Mechanisms of Shuttling Organic Matter (OM) Through Sulfidic Sediments of the Saint Lawrence Estuary

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Background

- The biogeochemical cycles of S, OM and Fe are intimately linked in sediments through the formation of iron-sulfur complexes.
- Oxide minerals sorb and sequester OM – e.g. the "iron shuttle"[1]; an estimated 0.15 x10^{18} g carbon resides in marine sediments[2] alone.

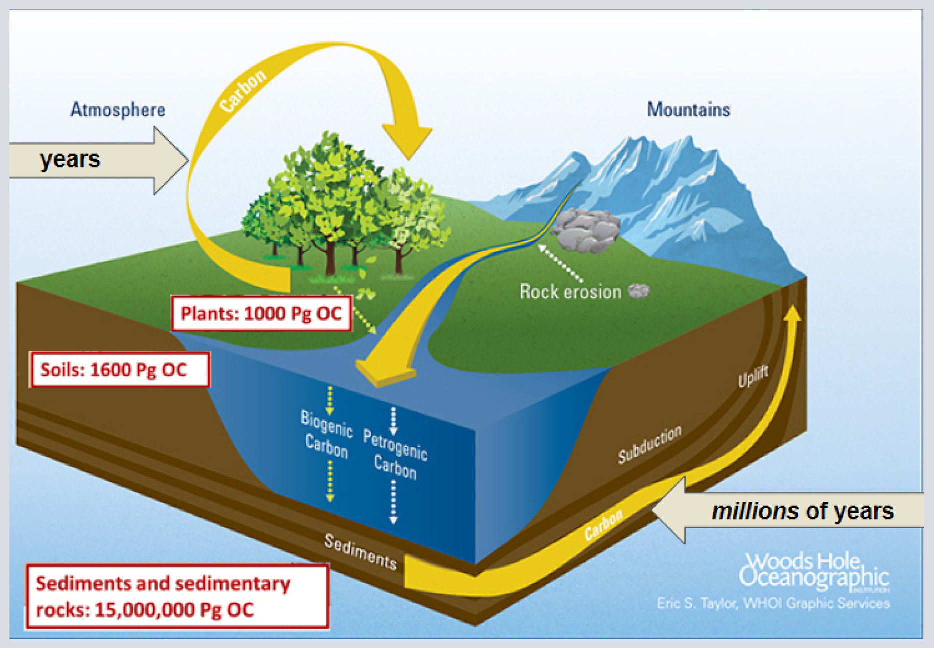


Fig. 1: Magnitudes and approximate residence times of Earth's organic carbon (OC) reservoirs[3,4]

- **Mackinawite (FeS)** may play an active role in sedimentary OM preservation, analogous to that of iron oxides.
- The mechanisms of transport of OM sorbed to iron minerals across the redoxcline are still poorly understood.

Fig. 2: Sediment sampling site: Quebec, Canada

Oxidizing Environment

Reducing Environment

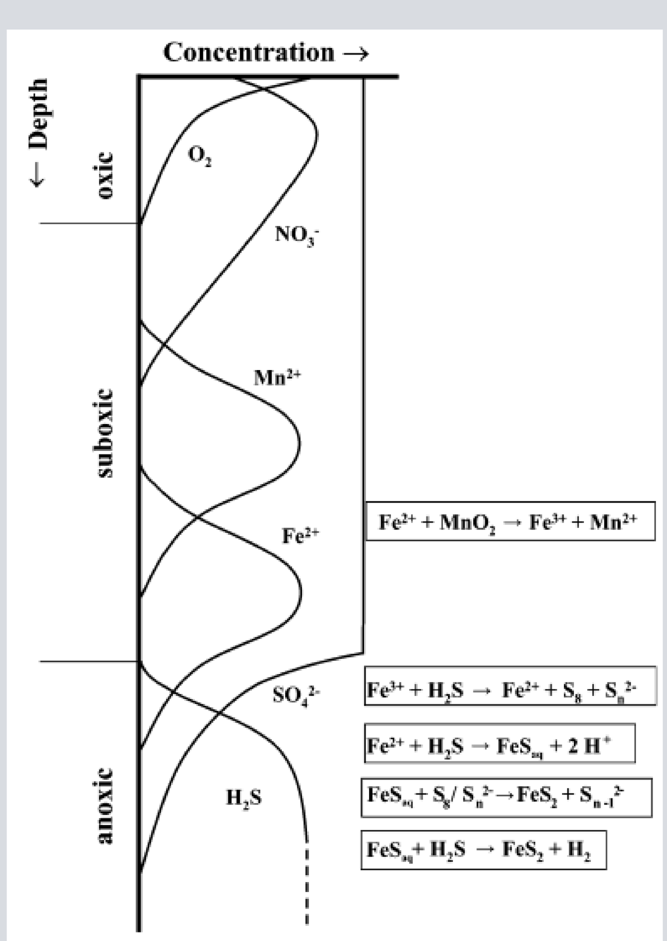
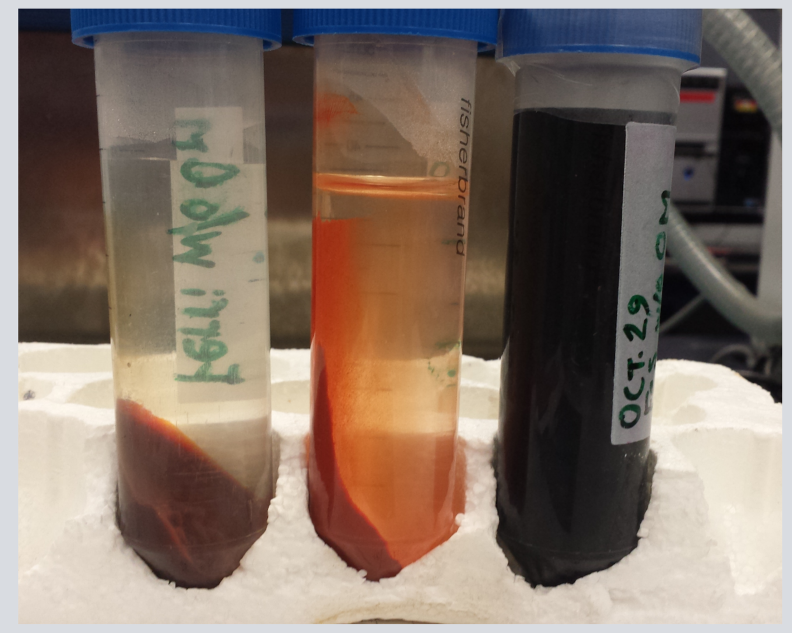


Fig. 3: Sediment core from SLE (*left*); idealized sediment redoxcline (*right*)[5]

Methods and Results

(I) Artificial Redox Cycle of Fe

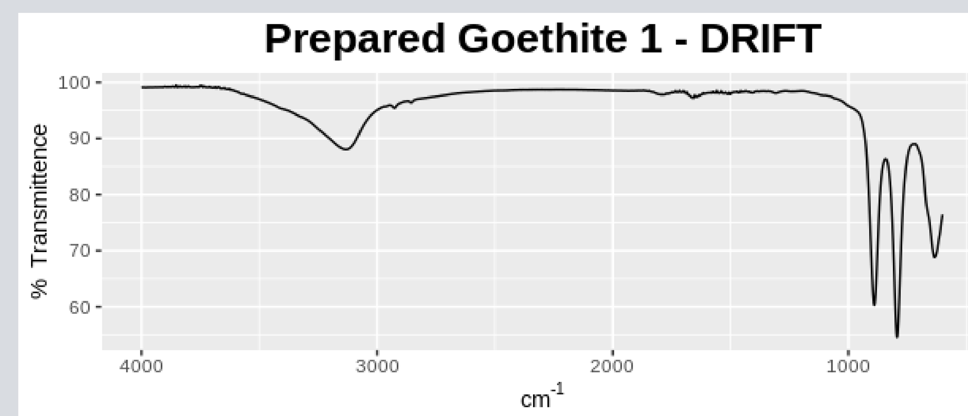
A model Fe redox shuttle has been developed:

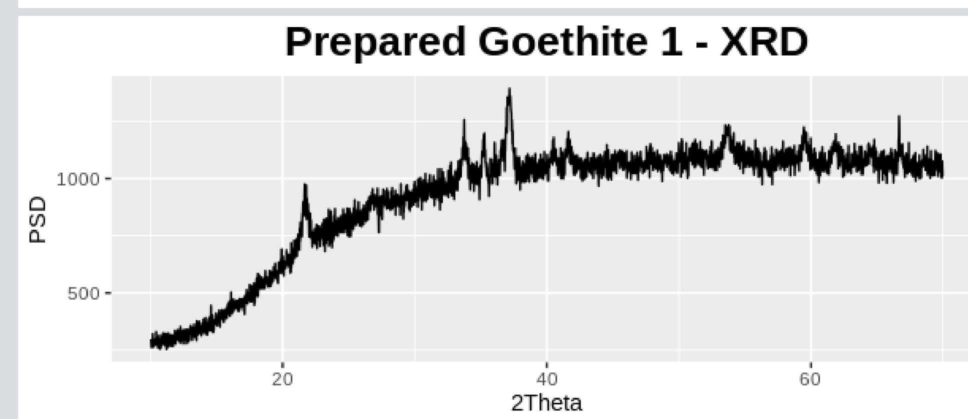


► Ferrihydrite $Fe(OH)_3$

► Goethite α-FeOOH

► Mackinawite FeS





Research Goals

To investigate the mechanism(s) of the iron shuttle for organic matter across the sediment redoxcline by:

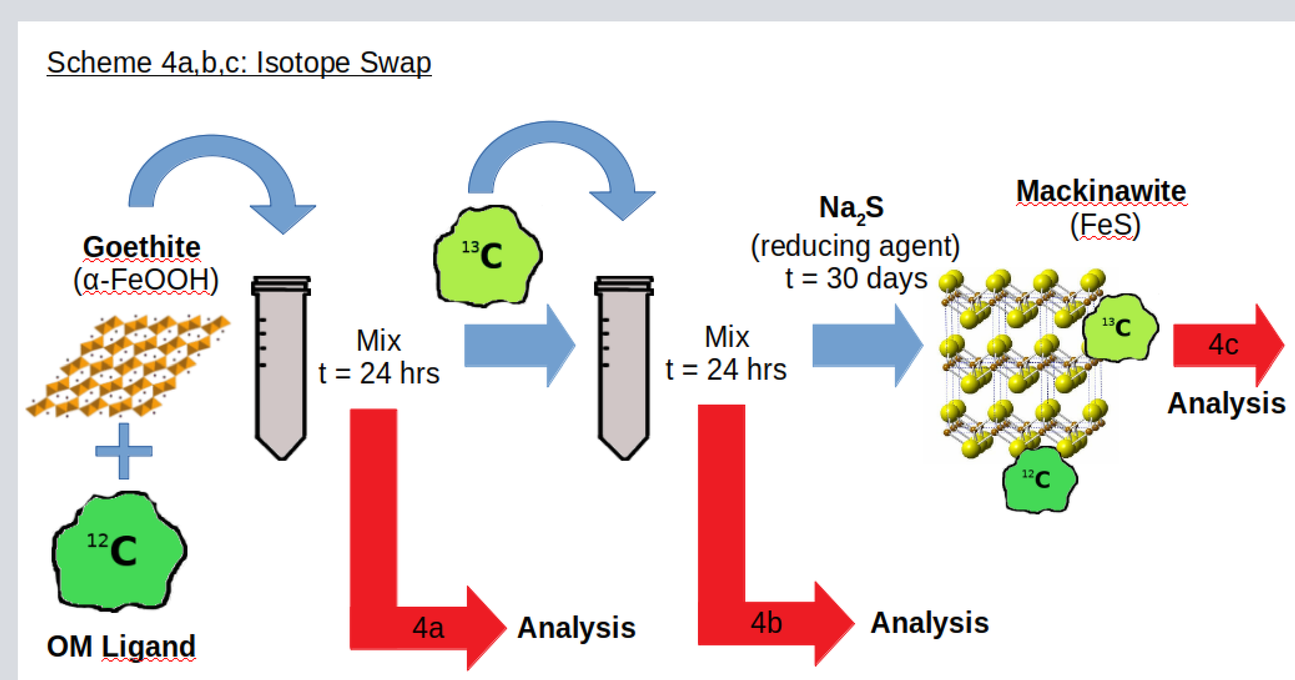
- Characterizing Fe solids across an artificial redox shuttle via XRD, Raman and FT-IR spectroscopy
- Using model organic ligands (aromatic and aliphatic counterparts) as sorbates demonstrating a gradient of Hard Soft Acid Base (HSAB) properties
- Following sorption of ligands across Fe phase transitions via Elemental Analysis – Isotope Ratio Mass Spectrometry (EA-IRMS) and ^{13}C-labeled ligands

in order to answer the following questions:

- Does iron oxidation state affect types/quantities of sorbed OM in sediments?
- Is there potential for desorption or competitive displacement of ligands bound to Fe^{III} during reduction to Fe^{II} in marine environments?

Methods and Results

(II) OM Competitive Displacement Scheme



(III) Shuttling OM across the redoxcline via Fe^{III}/Fe^{II}

Exploratory data by EA-IRMS:

Phase/Ligand	Average %OC[1]	*s*
Ferrihydrite/Catechol	9.66	0.13
(cycle to Goethite)	8.72	0.19
(cycle to Mackinawite)	Failed to precipitate	
Ferrihydrite/KHP	6.08	0.37
(cycle to Goethite)	5.73	0.16
(cycle to Mackinawite)	0.60	0.02
Ferrihydrite/Salicylate	3.06	0.21
(cycle to Goethite)	1.47	0.04
(cycle to Mackinawite)	0.91	0.11

[1]Initial Fe:OC in solution adjusted to 1:1; *n* = 3

Preliminary Conclusions and Next Steps

- Fe^{III} sorbs Catechol > Phthalate > Salicylate in agreement with the literature.
- Loss of sorbed OM observed for KHP & Salicylate upon reduction to mackinawite.
- Catechol inconclusive but failure to precipitate suggests reductive dissolution mechanism.
- Next steps include running iron shuttle schemes (e.g. see Scheme 4) for 30 days to obtain data.
- Future analysis of minerals by Transmission Electron Microscopy (TEM).

References

(1) A. Barber, J. Brandes, A. Leri, K. Lalonde, K. Balind, S. Wirick, J. Wang, Y. Gélinas (2017). Preservation of organic matter in marine sediments by inner-sphere interactions with reactive iron. *Scientific Reports*, 7: 366-381.

(2) S. Emerson and J. Hedges (1988). Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography*, 3: 621-634.

(3) Woods Hole Oceanographic Institution. https://www.whoi.edu/ (accessed Feb 04, 2020).

(4) J. Hedges, and R. Keil (1995). Sedimentary organic matter preservation: an assessment and speculative synthesis. *Marine Chemistry*, 49: 81-115.

(5) D. Rickard and G. Luther (2007) Chemistry of Iron Sulfides. *Chemical Reviews*,107, 514–562.

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