UNIVERSITY of STIRLING

Mineralogy and Speciation of Environmental Iron Nanoparticles with the ^{57}Fe Synchrotron Mössbauer Source

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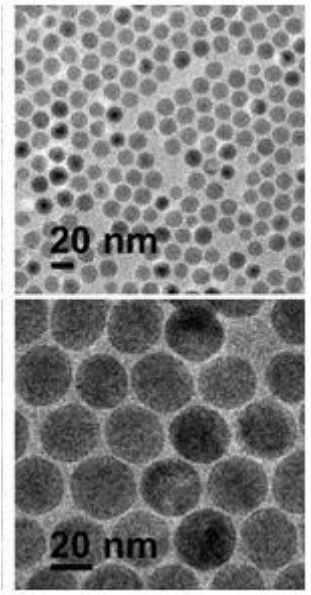
BE THE DIFFERENCE

Iron Nanoparticles

- Nanoparticles are submicron particles (<0.1 µm)
- Magnetic properties, high surface area, electron transfer processes, non-toxic (?), pigment
- Engineered iron nanoparticles
  - Used for treating industrial sites contaminated with chlorinated organic compounds.
  - Used in plastics, nanowires, coatings, nanofibres and textiles.
  - In certain alloys and catalyst application.
  - In magnetic data storage and resonance imaging.
  - Used in tissue repair, immunoassay, detoxification of biological fluids, hyperthermia, drug delivery and in cell separation.
  - As a gene carriers for gene therapy.
  - As magnetic sensing probes for in vitro diagnostics.
  - As drug carriers for targeted specific drug delivery.
- Environmental iron nanoparticles



TEM of magnetite nanoparticles (Sigma-Aldrich)

Iron biogeochemical cycle controls the carbon cycle

❑ Iron Hypothesis (Martin, 1990):

Iron is a limiting nutrient in the ocean, which controls primary productivity and thus atmospheric CO_2 levels.

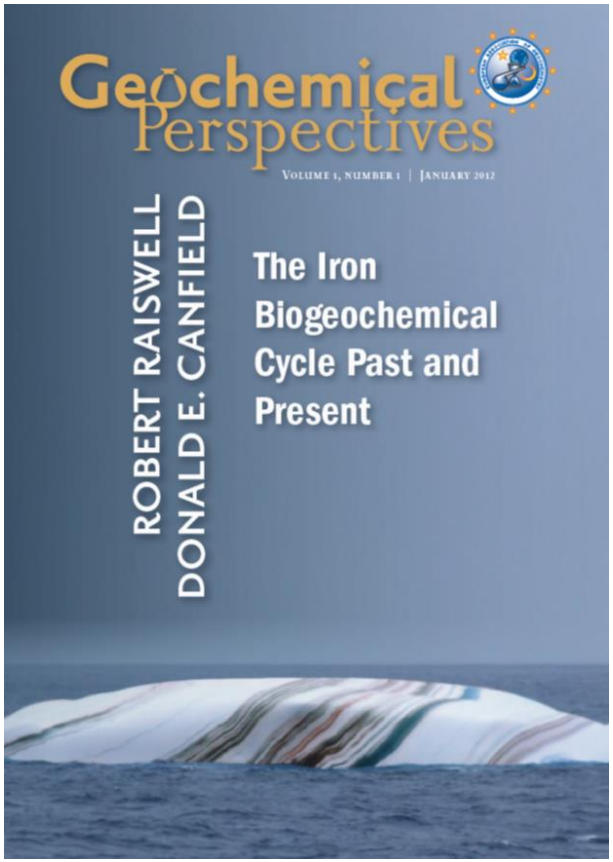
❑ Rusty Carbon Sink:

Over 20% of organic carbon in sediments is directly bound to reactive iron phases (Lalonde et al. 2012, *Nature*).

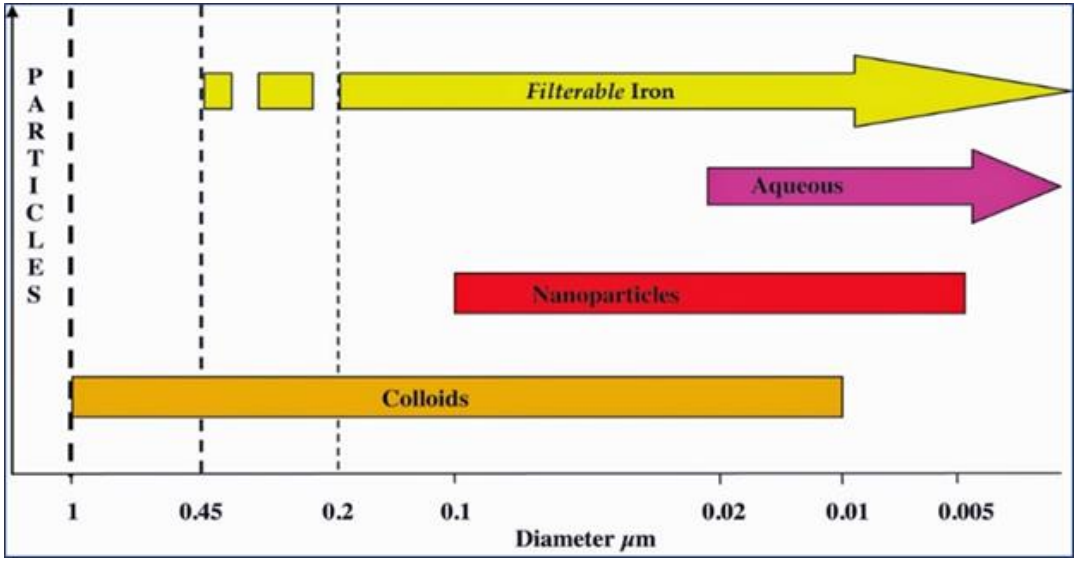
❑ Transport:

Iron and OC stabilize each other. High-latitude rivers with humic-rich may produce significant iron flux to the ocean.

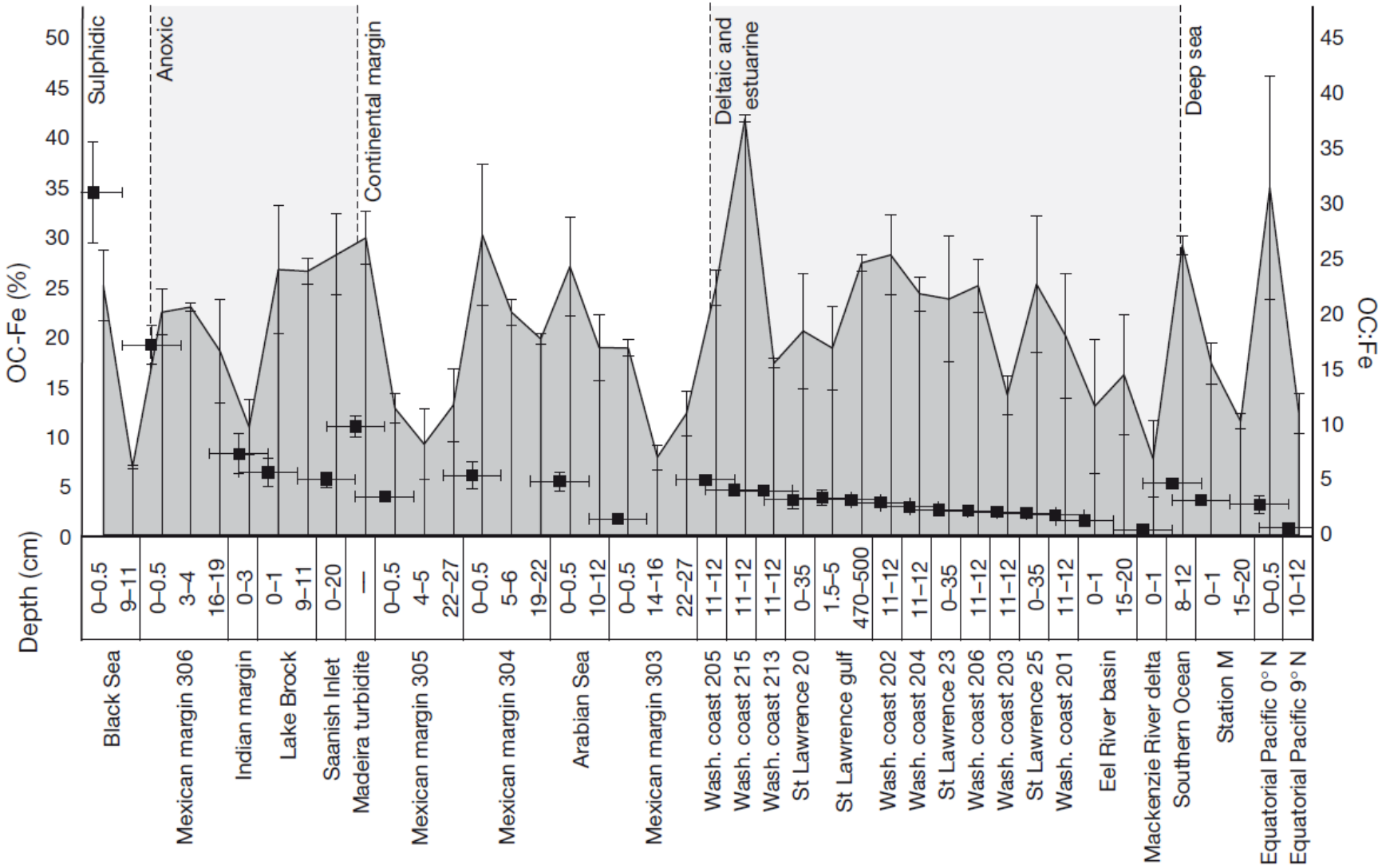
Towards a more mineralogical view …



"It is now more important than ever that a **more mineralogical view** is adopted in future studies of the iron biogeochemical cycle in order to **characterise colloids and nanoparticles**, and **define their role in aquatic environments**."



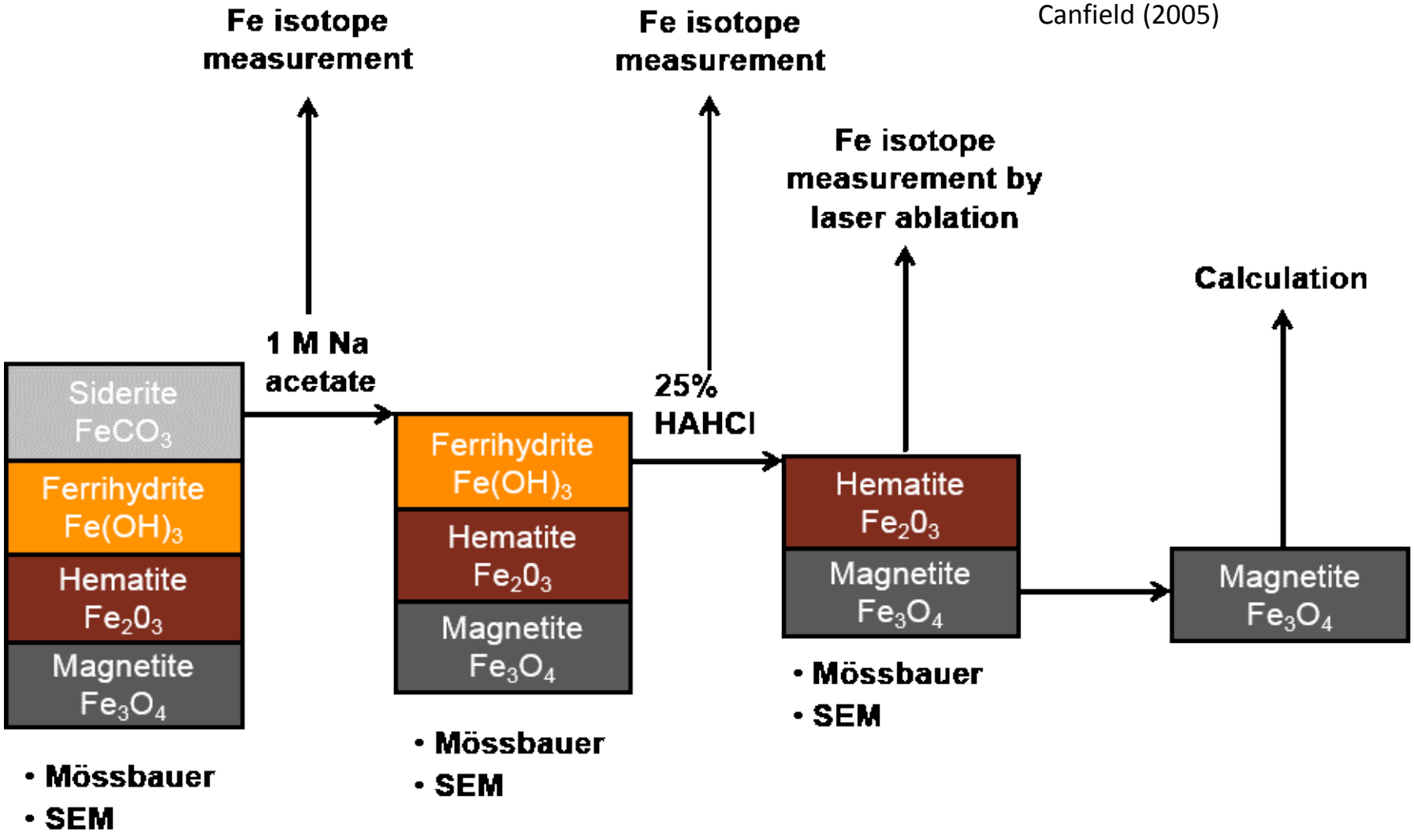
Rusty Carbon Sink



Lalonde et al. (2012) *Nature* **483**, 198-200.

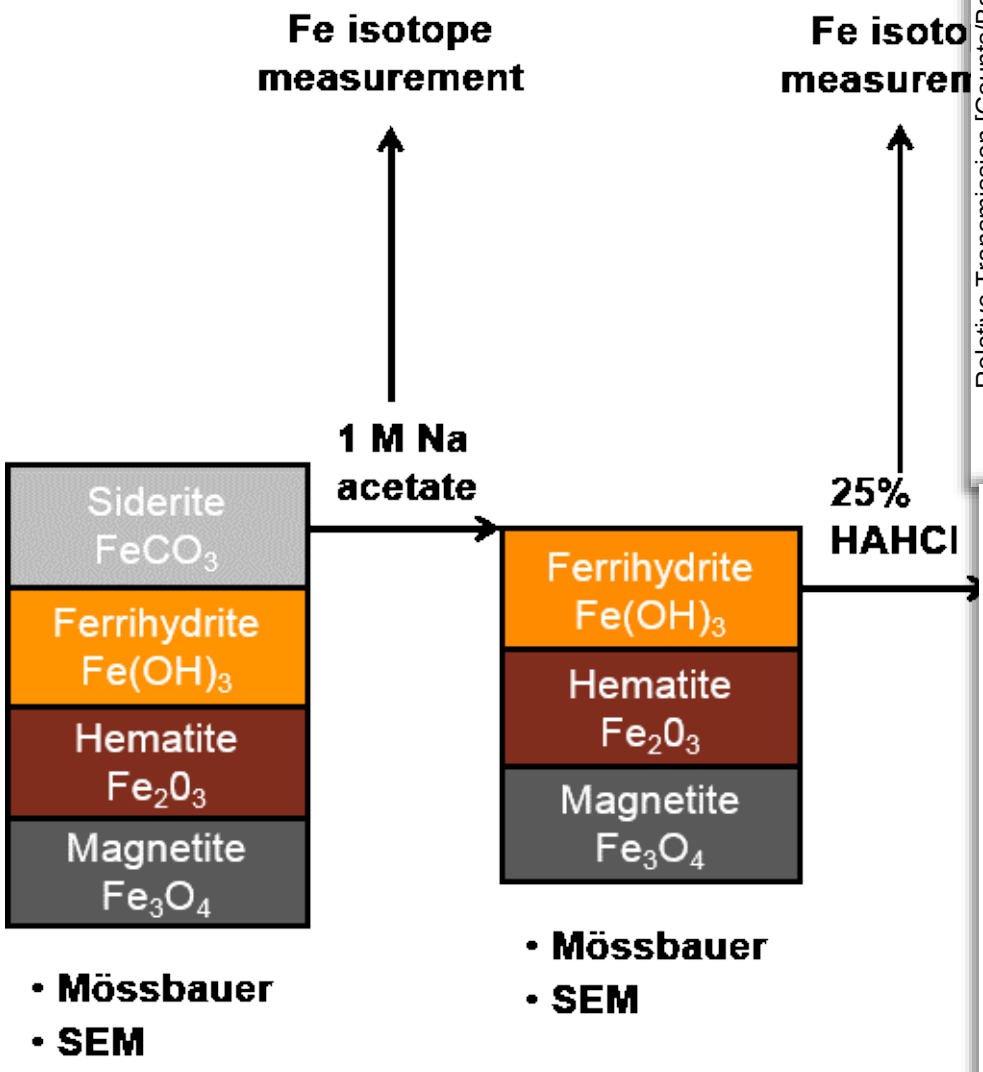
Sequential Extraction

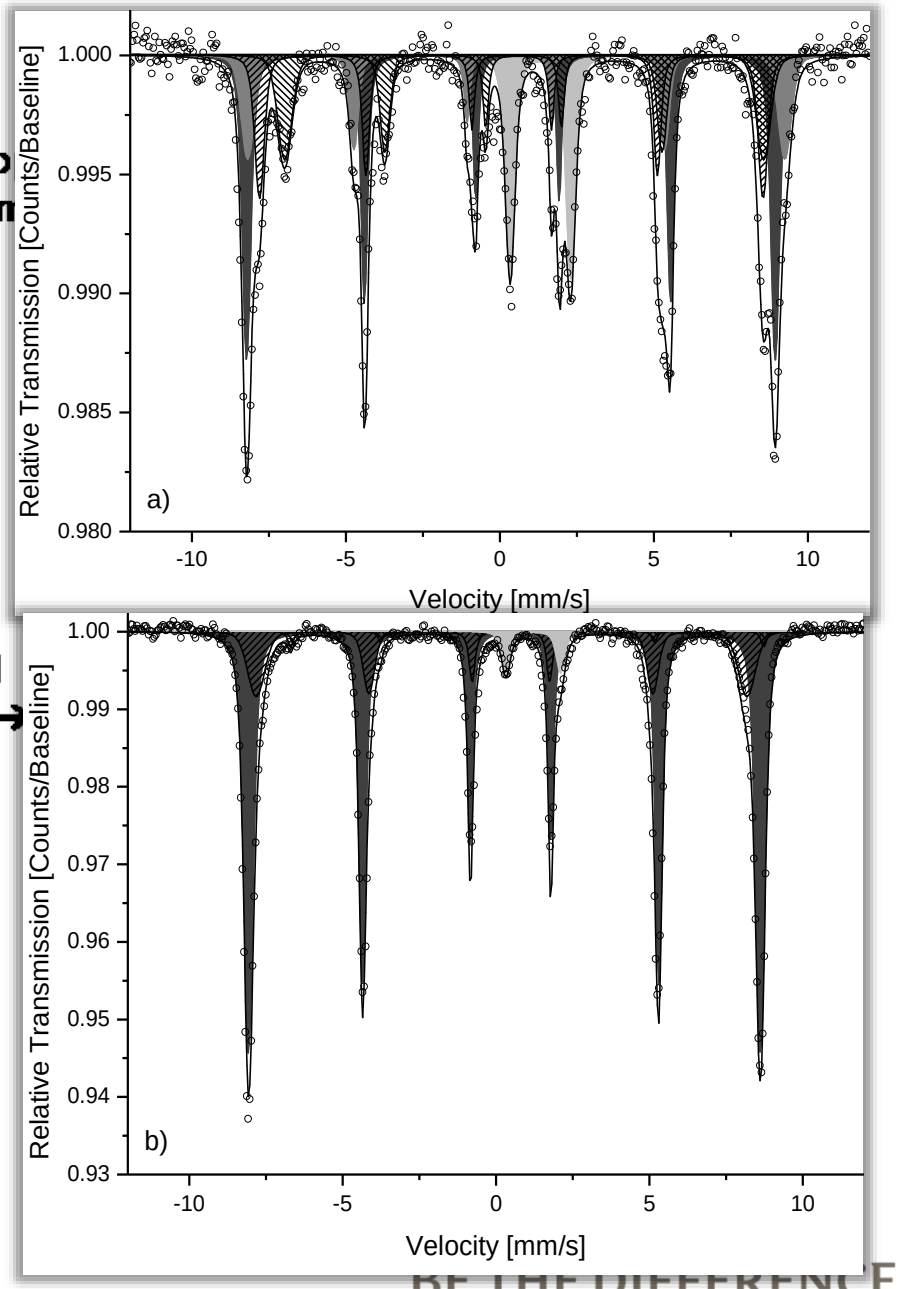
Sequential extraction steps modified from Poulton and Canfield (2005)



Schröder et al. (2016)

Sequential Extraction





Schröder et al. (2016)

Application of Mössbauer spectroscopy to marine sediments

Biogeosciences, 15, 1243–1271, 2018
https://doi.org/10.5194/bg-15-1243-2018

Biogeosciences Open Access EGU

Impacts of flocculation on the distribution and diagenesis of iron in boreal estuarine sediments

Tom Jilbert[1,2], Eero Asmala[1,2,3], Christian Schröder[4], Rosa Tiihonen[1,2], Jukka-Pekka Myllykangas[1,2], Joonas J. Virtasalo[5], Aarno Kotilainen[5], Pasi Peltola[6], Päivi Ekholm[7], and Susanna Hietanen[1,2]

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JGR

Journal of Geophysical Research: Biogeosciences

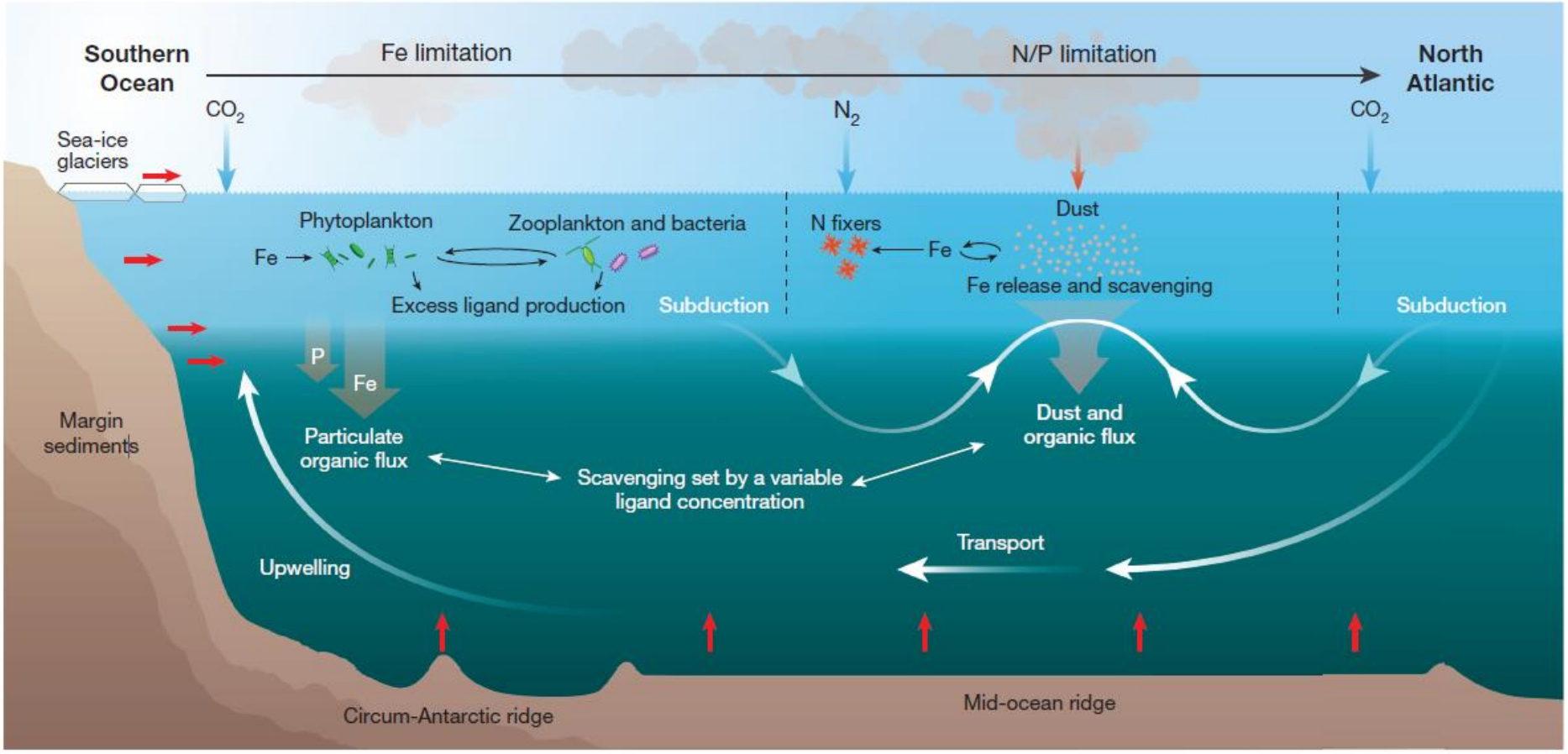
RESEARCH ARTICLE
10.1029/2018JG004649

Key Points:
- Extensive sediment resuspension may reduce reactive iron binding

The Role of Reactive Iron in the Preservation of Terrestrial Organic Carbon in Estuarine Sediments

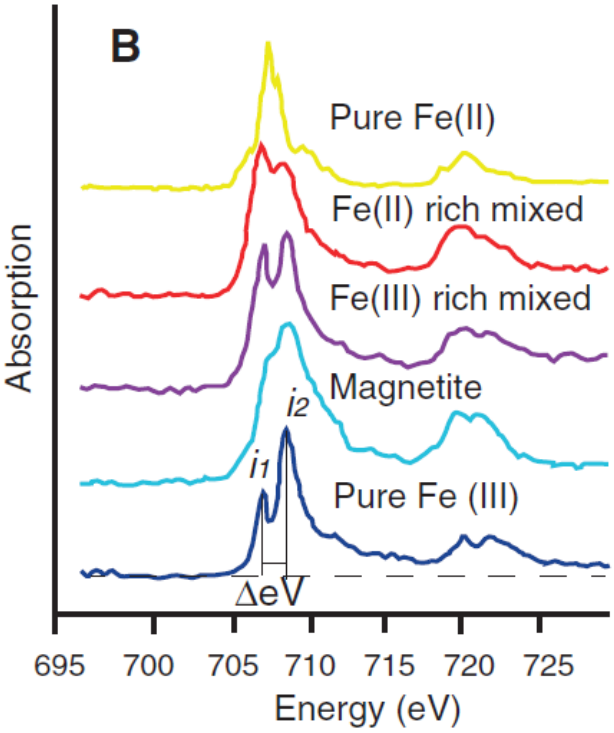
B. Zhao[1,2,3], P. Yao[1,2], T. S. Bianchi[3], M. R. Shields[3], X. Q. Cui[3,4], X. W. Zhang[3,4], X. Y. Huang[1], C. Schröder[5], J. Zhao[6], and Z. G. Yu[1,2]

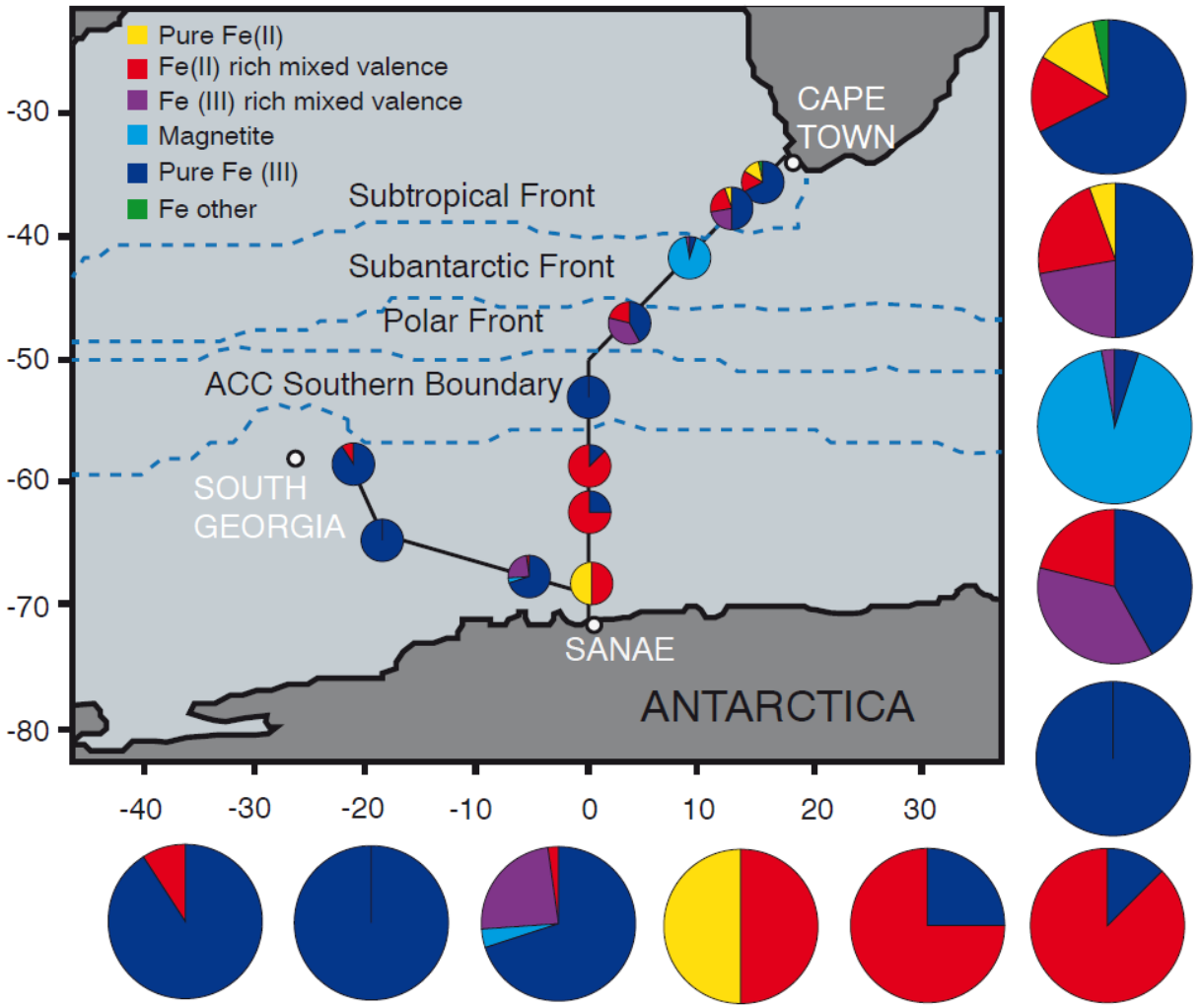
The integral role of iron in ocean biogeochemistry



Tagliabue et al. (2017) *Nature* **543**, 51-59.

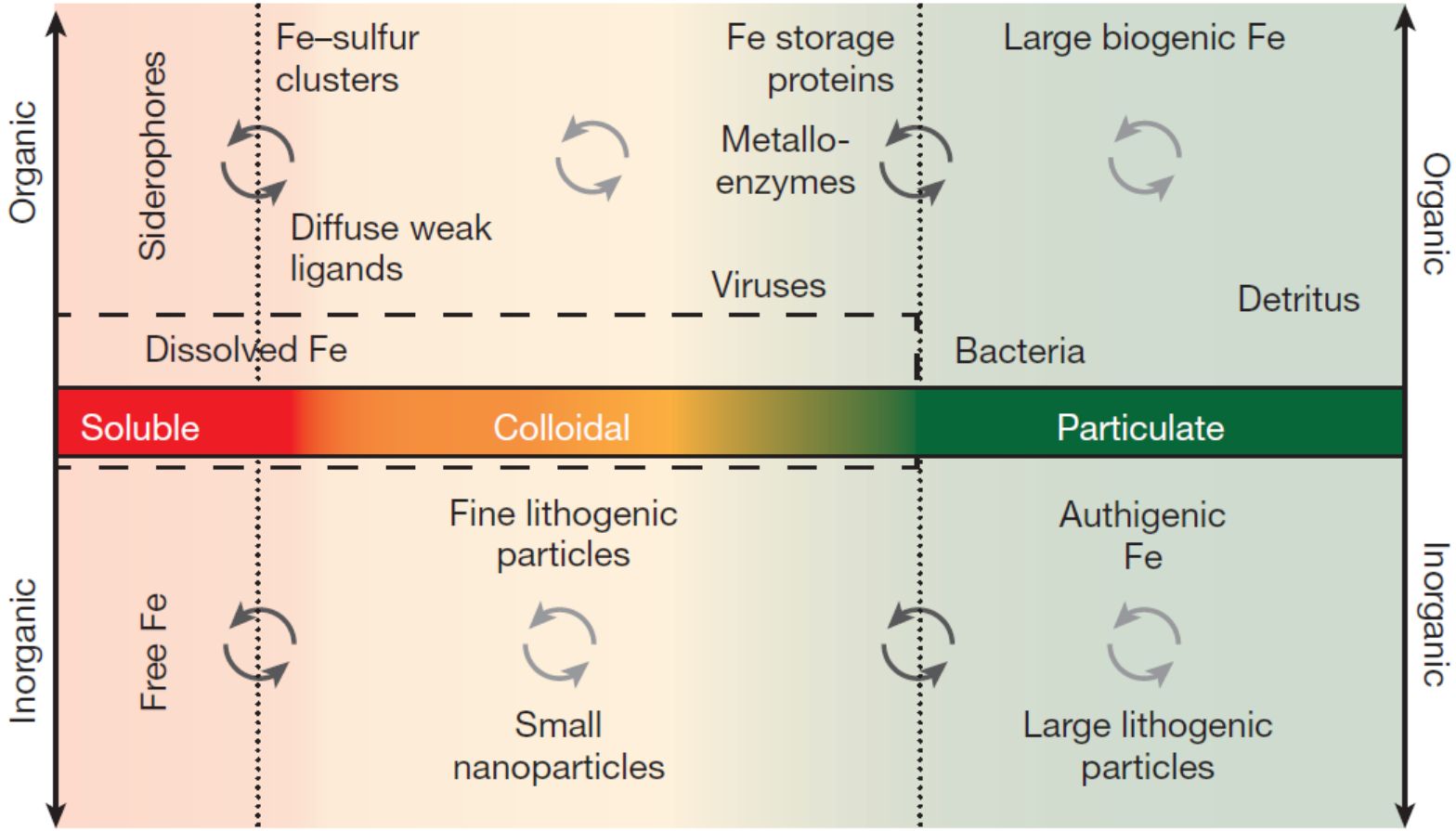
Iron Hypothesis





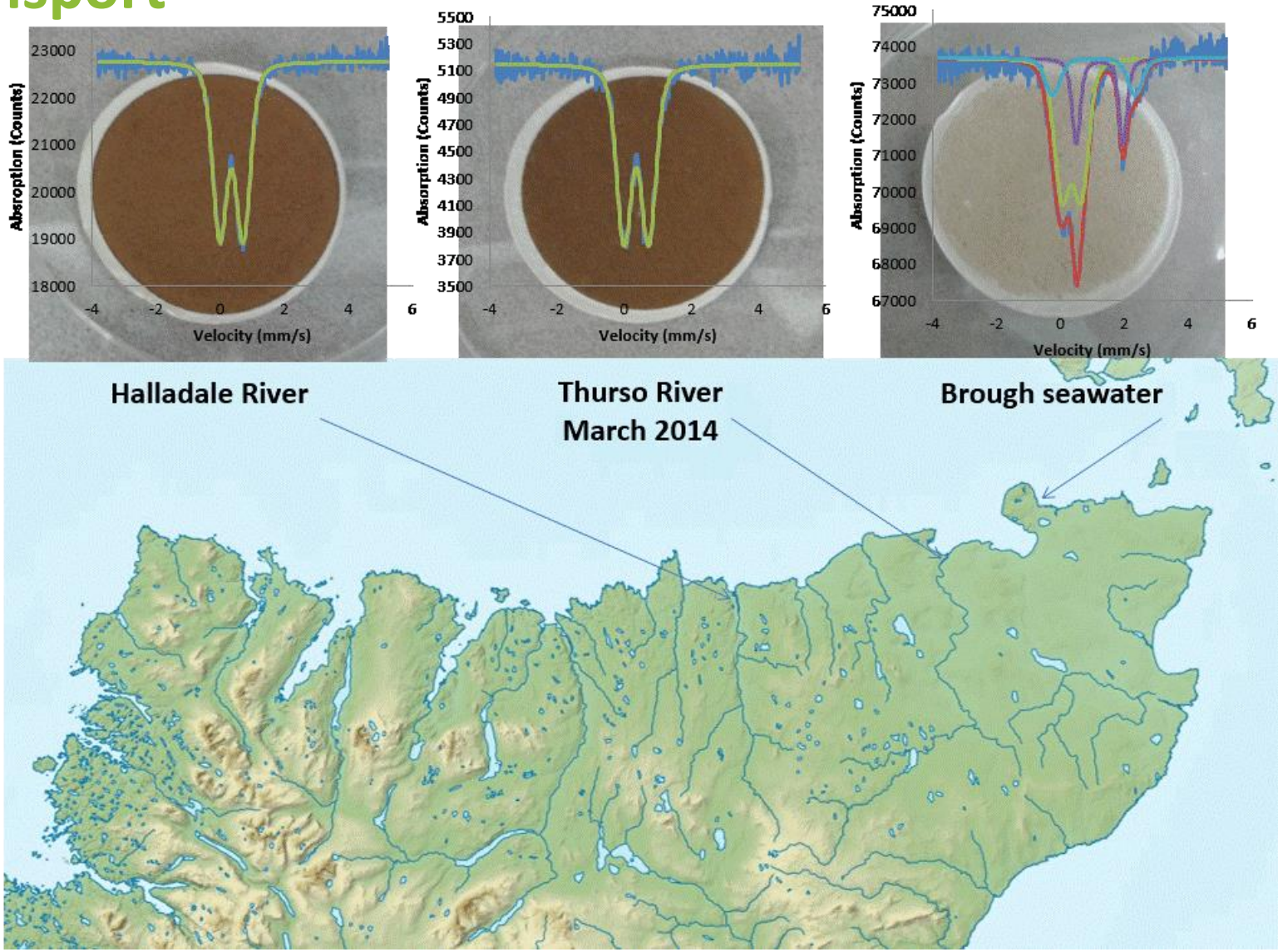
Von der Heyden et al. (2012) *Science* 338, 1199-1201.

Particulate and dissolved iron pools



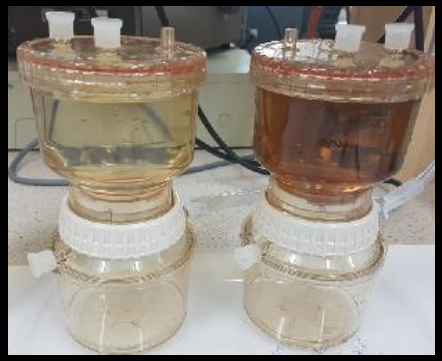
Tagliabue et al. (2017) *Nature* **543**, 51-59.

Transport



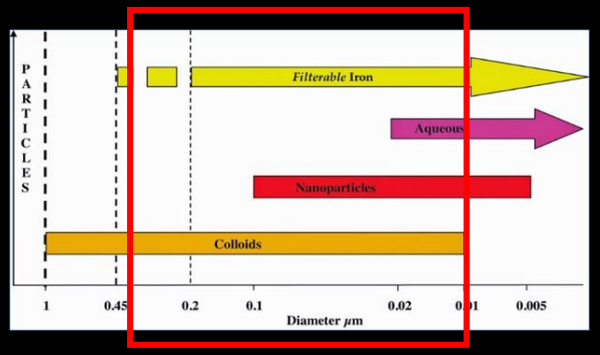
Schröder et al. (2016)

Nanoparticles/colloids: isolation and concentration

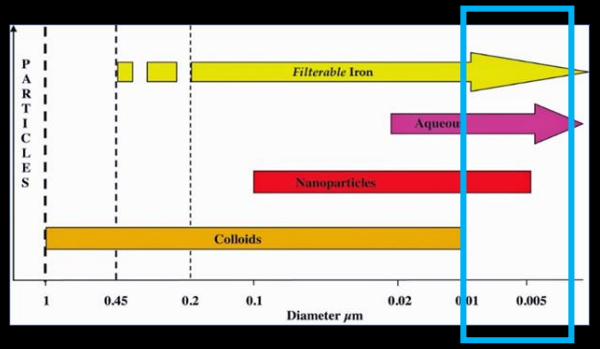


0.4 μm vacuum filtration

filtrate



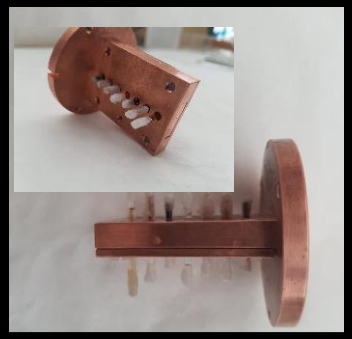
100 kDa (~10 nm) Jumbosep™ centrifuge



retentate

5 kDa (~1 nm) Amicon Ultra-15 centrifuge

retentate



Samples ready for SMS

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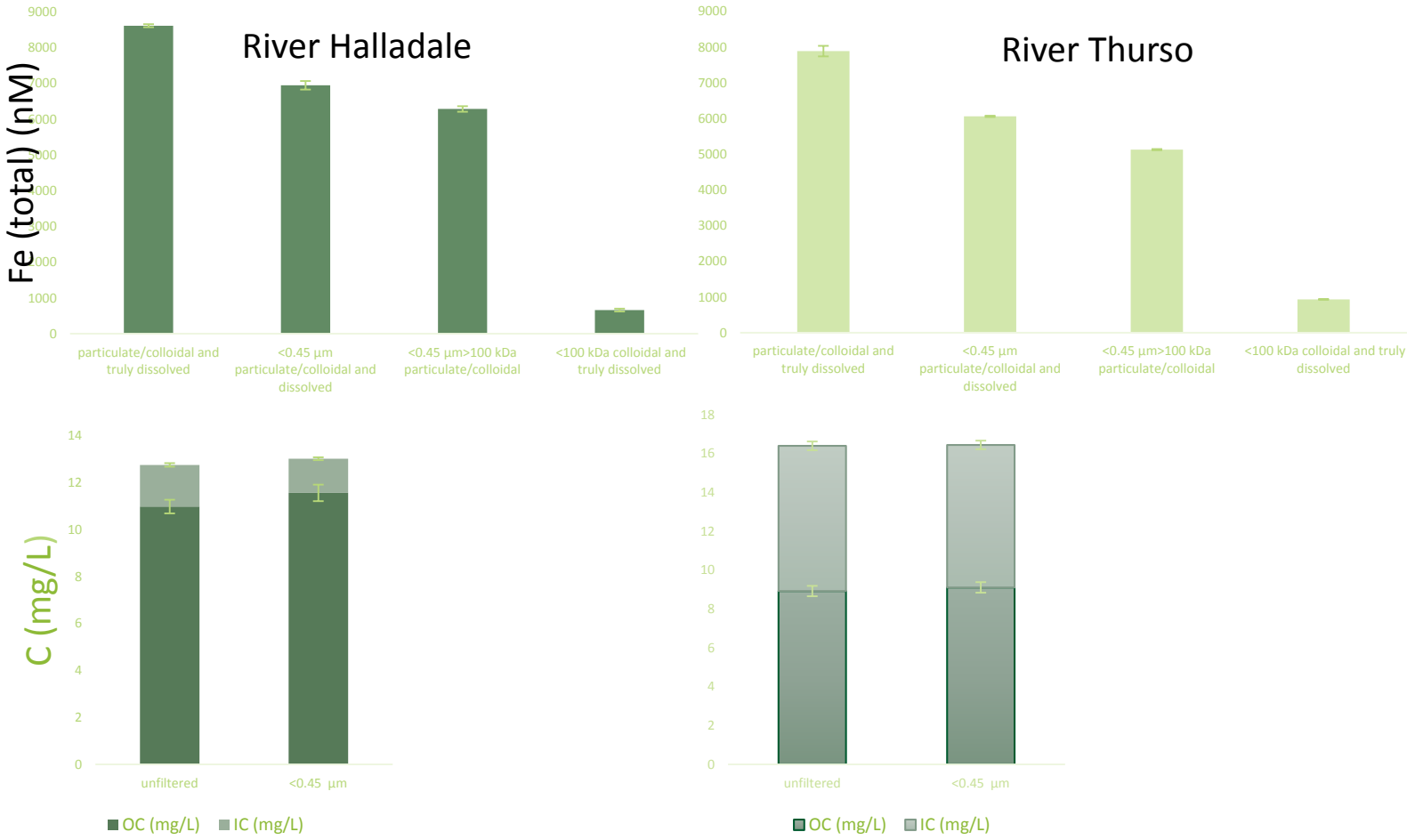
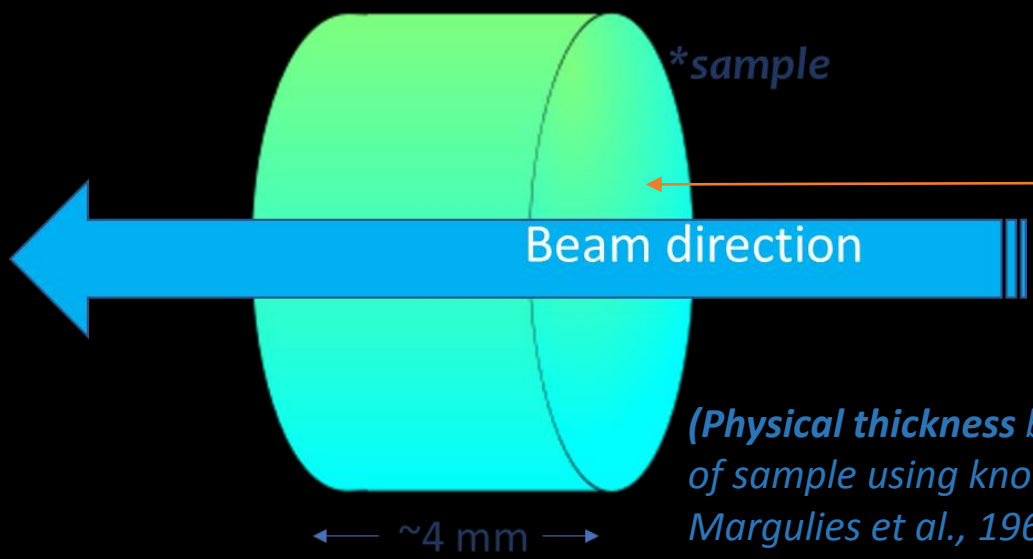
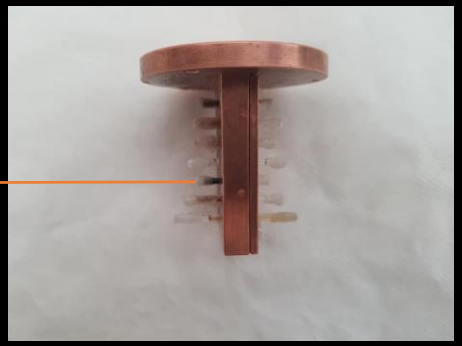
Size distribution of iron nanoparticles



SMS experiment: EV-310, ID18, ESRF (July 2018)

- Signal should not pass through glass
- Sample container needs to be long enough to reach optimum sample thickness
- Remove as much water as possible to maximise porosity and average density





*(**Physical thickness** based on calculated dimensionless thickness of sample using known element concentrations (adapted from Margulies et al., 1963) for River Halladale (April, 2017): **4.1 mm**)*

- Samples are in suspension, so, need be frozen for SMS
- Measurements down to liquid helium temperature (4.2 K)
- Nanoparticles display superparamagnetic behaviour

(< superparamagnetic blocking temperature to gain full mineralogical information)

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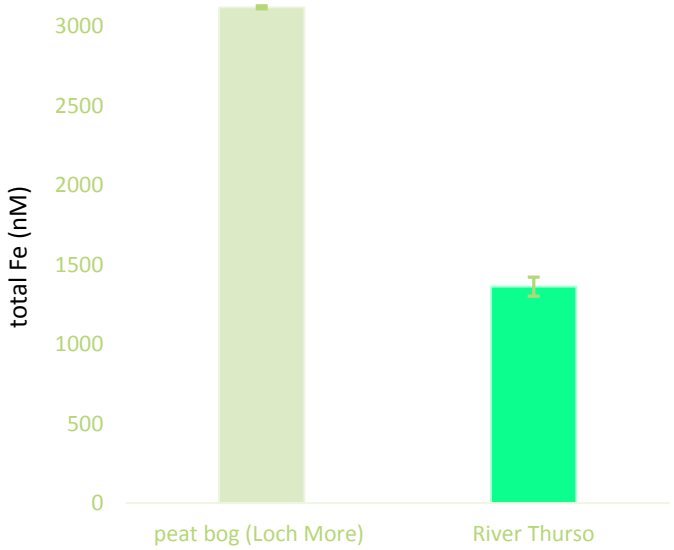
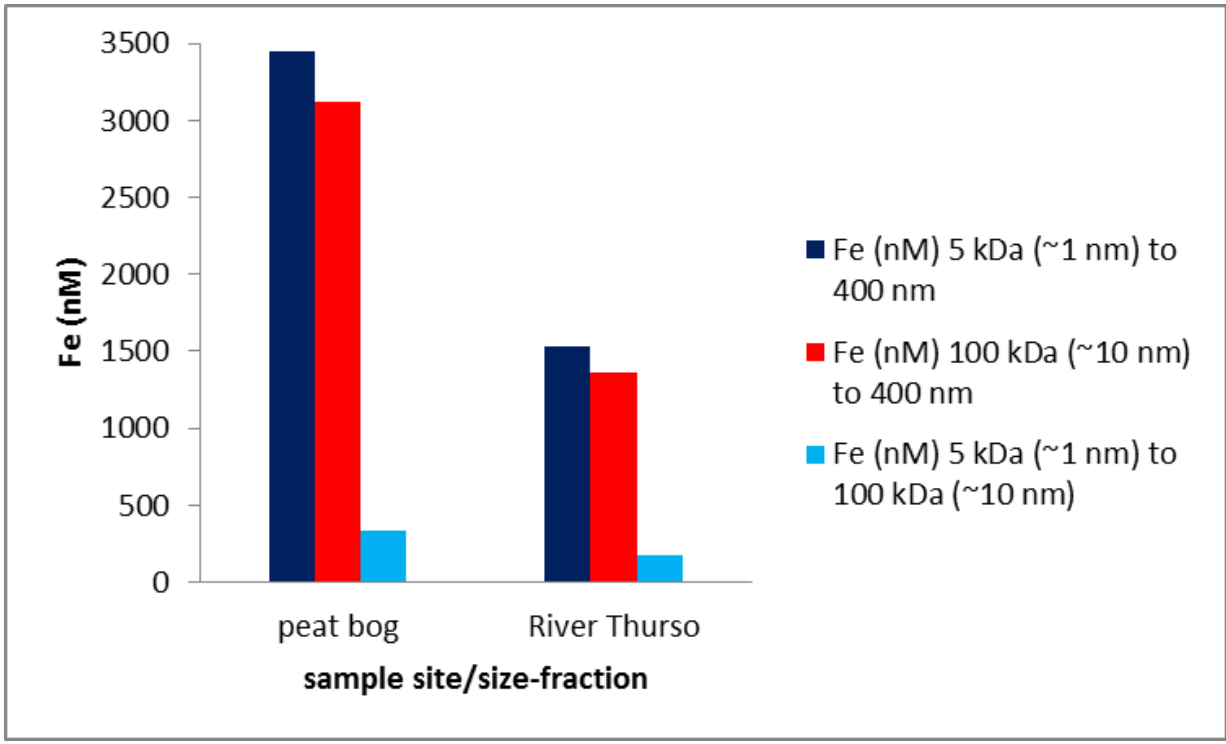


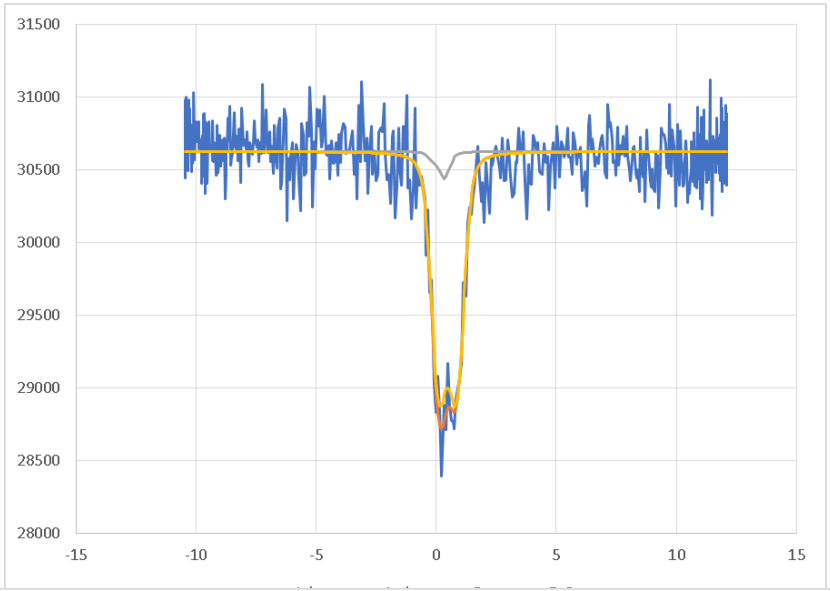
physical size fraction <0.4 μm>100 kDa (~10 nm)

total carbon (organic carbon = OC and inorganic carbon = IC): physical size fraction <0.4 μm>100 kDa (~10 nm)

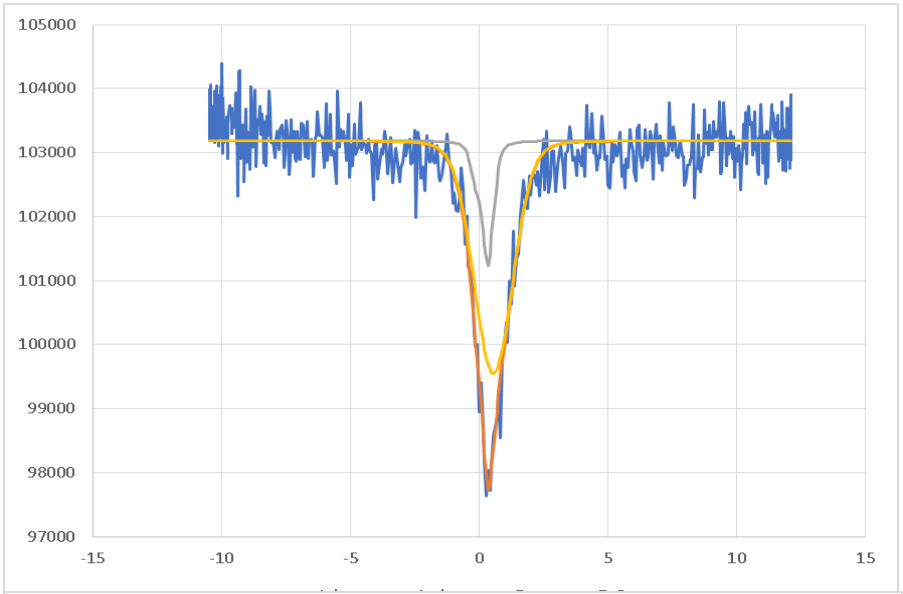
OC IC

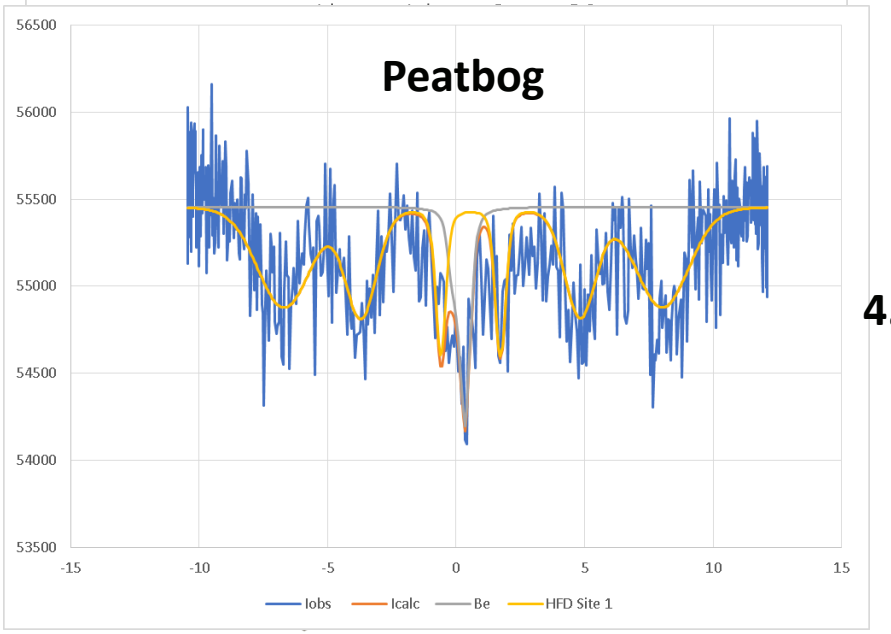


EV-310, SMS: Lepidocrocite (γ-FeOOH)!

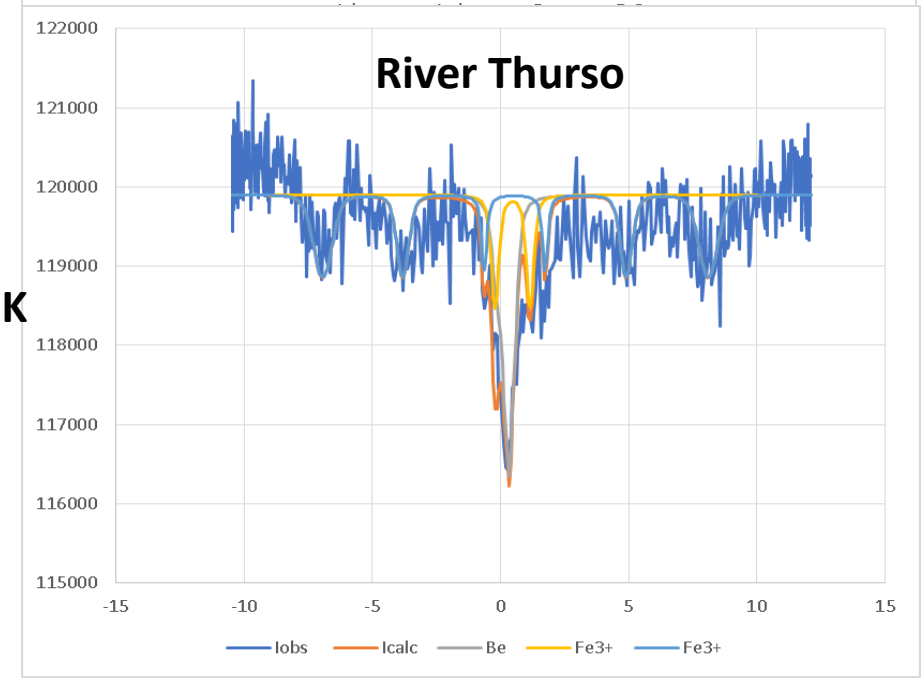


77 K





4.2 K



Conclusions

- ❑ This is work in progress
- ❑ Goal is to expand to more dilute marine samples
- ❑ Sample preparation needs to be optimized
- ❑ Currently exploring Field-Flow-Fractionation (FFF) at FZ Jülich

- ❑ Smaller beam size from EBS upgrade potentially enables:
  - ○ Investigation of even smaller sample volumes
  - ○ Investigation of individual particles
- ❑ Very precise sample handling needed
- ❑ Project funded by UK Science & Technology Facilities Council?

Thank you!

- Francois Muller
- ESRF ID18: Rudolf Rüffer, Alexandr Chumakov, Dimitrios Bessas, Jan-Philip Celse, Ilya Kupenko

Marine Alliance for Science and Technology for Scotland

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