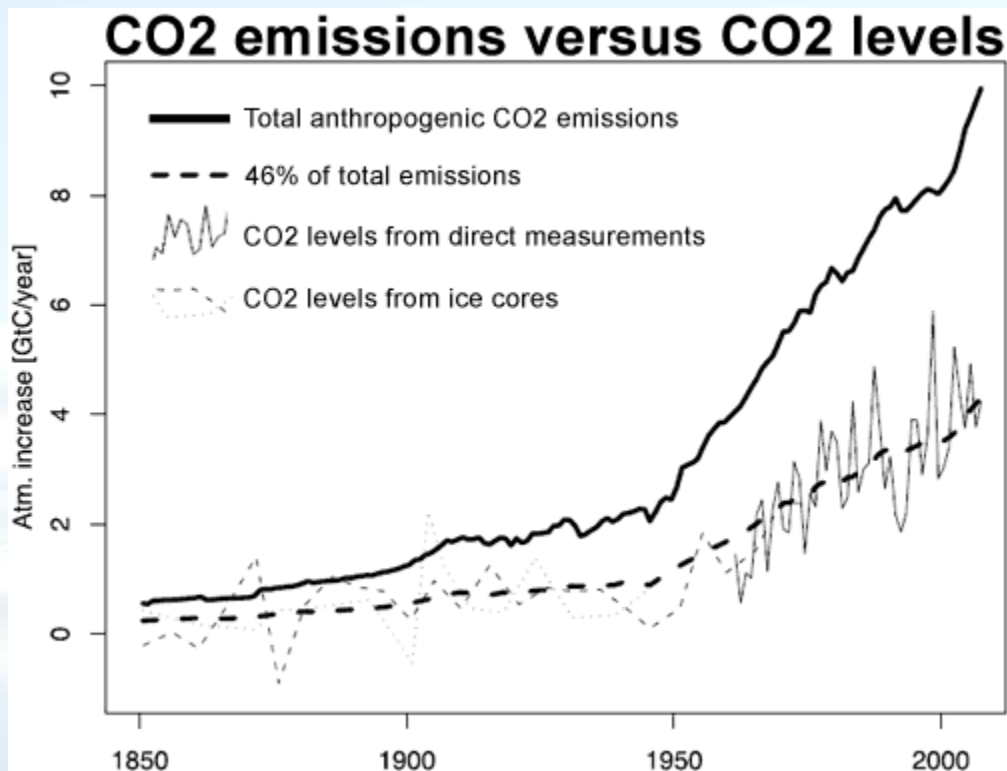


Application of iron L₃-edge XANES spectroscopy to colloid speciation

Bjorn P. von der Heyden
(Stellenbosch University)

Importance of Fe: Biogeochemical context



Unprecedented rise in atmospheric CO₂ levels, due to anthropogenic activities.

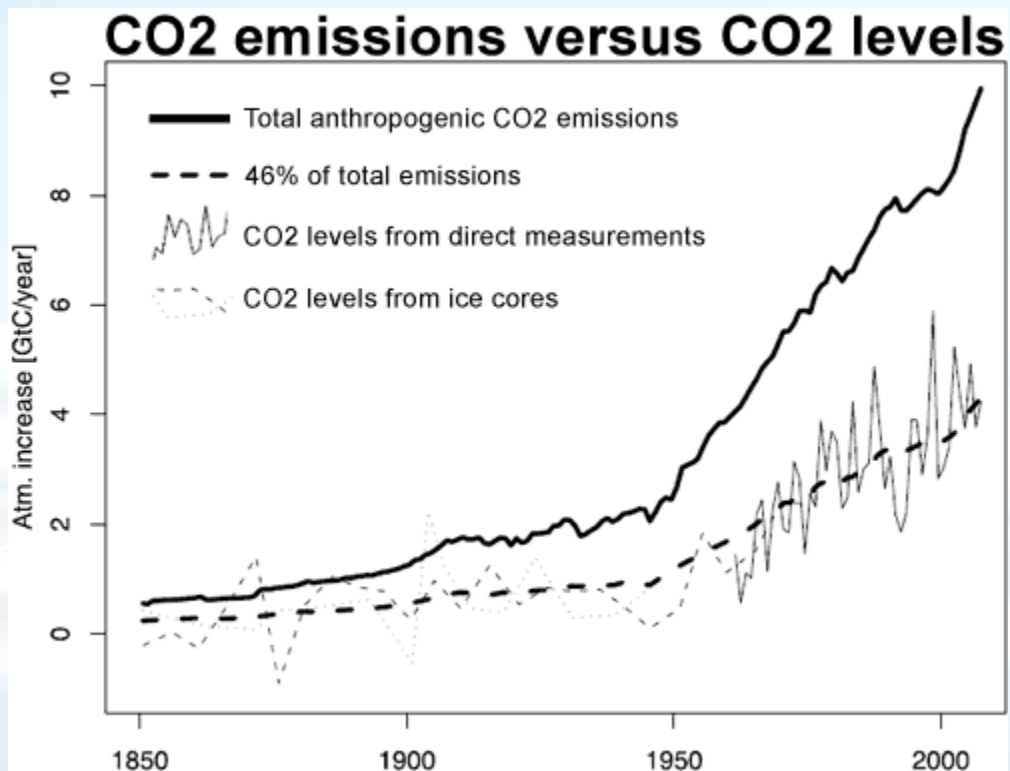


After Knorr, 2009

Sinks for atmospheric CO₂ include:

- 1) Terrestrial plants and soils
- 2) Marine phytoplankton (the ocean's "biological pump")
- 3) Seawater inorganic chemistry (the ocean's "physical/solubility pump")

Importance of Fe: Biogeochemical context



Unprecedented rise in atmospheric CO₂ levels, due to anthropogenic activities.



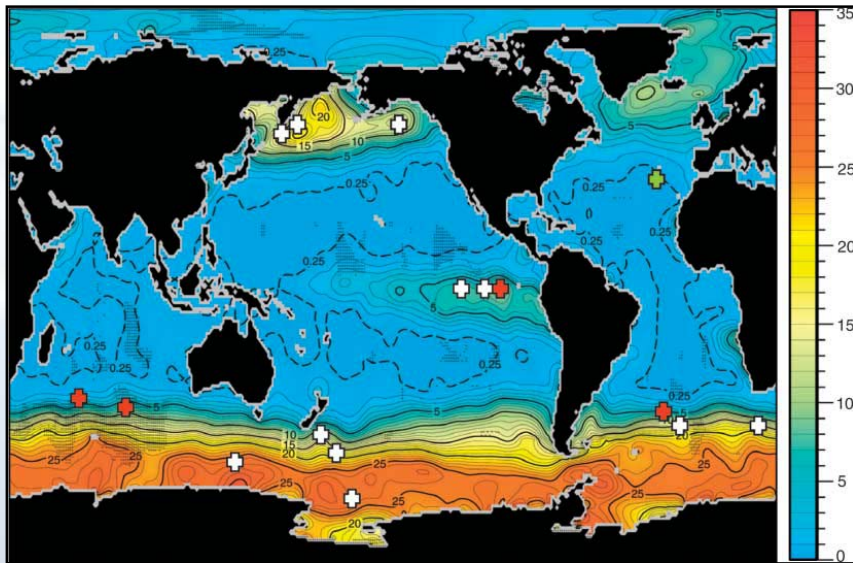
After Knorr, 2009

Sinks for atmospheric CO₂ include:

- 1) Terrestrial plants and soils
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- 3) Seawater inorganic chemistry (the ocean's "physical/solubility pump")

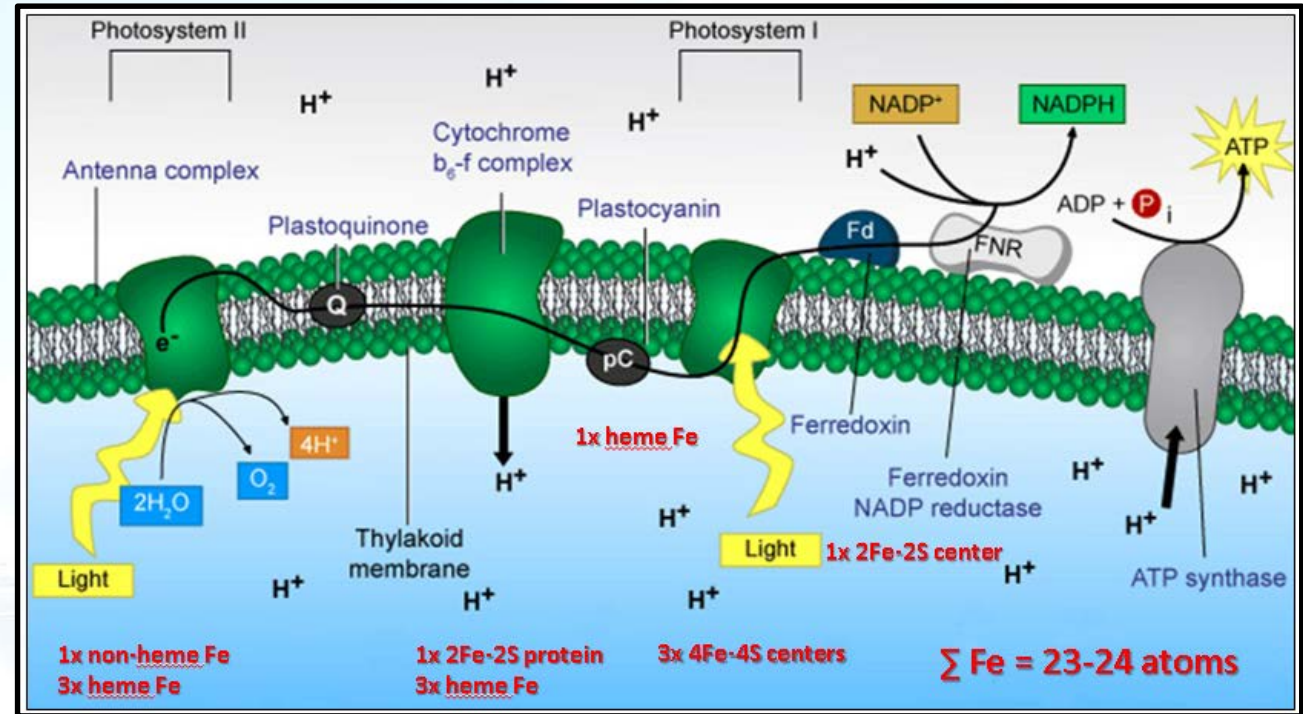
Importance of Fe: Biogeochemical context

HNLC status: Southern Ocean



Colour bar indicates surface mixed layer nitrate concentrations ($\mu\text{mol.L}^{-1}$)

After Boyd et al., 2007



Refs: Dept. Biol. Penn State (2004); Michel and Pistorius (2004)

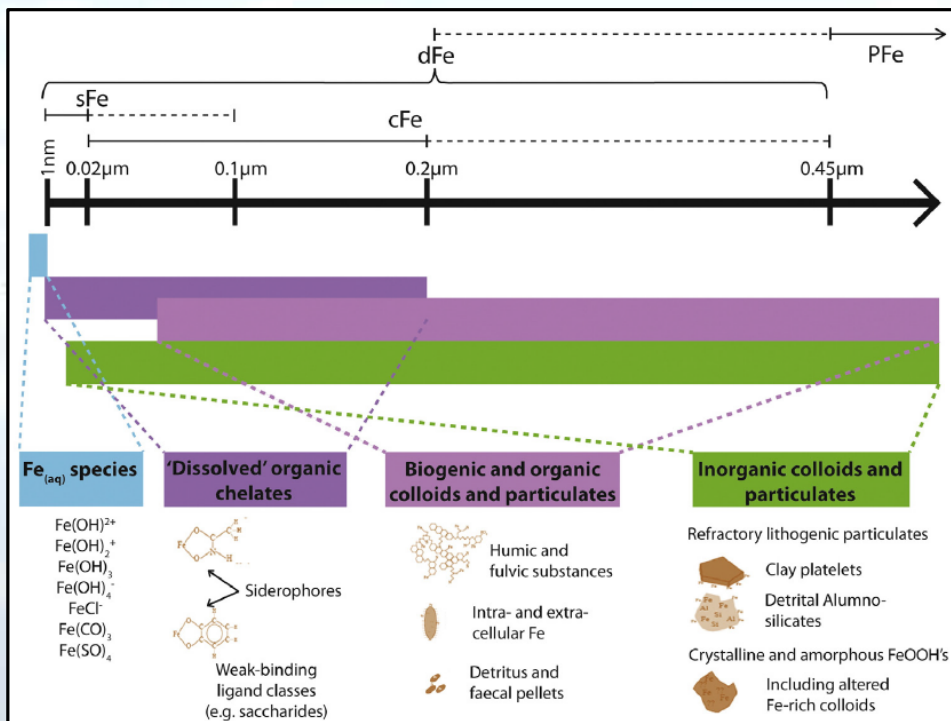
- Fe is an important trace element needed for the growth of photosynthetic organisms
- Constituent of the electron transport chain in the thylakoid membrane of cyanobacteria
- However, in large tracts of the world's oceans; low Fe concentrations limit primary productivity

S Fe speciation: Suspended colloids

Challenges:

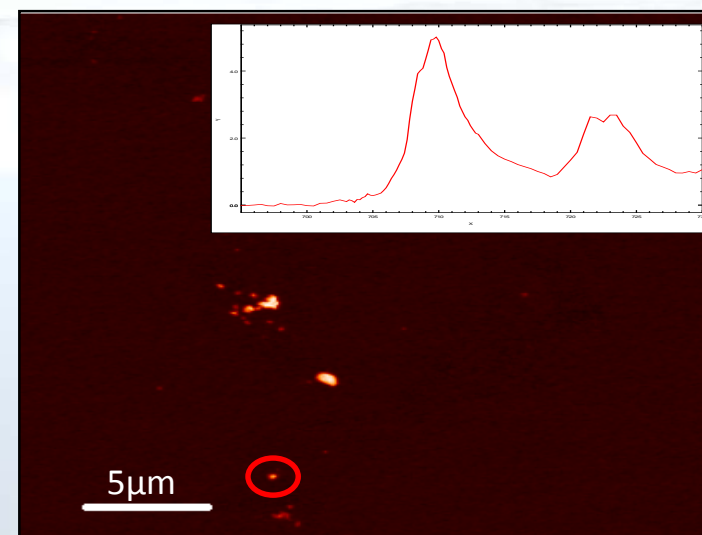
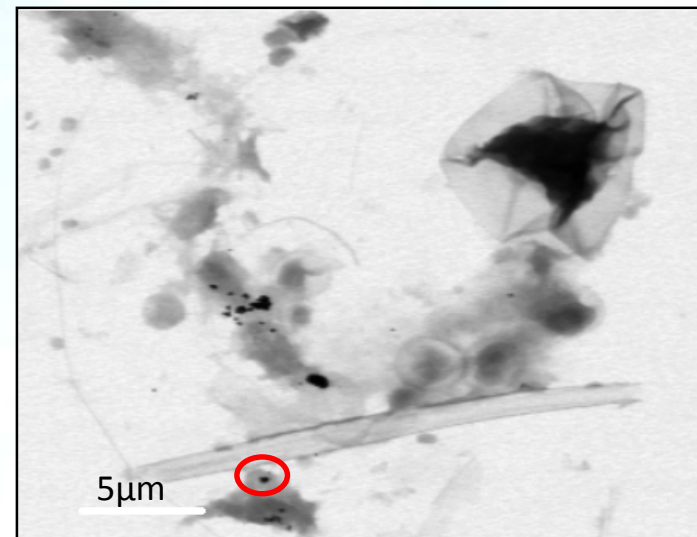
- Limited spatial or chemical data available
- Low concentration in seawater
- Small size: specialised techniques required for evaluation (e.g., XANES)

Fe size fractionation:



After von der Heyden and Roychoudhury, 2015

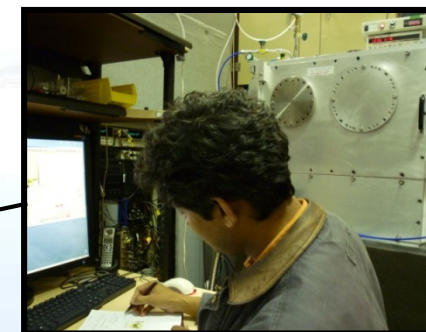
STXM maps:



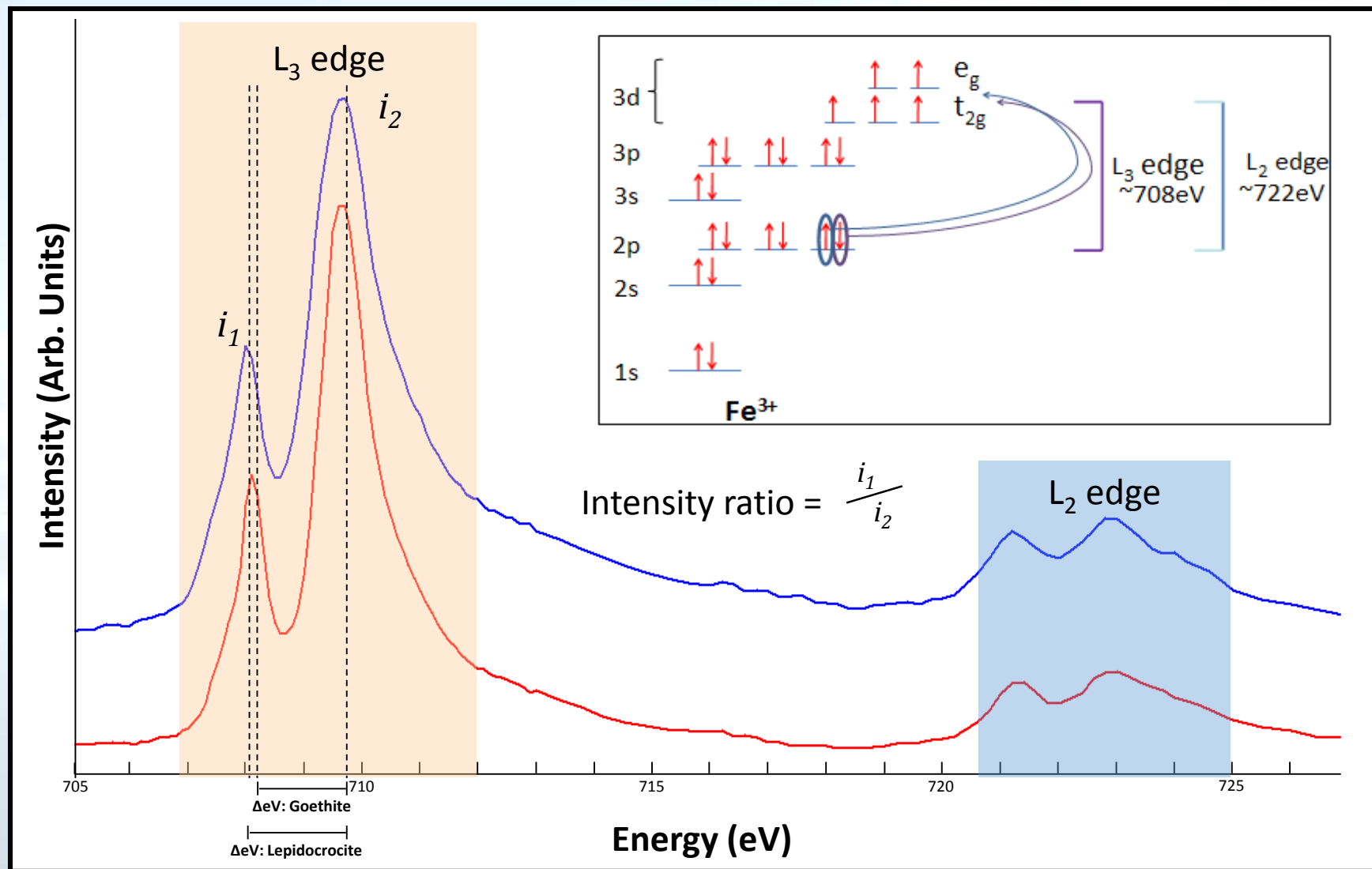
Fe speciation: Evaluation

Analysis:

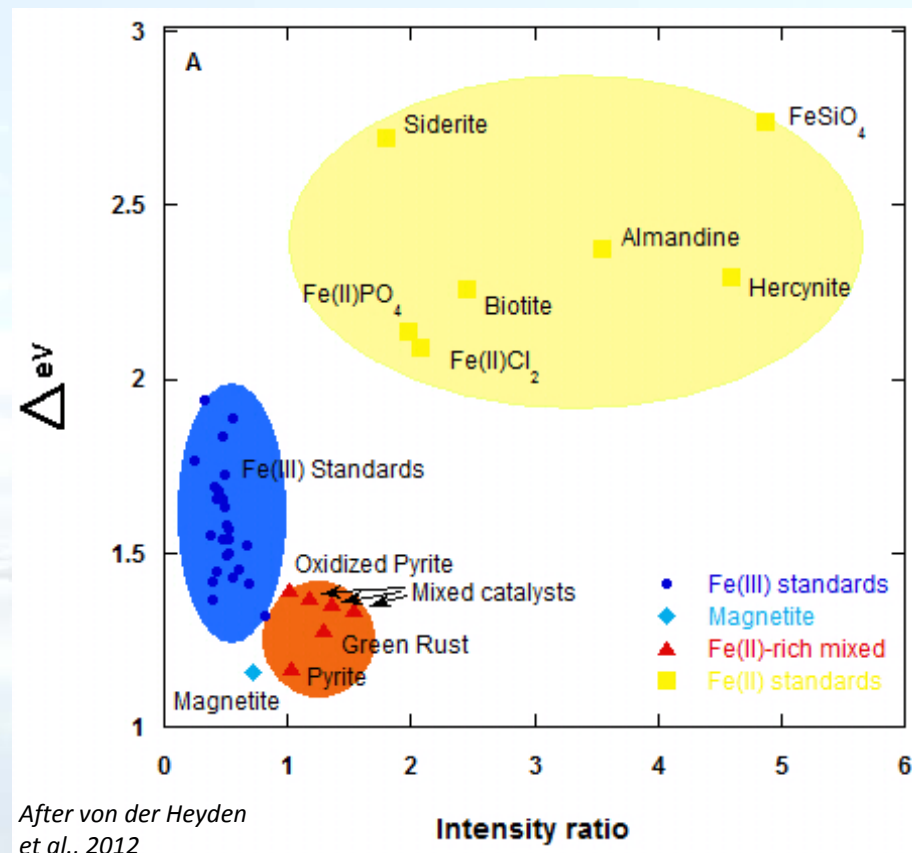
- Advanced Light Source: Lawrence Berkeley National Labs
- Beamline 11.0.2.: Molecular Environmental Sciences
- Scanning Transmission X-ray Microscopy (STXM)
- X-ray Absorption Near-edge Structure (XANES)
 - Conducted at the Fe $L_{2,3}$ -edge (*also Al K-, and C K-edges*)



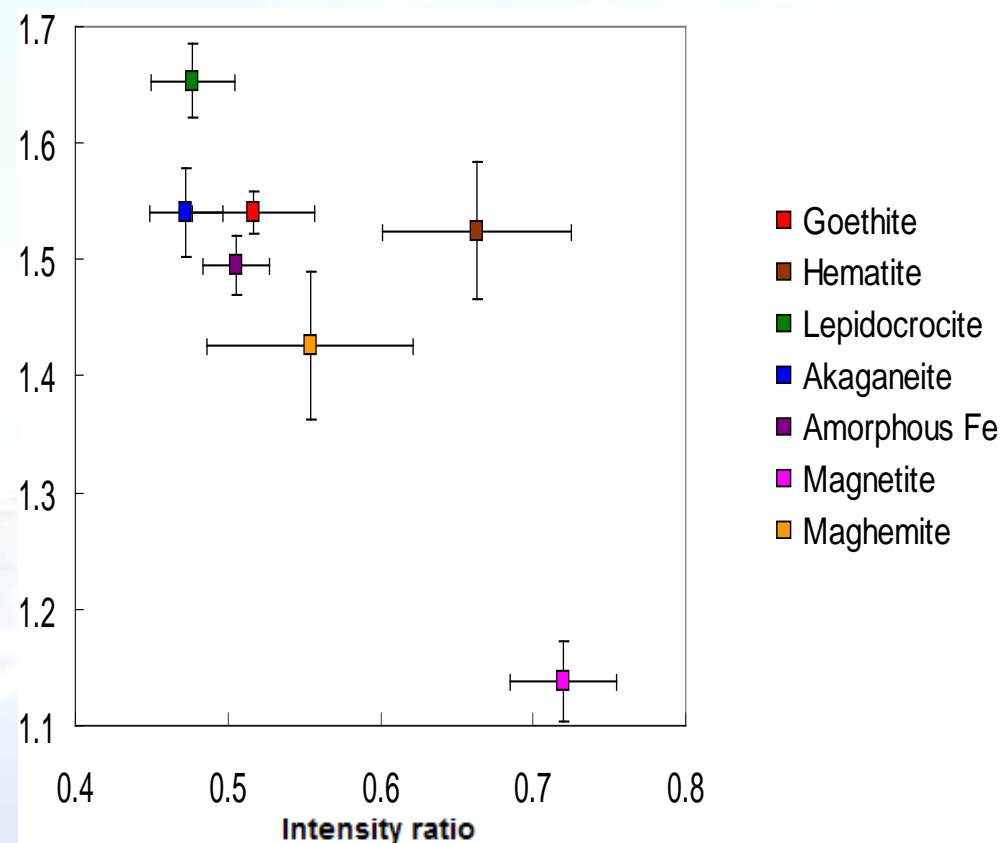
Fe L₃-edge spectroscopy



S Fe L₃-edge spectroscopy

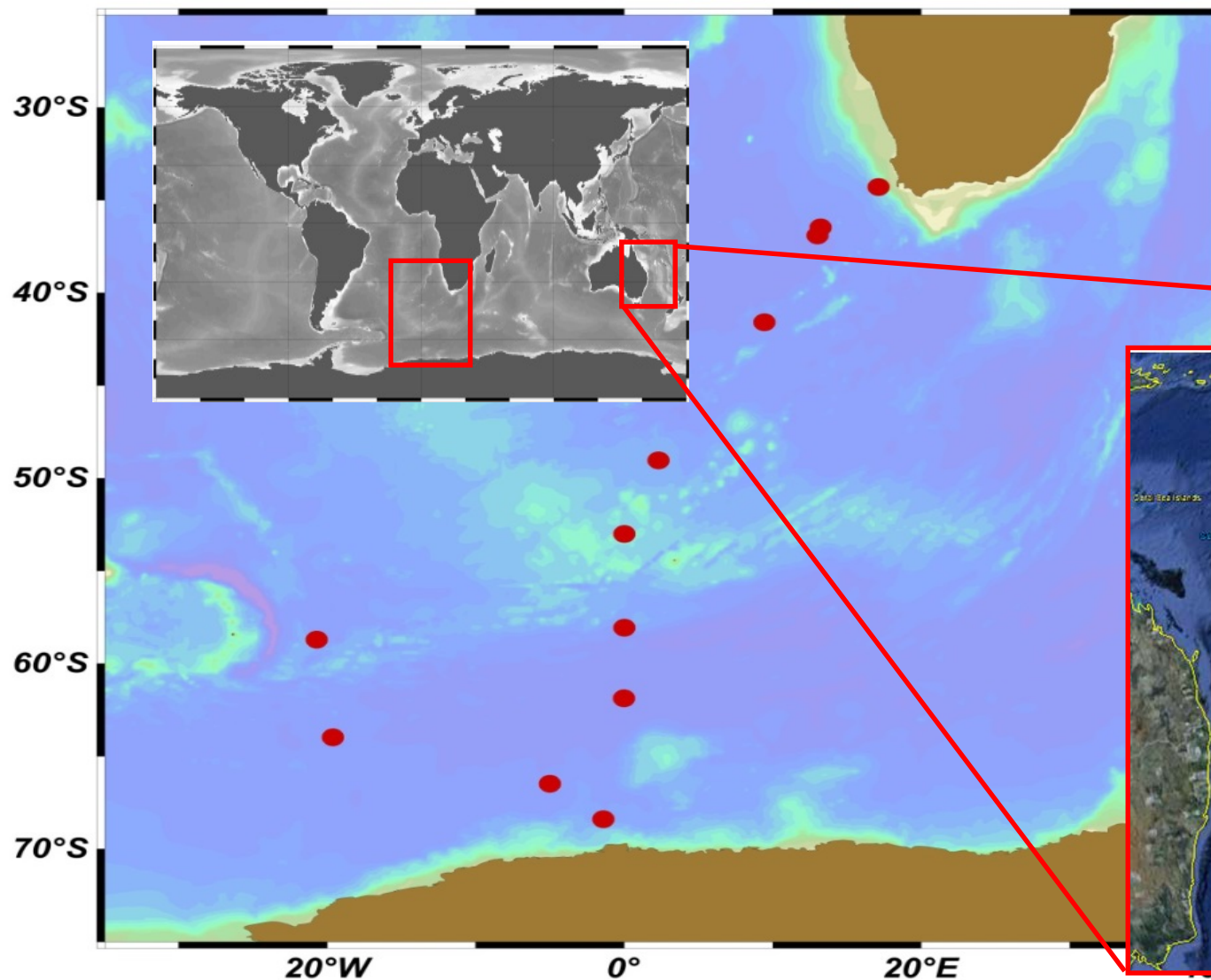


Literature standard Fe phases

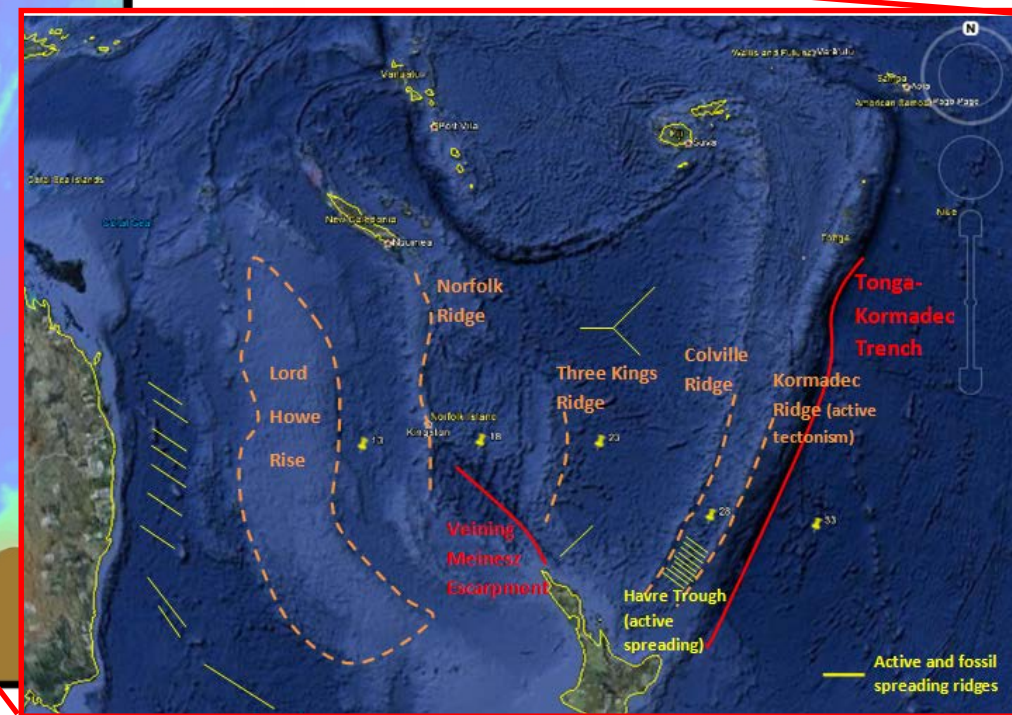


Standard Fe oxide and oxyhydroxide phases

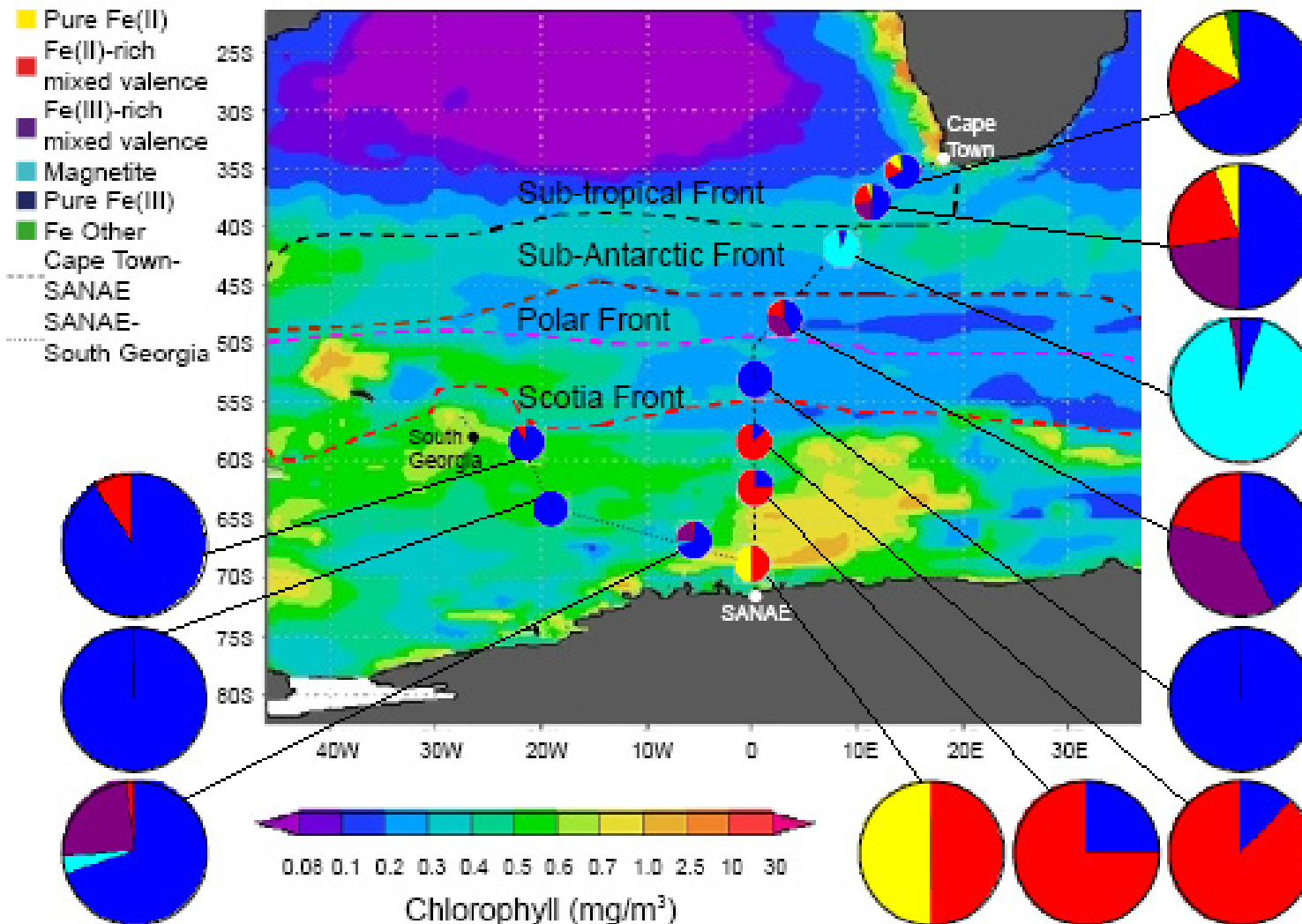
S Fe speciation: Open Ocean



- **Southern Ocean:** distribution of Fe mineralogy (von der Heyden et al., *Science*, 2012)
- **Pacific Ocean:** Fe-C associations (von der Heyden et al., *Environmental Science & Technology Letters*, 2014)



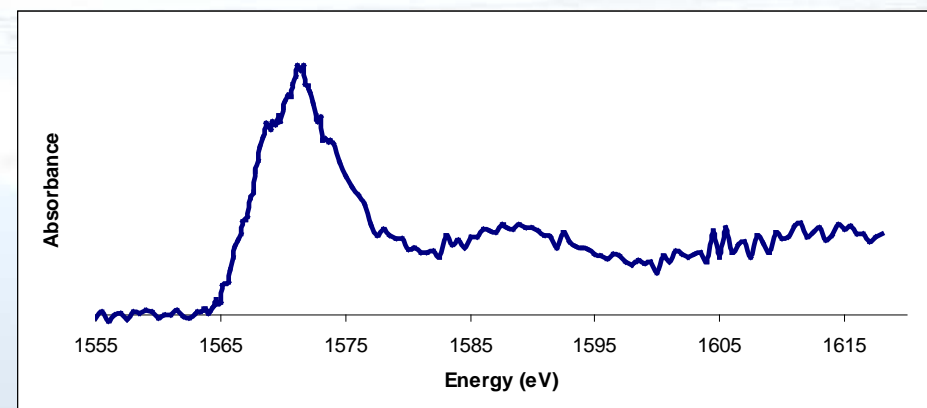
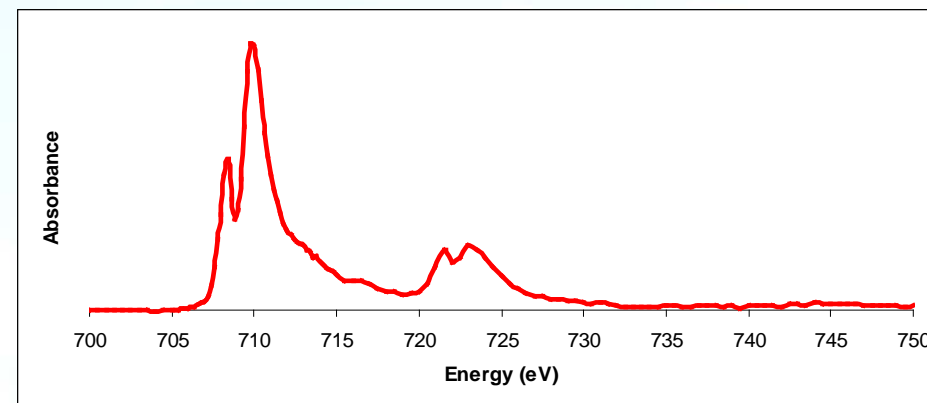
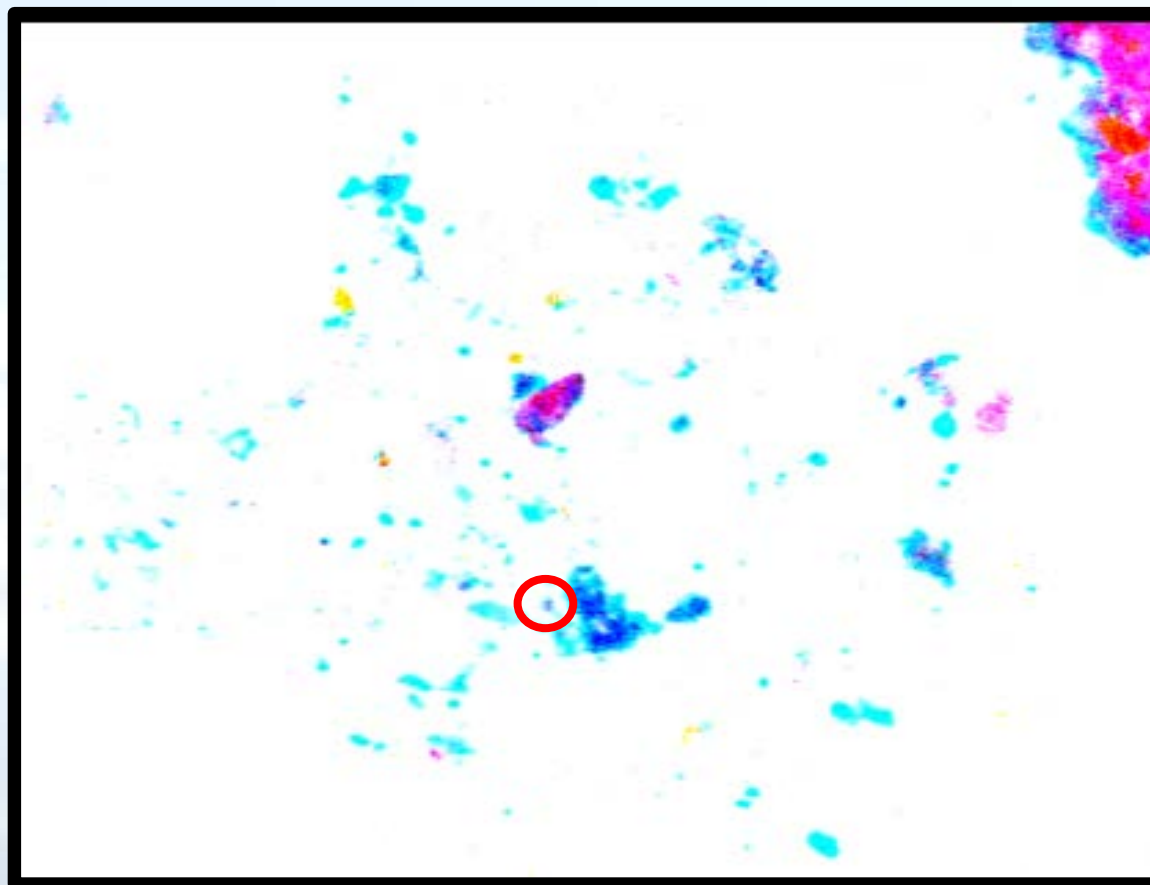
S Fe speciation: Southern Ocean



Distribution of Fe mineralogy in the Southern Ocean reflecting:

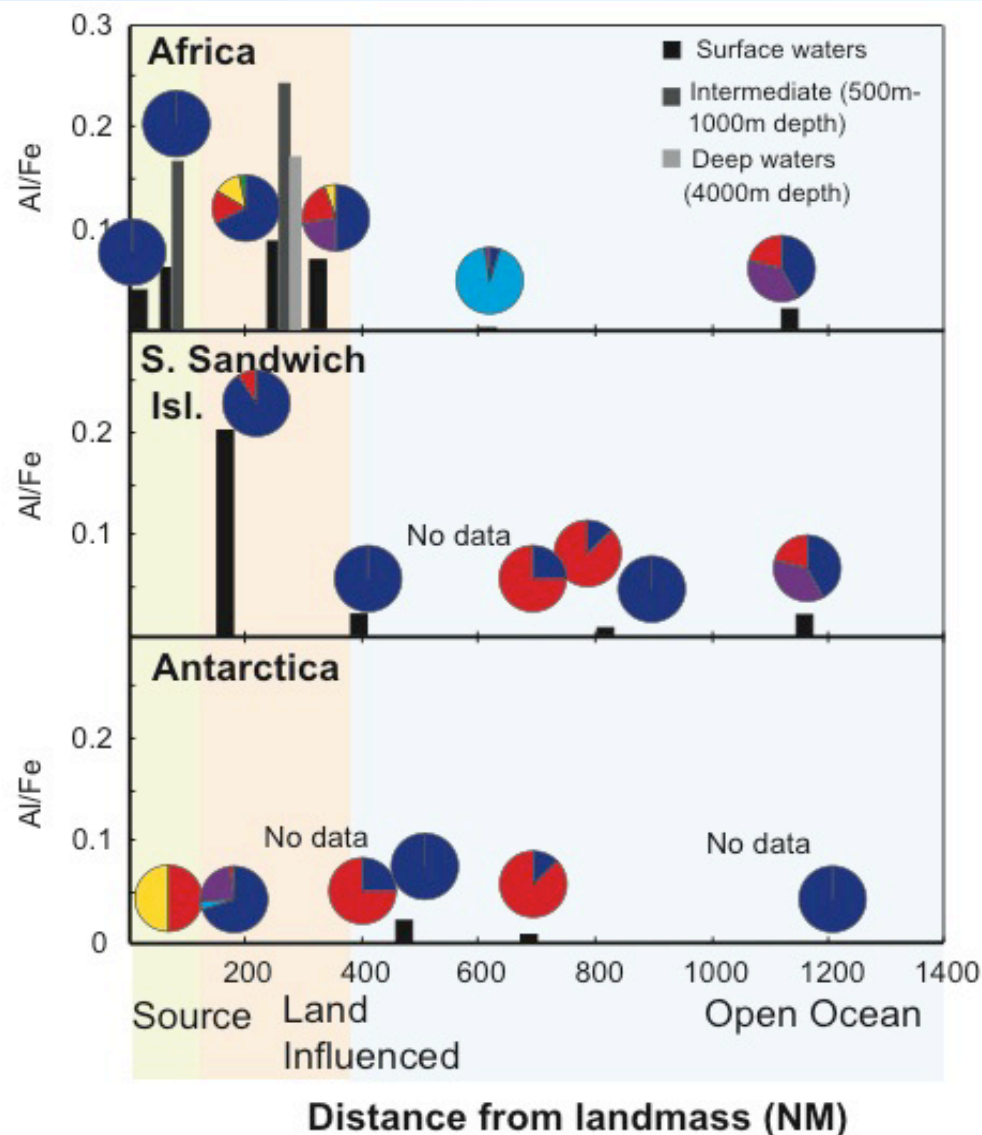
- High degree of heterogeneity
- Magnetite in the Sub-Antarctic Frontal Zone
- Increased prevalence of Fe(II) in the high latitudes
 - Biological control
 - Slower oxidation kinetics
 - Fe(II) sources
- Coinciding with greater chlorophyll

Fe speciation: Al substitution



Fluvial particles: Berg River, RSA

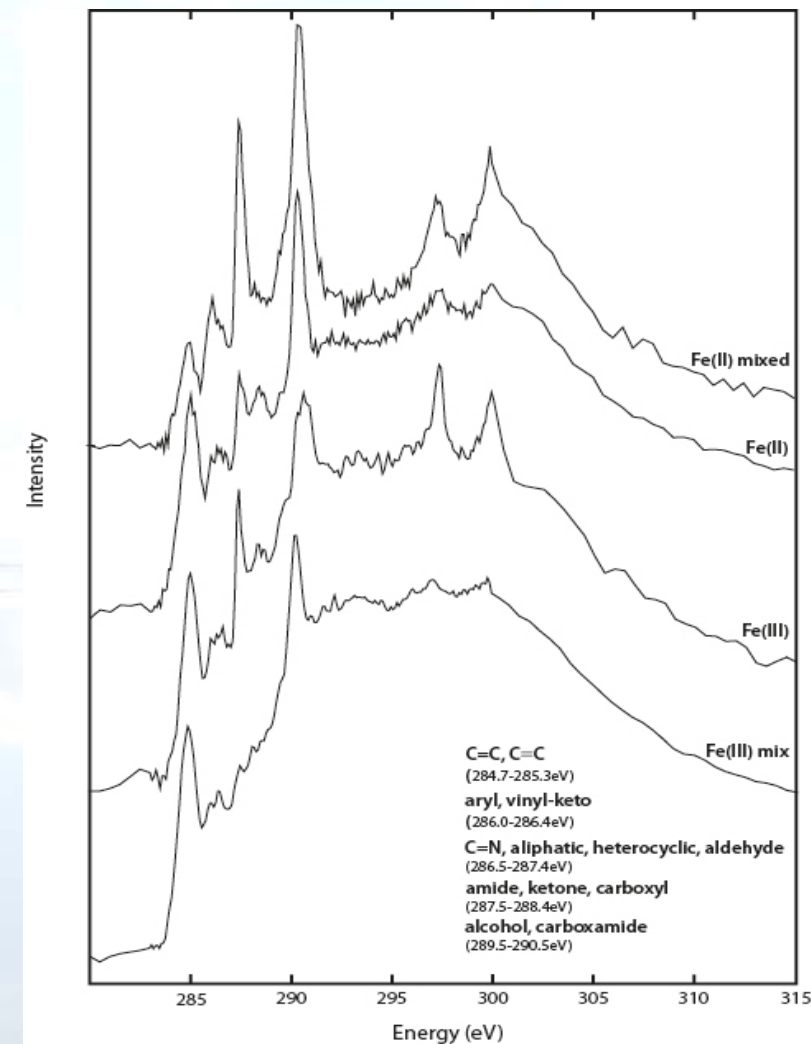
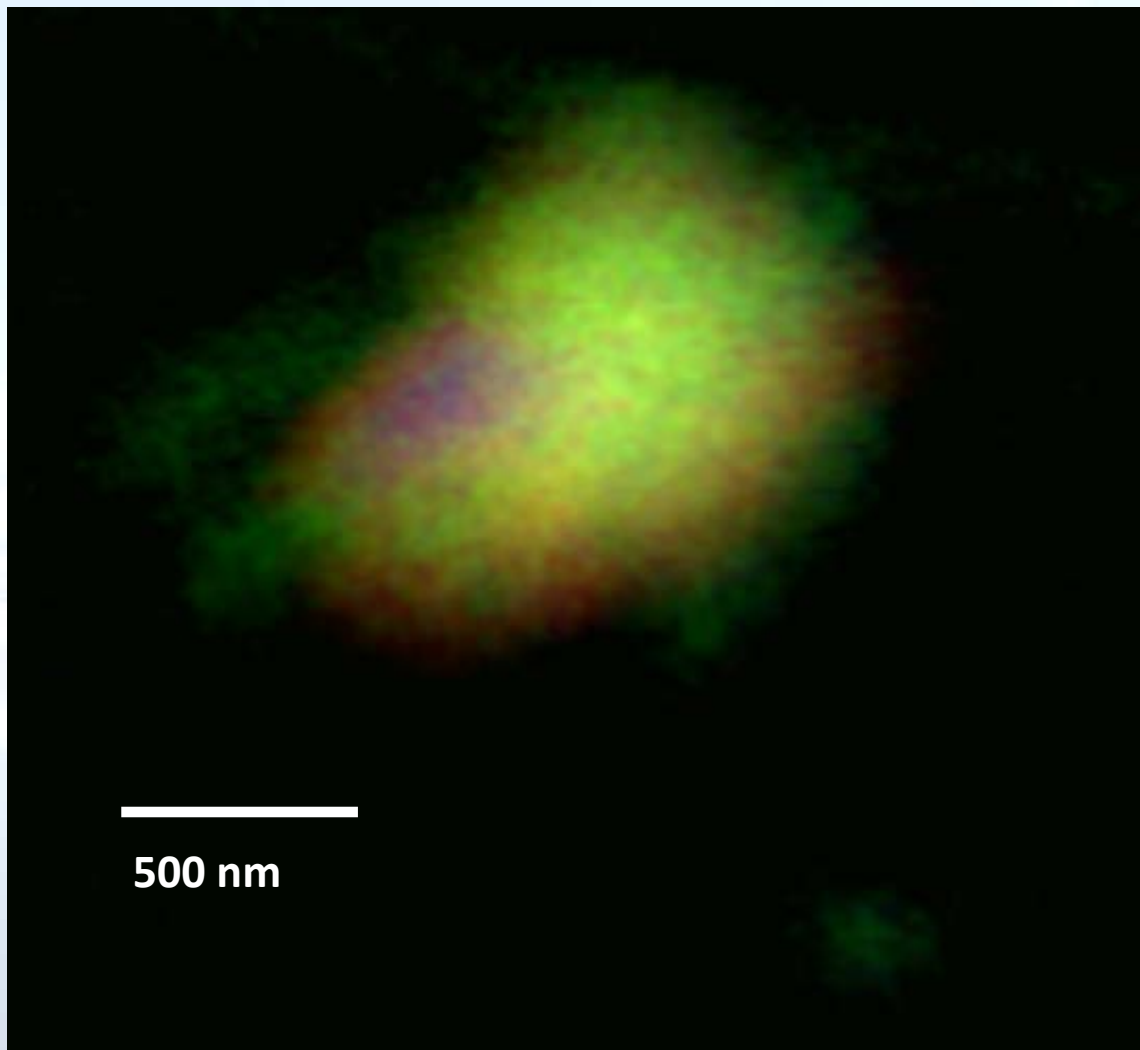
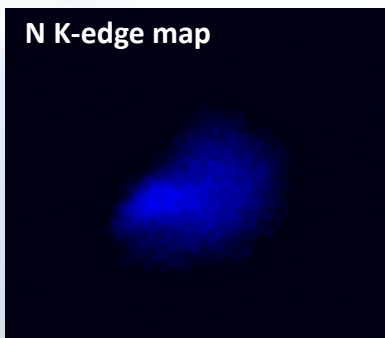
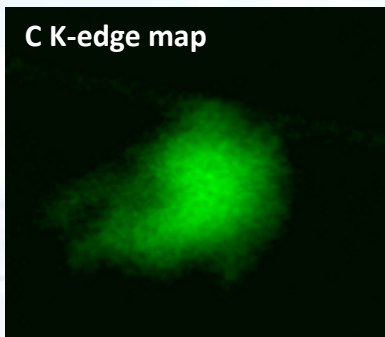
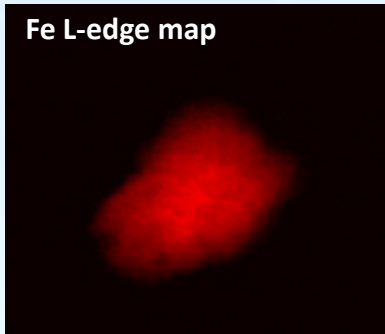
S Fe speciation: Al substitution



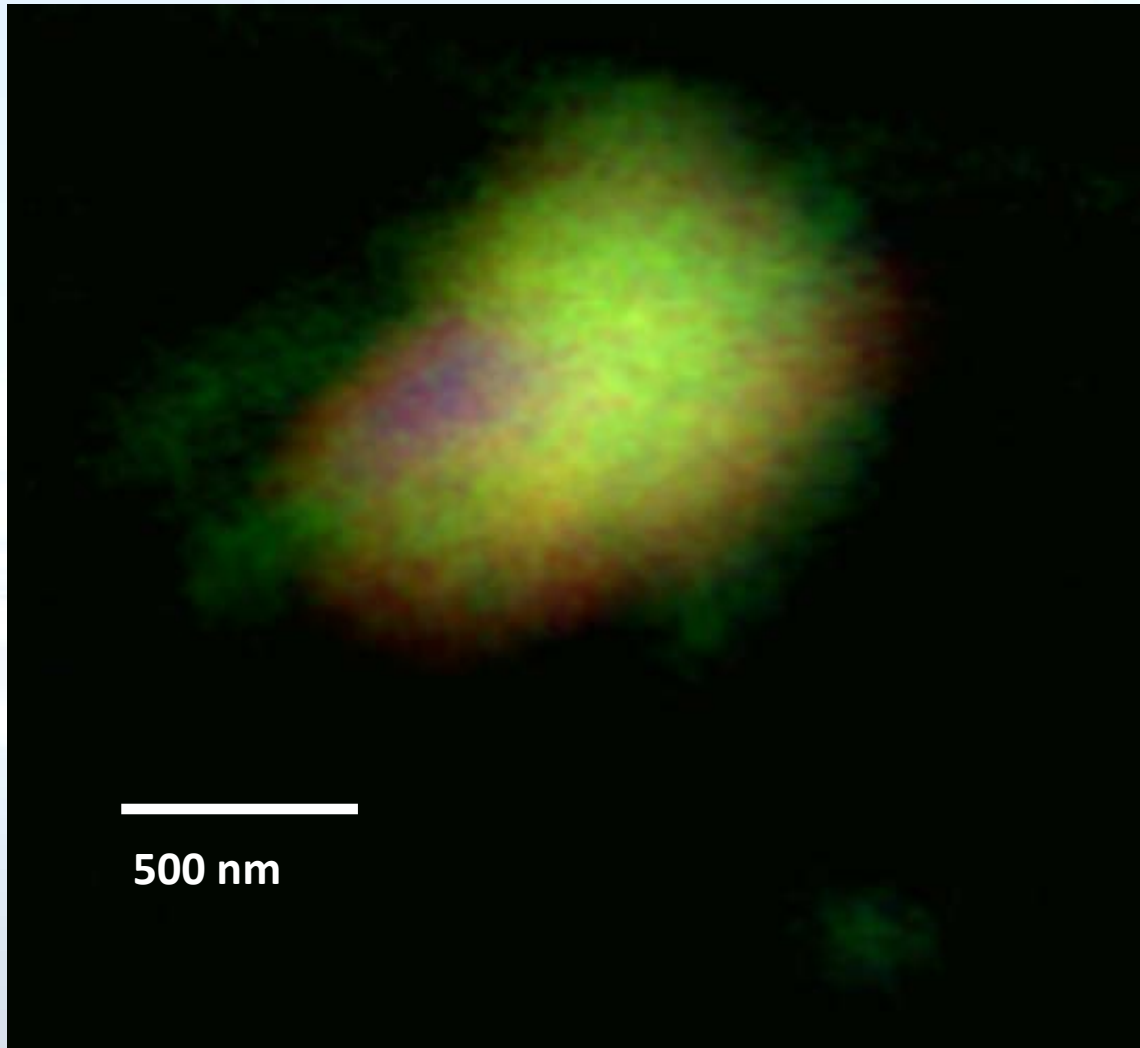
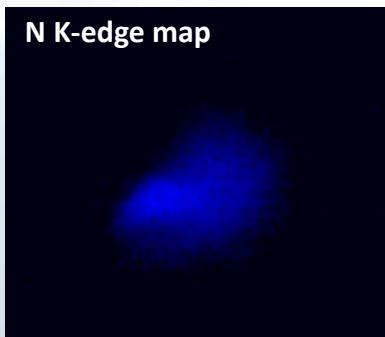
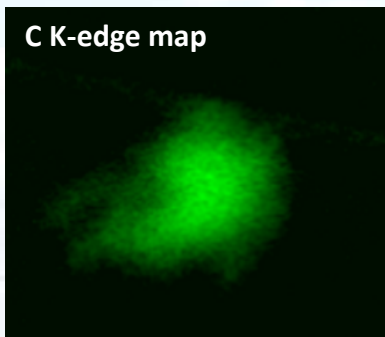
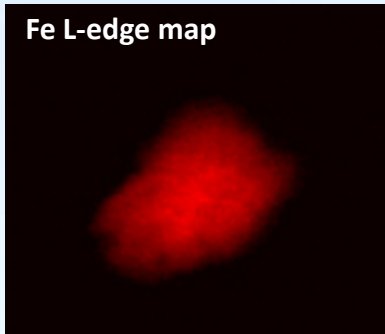
Distribution of Al/Fe ratios evaluated in particles collected in the Southern Ocean:

- Al/Fe ratios increase with distance from source, then decrease in Open Ocean
- Higher values at depth (0.17) relative to surface (0.08)
- Role as a chemical tracer
- Effects on solubility

Fe speciation: Associations with carbon



Fe speciation: Associations with carbon



Evaluation of particles from
Southern Ocean, Pacific Ocean,
two lacustrine environments:

- Fe(II) stable in a range of oxic aquatic environments
- Strongly *associated* with organic carbon
- Preferentially associated with alcohol and carboxamine functional groups

Concluding remarks

- Soft X-ray spectroscopy (i.e., the Fe $L_{2,3}$ -edge) is sensitive to changes in the local coordination of Fe minerals.
 - Used to evaluate the mineralogy and chemistry of small (10 nm diameter) Fe colloids.
 - Found to be heterogeneous in the Southern Ocean and in their associations with organic carbon
 - These characterised differences will reflect in their respective solubility, bioavailability and biogeochemical behaviour.
- Future work
 - This study: focus on the behaviour of these Fe classes under changing climatic conditions; focus on the speciation of other bioactive trace metal particulates (e.g., Cd)
 - Personal: Adapt the synchrotron-based X-ray skill set to Economic Geology questions (e.g., fluid inclusion and trace element speciation, characterisation of mine waste leaching products)
 - AfLS: Inclusion of a soft X-ray beam-line would be pertinent to Earth Scientists

Acknowledgements

People:



Prof. Alakendra
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Myneni



Dr. Thato
Mtshali



Raimund
Rentel



Dr. Tolek
Tyliczszak

Sponsors:



Thank-you!!!

“The ocean is a desert with its life underground and the perfect disguise above...”

Questions...?