What's af(Fe)cting OC-Fe interactions?

An experimental approach to understanding iron bound organic carbon in sediments

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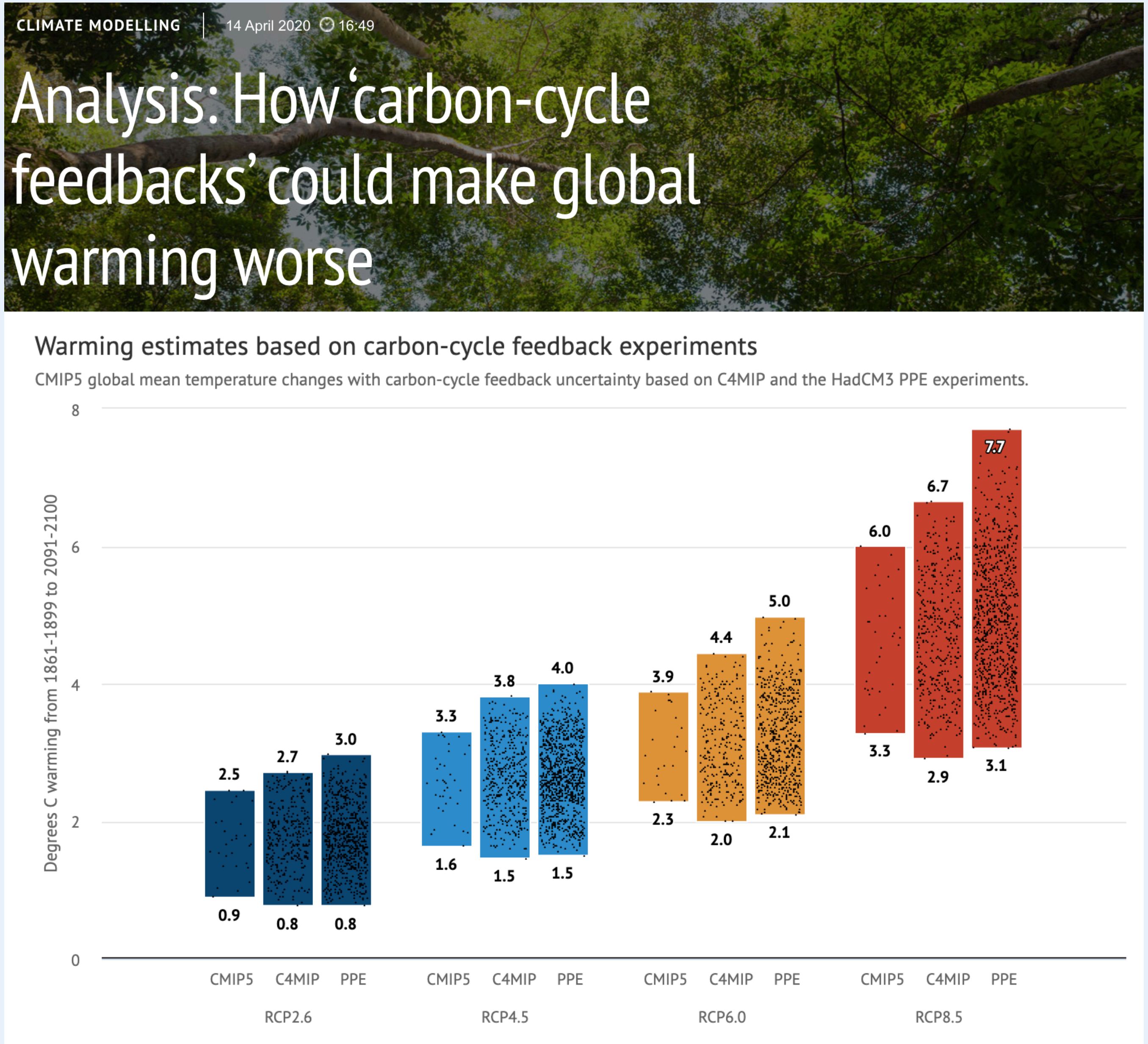
Aim: To understand why only a minority of (~22%) of organic carbon is preserved by reactive iron minerals in marine sediment. We investigate this by characterising the contribution of carboxyl groups in synthetic OC-Fe compounds to stability against chemical reduction of reactive Fe minerals.

@BenFisher_



Hausfather and Betts, 2020, carbonbrief.org

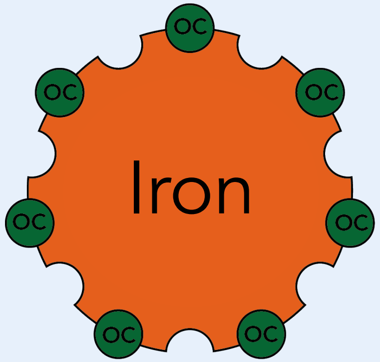
"Currently, only ~2% of sediment C stocks are located in highly to fully protected areas that prevent the disturbance of the seafloor."

"The lack of protection for marine C stocks makes them highly vulnerable to human disturbances that can lead to their remineralization to CO_2, further aggravating climate change impacts"

Atwood et al., 2020, Front. Mar. Sci

Preservation of sedimentary carbon

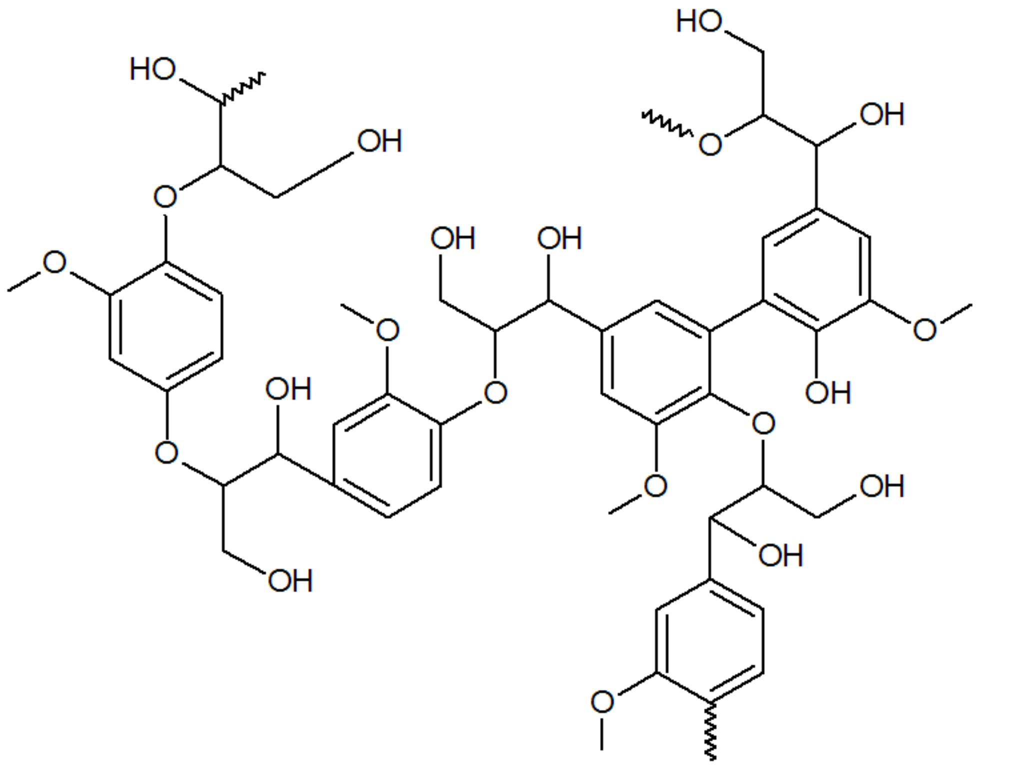
Of the ocean DOC pool, 1% becomes buried in sediment, ~22% is subsequently preserved by reactive iron minerals. *(Burdige, 2007, Lalonde et al., 2012)*

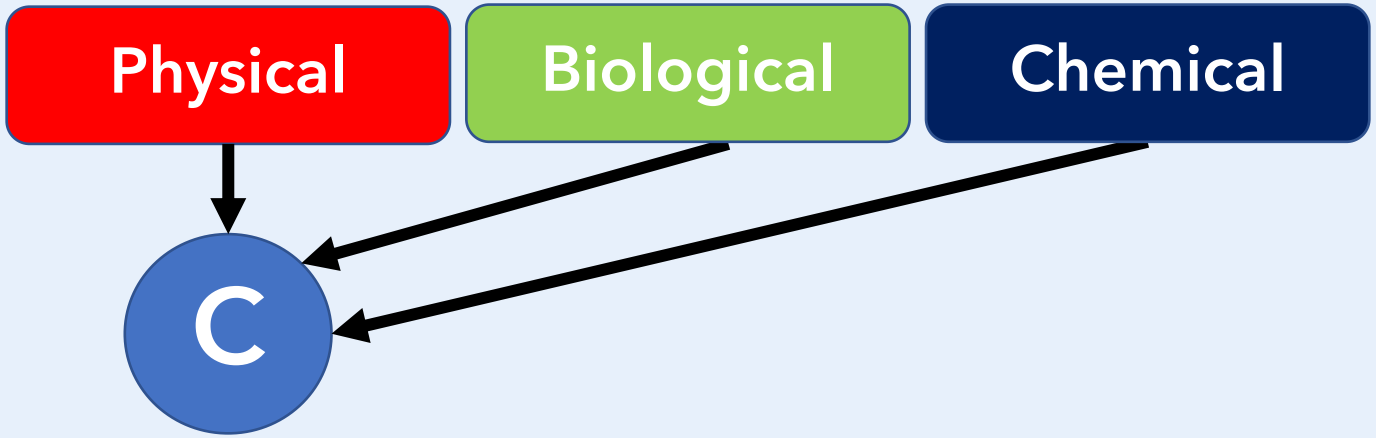


Why is some carbon preserved, and some not?

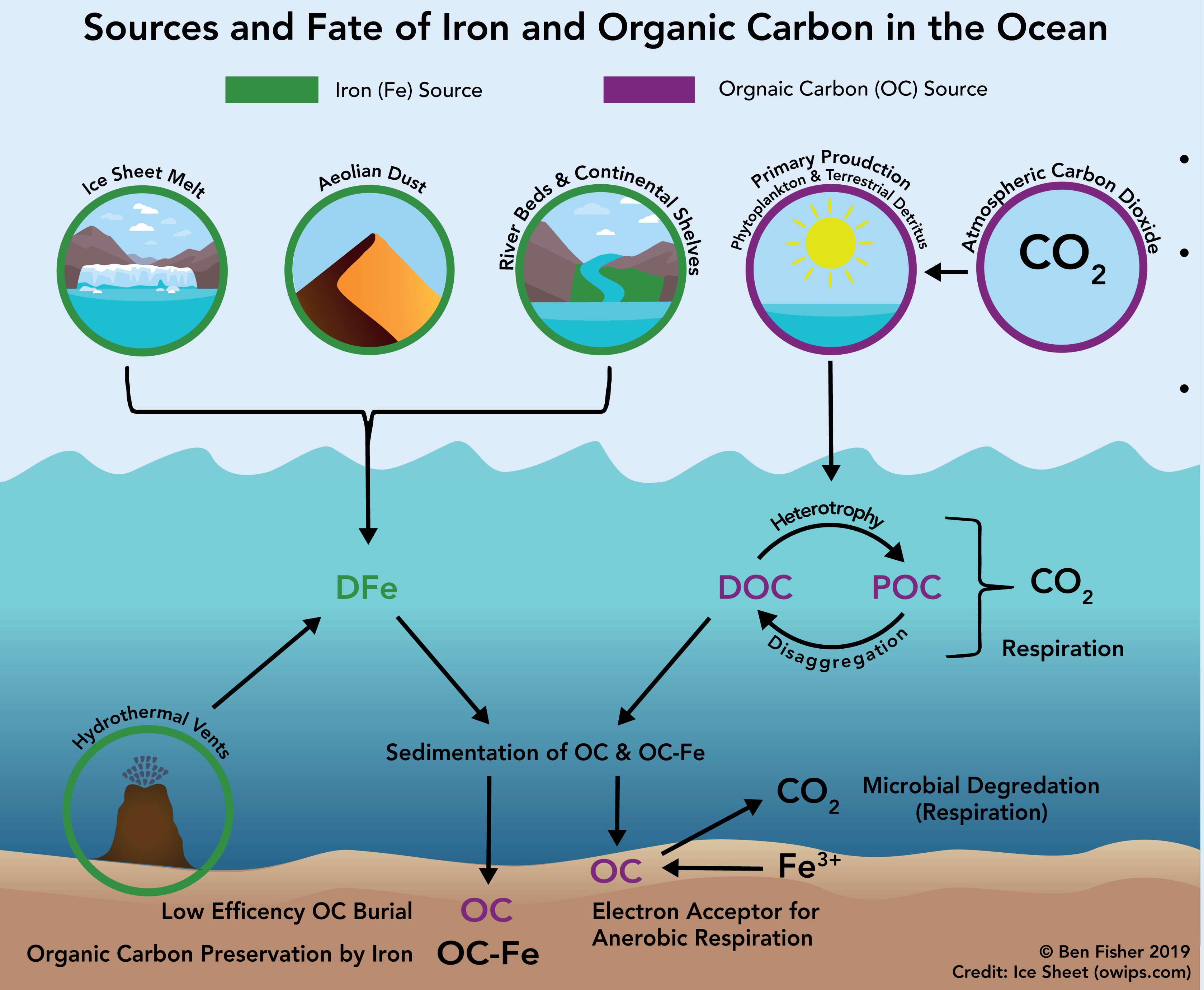
Inherent recalcitrance vs environmental factors

Lignin





Arndt et al., 2013
LaRowe et al., 2020



Variation creates uncertainty

Other C sources include:

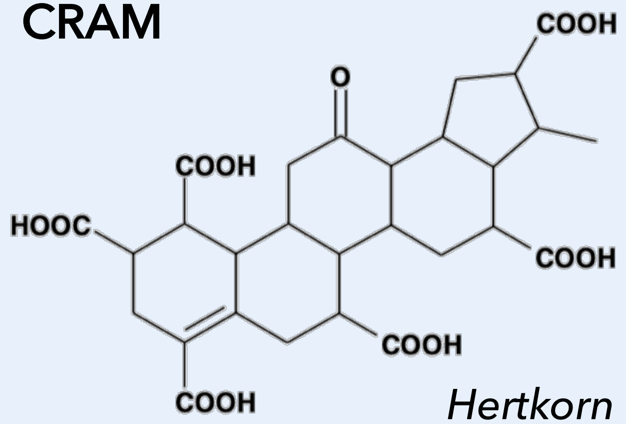
- Riverine (0.45 Pg C yr^{-1}) *(Meybeck, 1982; Li et al., 2017)*
- OC in groundwater liberated from summer permafrost thaw (14-71 kg km day^{-2}) *(Connolly et al., 2020)*
- Slope transport of soil and vegetation in fjord sediment *(Smith et al., 2015)*.

What happens to OC next?

Carbon at the seafloor

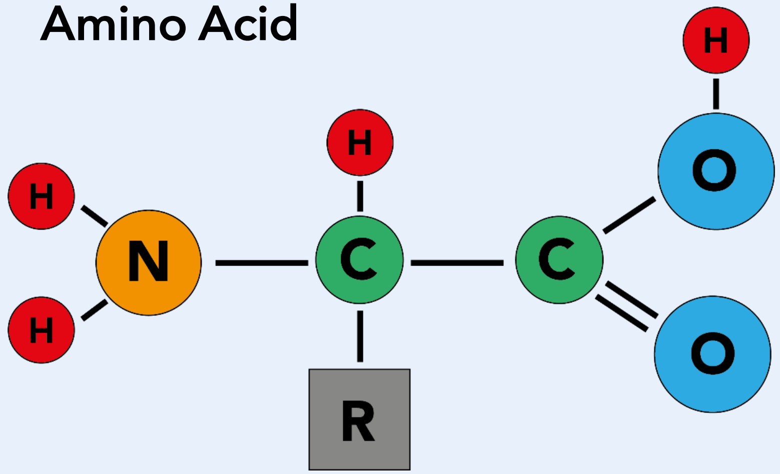
- **Where did it come from?**
  Amino acids: 10-15% *(Cowie and Hedges, 1992)*
  Carbohydrates: 5-10%, Lignin: 3-5% *(Cowie et al., 1992)*
  Lipids <5% *(Tissot and Welte, 1984)*
- **What does it look like?**
  Dominated by carboxyl rich alicyclic molecules (~62%) *(Hertkorn et al., 2006)*
  CRAM is highly transformed and functionalised *(Lam et al., 2007)*
- **How reactive is it?**
  Fe(III) forms stable mononuclear complexes with OC through carboxyl and hydroxyl groups. *(Karlsson et al., 2010,2012, Mikutta 2011)*

CRAM

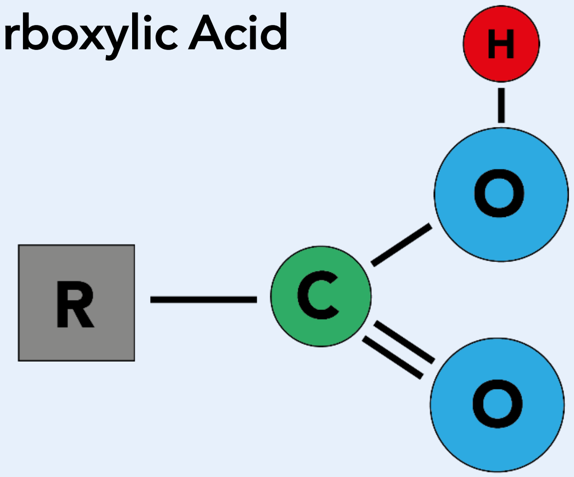


Hertkorn et al., 2006

Amino Acid



Carboxylic Acid



Experimental approach

Hypothesis:

Different organic carbon moieties will create differential stability of iron organominerals, resulting in differential rates of extractability for the iron phase and associated OC.

Method:

Create synthetic sediments with known iron and carbon content

Measure Fe + C

↓

Differ the structure of carbon used (no. of COOH groups)

↓

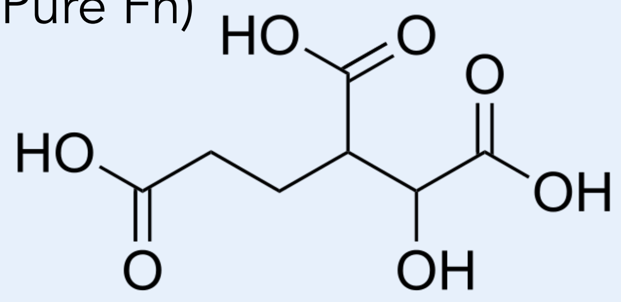
Reductively dissolve the organomineral (CDB)

N.B Reductive dissolution by CDB is used as a proxy for preservative strength, the stronger the preservation the more difficult to extract.

Measure Fe + C

Carbon moieties

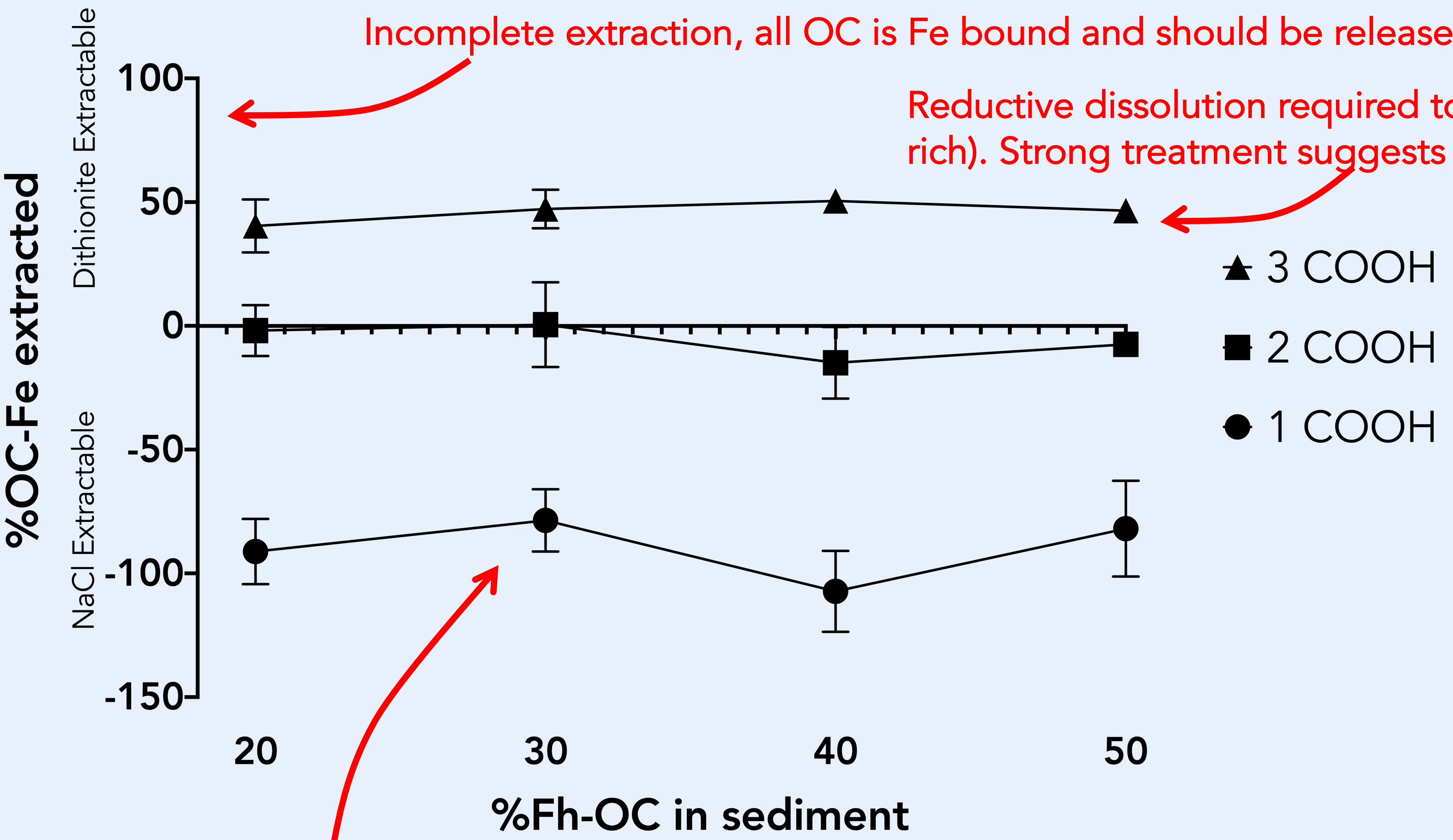
0 COOH (Pure Fh)
1 COOH
2 COOH
3 COOH



Extractability of Carbon

Incomplete extraction, all OC is Fe bound and should be released.

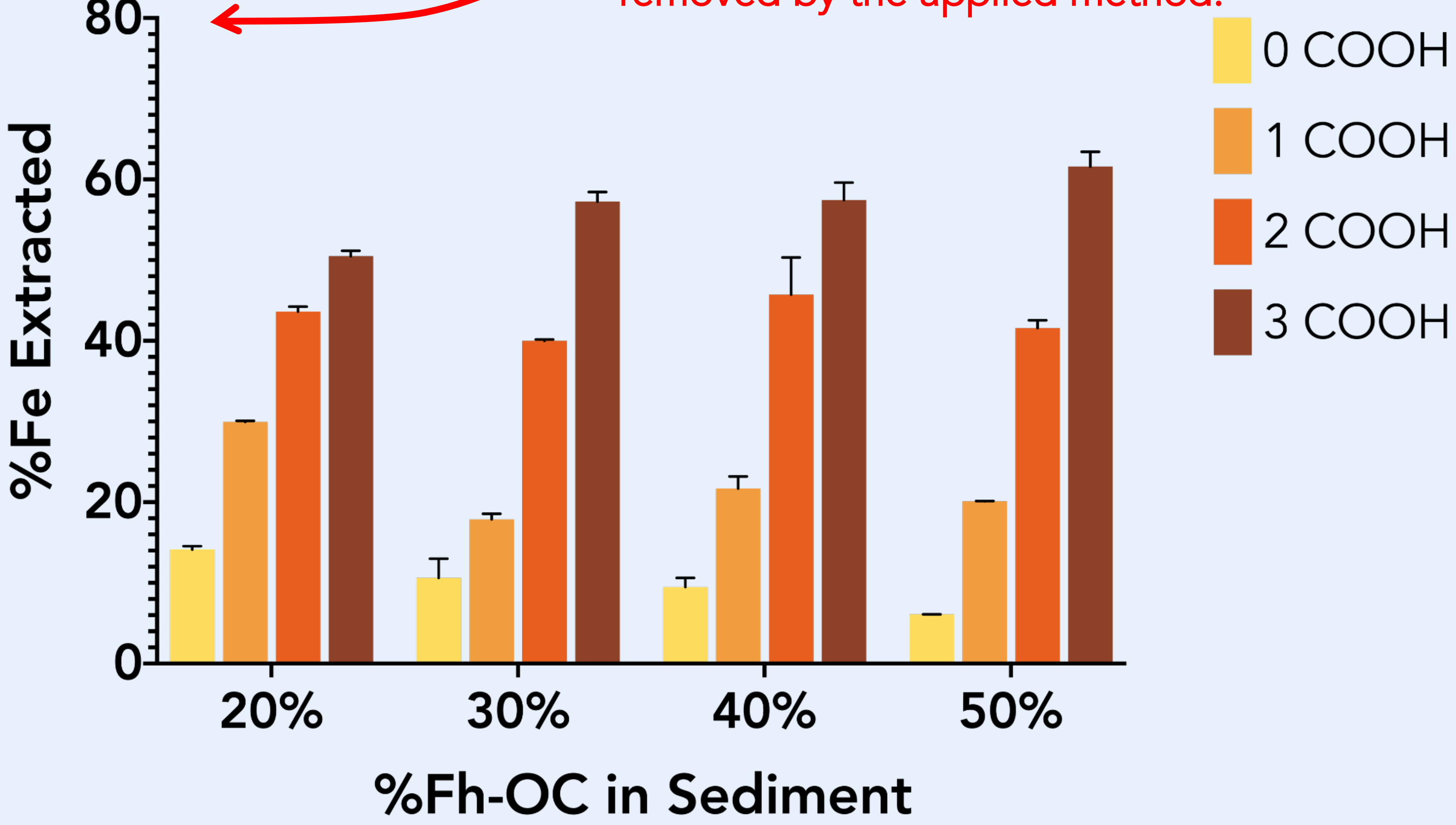
Reductive dissolution required to remove 3 COOH OC (carboxyl rich). Strong treatment suggests strong bonding/preservation.



The majority of structurally simple OC (1 COOH) is removed by NaCl, suggests weaker bonding and preservative effect.

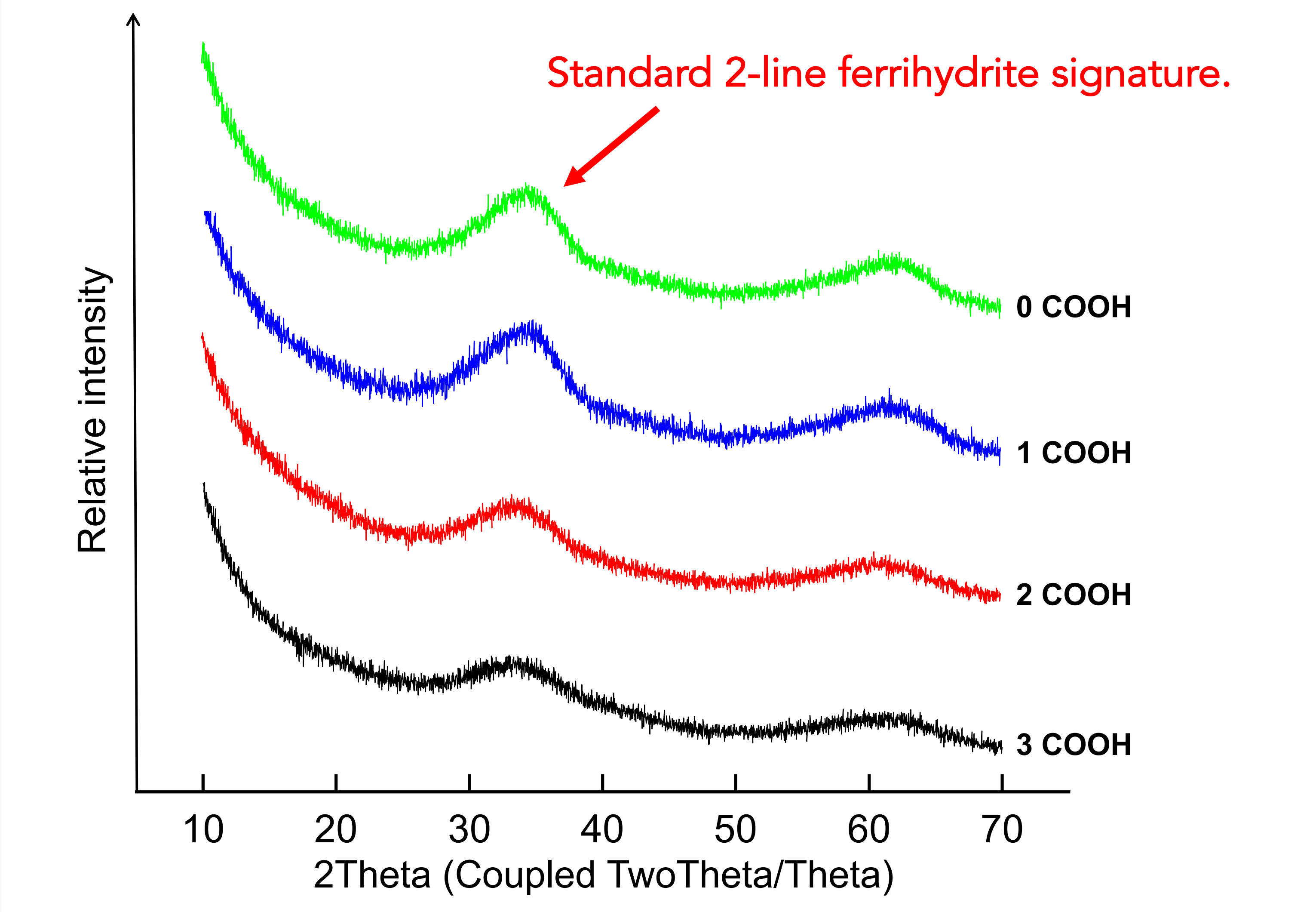
Extractability of Iron

Incomplete extraction, all Fe is easily reducible so should be removed by the applied method.



Stepwise trend shows that carboxyl rich organic acids liberate the most Fe from their associated minerals upon reduction.

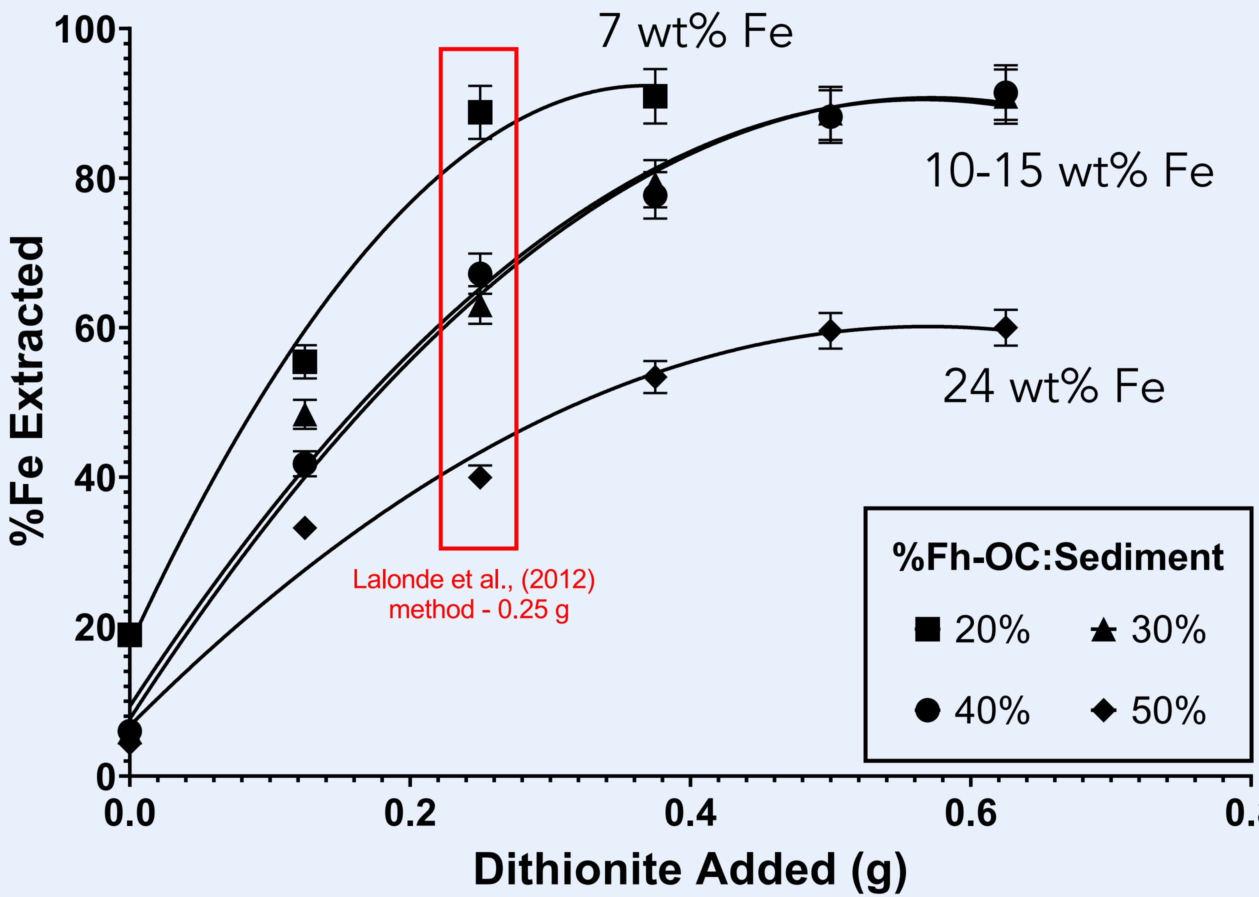
Stability of organominerals (XRD)



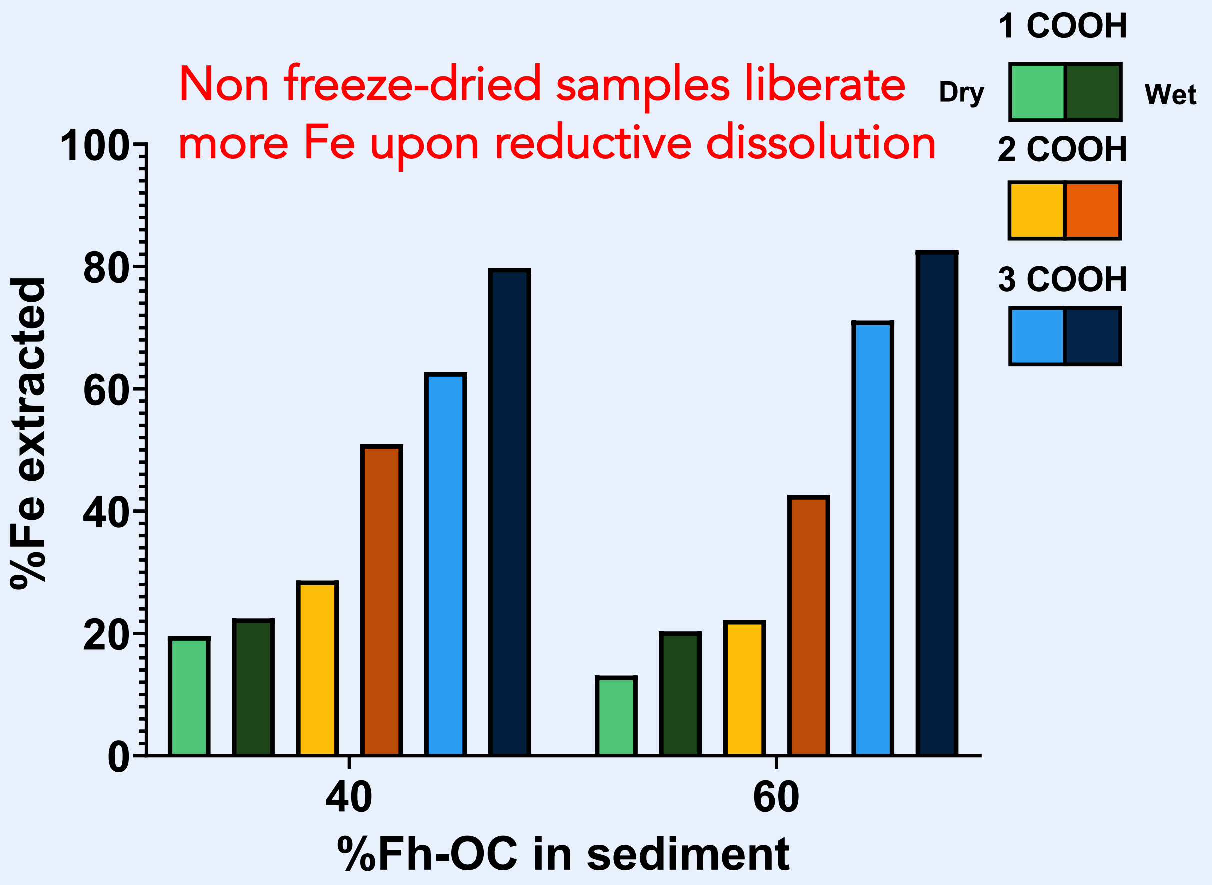
Organic associated Fe minerals become more amorphous and less stable as the carboxyl richness in the organic component increases. The peaks soften in amplitude.

Repurposing for method testing

Sodium dithionite saturates at ~10 wt% Fe, heterogenous sediments or iron rich should increase dithionite addition



Non freeze-dried samples liberate more Fe upon reductive dissolution



Conclusions and implications

- Carboxyl richness of organic compounds is a deterministic factor for OC-Fe stability.

  Structurally complex, less degraded carbon is most strongly preserved. Could we change the type of carbon reaching the seafloor?

- Iron minerals become more amorphous as carboxyl content increases.

  Iron is less stable when associated with more complex carbon, it takes a more gel like form and more is released when the mineral is reduced. Importance of sediment protection.

- Estimations of OC-Fe for natural sediments are likely underestimating the importance of this mechanism by ~33%.

  The current way we measure preserved carbon in sediment appears to be inefficient. Underestimating the amount of preserved carbon has big implications for BGC and climate models.

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