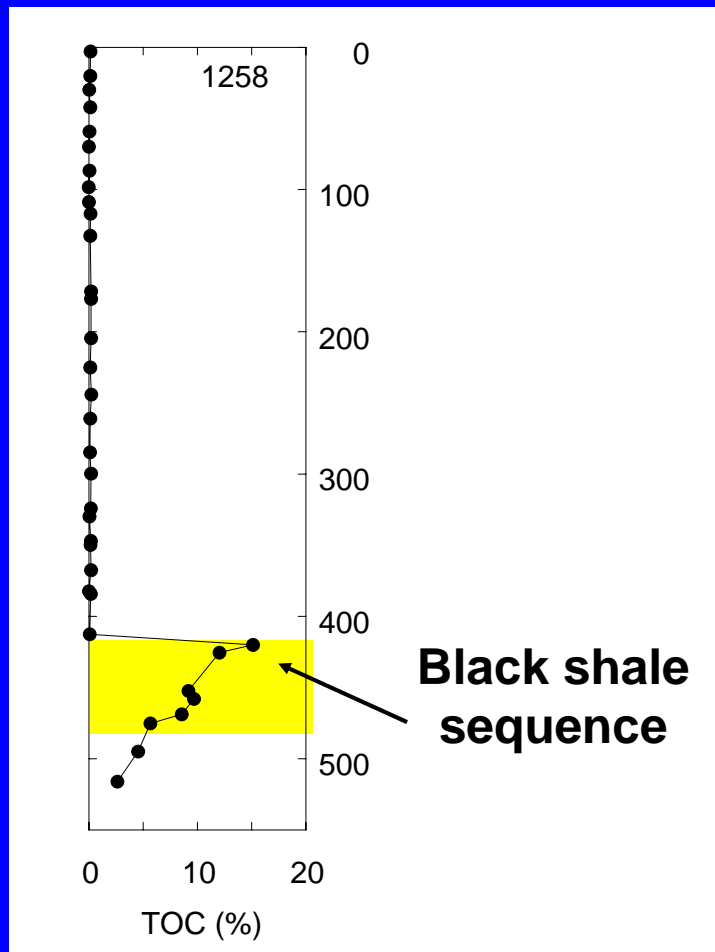
Acknowledgements for Support:
Leg 207 Shipboard Scientific Party,
Deutsche Forschungsgemeinschaft and Max Planck Society

Black shales and Diagenesis: Processes and Proxies



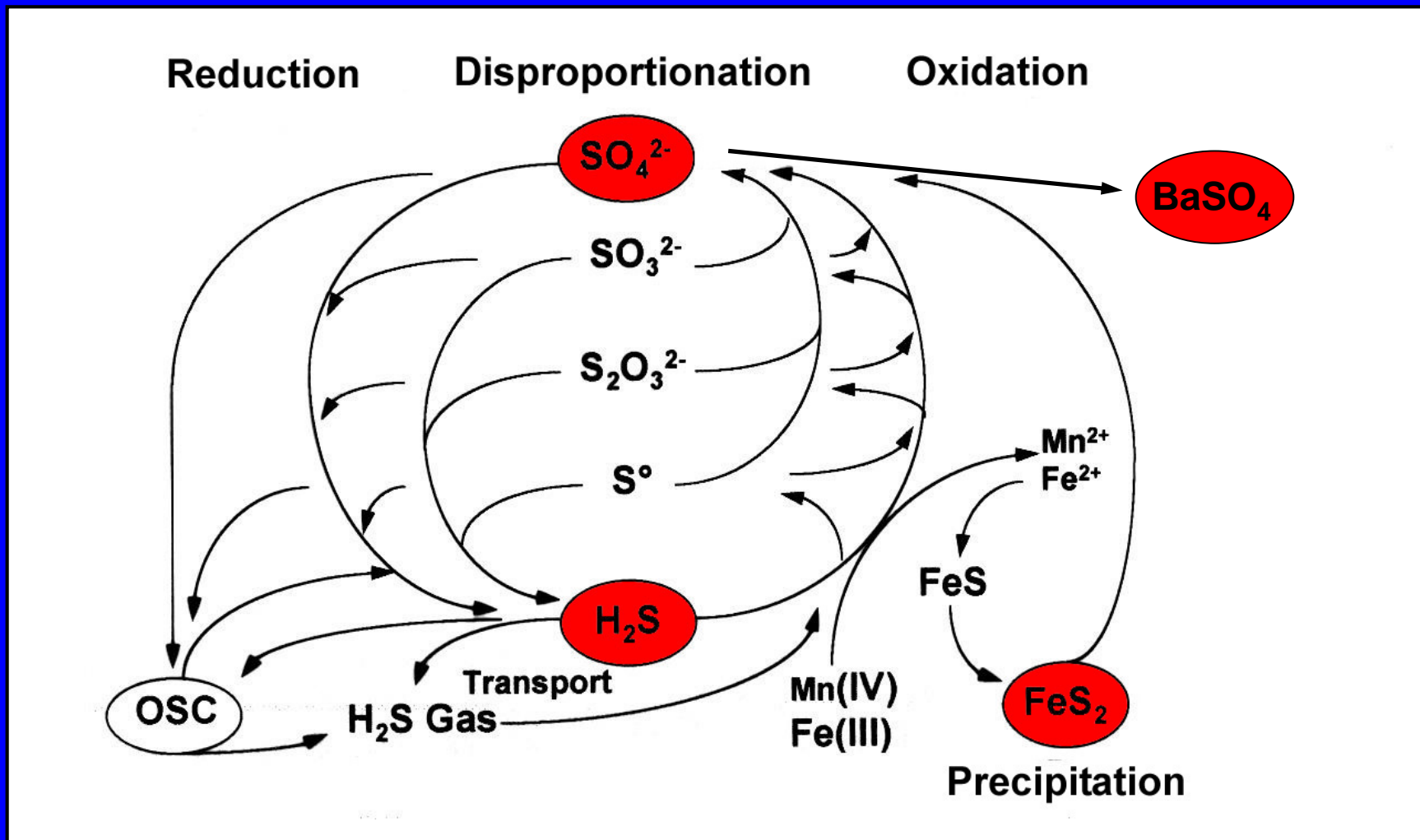
- Authigenic sulfur phases
- Pore water modeling (SO_4 - CH_4 -Ba)
- S and O isotope biogeochemistry

Black shales in Leg 207 sediments and pore water response

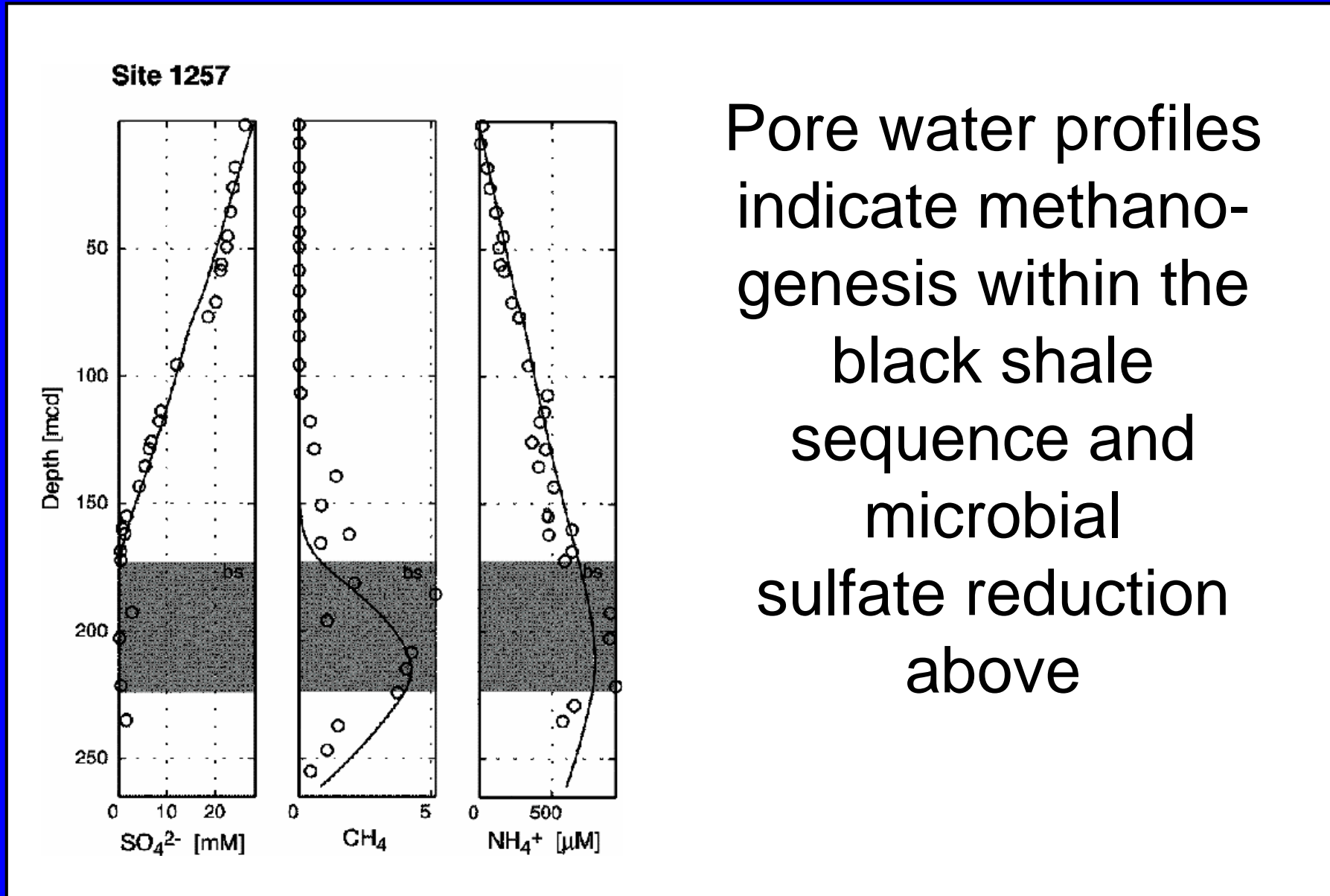


Pore water response
(normalized to top of black shales)

Sedimentary sulfur phases: Recorders for microbial activity, sulfur cycling and coupling to metals



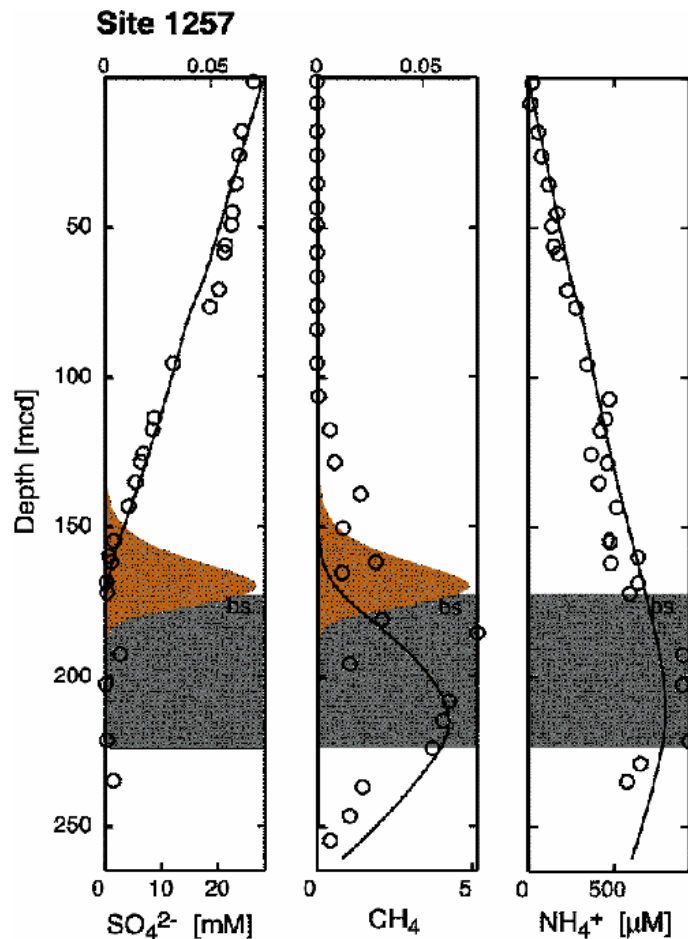
Pore waters as recorders of biogeochemical elements transformations



Pore water profiles indicate methanogenesis within the black shale sequence and microbial sulfate reduction above

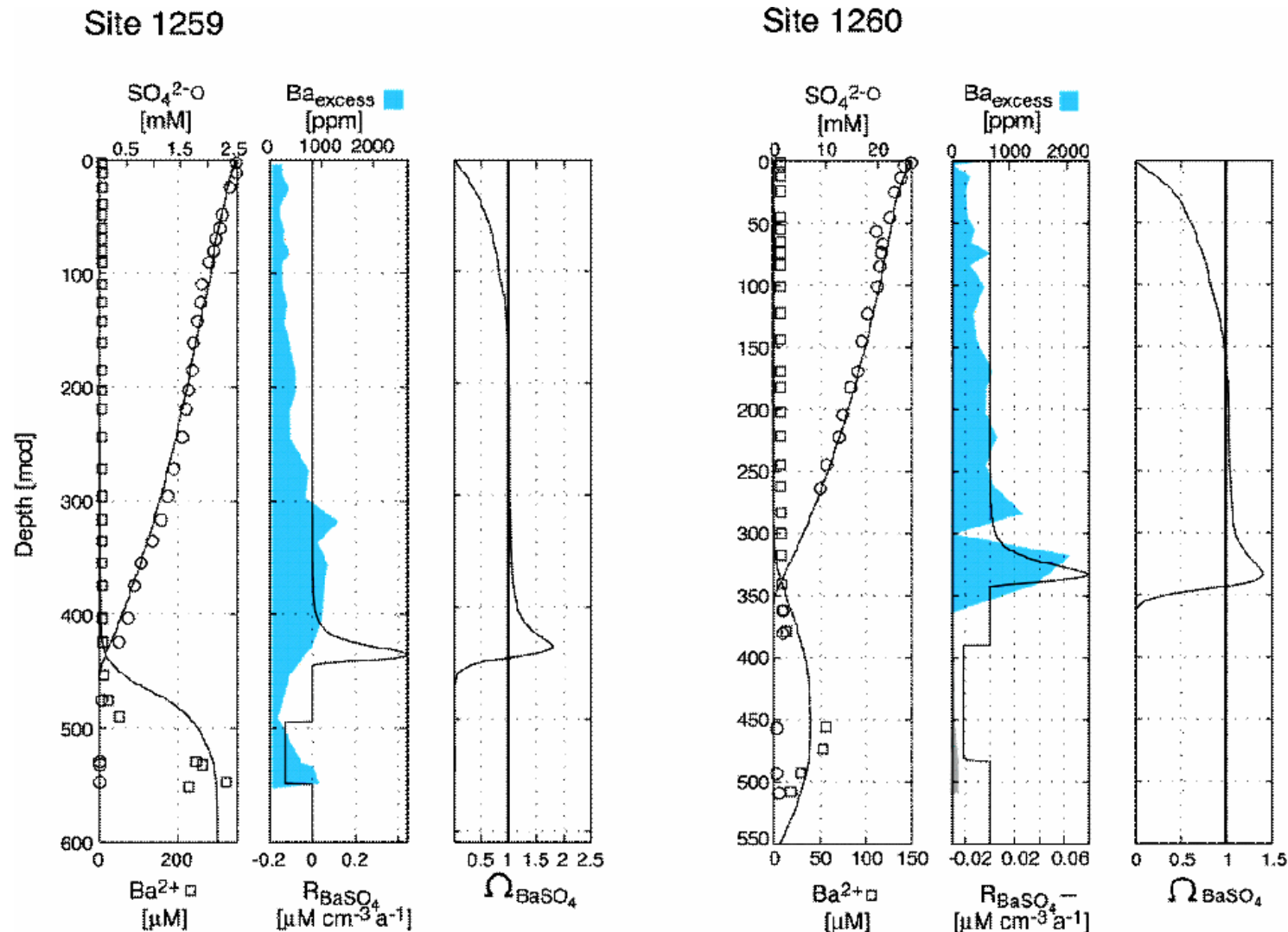
Anaerobic Oxidation of Methane

Methane Oxidation Rate [$\mu\text{M}\cdot\text{a}^{-1}$]

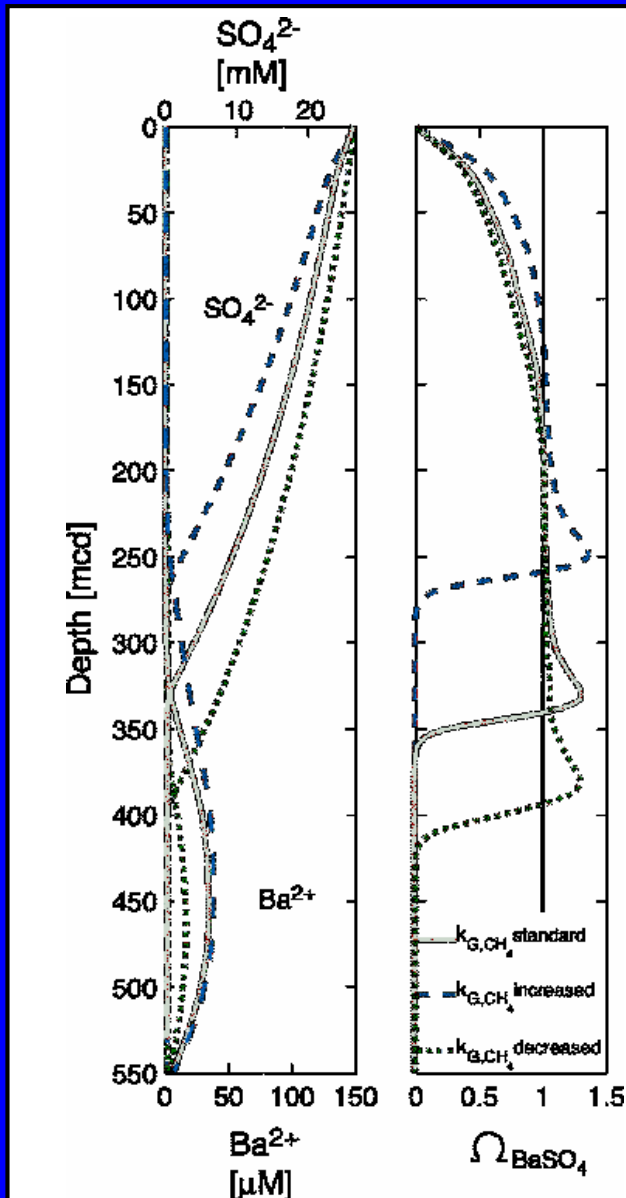


Modeling of pore water profiles indicate anaerobic oxidation of methane at the sulfate-methane transition associated with sulfate reduction

Dissolution and Precipitation of Barite: Measured Ba excess and rate modeling



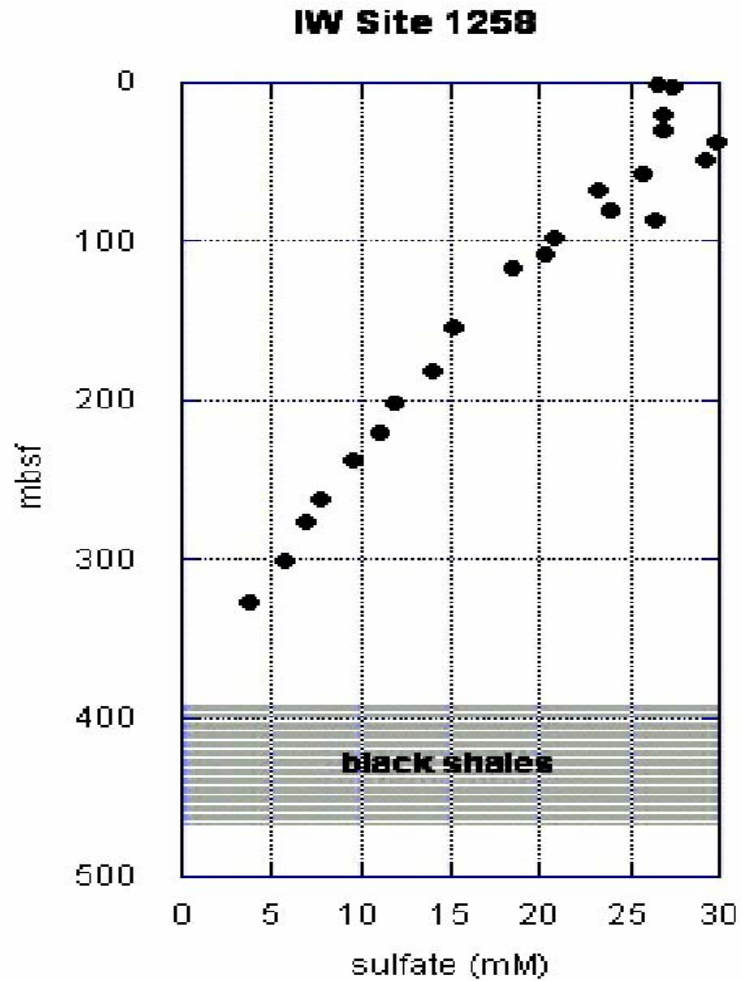
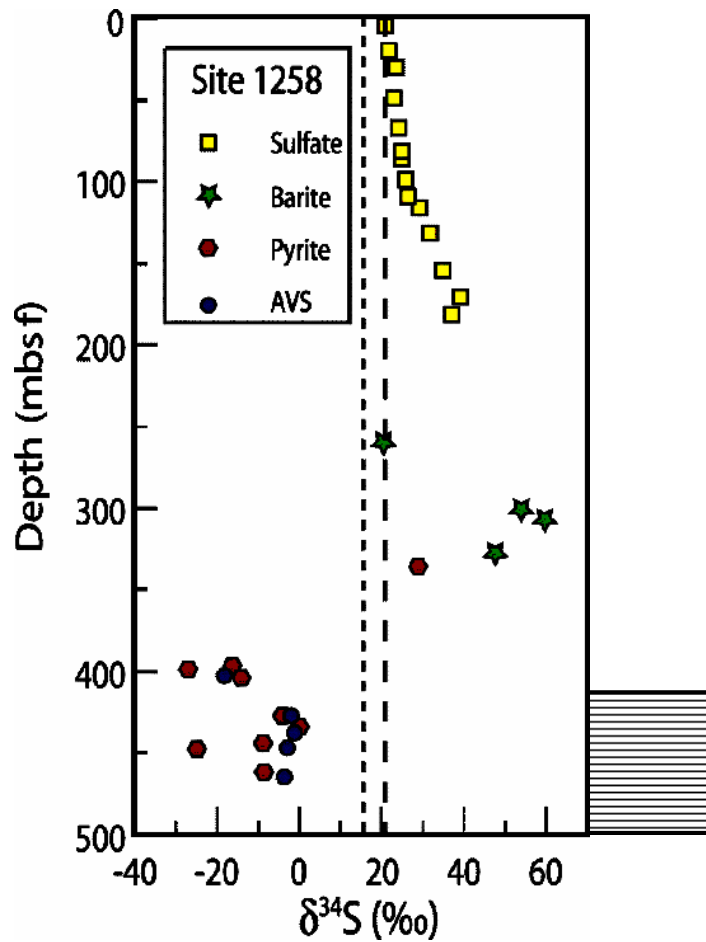
Methanogenesis & Pore Water Gradients



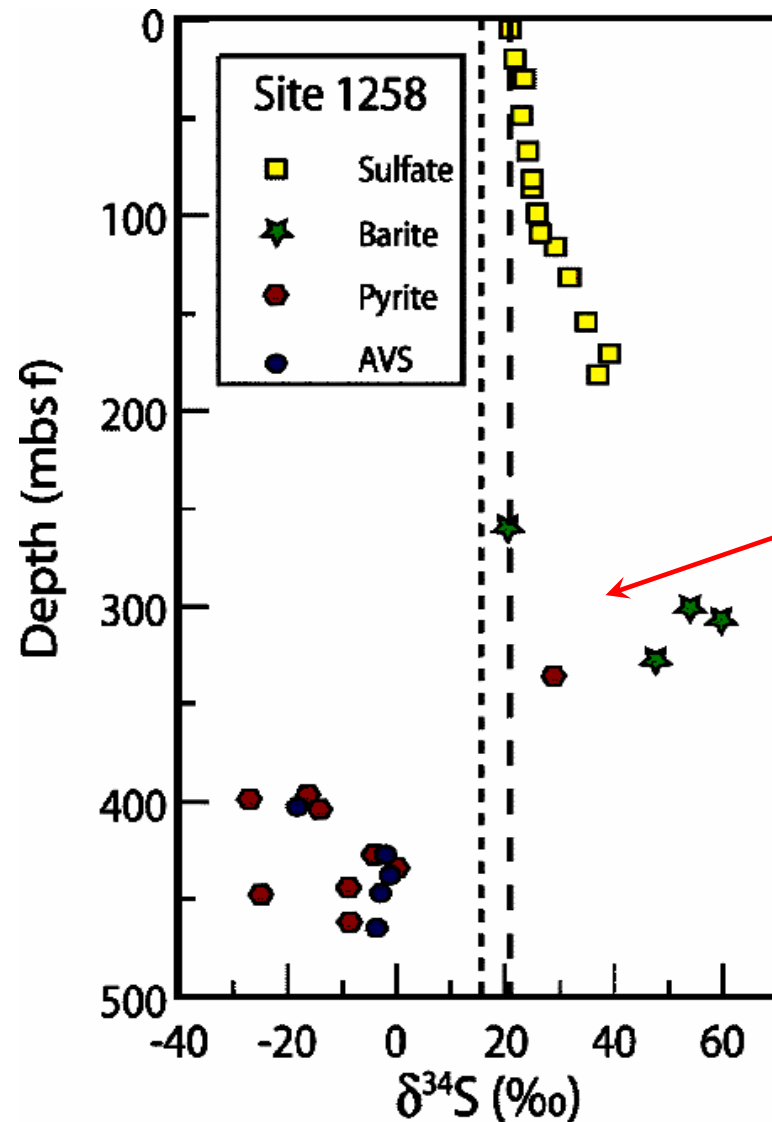
Sulfate-barium-gradients are controlled by methanogenesis rate in the black shales:

Implications for characteristic S and O isotope enrichments in authigenic sulfur phases

Sulfur isotope biogeochemistry

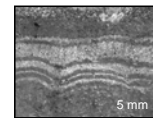


Sulfur isotope biogeochemistry



Isotopic composition of dissolved sulfate as indicator for ongoing microbial sulfate reduction

Heavy barite and pyrite above black shales as recorders for AOM

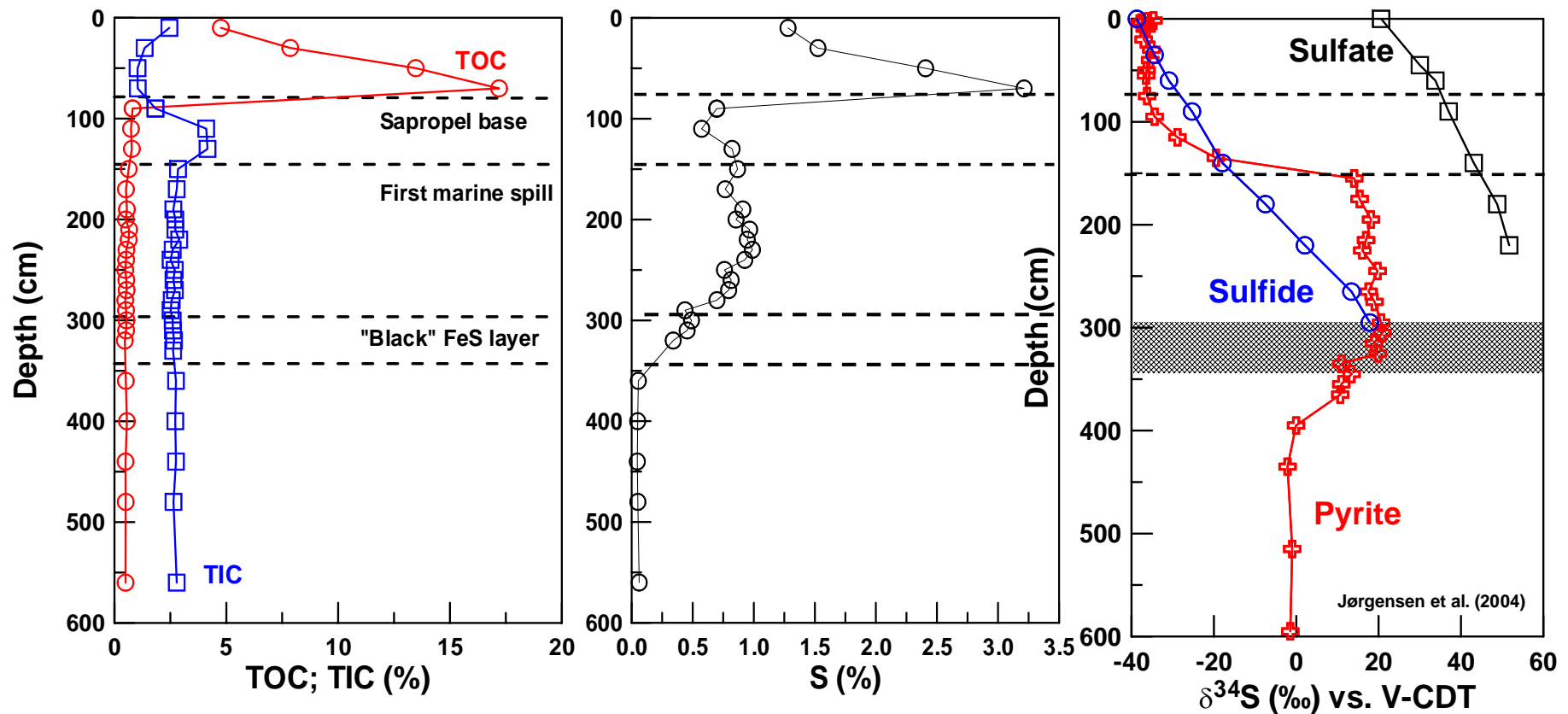


Authigenic pyrite concretion and euhedral crystals

Pyrite and AVS in black shales reflect early reactions in the sulfur cycle

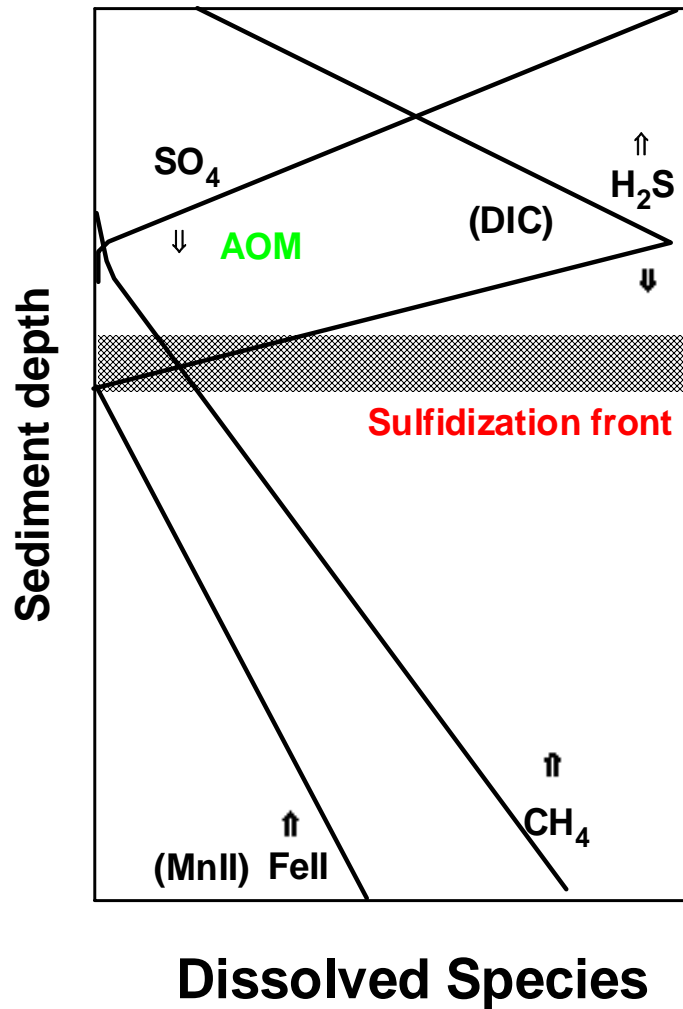
Similar results at all sites

Black Sea sediments as a Model System



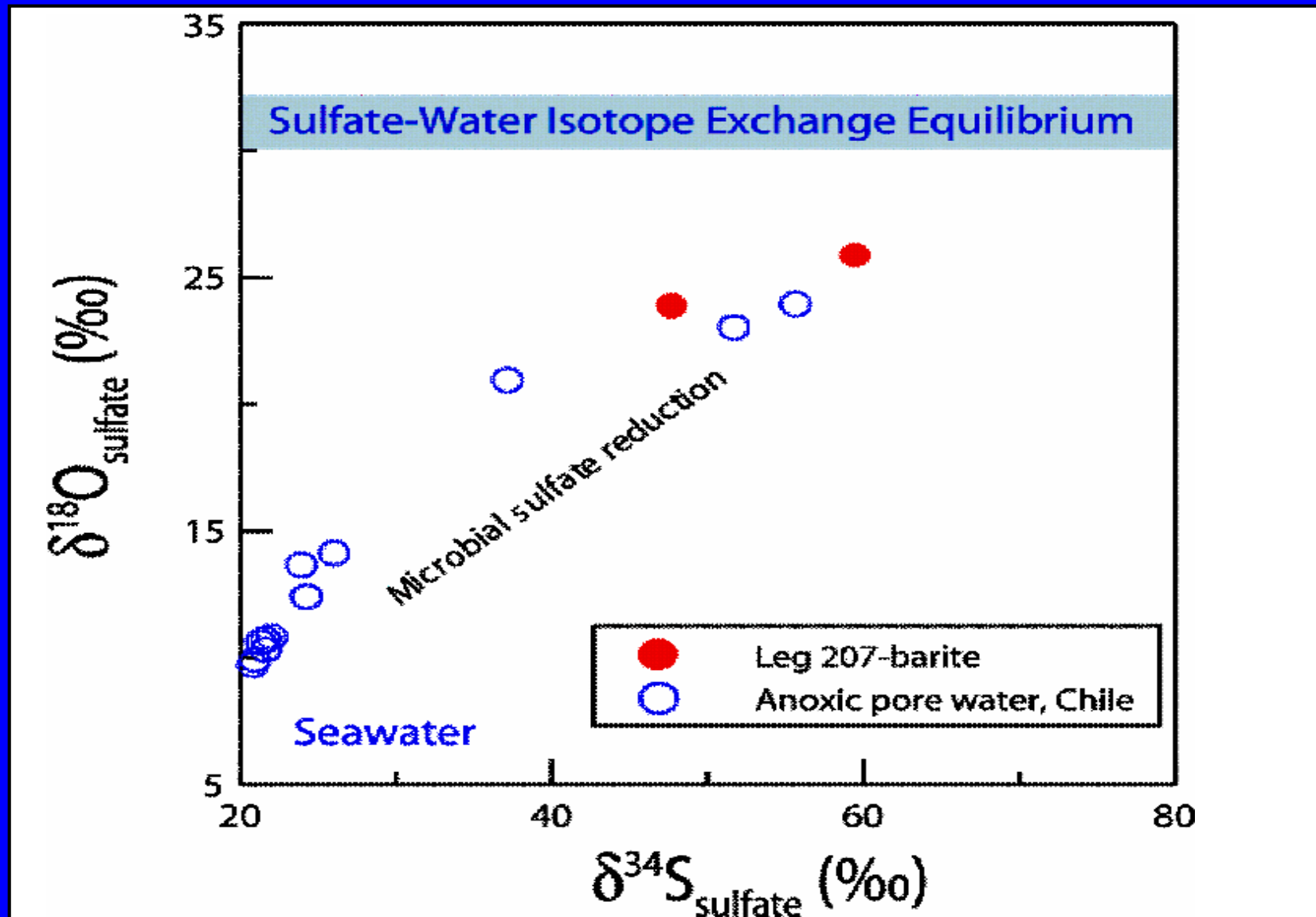
**Diagenetic Sulfidization as a Process
leading to Decoupling of C and S and heavy Sedimentary Sulfides**

Black Sea sediments as a Model System

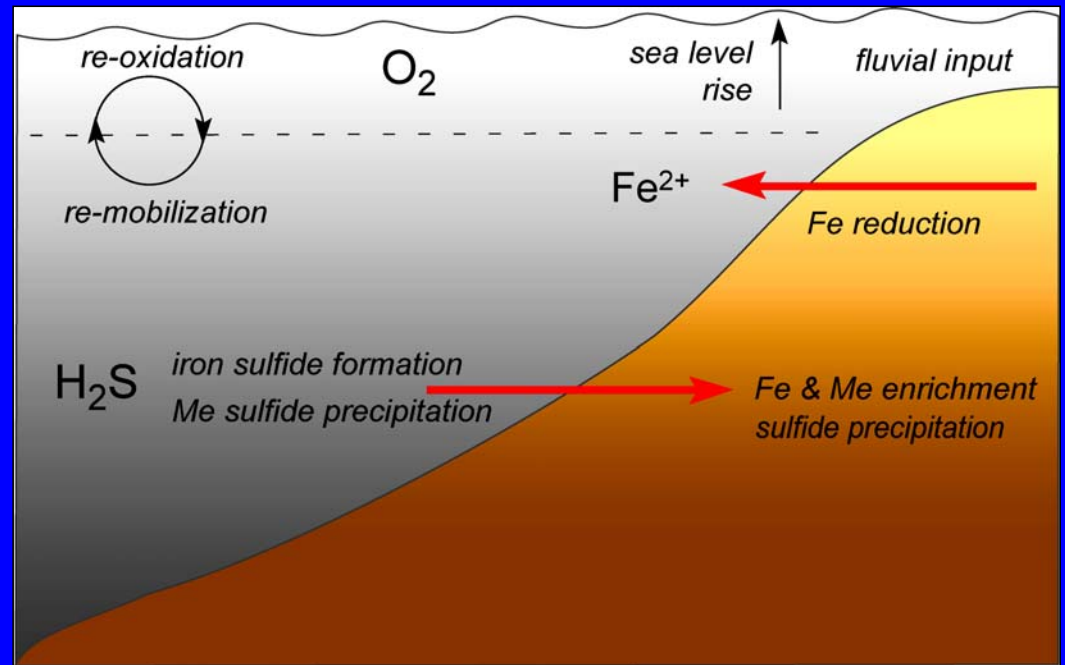
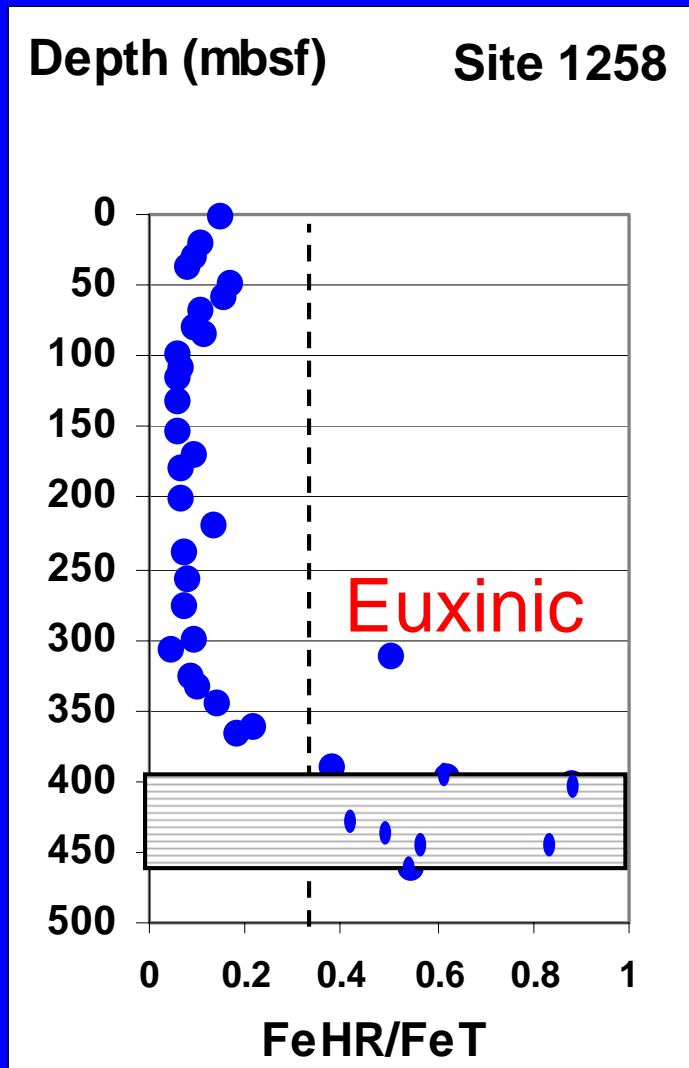


**Anaerobic Methane
Oxidation
as the Driving Force**

S and O isotope co-variations in authigenic barite: Recorders of pore water composition and enzymatic intracellular activity

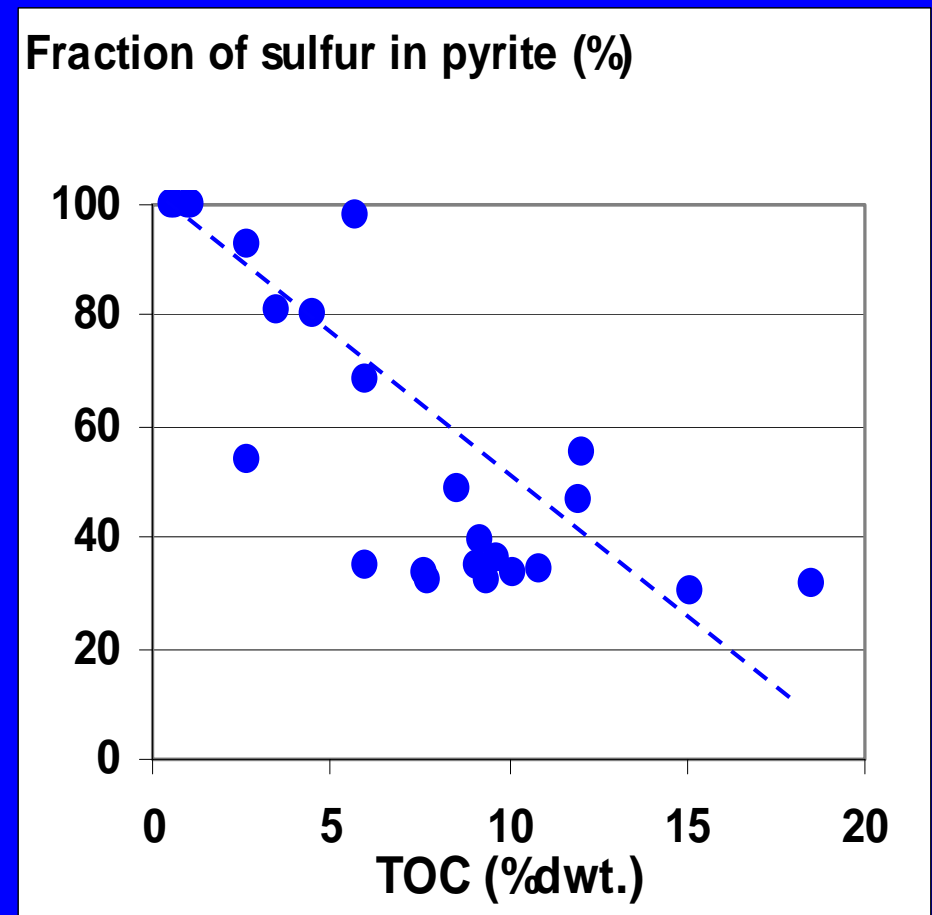
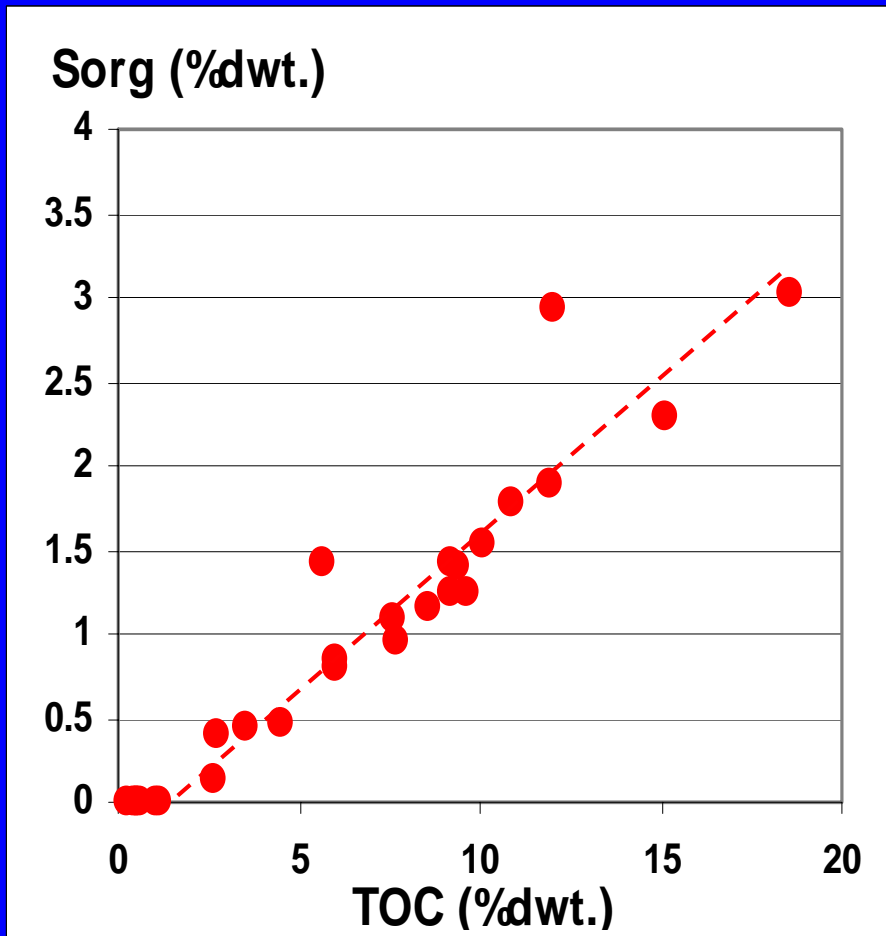


Euxinic conditions during black shale formation



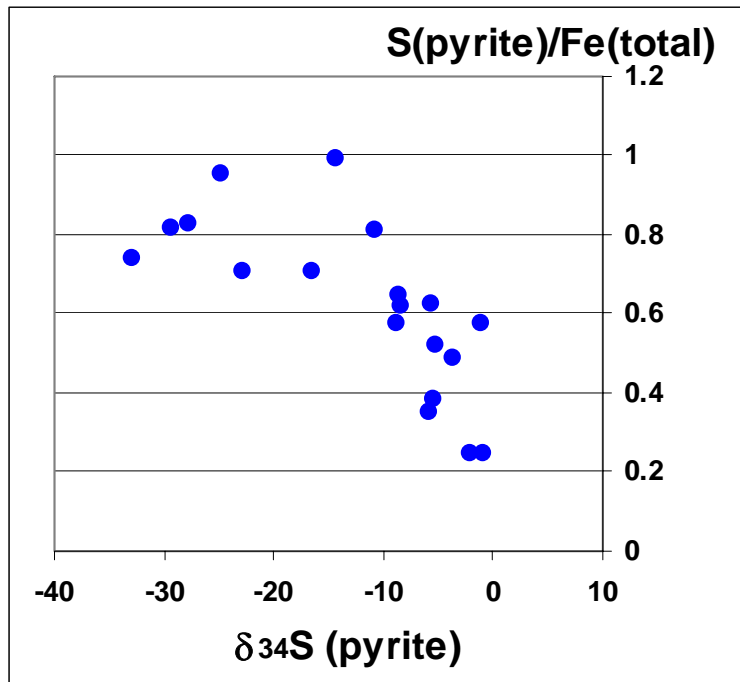
Pyrite formation in the water column

Sulf(id)urization of iron and organic matter in black shales



- The relative importance of sulfurization of organic matter increases with its content

Sulfur isotope partitioning into pyrite of black shales

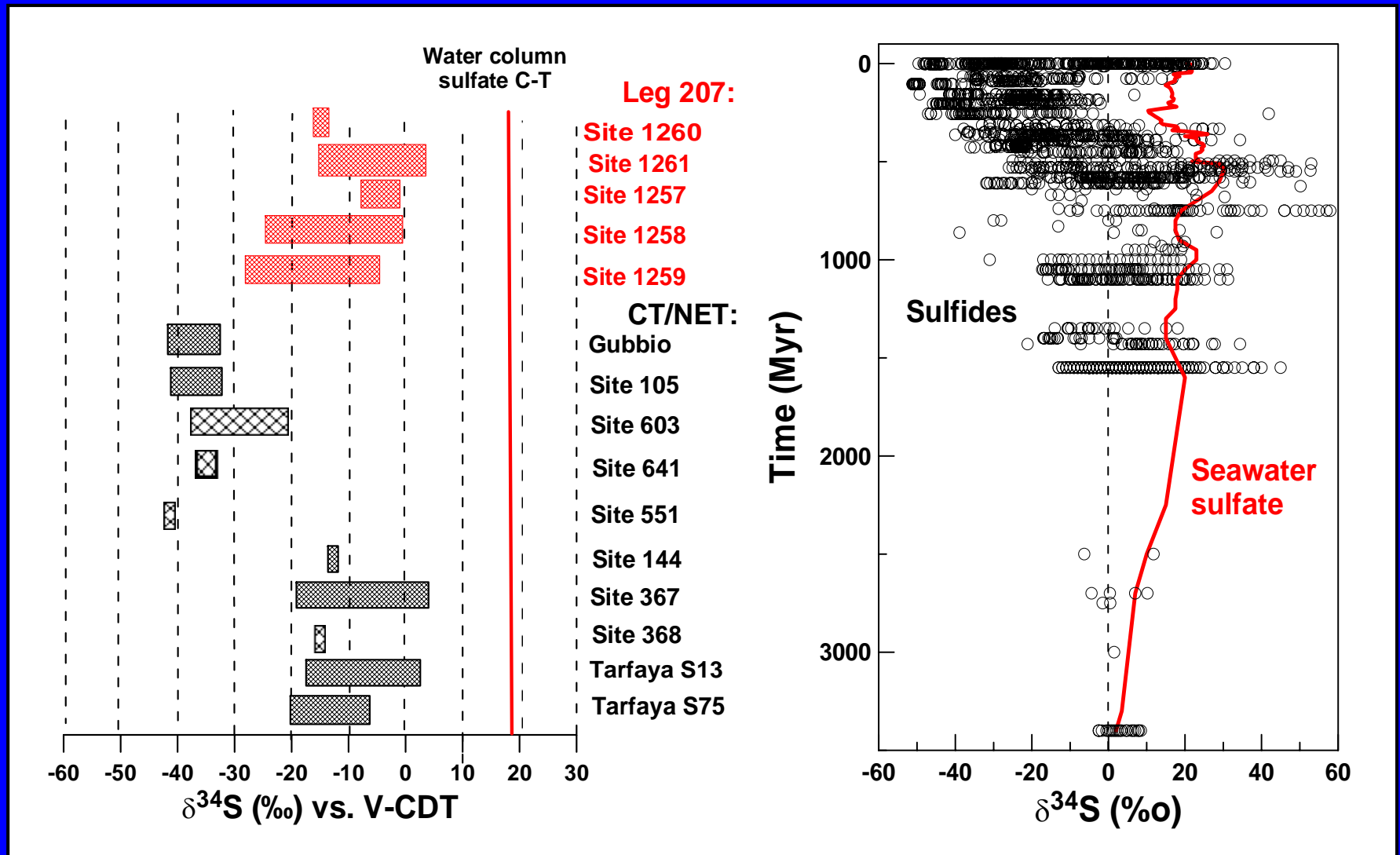


**Iron and S isotope
geochemistry**

Similar trend for TOC

**Enhanced S redox
cycling
at higher TOC**

Heavy sulfur isotopes in pyrite: Recorders for AOM vs. closed system



CT/NET data: Böttcher & Kuypers (unpublished)

Data: Canfield, Strauss, Böttcher

Conclusions

- Pore waters in sediments at Demerara Rise reflect biogeochemical processes dominated by sulfate reduction associated with anaerobic methane oxidation
- The depth of the sulfate-methane transition zone, as well as the availability of sulfate at depth are exclusively controlled by the production of methane in the black shale sequences
- Activity of deep biosphere microbial activity is reflected in the sulfur isotopic composition of the different sulfur-containing phases
- **Reactive iron contents indicate water column derived pyrite in black shales. Also mirrored by S isotope data.**
- The relative importance of sulfurization of organic matter depends on the availability of organic matter
- **Isotopically heavy sulfate and pyrite mineral phases are suggested to be indicators for anaerobic methane oxidation**