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 \(0.15 \times 10^{18}\) g carbon resides in marine sediments\(^2\) alone. 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.

**Background**

**Methods and Results**

**(I) Artificial Redox Cycle of Fe**

A model Fe redox shuttle has been developed:

- Ferrihydrite Fe(OH)\(_3\)
- Goethite \(\alpha\)-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?

**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.

**Figure 1:** Magnitudes and approximate residence times of Earth’s organic carbon (OC) reservoirs\(^3,4\)

**Figure 2:** Sediment sampling site: Quebec, Canada

<table>
<thead>
<tr>
<th>Phase/Ligand</th>
<th>Average %OC</th>
<th>s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrihydrite/Catechol</td>
<td>9.66</td>
<td>0.13</td>
</tr>
<tr>
<td>(cycle to Goethite)</td>
<td>8.72</td>
<td>0.19</td>
</tr>
<tr>
<td>(cycle to Mackinawite)</td>
<td>Failed to precipitate</td>
<td></td>
</tr>
<tr>
<td>Ferrihydrite/KHP</td>
<td>6.08</td>
<td>0.37</td>
</tr>
<tr>
<td>(cycle to Goethite)</td>
<td>5.73</td>
<td>0.16</td>
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<tr>
<td>(cycle to Mackinawite)</td>
<td>0.60</td>
<td>0.02</td>
</tr>
<tr>
<td>Ferrihydrite/Salicylate</td>
<td>3.06</td>
<td>0.21</td>
</tr>
<tr>
<td>(cycle to Goethite)</td>
<td>1.47</td>
<td>0.04</td>
</tr>
<tr>
<td>(cycle to Mackinawite)</td>
<td>0.91</td>
<td>0.11</td>
</tr>
</tbody>
</table>

\(^4\) Initial Fe:OC in solution adjusted to 1:1; \(n = 3\)

**References**


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