Metal speciation and ligand production

Kristen Buck

Organic complexation by CLE-AdCSV

$$Fe' + L_i \Leftrightarrow FeL_i \qquad Cu^{2+} + L_i \Leftrightarrow CuL_i$$

Fe: Rue and Bruland 1995, Abualhaija and van den Berg 2014;
Cu: Campos and van den Berg 1994

CLE: Competitive Ligand Exchange

$$Fe' + L_i \Leftrightarrow FeL_i$$

$$+$$

$$SA$$

$$\Updownarrow$$

$$Fe(SA)$$

$$Cu^{2+} + L_i \Leftrightarrow CuL_i$$

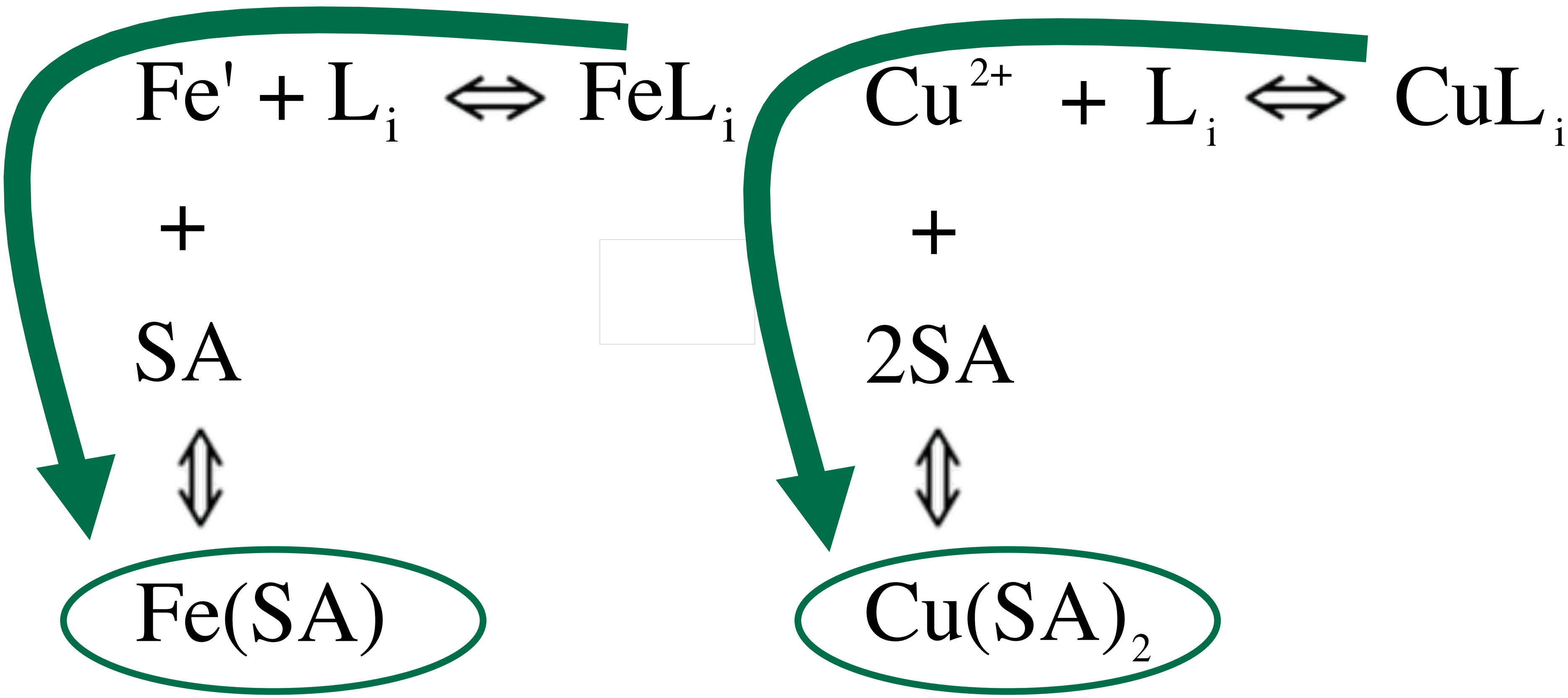
$$+$$

$$2SA$$

$$\Updownarrow$$

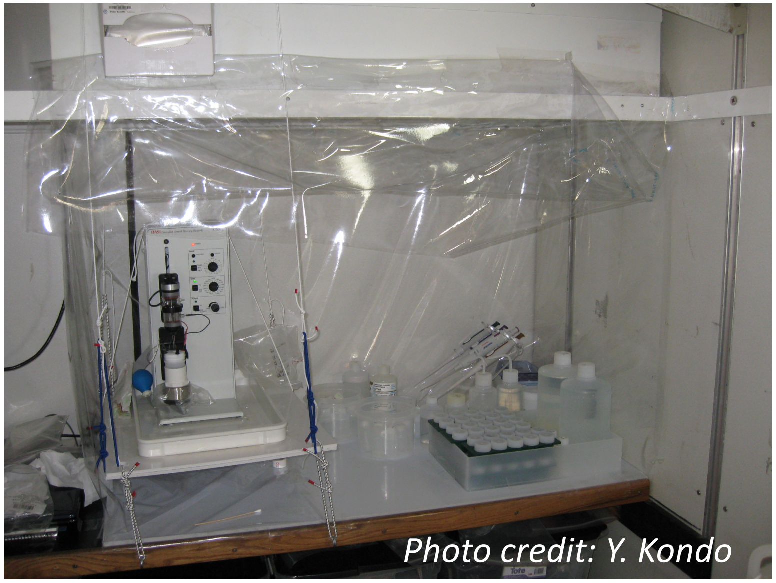
$$Cu(SA)_2$$

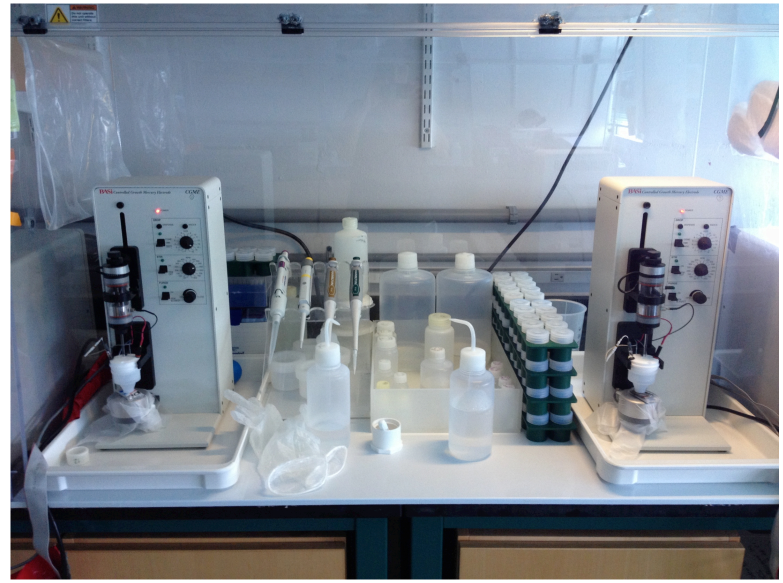
CLE: Competitive Ligand Exchange

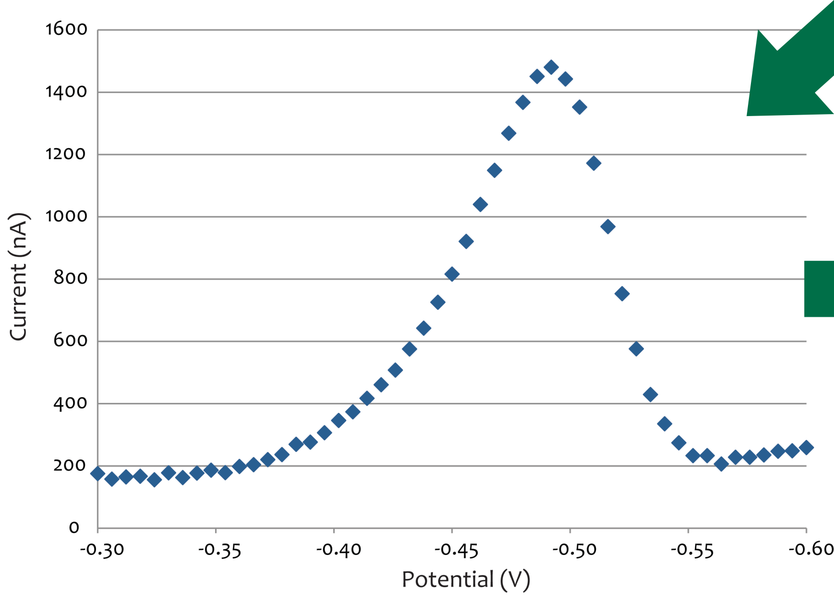


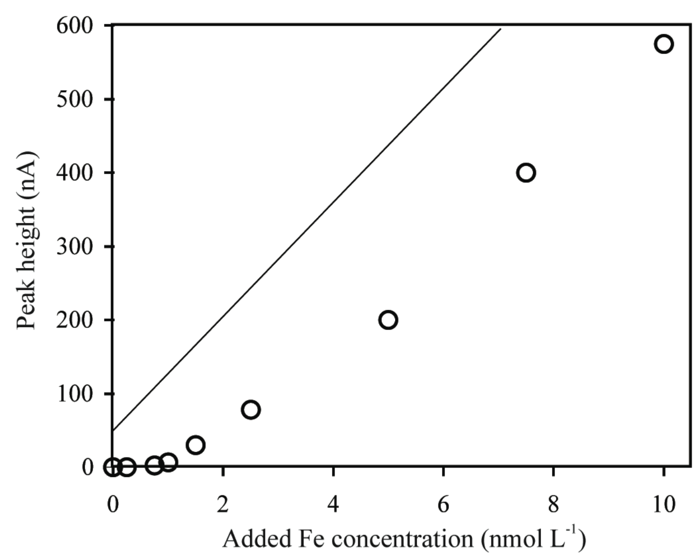
These SA complexes then measured by Adsorptive Cathodic Stripping Voltammetry (AdCSV)

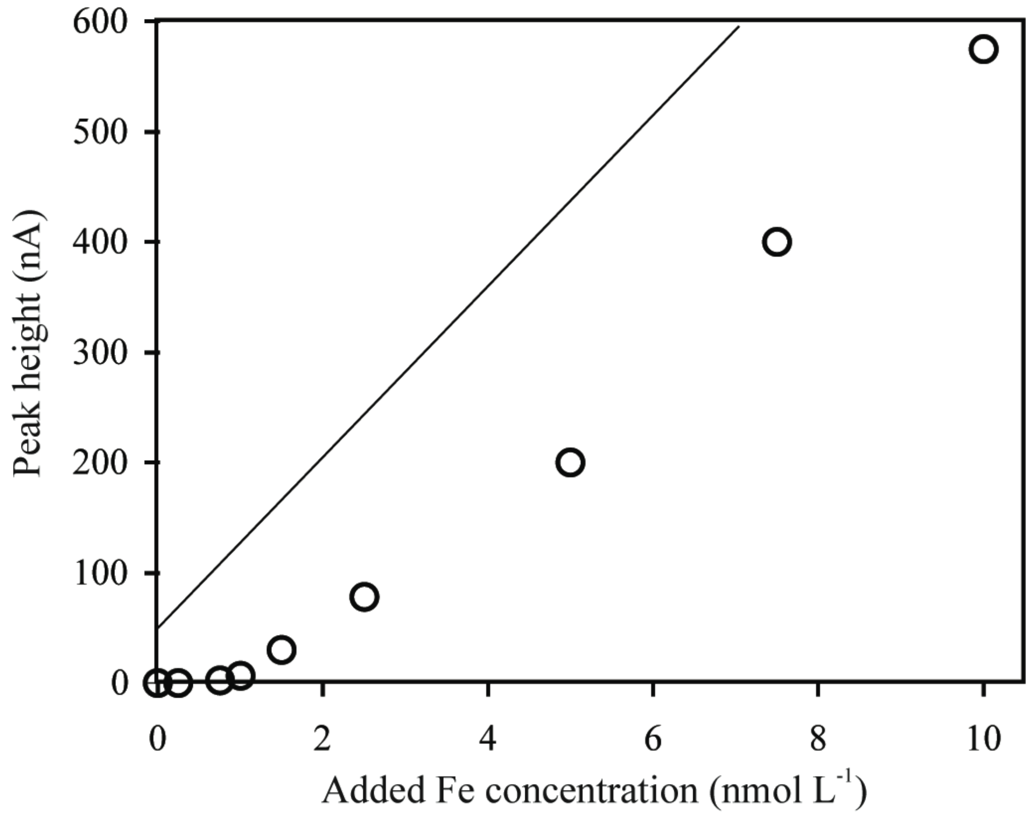
Adsorptive Cathodic Stripping Voltammetry (AdCSV)





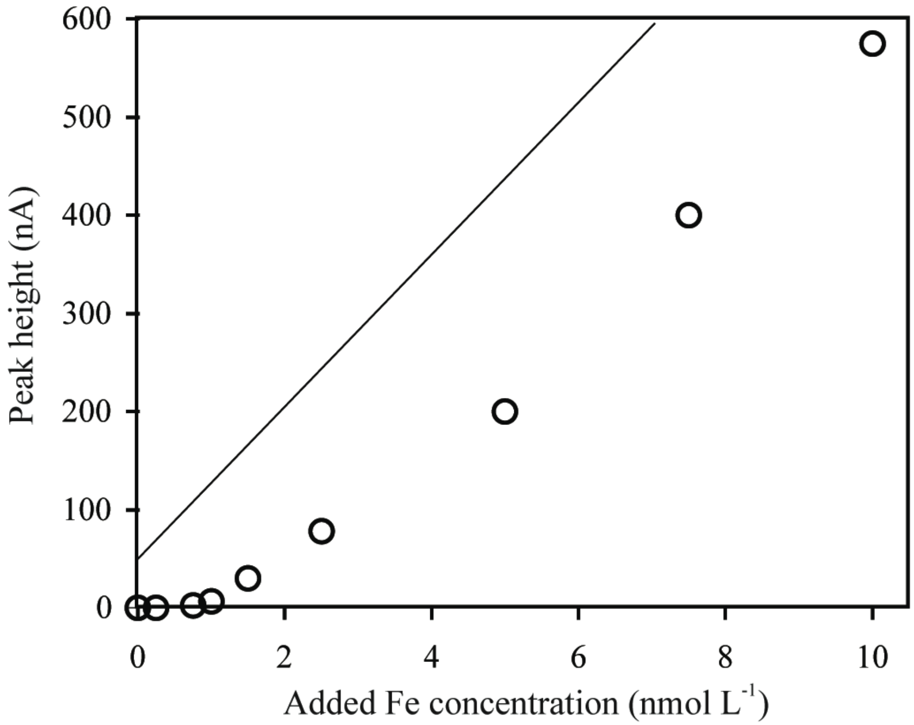




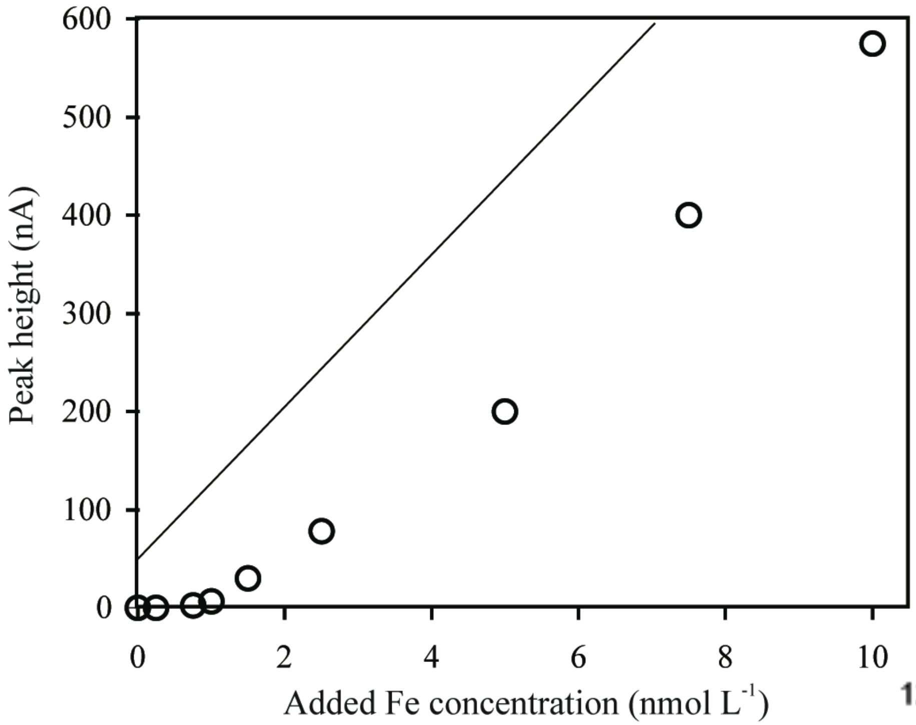


Data Interpretation

$[L_i]$ and conditional binding constants K_i

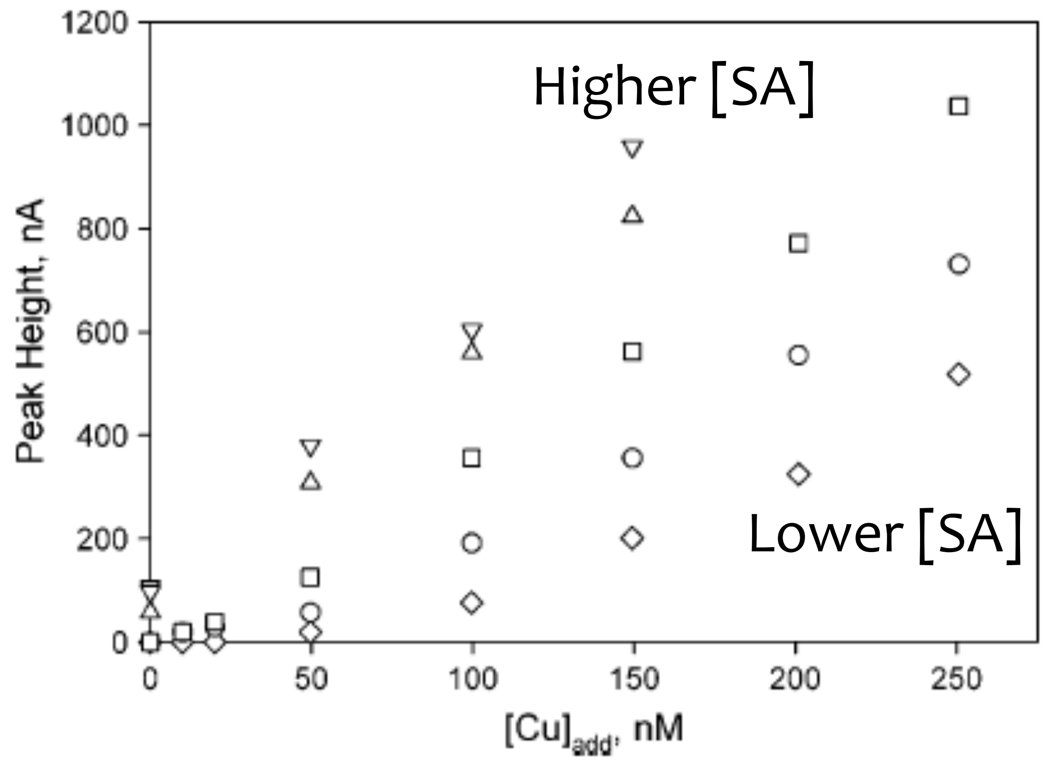


Limitation: limited information about FeL in these titrations



Limitation: limited information about FeL in these titrations

Solution: multiple analytical windows (MAW)

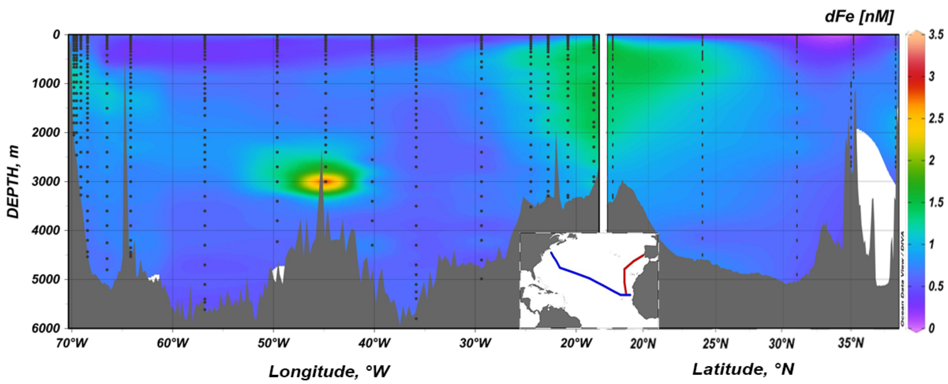


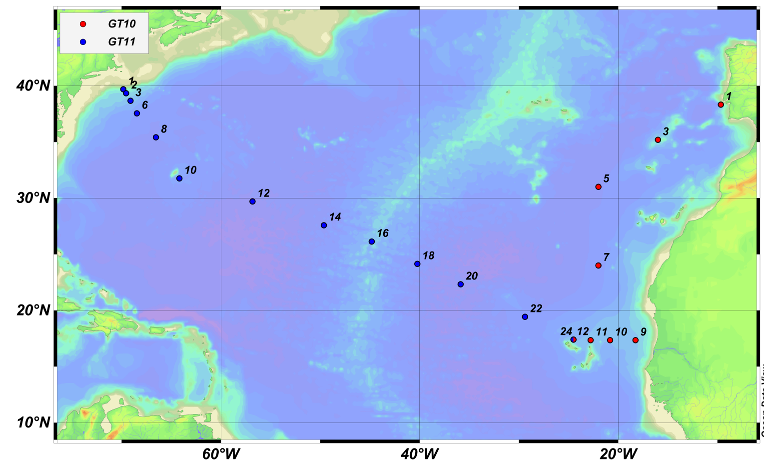
Relevant Background

- Organic complexation is critical in Fe cycling
  - Inorganic Fe solubility is low
  - Dynamic ligands required to model global Fe cycle
- The strongest ligands exert greatest influence
  - These bind ambient Fe, Cu (bioavailability, solubility)
- Excess strong ligands (i.e., eL_1) drive Fe cycling
  - Best candidate = siderophores

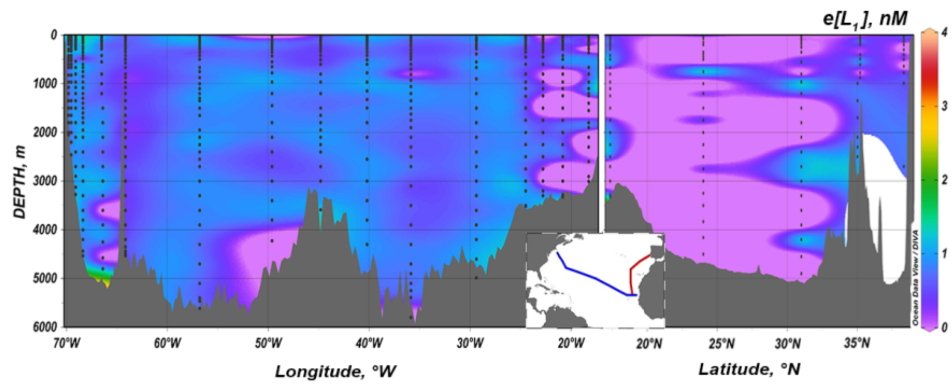
North Atlantic (NAZT)

dFe

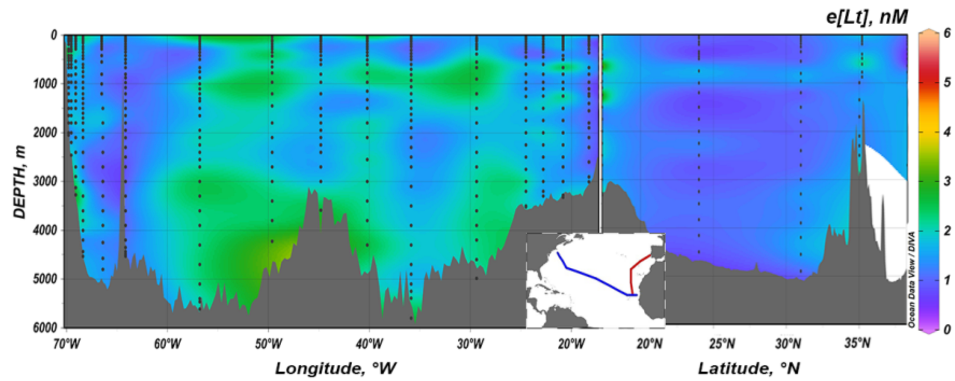




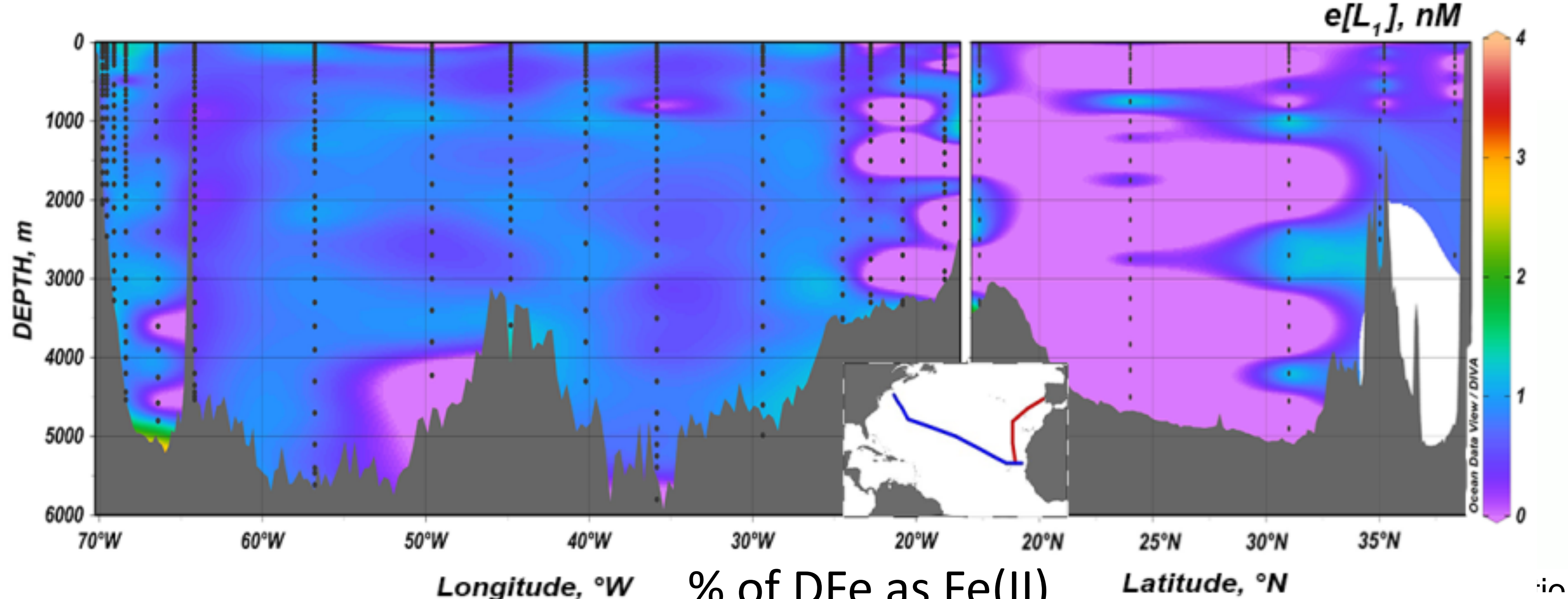
eL_1



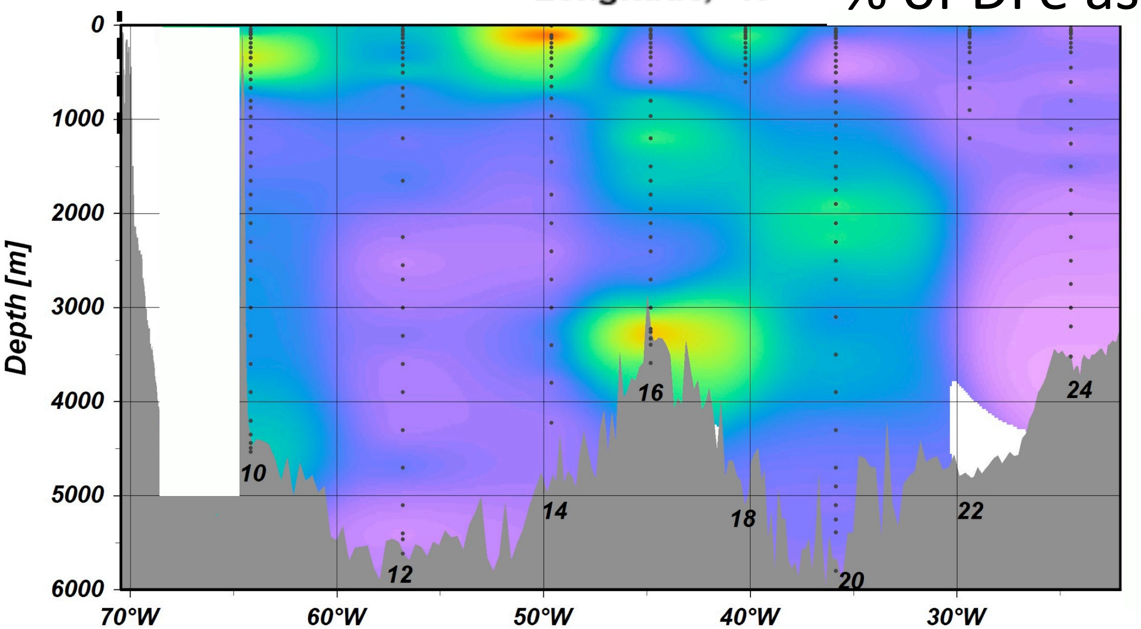
eL_T



Buck et al. 2015; Hatta et al. 2015; Sedwick et al. 2015



% of DFe as Fe(II)



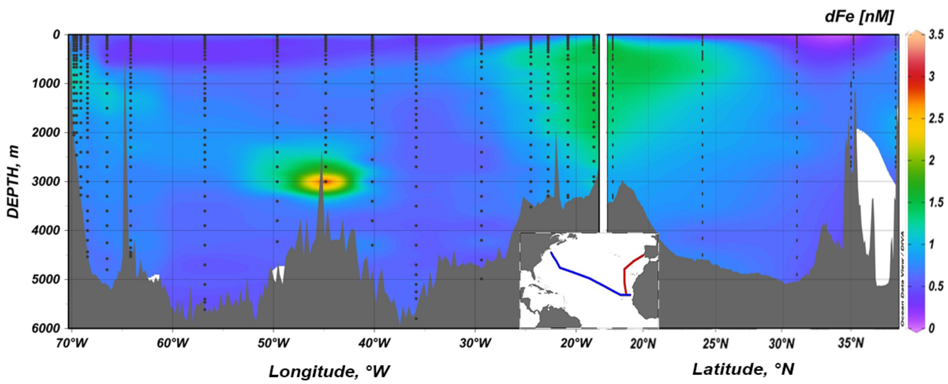
Buck et al. 2015; Sedwick et al. 2015

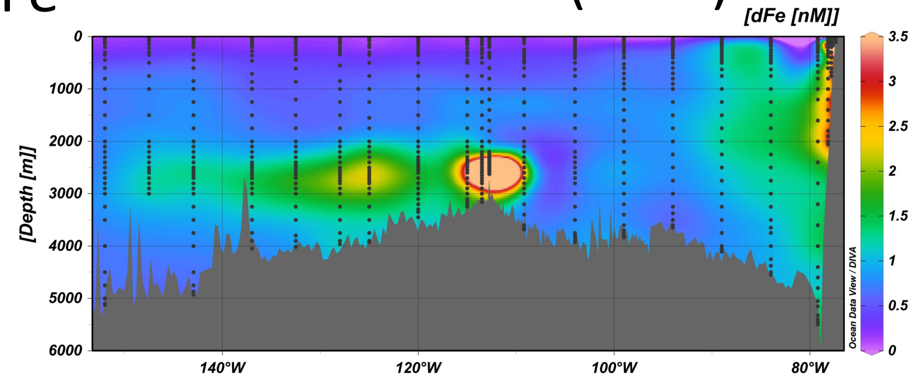
- Minima in eL_1 with high % Fe(II)
  - Bio response?
  - Storage?

North Atlantic (NAZT)

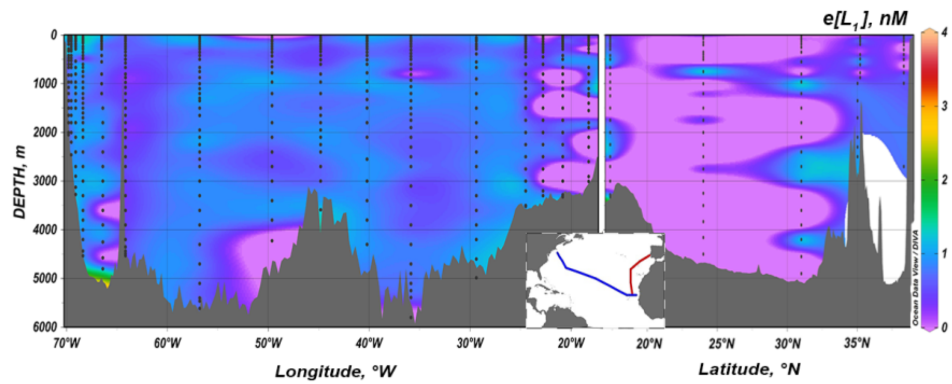
dFe

East Pacific (EPZT)





eL_1



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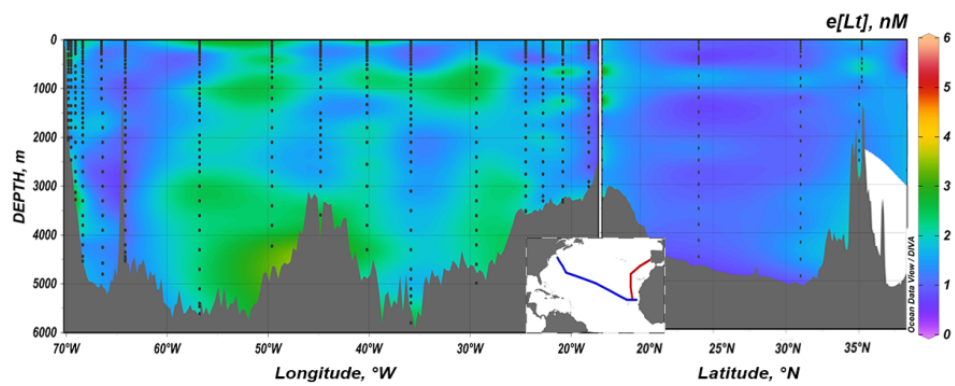
kristenbuck@usf.edu

eL_T



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kristenbuck@usf.edu

Buck et al. 2015; Hatta et al. 2015; Sedwick et al. 2015

Resing et al. 2015; Buck et al. in prep.

eL_1

UNPUBLISHED DATA
kristenbuck@usf.edu

DOC

Craig Carlson, UCSB

UNPUBLISHED DATA
carlson@lifesci.ucsb.edu

eL_T

UNPUBLISHED DATA
kristenbuck@usf.edu

EPZT Water Mass Analysis:

Brian Peters, Karen Casciotti

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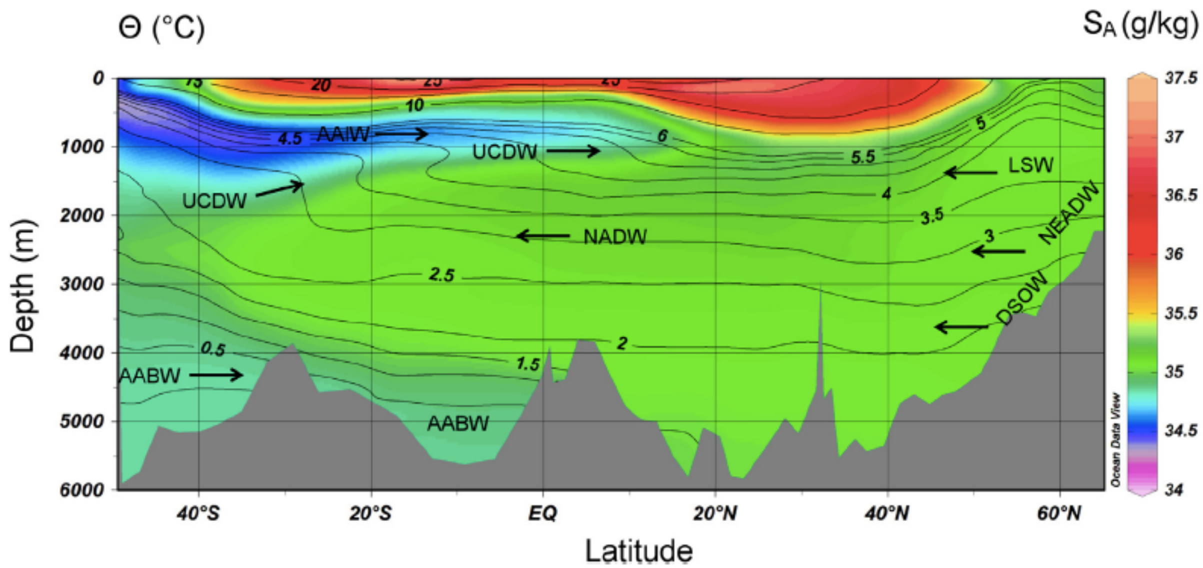
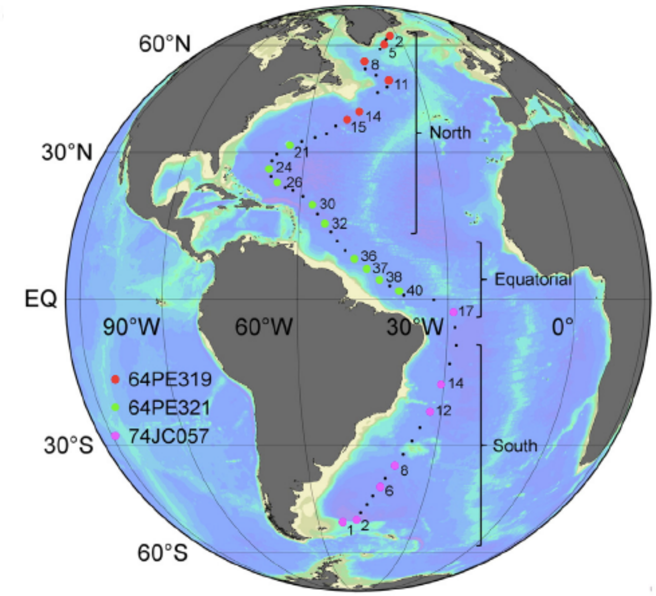
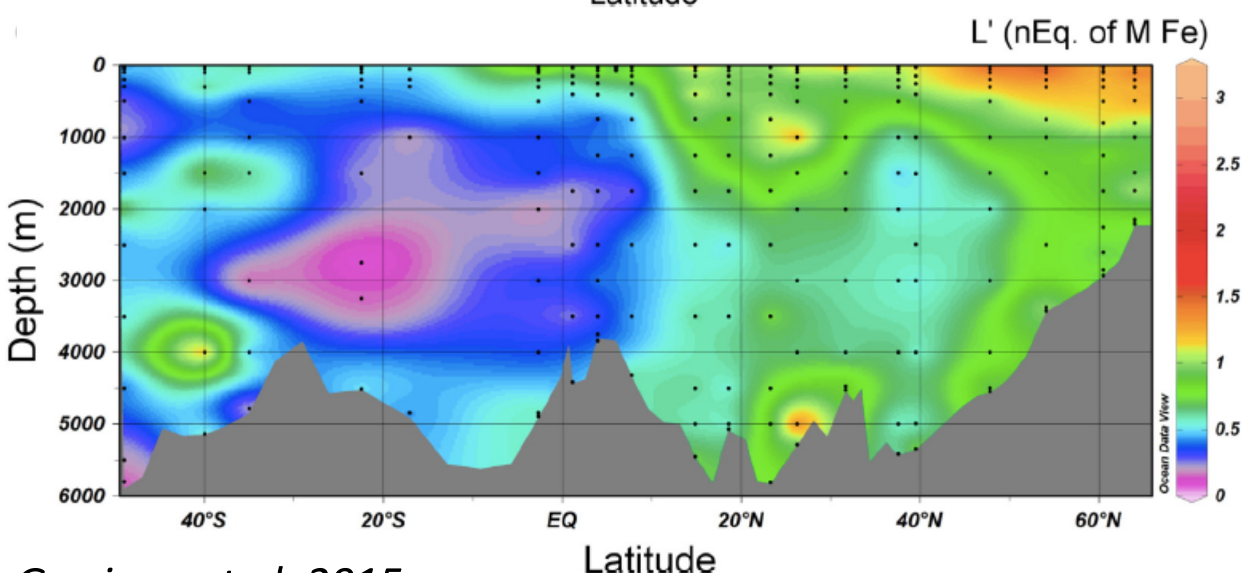
kristenbuck@usf.edu

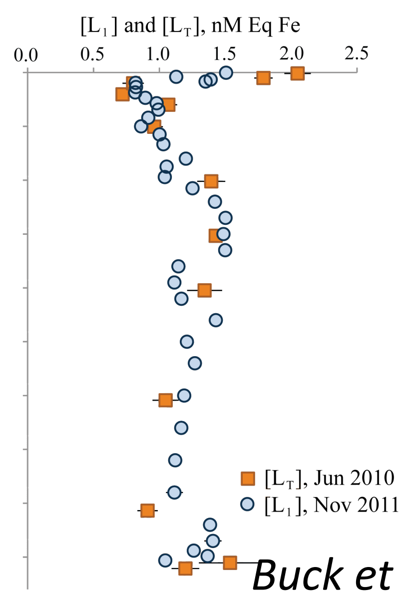
- Pacific Deep Water
  - Oldest water mass
  - Minima in eL_1, eL_T

Dutch GEOTRACES, W Atlantic







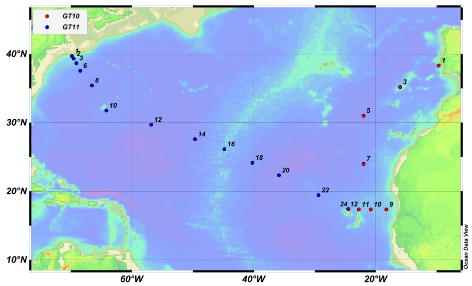


Gerringa et al. 2015

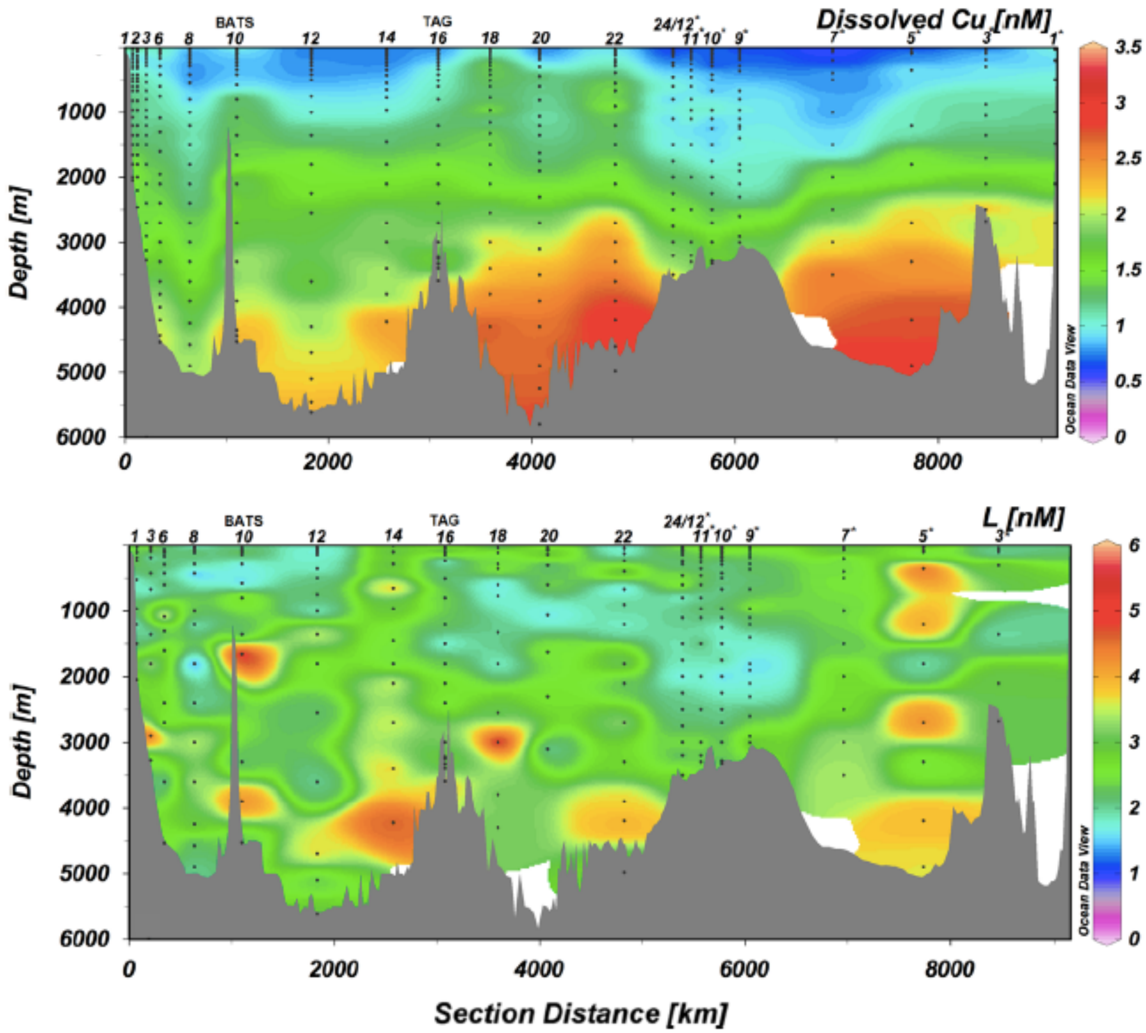
Buck et al. submitted

How to explain trends in eL_1

- Water mass dilution
- Ligand saturation by trace metals
  - Is DFe increasing, converting eL_1 to FeL- no?; saturation with other TMs?
- Bacterial degradation of L_1
  - Who eats L_1? Bioavailability of siderophores?
- Abiotic scavenging of eL_1
  - Are particles a source of ligands or a sink?
  - More evidence for FeL scavenging than eL_1?



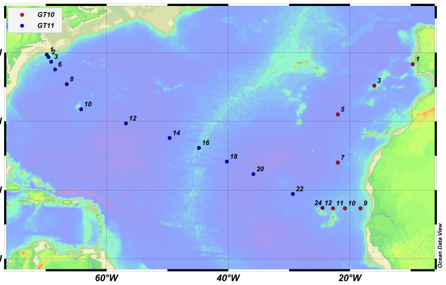
Copper speciation



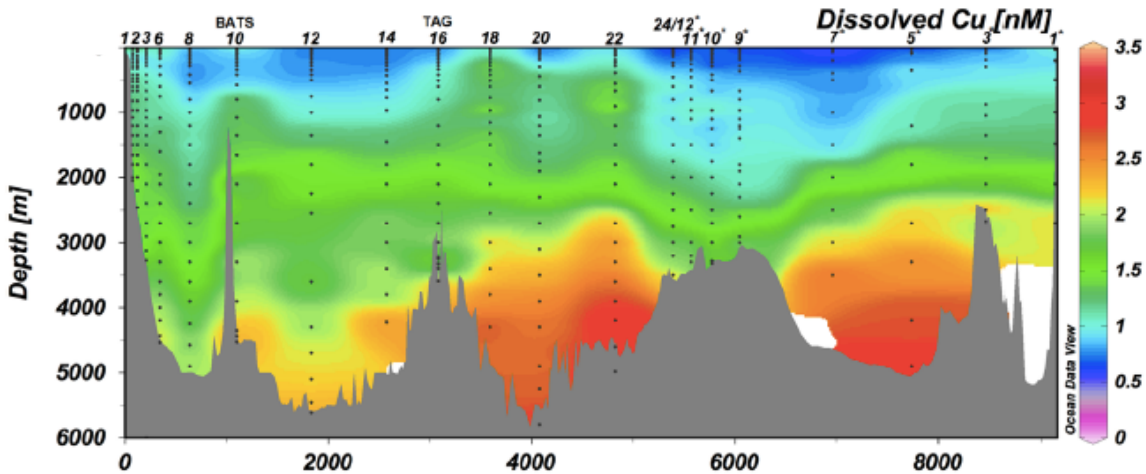
Dissolved Cu concentrations: Increase with depth

Cu-binding ligands relatively uniform with depth

Jacquot and Moffett 2015

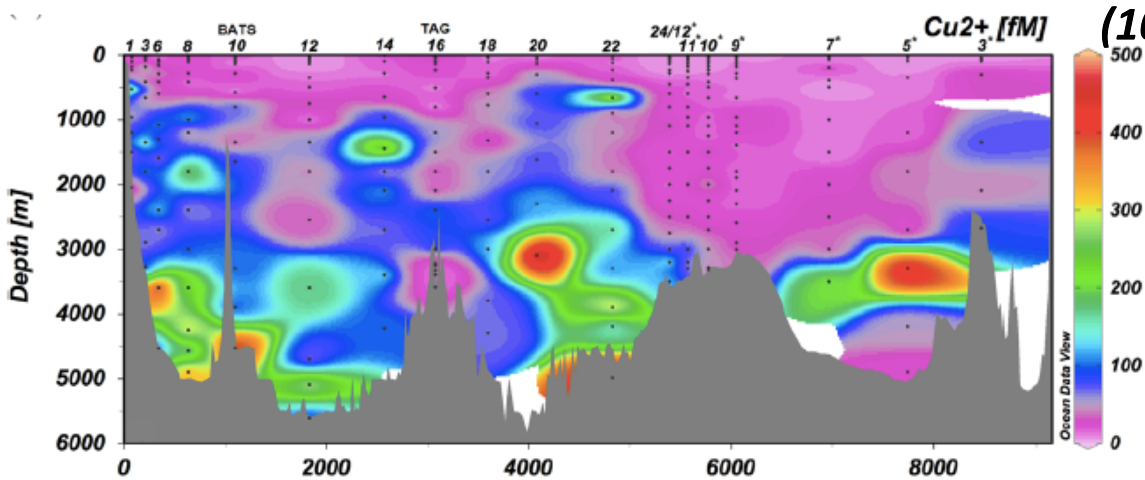


Copper speciation



Dissolved Cu concentrations: Increase with depth

$(10^{-12.3}$ *M)*



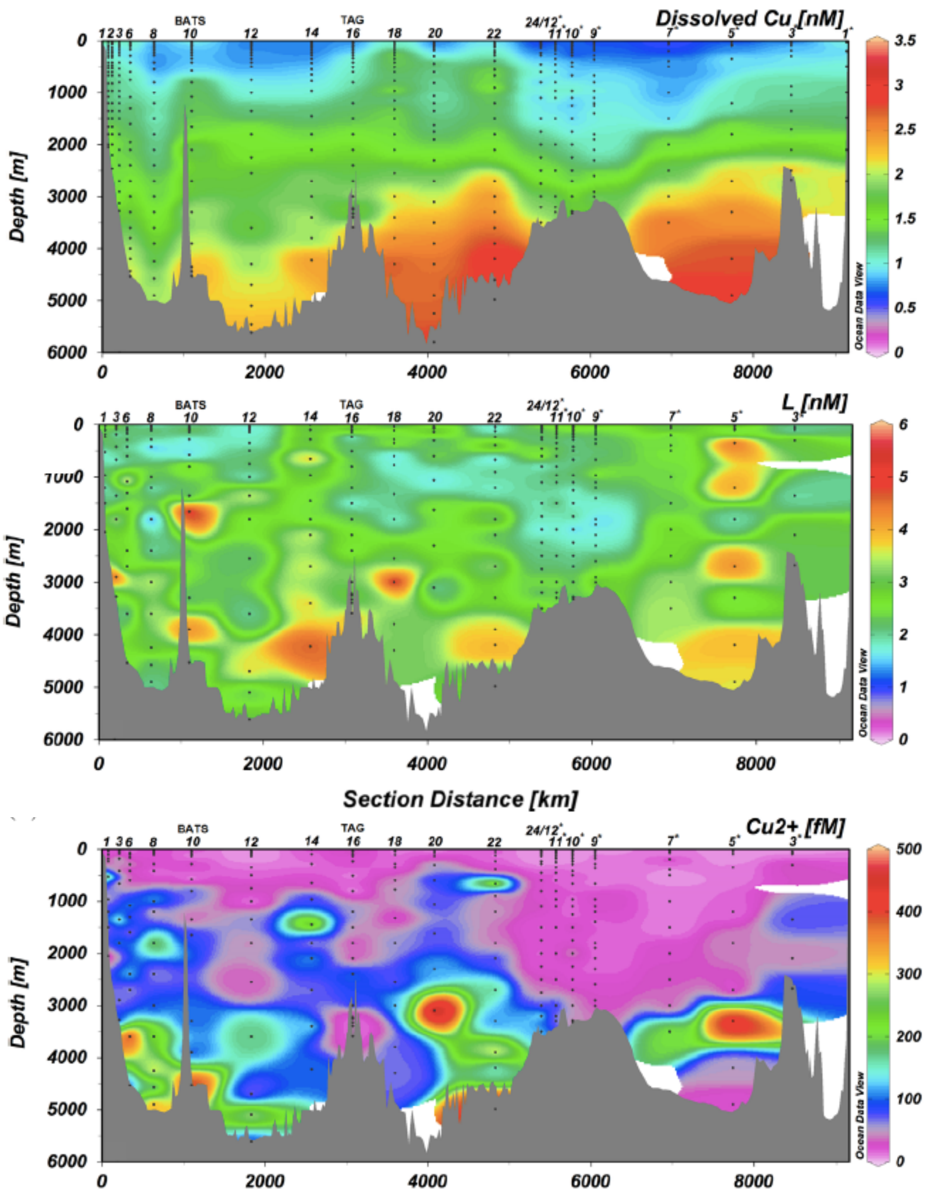
Cu-binding ligands relatively uniform with depth

= Low excess L at depth, higher Cu^{2+}

Jacquot and Moffett 2015

North Atlantic (NAZT) | East Pacific (EPZT)

dCu



L

Cu^{2+}

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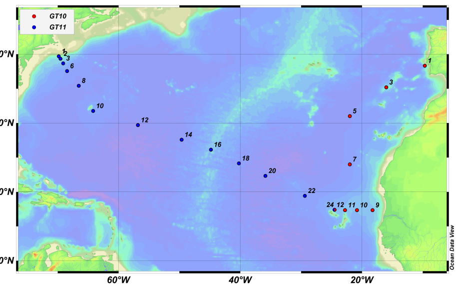
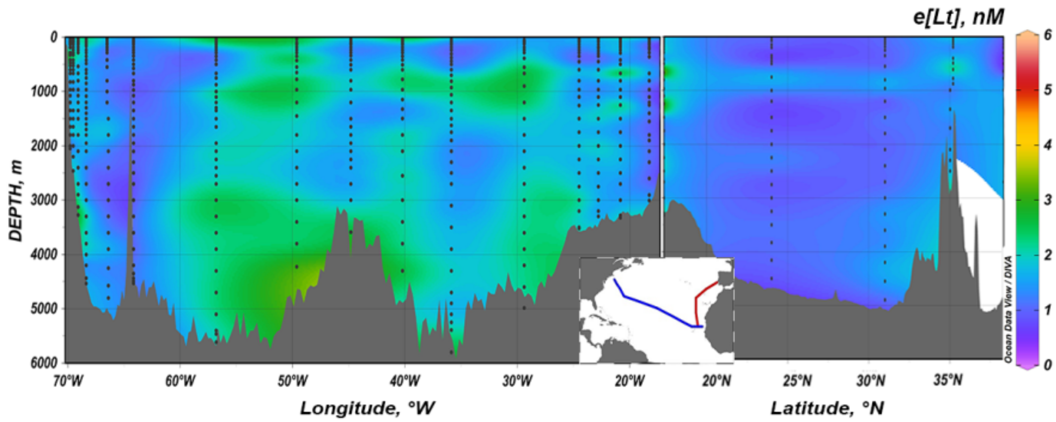
aruacho@ucsd.edu
kbarbeau@ucsd.edu

Jacquot and Moffett 2015

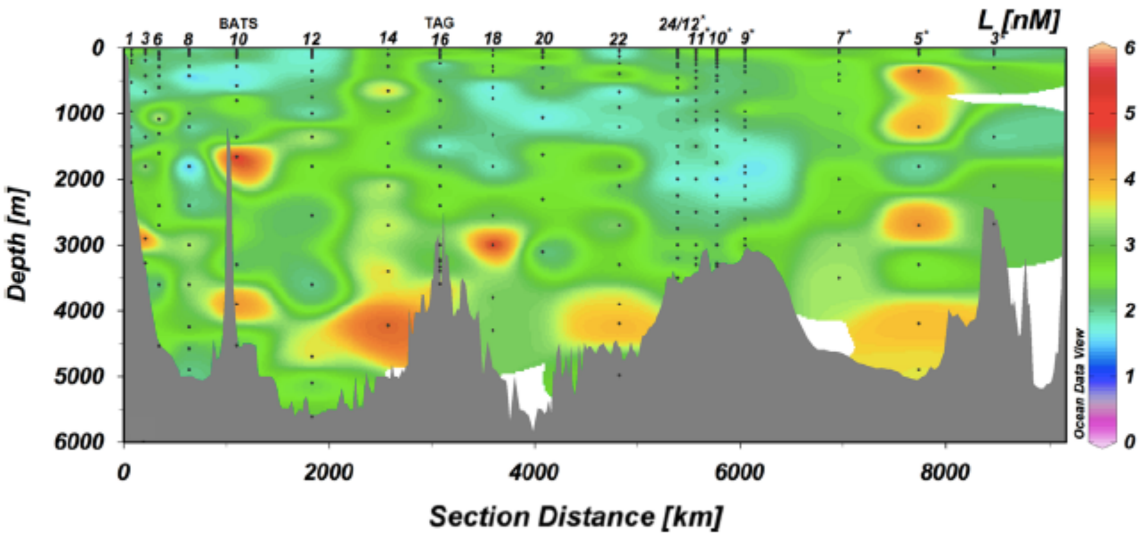
Angel Ruacho, Kathy Barbeau, unpubl.



Overlap in Fe and Cu ligands



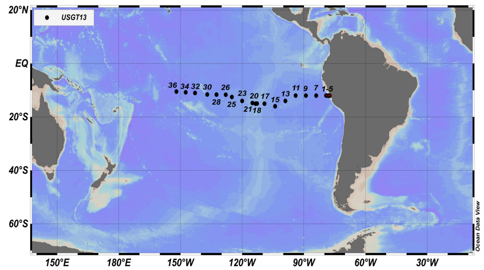
Excess Fe-binding ligand concentrations



Cu-binding ligand concentrations

=> Some eL_{Fe} binds Fe *and* Cu; L_2 for Fe

Jacquot and Moffett 2015, Buck et al. 2015



Overlap in Fe and Cu ligands

UNPUBLISHED DATA
aruacho@ucsd.edu
kbarbeau@ucsd.edu
kristenbuck@usf.edu

Excess Fe-binding ligand concentrations

Cu-binding ligand concentrations

=> Some eL_{Fe} binds Fe *and* Cu; L_2 for Fe

Kristen Buck, Angel Ruacho, Kathy Barbeau, unpubl.

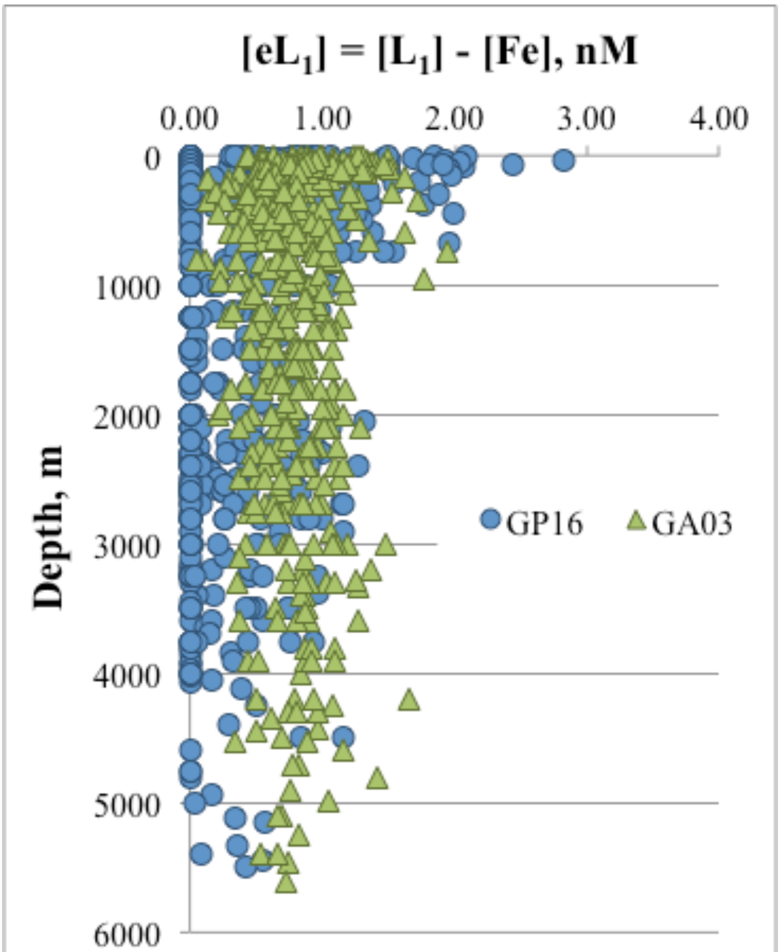
From GEOTRACES Surveys:

- Fe-binding ligands in excess of [Fe]

- Apparent loss of excess in strongest Fe ligand class between basins, along water masses, but gain in excess weaker ligands; higher Cu, L and Cu^{2+} in EPZT deep waters compared to NAZT

- Some of these ligands, especially L_2-type at depth, bind both Fe and Cu

eL_1 trends: ligand production or release?

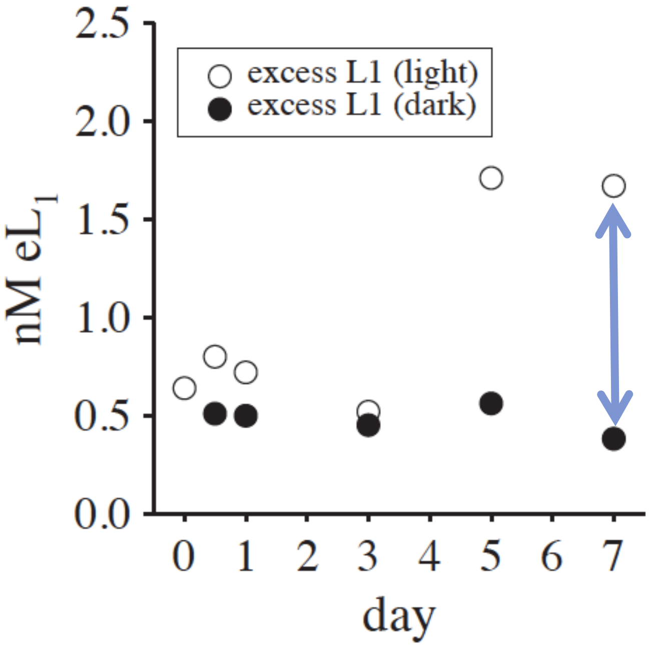


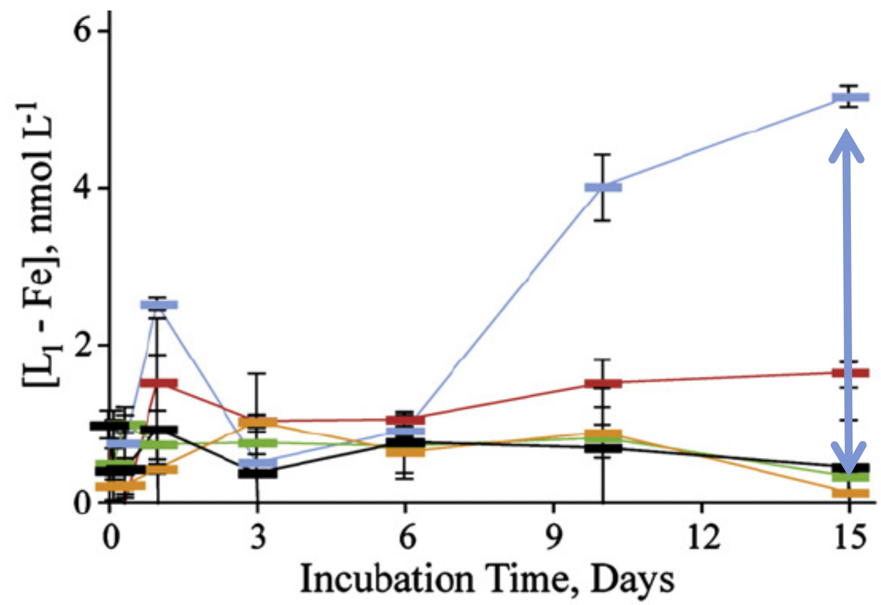
- Highest eL_1 in upper water column of Pacific
- Local maxima in eL_1 in AAIW of Atlantic and Pacific sections; also "Green Belt" in Bering Sea

Buck and Bruland 2007; Buck et al. 2015; Buck unpubl.

Ligand production by diatom communities

$eL_1 = L_1 - Fe$



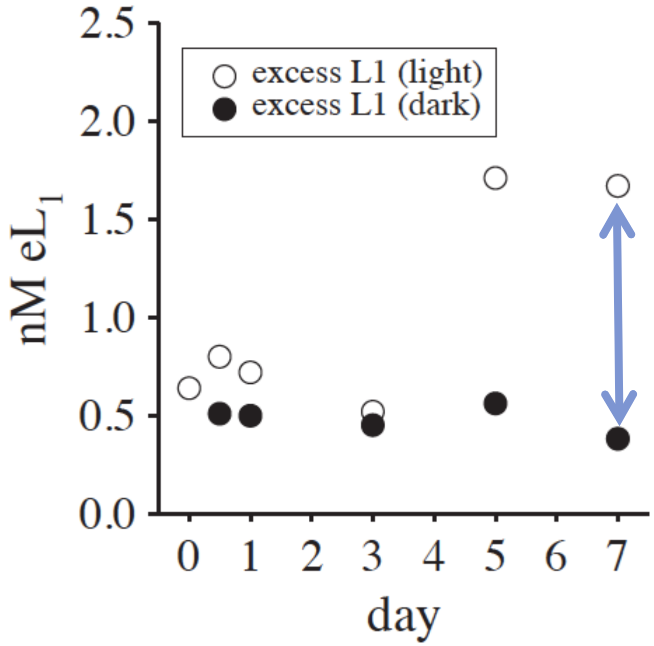


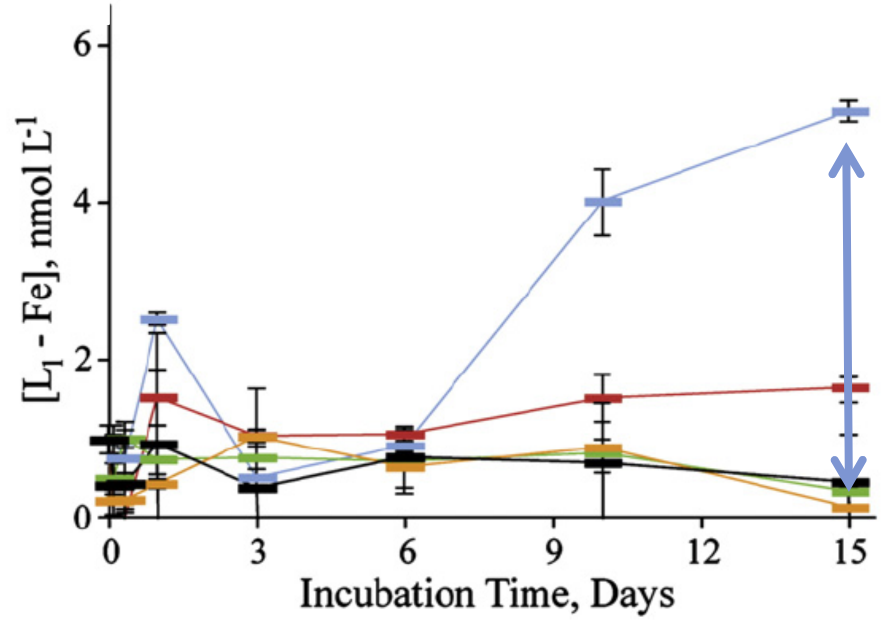
King et al. 2012

Buck et al. 2010

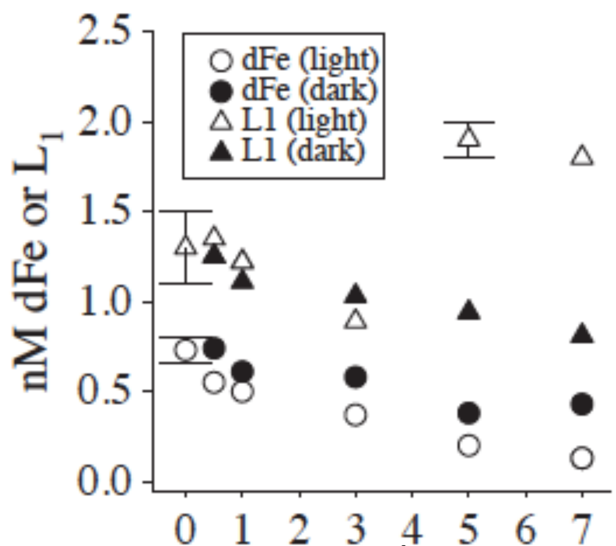
Ligand production by diatom communities

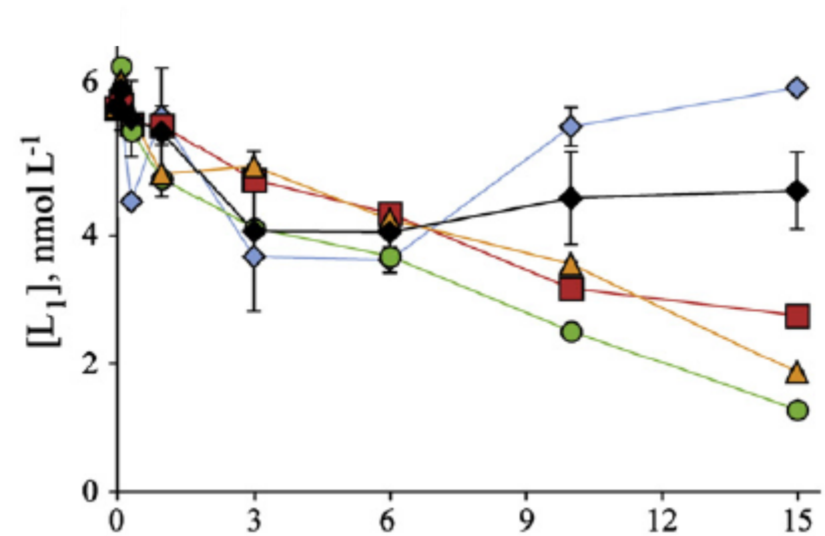
$eL_1 = L_1 - Fe$





total ligand, $[L_1]$



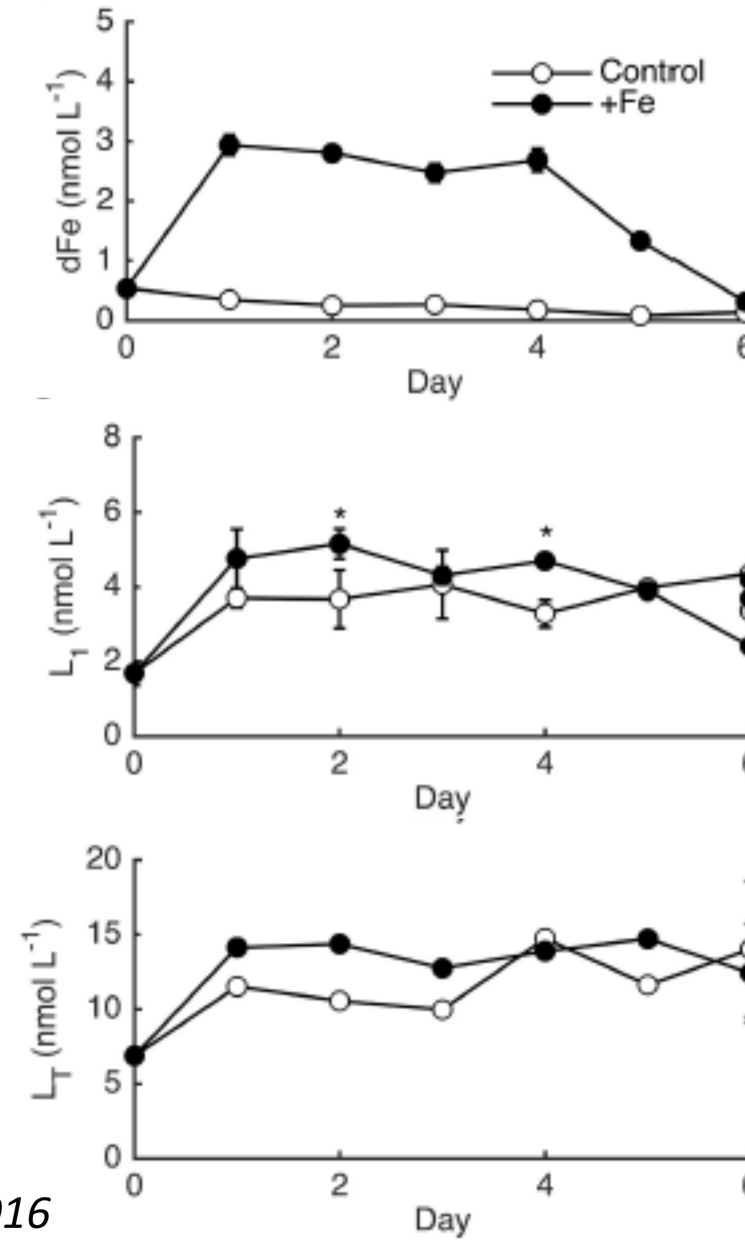


King et al. 2012

Buck et al. 2010

Ligand production by diatom communities

and/or ligand release with uptake of DFe?



Bundy et al. 2016

Moving Forward

- What is FeL? Is all DFe organically complexed?
  - Inert (to CLE-AdCSV) Fe phases, Biogenic Fe
  - Do diatoms produce L_1 and/or is it bacteria? Trigger?
  - What happens to L with FeL acquisition?
- Where does the free ion model apply?
  - Contributions of Fe′ vs. FeL
  - Toxicity vs. limitation modes of Cu bioavailability
  - Is there meaningful Cu(I) in the (surface) ocean?
- Ligand class distinctions; do weaker L matter?
- What leads to eL_1 loss?

The End