COST Action 735 Workshop on

"Iron Bioavailability in the Surface Ocean"

IFM-GEOMAR, Kiel, Germany, 1-2 February 2010

Workshop Summary and Report
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The meeting was attended by 36 people from 9 countries, with 22 of those attending being supported directly by COST Action 735. The aim of the meeting was to critically examine and discuss the issues associated with iron bioavailability in the surface ocean and to identify the key ocean biogeochemical processes relevant to this. This topic is crucial to our understanding of the role of iron in ocean productivity, not only for the High Nutrient Low Chlorophyll (HNLC) regions which are strongly iron limited, but also in the Tropical oligotrophic gyres where productivity is limited by the availability of fixed nitrogen, and the direct fixation of atmospheric nitrogen by marine organisms may be influenced by iron supply and bioavailability.

The organization of this meeting was undertaken as part of the activities of Working Group I ('Short-lived trace gas production and biological feedbacks') in Cost Action 735. The participants at the meeting were chosen so as to include researchers actively working on aspects of iron bioavailability and to represent a wide range of different disciplines and approaches to this topic. A number of early career scientists were also able to attend the meeting and take part in the discussions.

The meeting agenda (see appendix) was designed around a series of thematic discussion sessions, each focusing on a different aspect of iron biogeochemistry and its relationship to the question of bioavailability. The key questions and parameters identified during each session are discussed below:

What is bioavailable iron?

Dr Croot in his introduction to the meeting posed the question, what exactly is bioavailable iron? He further suggested that presently within the marine community we do not have a consistent terminology for its use, as the term is applied to different experimental derived chemical lability measurements (including redox) as well as to biological growth rates. Additionally he pointed out that a standard definition (see below) for bioavailability, as used in pharmacy and medicine, is a rate based measurement and not a concentration as is frequently used in the oceanographic context.

Definition (Wikipedia): *Bioavailability is a measurement of the* ***rate*** *and* ***extent*** *of a therapeutically active drug that reaches the systemic circulation and is available at the site of action. It is denoted by the letter F.*

Finally Dr Croot suggested that as most of the uses of the term "bioavailability" with respect to iron in the ocean relate to equilibrium or thermodynamic analysis and not to rate measurements, that the community look towards rate based measurements for this term and developing common terminologies for the other measurements.

Possible definitions of common terms for iron bioavailabiltiy in the surface ocean

Bioavailable iron – the *concentration* of iron in seawater that is able to be taken up by the biota within the time frame of cell division at optimal growth rates.

Iron Bioavailability – the *rate* at which iron is taken up by the biota

The invited speaker for this theme was Prof. Mark Wells from the University of Maine in the USA and his presentation was entitled: "*Iron Bioavailability: Where are We and Where do we need to Go?*". Prof. Wells had also participated in, and organized, the seminal Bermuda workshop on 'Iron chemistry in seawater and its relationship to phytoplankton" held in May 1994 (Wells et al. 1995), out of which a number of key papers were published in a special issue in Marine Chemistry in 1995. Prof. Wells in his talk chose to examine how far we had progressed since 1994 and highlighted 3 key questions (see below) that were originally posed at the Bermuda workshop (Wells et al. 1995).

What are the chemical speciation and forms of iron among the soluble, colloidal and particulate fractions, including the rates and mechanisms of transformations among these forms?

What are the inter-relationships between the chemical speciation of iron and the microbial community?

How do microbes adapt biochemically and physiologically to Fe availability in the ocean?

In his talk, Prof Wells, gave an overview of recent observations in the field and very kindly shared with the meeting some of his unpublished data from recent work in the North Pacific. In assessing our progress in the field of iron chemistry since the Bermuda meeting, Prof Wells examined the questions arising from that meeting and in turn showed data produced in the intervening time period and the new questions or key issues that had arisen (see below).

Key issues raised in **Bermuda** and the *new questions* arising from subsequent work.

What is the composition and source of the ligands?

The combination of few data and different methods/analytical windows complicate comparisons among ligand data from different sites/studies — Do ligand concentrations really differ among regions?

Are their two main Fe(III) complexing ligand classes controlling Fe speciation in seawater, and if so how do their absolute concentrations and conditional constants differ over spatial and temporal scales?

Do Humic Acids comprise a significant or predominant fraction of the stronger Fe(III) ligand class (vs. siderophores)? If so, how does this affect Fe availability to marine phytoplankton?

Do they exist within the soluble or colloidal organic phase?

Does the partitioning of Fe among colloidal and soluble complexes affect Fe availability?

Can marine phytoplankton survive and flourish by harvesting only inorganic (Fe') from seawater?

Some (most?) marine prokaryotes have the capacity to produce and release siderophores, but do siderophores significantly enhance their Fe uptake in seawater?

New questions arising since Bermuda.

To what extent does iron availability depend upon Cu (or other metal) availability?

Fe(III) and Fe(II) complexing ligands appear to affect Fe redox processes in surface waters - how does this impact Fe bioavailability?

Group discussion then focused on the following:

- Influence of ligands on iron redox cycles – acceleration or retardation of Fe(II) oxidation?
- Possible role of humic substances (Laglera et al. 2007; Laglera and Van Den Berg 2009) in binding Fe in seawater, does this method truly measure humics? Are humic-Fe complexes bioavailable?
- Strong correlations exist between deep water and humic fluorescence in the Pacific (Kitayama et al. 2009; Tani et al. 2003) and between Fe solubility and AOU in the Mauritanian upwelling (Schlosser and Croot 2009). Can Fe solubility in deep waters be parameterized using this approach?
- Zooplankton grazing on phytoplankton releases iron binding ligands (Sato et al. 2007). How important is this pathway for the production of ligands?
- What are the functional groups in L1 and L2? Are there really two ligand classes or are they an artifact of the measurement techniques?
- Are ligands in the colloidal phase? Recent evidence suggests this is the case (Boye et al. 2005; Cullen et al. 2006) and that this size range is critical to understanding the variability in dissolved Fe concentrations (Bergquist et al. 2007). Are these ligands more easily scavenged than those in the soluble phase?
- Do ligands release the Fe? What is the lability of these complexes?
- Role of Cu/Fe coupled system in cells (Maldonado et al. 2006)
- Elevated Fe(II) but still iron limited phytoplankton (Croot et al. 2008; Roy et al. 2008). How can this occur?
- Measurements now exist for known Siderophores in the ocean (Mawji et al. 2008). Is this siderophore Fe bioavailable?
- Are there regional impacts on iron bioavailability?

Iron solubility and bioavailability

Dr Yeala Shaked from Israel was the invited expert for this session and she presented a comprehensive overview of the uptake processes for iron currently identified in marine phytoplankton and bacteria. Dr Shaked showed evidence for a common mechanism by which marine eukaryotic and prokaryotic phytoplankton acquire iron which involves a reduction step mediated by plasma-membrane reductases closely coupled with transport into the cell that facilitate the reductive release of organically bound iron (Shaked et al. 2005; Shaked et al. 2004). This pathway is supported genetically and experimentally and is thought to enable phytoplankton to access the heterogeneous pool of iron complexes in the ocean. The reductive pathway is thought to prevail in open ocean phytoplankton over that of direct siderophore uptake mostly since the former provide a general mechanism for acquiring many Fe complexes while the later is too specific for a dilute solution such as seawater. Dr Shaked's suggestion replaces an earlier paradigm (Hutchins et al. 1999) that prokaryotes acquire siderophore bound iron by specific receptors, while eukaryotes acquire tetrapyrrole iron by reducing it prior to transport.

Discussion on this theme was focused on the following

- If the reductive pathway dominates then the bioavailability of a specific Fe complex is defined by its reducibility. What makes a Fe complex reducible by transmembrane reductases?
- Although organically bound iron is accessible to microorganisms via the reductive pathway, unchelated iron (Fe') is always far more available for uptake (which also include a reduction step). Therefore the chemical lability and rate of Fe' release from a complex are still essential variables determining its bioavailability. Given the importance of Fe' in uptake, photochemical processes that may increase its concentrations (most likely as Fe(II)) are important to evaluate in the ocean.
- Colloidial iron, an important fraction of iron in the ocean has not shown to be directly available for phytoplankton (other than the soluble iron being released from them). Do phytoplankton posses a mechanism for making adsorbed FeOx (more) available?

- Is the conditional log K of iron-organic complexes related to its redox potential and ability to undergo reduction by the cells? Are the functional groups of the ligands or its stereoscopic structure influence its reducibility?
- Are larger cells favoured for processes involving iron uptake by cells via reduction of iron complexes at the cell surface?
- Experiments with phytoplankton are currently designed to minimize the influence of bacteria. Thus the importance of symbiosis between bacteria and phytoplankton may be underestimated – can we design experiments to tackle this issue?

Recycling iron: Photochemistry & Grazing

Two presentations were included in this theme. The first talk was from Dr Kathy Barbeau, an invited expert from the Scripps Institute for Oceanography in the USA. Dr. Barbeau gave an overview of photochemical production of Fe(II) (Barbeau 2006) from siderophores isolated from the marine environment and also included some of her groups recent work on the uptake of Fe from heme compounds which shows how some bacteria can recycle iron (Hopkinson et al. 2008). The second presentation was by Dr Geraldine Sarthou from the University of Brest in France, and she focused on the role of zooplankton grazing on the regeneration of iron from particulate to soluble forms in the ocean.

A lively group discussion session resulted, where the following related topics were discussed:

- The concept of an Fe ratio has recently been applied to ocean studies (Boyd et al. 2005), this is analogous to the f ratio used for nitrogen in the ocean (Eppley and Peterson 1979). Is this a valid approach? Are analogies with the nitrogen cycle useful in this context? N_2 gas is bioavailable to some organisms but is not included in the f ratio concept. Nor is DON included in the f ratio, but the analogous form of Fe is thought to be the most bioavailable form.
- Porphyrin type ligands are they L1 or L2? It appears that the binding strength of Protoporphyrin IX was previously overestimated in earlier studies (Rue and Bruland 1995; Witter et al. 2000), as more recent studies (Schlosser and Croot 2008) indicate that complexation is non-existent or weak at best.

- Viral lysis has been identified as a pathway for Fe regeneration in the laboratory (Gobler et al. 1997), and in the open ocean (Boyd et al. 2005) including iron enrichment experiments (Higgins et al. 2009). However it is unclear how important this pathway is due to uncertainties in viral lysis rates.
- Is there a temperature effect for photochemistry, in particular for ligand to metal charge transfer (LMCT) reactions? Dr. Barbeau presented preliminary data on the marine siderophore Aerobactin (Küpper et al. 2006), which apparently has different Fe(II) yields as a function of temperature.
- The issue of bacteria/phytoplankton synergism was also revisited in light of new work using Vibrioferrin (Amin et al. 2009a; Amin et al. 2009b) that suggests a mutually beneficial exchange between phytoplankton and bacteria.
- Fe(II) ligands – what they could be? Possible candidates include thiols, iron sulfur proteins…or are they really Fe(III) ligands?
- What species of Fe(II) do the FeLume methods (Croot and Laan 2002; Hopkinson and Barbeau 2007; Rose and Waite 2001; Ussher et al. 2005) actually detect? This still seems to be an unknown quantity with important implications for Fe(II) redox (Croot et al. 2007).
- Is the Fe(II) method of Hansard et al. (2009), which involves prior acidification of samples, really measuring Fe(II) or is it better as a proxy for easily reducible (hence bioavailable) Fe?
- Are recycling processes, as we understand them, represented accurately in models?
- What is the importance of sugars and other metabolites in the complexation of iron? While they may be thermodynamically weak they may be important kinetically.
- Different effects from grazers on iron regeneration rates (Barbeau et al. 2001; Barbeau and Moffett 2000; Barbeau et al. 1996; Sarthou et al. 2008; Tovar-Sanchez et al. 2007)
- Do grazers alter the iron redox speciation? Does the passage time through the low pH environment of the stomach or vacuole enough to allow reduction to Fe(II)?
- Remobilization of resuspended sediment particles by grazing – is this important for coastal and shelf regions?

- Impacts of Climate change – what do we really know? It appears that information on the ligands is the critical point as the effects on the inorganic chemistry is reasonably well described (King et al. 1995; Liu and Millero 1999; Liu and Millero 2002; Millero and Sotolongo 1989; Millero et al. 1987; Santana-Casiano et al. 2004; Santana-Casiano et al. 2006).

Bioreporters & Genomes

In this session two presentations were made. Firstly Prof. Julie La Roche (IFM-GEOMAR, Kiel, Germany) gave an overview into the iron acquisition systems currently identified in marine diatoms through genomic approaches and in particular what genes are expressed under iron limitation. The second talk was by the invited expert, Dr Robert McKay (Bowling Green University, USA), who explained the current approaches for using bioreporting organisms as indicators of iron bioavailability in the marine environment. He also explained some of their current limitations and potential for use in the future.

- Can bioreporters give information about assimilation rates? Currently the calibration of bioreporters is done against EDTA buffered solutions and represent concentrations of bioavailable iron not uptake rates.
- Further calibration of bioreporters against non EDTA solutions important.
- Need to develop and encourage measurements of genetic expression as a means to detect bioavailability.
- Choice of environmentally relevant bioreporters, previously they were mostly estuarine cyanobacteria that were used, new developments of open ocean *Synechococcus* cyanobacteria are promising.
- It is important to know how fast do the bioreporter cells react to changes in iron availability and how quickly is the reporter switched on…what is the minimum incubation time for using a bioreporter?
- Efforts to prevent grazing of the bioreporters, the development of the porous underwater chamber (Hassler et al. 2008) may help in this.
- Important to have a built in self-destruction for bioreporter cells in case they are released into the wild.
- Currently most of what we know on iron uptake systems from the marine environment is from comparison with known uptake systems, many of which are from yeasts and terrestrial bacteria and so the possibility of other unknown

uptake systems inherent in marine bacteria and phytoplankton is high. How does *Prochlorococcus* obtain Fe in the open ocean?

Model Parameterizations

The presentation in this theme was a joint one between Dr Alessandro Tagliabule (LSCE, Paris, France), who focused on the current state of iron modelling in Global Climate Models (GCMs), and Dr Christoph Völker (AWI, Bremerhaven, Germany) who explained the situation for higher resolution regional models.

Despite this being the last discussion session during a long day of talks, this session provoked a good exchnage between the modellers and the experimentalists. The key topics of discussion were as follows:

- The relationship between DOC and iron binding ligands observed at DYFAMED (Wagener et al. 2008), allows interesting model experiments to be made. Is this relationship valid? It was proposed recently for iron in the ocean (Hiemstra and Van Riemsdijk 2006) based on the Non- Ideal Competitive Adsorption (NICA) model (Kinniburgh et al. 1999) However the relationship found by using this model is apparently invalidated by the production of high binding strength siderophores.
- Is there a universal relationship between Phytoplankton biomass and iron binding ligands in near surface waters (Gerringa et al. 2006)?
- How is the scavenging of iron represented in models? Is scavenging in surface waters related to bioavailability or to other process? Is Th really a good model for the scavenging of Fe in the ocean?
- How do the modelers tackle the lack of data for some processes?
- Two speed approach to the modeling of iron in the ocean, need to separate the fast and slow reactions – the typical time step in model is 1 hour.
- Very important to have a complete ligand database for iron for use in models and for comparative purposes for those working in the field.
- Property plots of Fe(II)/FeT against FeT is this valid? (Similar arguments have been expressed with regard to the term fractional aerosol solubility)
- Is there a universal relationship between Fe concentration and the ligand concentration (Buck et al. 2007) ? A database would help answer this question.

February 2

Databases, final discussions and outcomes

At the beginning of the final discussion session, Tom Bell (UEA, Norwich, UK) gave a presentation on the role of the SOLAS project office in facilitating project integration and database construction. He presented initial results from Dr Alex Baker's (UEA, Norwich, UK) database for aerosol deposition to the ocean which was highly applicable to current efforts of this meeting. A further short presentation was made by Dr Thibaut Wagener (IFM-GEOMAR, Kiel, Germany) on observations of temporal changes in bioavailability. This presentation was on behalf of Dr Cecile Guieu (CNRS, France) who unfortunately could not attend the meeting.

In the final discussion session the following issues/comments emerged:

- Agreement that a database for iron redox and organic speciation (ligands) needs to be constructed.
- That there could be in the future a database of bioreporter measurements.
- That information on the phytoplankton community structure is also useful for assessing iron bioavailability qualitatively.
- Biologists want a better definition for ligand properties …chemists wish this too but it is not practical…it is most likely misleading to suggest that there are defined structural differences between the ligand classes determined by voltammetry.
- Assimilation rate from radioisotopes/natural isotopes with the oxalate wash methods (Tang and Morel 2006; Tovar-Sanchez et al. 2003).
- There is no way presently to incorporate bioreporter data into GCMs.
- Chemical lability methods as a proxy for bioavailability – differs from the past where strong Fe(III) ligands were used for exchange reactions(Wells 1989; Wells and Mayer 1991). Instead this could now include a reducing component in the assay.
- Importance of including meta-data, PAR or global radiation, biological data collected simultaneously with speciation or concentration data.
- Information on iron quotas important for different phytoplankton species for inclusion in models.

- Is the rate of reduction a good proxy for bioavailability…EDTA media good for concentration based growth rate assessments but does not adequately reflect the natural iron speciation.
- Fe' is a good measure of iron bioavailability…but could include Fe(II) and natural measurements are equilibrium Fe' …underestimation?
- What is the overall importance of siderophores in the ocean?
- The relationship between Fe and other nutrients and trace metals is also important to consider.
- How is the bioavailable iron partitioned into the cell with time under iron limitation? Is it for the photosystem first then for cell division/biomass?
- Seasonal changes in iron solubility may be related to pre-existing seawater conditions. Is the prehistory of the watermass important for interpreting the response?
- More work is yet needed on the interactions between the microbial and phytoplankton communities and their influence on iron solubility and organic speciation.
- Ligand production pathways: How much is from metabolite production or siderophores under iron stress?
- Do we need a definition for iron bioavailability…definition for other nutrients…rate based or concentration based…

Products and outcomes

This meeting proved to be an excellent opportunity for the exchange of ideas and information between the participants. At the end of all the discussions the following outputs were agreed:

➢ An article summarizing the current state of work in bioavailability which synthesizes our present understanding of the processes that effect iron bioavailability in the surface ocean and provide guidelines for future work in order to better link measurements of iron speciation with bioavailability for both field work and ocean models. This article will be submitted to either a normal peer-reviewed journal (e.g. Marine Chemistry) or a peer-reviewed open-access journal (e.g. Biogeosciences discussions). Other articles may also be submitted to the same journal on specific topcis related to the overall theme of the meeting.

- Webpage for iron bioavailability links as a forum for information exchange and for details of upcoming meetings. That already there existed overlaps between existing science programs was identified and such a webpage may help facilitate the links between these programs
- It was reccomended that a database for iron ligand and redox measurements be constructed and could be joined with existing efforts to archive data collected during upcoming GEOTRACES cruises. The chairs of both the international SOLAS and GEOTRACES programs and the related COST Actions 735 and 801 will be informed of this reccomendation (see appendix III).
- Proposal for a joint workshop between this COST Action, 735, and COST Action 801 (GEOTRACES) on issues to do with a central database for metal speciation measurements (see appendix III).
- Student exchanges between laboratories via COST Action 735 STSM should be encouraged. For exchanges where COST funds can not be used, alternative fundins sources should be explored.
- Possiblity of intercalibration experiments for Fe speciaiton at the TENATSO site in Cape Verde. These efforts would complement existing plans within GEOTRACES for shipboard intercalibrations for trace metal speciation.
- Examine the possibility of an ESF meeting/workshop to be held in 2 years time on the subject of trace metal bioavailability.

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Appendix II: ***Workshop Agenda***

February 1, 2010

09:00 *Welcome and general introduction*: **Peter Croot (Germany)**

09:15 *What is bioavailable iron?* **Peter Croot**

09:30 Overview Lecture: *Where are we and where do we need to go?* **Mark Wells (USA)**

10:30 Coffee Break – Informal Discussions

11:00-12:30 **Discussion session – Iron Solubility and bioavailability**

11:00 *Iron Solubility in the Ocean* **Peter Croot**

11:15 *Thoughts on Iron Bioavailability and Uptake* **Yeala Shaked (Israel)**

12:00 Open discussion – Iron Solubility and bioavailability

12:30 Lunch – Informal Discussions

13:30-14:30 **Discussion session – Recycling iron: Photochemistry & Grazing**

13:30 *Recycling iron – Photochemical and biological processes* **Kathy Barbeau (USA)**

14:00 **–** *Fate of Fe during mesozooplankton grazing* **Geraldine Sarthou (France)**

14:30 Open discussion – Recycling iron: Photochemistry & Grazing

15:00 Coffee Break – Informal Discussions

15:30-16:30 **Discussion session – Bioreporters & Genomes**

15:30 *Genomics-Enabled Approaches to Explore Diatom Ecophysiology: Life at low iron concentrations* **Julie La Roche (Germany)**

15:50 – *Whole cell iron reporters: Putting the "Bio" into "Bioavailability"* **Robert McKay (USA)**

16:10 Open discussion – Bioreporters & Genomes

16:30-17:30 **Discussion session – Model Parameterizations**

16:30 Recent insights about iron and consequences for modelling the global iron cycle **Alessandro Tagliabue (France)** and **Christoph Völker (Germany)**

17:00 Open discussion – Model Parameterizations

19:30 Joint Dinner at Restaurant (Kieler Brauerei)

February 2, 2010

09:00 SOLAS Integration: Databases **Tom Bell (UK)**

10:15 Atmospheric/Oceanic controls on bioavailability Cecil Guieu (France)

presented by **Thibaut Wagener (Germany)**

10:30 Coffee Break – Informal Discussions

11:00 **Final Synthesis and Recommendations for Future work Peter Croot**

Appendix III: Email sent to GEOTRACES and SOLAS Chairs regarding Proposal for joint SOLAS-GEOTRACES workshop for metal complexation database

Dear All,
I am emailing you in your role as chair of the international SOLAS or GEOTRACES programs with regard to a proposal for a joint workshop on constructing a database for metal complexation data.

Earlier this week a workshop was held in Kiel on 'Iron bioavailability in the surface ocean', the workshop was funded via the SOLAS related COST Action 735. Participants at the workshop clearly identified that currently the marine science community is missing a comprehensive and complete database for iron speciation measurements (redox and organic) which would be of assistance to both modellers and observationalists. The construction of such as database could be along the lines of the highly successful database for DMS (Kettle et al., 1999) which now allows easy web based access (http://saga.pmel.noaa.gov/dms/). It was acknowledged that efforts were already underway to archive iron speciation measurements (though they are not core parameters) taken on upcoming GEOTRACES cruises to the GEOTRACES database held at BODC, but this may not include historical datasets or non-GEOTRACES work. Thus it is envisaged that a single database for all iron speciation measurements with links to the other datasets from the same cruises would be a useful tool for both the SOLAS and GEOTRACES communities.

Thus the participants of the Kiel meeting proposed that I, in my role as convener of the meeting in Kiel, should email the chairs of the respective programs and chairs of the related COST Actions in Europe to propose a joint database, not only for iron but also for other bioactive metals where data exists (Zn, Co, Cd, Cu etc) and simultaneously to propose a joint workshop between COST Actions 735 and 801 on the construction of such a database. Additional support for such a meeting may be requested from international GEOTRACES or SOLAS to allow more non-European participants to attend.

The full workshop report of the Kiel meeting will be available next week and I will forward it on to you once it is completed.

Thanks for your help in this matter.
Yours sincerely

Dr Peter Croot

Appendix IV:

Reference List:

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