Scientific Report

ESF Exploratory Workshop

The Reactivity of Iron Minerals in Natural Aquatic Systems

5-7 October 2005, Bayreuth, Germany

Organizers:

Dr. Stefan Peiffer (principal applicant)
Professor
Chair of Hydrology, University of Bayreuth
D-95440 Bayreuth
Germany
fon: +49-921-552251
fax: +49-921-552366
e-mail: hydrology@uni-bayreuth.de

Dr. Bo Thamdrup (could not participate in the final workshop)
Associate professor
Institute of Biology
University of Southern Denmark
Campusvej 55, DK-5230 Odense M
Denmark
fon: +45-6550-2477
fax: +45-6593-0457
e-mail: bot@biology.sdu.dk

1. Executive Summary

The workshop was held from October 5th to Oct 7th 2005 at the Science Centre of the University of Bayreuth, Thurnau Castle. It hosted 21 scientists from 11 countries. Two of the participants who originally planned to come had to cancel shortly before the workshop started (Stefan Haderlein, Bo Thamdrup).

The initial motivation of the workshop was to identify common research questions between groups from various scientific disciplines and to evaluate strategies for joint studies that combine the various methodologies. The workshop was divided in a presentation and a discussion section which was used to identify research needs and perspectives.

Major research needs had been identified in two fields.

Molecular-level processes

Understanding processes at the molecular level is crucial to underpinning work at the interface between the bio- and the geosphere. Molecular level studies are needed to generate hypotheses at larger scales and vice versa. They are vital to verify the environmental relevance of processes studied in the laboratory. It is meaningful to use laboratory studies to define boundary conditions with a limited number of variables.

It appeared, however, that it means different things to the different communities. Biology studies at the level of proteins and genes, while the geosciences look at the atomic or subatomic level. Both views are very important and need to be considered in parallel. Critical aims where identified for both disciplines. Ultimately, these studies should be developed to help identify whether a given processes is biotic or abiotic. A unifying theme identified is a better understanding of electron flow to/from iron minerals and the microbe-mineral interface (nano-scale), through mineral assemblages and also through complex microbial communities (e.g. biofilms). Tools have been identified that need to be modified or even developed in order to study these processes.

The connection between surface speciation and transformation processes at mineral/water interfaces is poorly understood. Process knowledge on a molecular level gains the understanding of processes in natural systems. It was regarded a general problem that handling of redox sensitive mineral phases can be critical which suggests a need for mineral characterization facilities in dedicated anaerobic facilities.

Environmental Significance of Iron

Several key questions had been identified as a future scientific focus and extensively discussed:

- The link between iron and the carbon and phosphorus cycles,
- mining and the environment,

- the stability of arsenic in contaminated soils and groundwaters by remediation using Fe,
- the environmental relevance of the reduction of structural bound Fe(III) of non-oxyhydroxides,
- in situ determination of rates of Fe(III)-reduction.

The discussion helped to formulate perspectives for future research initiatives. The participants at the workshop have identified themselves as part of a larger group or European scientists in the field of environmental biogeochemistry and also biotechnology related to the element iron that should be brought together in one of the ESF Instruments to promote science in Europe. An *A La Carte Scientific Programme* appeared to be most promising for the group.

Essentially, the programme as a whole needs to lead to a set of novel, fundamental and quantitative knowledge of a series of processes related to iron biogeochemistry and possible applications to biotechnology.

2. Scientific Content

2. 1 The motivation for the exploratory workshop

The element iron plays a prominent role in the environment. It affects the cycling of elements, nutrients and contaminants through manifold surface and transformation reactions that are due to its various chemical properties:

Iron tends to coordinate as both, ferrous and ferric iron with a large number of complexing agents thereby affecting their redoxchemical properties.

The high coordination affinity of iron ions particularly to water molecules but also to natural organic compounds leads via condensation processes to the formation of colloidal systems that occur in a wide size spectrum from monomeric over polynuclear species to microcrystalline species of high reactivity.

Iron forms a wide number of minerals with varying surface reactivity, which is controlled by the chemical structure of the minerals (incorporation of foreign ions, Fe(II)/Fe(III)-mixed oxides). Various iron minerals have semiconducting properties (pyrite, magnetite), which has important consequences with respect to electron transfer reactions.

Due to the abundance of iron in the geosphere, the qualitative relevance of these properties for material turnover in aquatic systems has attracted attention in various disciplines of the environmental natural sciences. In this ESF workshop the following key questions had been addressed:

By which mechanisms do surface redox interactions between adsorbed Fe(II) and surface Fe(III) groups proceed and what is their role in mineral transformations?

What kind of iron oxide nanoparticles are present in sediments and how abundant are they?

How do microorganisms transfer electrons to ferric oxide ?

How can our knowledge about the rates of redox transformations involving iron in natural environments be improved by profiting from recent progress in spectroscopy, microscopy, and field sampling techniques.

It was the objective of the ESF exploratory workshop to identify common research questions between groups from various scientific disciplines, such as microbiologists, geochemists, spectroscopists, or limnologists, and to evaluate strategies for joint studies that combine the various methodologies. The workshop, at which leading European scientists in the field of iron biogeochemistry had participated, was divided in a presentation and a discussion section which was used to identify research needs and perspectives.

2.2 Research needs –Unresolved scientific questions

2.2.1 Molecular-level processes

Understanding processes at the molecular level is crucial to underpinning work at the interface between the bio- and the geosphere. It appeared, however, that it means different things to the different communities. Biology studies at the level of proteins and genes, while the geosciences look at the atomic or subatomic level. Both views are very important and need to be considered in parallel. The following critical aims where identified:

Geosciences:

- A better understanding of chemical bonding and its effect on reactivity with respect to redox processes, dissolution, nucleation/transformation, and sorption (effect of geometry) is required.
- Recognition of the importance of isotope fractionation. Isotope fractionation is especially important to integrate into research programmes given the critical gaps in our theoretical understanding of Fe mineral transformations. Its knowledge also facilitates characterization of field samples in the laboratory.
- Running molecular-scale experimental and computation (molecular dynamics) programmes in parallel.

Biology

- Better understanding of the diversity of organisms mediating redox transformations of iron (oxidative and reductive). The identification of genes and proteins involved for these transformations is required for (1) mechanistic studies; kinetics, specificity etc. and (2) molecular probes for field related studies (distribution and activity).
- Identification of critical controls on microbial activities (limiting nutrients, role of organics in shuttling/chelating, electron donor requirements, mineralogical constraints).

Ultimately, these studies should be developed to help identify whether a given processes is biotic or abiotic.

A unifying theme identified is a better understanding of electron flow to/from iron minerals and the microbe-mineral interface (nano-scale), through mineral assemblages and also through complex microbial communities (e.g. biofilms).

Tools required

- New molecular biology/ecology tools including genetic markers for the identification of key processes
- Spectroscopic techniques with enhanced sensitivity. Can we monitor in situ surface changes at the molecular scale using synchrotron techniques?

- Analytical tools with improved spatial separation (both in the solid and in the aqueous phase).
- Better control on redox states in experimental systems.
- We need to develop functional probes and techniques to monitor microbial activities.
- What are the best tools we can use to determine Fe speciation in natural environments ?

Upscaling

Molecular level studies are needed to generate hypotheses at larger scales and vice versa. They are vital to verify the environmental relevance of processes studied in the laboratory. It is meaningful to use laboratory studies to define boundary conditions with a limited number of variables (preferably one). Subsequently the derived hypothesis should be tested in the field. Questions arising are:

- Can we link via intermediate scales, such as enrichment cultures?
- What is the role of isotopes for process identification particularly in field studies ?
- Modelling can be a crucial tool for hypothesis generation and testing, e.g. the importance of reactive transport modelling to understand groundwater processes.

Mineral nucleation and transformations

The connection between surface speciation and transformation processes at mineral/water interfaces is poorly understood. Process knowledge on a molecular level gains the understanding of processes in natural systems. Open questions are:

- Kinetics of processes, detailed chemical speciation, impact of surface properties and shape on reactivity, the effect of other elements on transformation (e.g. critical controls of P),
- interactions with natural organic matter, and how it impacts on the processes,
- What controls the reactivity of iron phases ?
- Surface specificity versus bulk mineral properties
- Do conduction bands of ferric oxides serve as electron acceptors (at least at low pH) ?

It is regarded a general problem that handling of redox sensitive mineral phases can be **c**ritical which suggests a need for mineral characterization facilities in dedicated anaerobic facilities. Increased interdisciplinarity in the study of the solids with emphasis on anoxic facilities is required.

2.2.2 Environmental Significance of Iron

Key questions had been identified in selected fields of environmental biogeochemistry:

The link between iron and the carbon and phosphorus cycles

- How is the bioavailability of nutrients and toxic substances affected by their coordination to surfaces of iron minerals ? To what extent are adsorbed reactants available to organisms ? How is biodegradation of organic substances (including pesticides) influenced by sorption to mineral surfaces?
- How is weathering of minerals influenced by organic acids (Mechanisms behind *ligand enhanced dissolution*)

Mining and the environment:

- How is the transformation of secondary Fe minerals affecting the long term attenuation of heavy metals in mining waste leachates ?
- Changes in local structure of sorbed cations and anions during phase transformation

Stability of arsenic in contaminated soils and groundwaters by remediation using of Fe:

- How stable are arsenic containing secondary Fe phases in the long term under different geochemical conditions?
- Adsorbed As vs. As incorporated in the crystal lattice
- Phase transformation/ion diffusion
- Effects of As speciation (As(V), As(III), methylated arsenic, arsenic sulphur species)

Is the reduction of structural bound Fe(III) of non-oxyhydroxides environmentally relevant?

Fe(III) phosphates - open questions

- Why are the Fe(III) phosphates preserved in several environments, although their reduction is thermodynamically more favorable than the reduction of oxyhydroxides?
- What is the potential of authigenic Fe(III) phosphate formation and preservation for removing P from nutrient rich environments?

Fe(III) in clay minerals - Open questions

- Is lattice bound Fe(III) a suitable substrate for iron reducing bacteria in marine sediments and contaminated sites?
- Is it possible to confine the accessibility of the structural Fe(III) for dissimilatory iron reduction regarding the need of electron shuttles and thermodynamic constraints.

- Is microbial mediated reduction of structural Fe(III) indeed relevant for the weathering of silicates and the formation and transformation of clay minerals?
- What determines the reactivity of Fe(II) in the octahedral sheet of smectites?
- Generally: Are (iron-reducing) bacteria capable of reducing the structural Fe(III)? Under which conditions is bacterially mediated reduction of lattice bound Fe(III) important in natural environments?.

In situ determination of rates of Fe(III)-reduction

The development of a method to determine in situ rates of Fe-reduction remains a scientific challenge but is one of the prominent tasks in environmental biogeochemistry.

2.3 Perspective

The participants at the workshop have identified themselves as part of a larger group or European scientists in the field of environmental biogeochemistry and also biotechnology related to the elements iron that should be brought together in one of the ESF Instruments to promote science in Europe. After discussion with the representative of ESF, Prof. Meincke, an *A La Carte Scientific Programme* appeared to be most promising for the group.

The Scientific Programme needs to be divided into maximum 6-7 work packages that in themselves should be highly coordinated and that should each be internally inter- and multidisciplinary. This means they should each combine at least 2-3 subtopics from geochemistry, material sciences, microbiology, genetics, spectroscopy, modelling, mineralogy, hydrology, engineering etc.

Essentially, the Programme as a whole needs to lead us to a set of *novel, fundamental and quantitative* knowledge of a series of processes related to iron biogeochemistry and possible *applications to biotechnology*. Among these worth pursuing are:

- Creation of a systematic database with primary and secondary data pertaining to the physico-chemical properties of inorganic and biogenic iron phases; this would include parameters affecting synthesis, stability, size, shape, aggregation behaviour, speciation, redox, dissolution/ precipitation rates, transformation kinetics, surface properties and binding characteristics; passivation, isotopic tracers/signatures; this is mostly fundamental research to streamline the huge variety in the pertinent data available (i.e., create a coherent and self consistent data base); upscaling issues both in space and time;
- Develop methodologies for in situ, time resolved and nanoscale monitoring and quantification of reactions at lab and field scale; link to pilot and regional scales, water treatment; EU clean water act implications; etc;
- Define novel questions and possible pathways to advance the quantification of the processes, mechanisms, the role, application and use of iron oxides as

scavengers for toxic substances (metals, organics, agricultural products – phosphate, nitrate); this needs to include both fundamental and applied work;

- Quantify and characterize the genera, role and functions, physiology, systems and structural biology of microorganisms in biosynthesis and biotransformation of iron phases in nature and their effect on reactivity; templating functions; link between pure, mixed cultures and natural assemblages; link to sedimentation rates; novel molecular techniques;
- Development and application of diagenetic regional to global scale monitoring combined with modelling to aid forecasting of the behaviour of iron in aquatic sediments; link to diurnal, seasonal and longer time scale effects; link to climate;
- Biotechnology, biomimetics and bio”corrosion”, nanomagnets etc; role/functions, possible applications and markets; links to design and manufacturing etc; here also link to (bio)remediation strategies and technology developments;

All this informations will be merged into a complex and comprehensive model for the global biogeochemistry of iron that will help explain how the iron cycle is working in the modern world and how this has changed through Earth’s history and possible create a predictive tool for the affects and consequences that will happen in the future.

Overall, all these work packages will need:

- Data from in situ experiments with well-controlled and cross-laboratory tested precipitates, bacterial strains etc. ,
- sampling and monitoring tools for short and long term lab and field monitoring,
- modelling efforts from the molecular to the global scale

Deliverables will be

- a self-consistent database aiding with our understanding of abiotic and biotic processes and mechanisms
- a quantitative measure of the important molecular level pathways leading to and affecting the global biogeochemical cycling of Fe.

3 Final Programme

Thursday, Oct 4th		
20:00	Dinner/Ice-Breaker	
Wednesday, Oct 5th		
8:30 - 8:45	Opening Stefan Peiffer	
8:45 – 9:00	Remarks from the ESF (Prof. Jens Meincke, representative of ESF)	
9:00 – 9:45	European research funding (Robert Debusmann, University of Bayreuth)	
9:45 – 10:15	Infrastructure opportunities of the Bayreuth Center of Ecology and Environmental Research (Dr. Thomas Gollan, BayCEER)	
10:15 – 10:45	Coffee break	
10:45 – 11:15	Mössbauer Spectroscopy at the BGI in Bayreuth, European Research Infrastructure: Transnational Access (Dr. Catherine McCammon)	
I Abiotic processes		
11:15 – 11:35	Thilo Behrends	Iron minerals other than iron oxyhydroxides as substrates or products of microbial iron reduction
11:35 - 11:55	Liane G. Benning	Time resolved nucleation, growth and aggregation kinetics of iron based nanoparticles.
11:55 – 12:15	Stefan Haderlein	Redox reactions and phase transformation processes at iron mineral surfaces
12:15 – 12:35	Thomas Hofstetter	How do interactions of structural and surface bound Fe affect surface reactivity of iron minerals
12:35 - 14:00	Lunch break	
14:00 – 14:20	Christian Koch-Bender	Redox reactions of nano-sized iron oxides - The mineral view
14:20 - 14:40	Stefan Peiffer	Can bulk parameters help predict iron mineral surface reactivity towards sulphide ?
14:40 – 15:00	Dieke Postma	Reactivity of iron oxides in sediments and the road towards measurement of

		in situ rates of iron reduction
15:00 – 15:20	Lars Lövgren	Studies of the coordination of ions at the iron oxide/water interface
15:20 – 15:40	José Torrent	Some questions about the origin, concentration, and reactivity of ferrimagnetic Fe oxides in soils
15:40– 16:10	Coffee Break	
16:10 -.17:30	Discussion Abiotic Processes	
19:00 - 20:00	Dinner	
Thursday, Oct 6th.		
II Biotic Processes		
8:40 – 9:00	Frederic Jorand	Role of bacteria in the formation of extracellular green rust or magnetite and reactivity of GR with bacteria.
9:00 – 9:20	Stephan Kraemer	Geochemical mechanisms of biological iron acquisition
9:20 – 9:40	Kirsten Küsel	What do we know about the mechanisms of microorganisms to reduce Fe(III) oxides under acidic and pH neutral conditions?
9:40 – 10:00	John Lloyd	Electron transfer to Fe(III) minerals and its role for biogeochemical cycles.
10:00 – 10:20	Kristina Straub	Relationship of anaerobic Fe(II)-oxidizing bacteria and the Fe(III)-minerals formed
10:20 – 10:40	Katrin Wendt-Potthoff	Fe(III) reduction in sediments with strong pH gradients - laboratory and field measurements
10:40 – 11:10	Coffee Break	
11:10 – 12:30	Discussion Biotic Processes	
12:30 – 14:00	Lunch break	
III Field studies		
14:00 -14:20	Corey (M. Sc.) Archer	Using Fe isotopes as tracers of inorganic redox and microbial Fe reduction processes

14:20 – 14:40	Valentina Parfenova	Microorganisms inhabiting bottom sediments of Lake Baikal that are actively involved in the turnover of iron minerals
14:40 – 15:00	Xavier Châtellier	Monitoring the cycle of iron in soils and streams through laboratory and field experiments.
15:00 – 15:20	Maria Letizia Colarieti	Mechanisms and rates of redox reactions in soil and groundwater involving phenolic compounds and iron oxides
15:20 – 15:40	Coffee Break	
15:40 – 16:10	Yigal Erel	Combining Fe and Pb isotope measurements in order to identify sources and processes in soils and groundwaters which affect mobility and bioavailability of metals
16:10 – 16:30	Jan Wiederhold	Iron isotopes - a new tool to trace the biogeochemical iron cycle in soils
16:30 – 16:50	Gudrun Massmann	Estimation of iron turnover rates in larger-scaled natural systems recharged by bank filtration
16:50 – 17:10	Simon Poulton	Behaviour of iron oxide nanoparticles during transport, sedimentation and early diagenesis and implications for paleoenvironmental reconstruction
17:10 – 19:00	Discussion	
19:30 -	Dinner	
Friday, Oct 7th.		
8:30 – 11:00	Discussion and conclusion, planning of new initiatives	
11:00	Departure	

4 Final List of Participants

Corey Archer (M. Sc.)
Department of Earth Sciences
University of Bristol
Wills Memorial Building
Bristol BS8 1RJ
c.archer@bristol.ac.uk

Dr. Thilo Behrends
Faculty of Geosciences
Department of Earth Sciences, Biogeochemistry
Utrecht University
P.O. box 80021
NL-3508 TA Utrecht
e-mail: behrends@geo.uu.nl

Dr. Liane G. Benning
Earth and Biosphere Institute
School of Earth and Environment
University of Leeds
Leeds LS2 9JT
UK
e-mail: liane@earth.leeds.ac.uk

Dr. Xavier Châtellier
CNRS;
Geosciences Rennes
University of Rennes 1, Campus de Beaulieu,
Batiment 15, Avenue du General Leclerc, 35042 Rennes Cedex, France
Email: xavier.chatellier@univ-rennes1.fr

Dr. Maria Letizia Colarieti,
Dipartimento di Ingegneria Chimica dell'Università "Federico II"
P.le Tecchio 80
I-80125 Napoli
email: colariet@unina.it

Dr. Yigal Erel
Inst. Earth Science
The Hebrew University of Israel
Jerusalem, 91904
Israel
email: yerel@vms.huji.ac.il

Dr. Thomas Hofstetter
EAWAG/ETH
Department W+T
P.O. Box 611
Ueberlandstr. 133
CH-8600 Dübendorf
Switzerland
email: thomas.hofstetter@eawag.ch

Dr Frederic JORAND
LCPME UMR 7564 CNRS-UHP
405, rue de Vandoeuvre
54600 VILLERS
FRANCE
email : jorand@pharma.uhp-nancy.fr

Dr. Stephan Kraemer
Institute of Terrestrial Ecology
ETH SGC Room D12
Grabenstrasse 3
CH-8952 Schlieren
Switzerland
email: kraemer@env.ethz.ch

Dr. Christian Koch-Bender
Department of Natural Sciences
Royal Veterinary & Agricultural University
Thorvaldsensvej 40
DK-1871 Frederiksberg C. - Copenhagen V,
email: cbk@kvl.dk

Dr. Kirsten Küsel
Friedrich-Schiller-Universität Jena
Institut für Ökologie
Carl - Zeiss - Promenade 10
D-07745 Jena
Germany
e-mail: Kirsten.Kuesel@uni-jena.de

Dr. John Lloyd,
University of Manchester, Department of Earth Sciences,
Manchester, M13 9PL, Lancashire,
UK
e-mail: jon.lloyd@man.ac.uk

Dr. Lars Lövgren
Oorganisk kemi
Kemiska institutionen
Umeå universitet
901 87 UMEÅ
Sweden
e-mail: lars.lovgren@chem.umu.se

Dr. Gudrun Massmann
Institut für Geologische Wissenschaften
Fachbereich Geochemie, Hydrogeologie, Mineralogie
Arbeitsgruppe Hydrogeologie'
FU-Berlin
Malteser Str. 74-100, 12249 Berlin
email: massmann@zedat.fu-berlin.de

Prof. Stefan Peiffer
Chair of Hydrology
University of Bayreuth
D-95440 Bayreuth
'el.: ++0049-921-552251
Fax: ++0049-921-552366
E-Mail: s.peiffer@uni-bayreuth.de
www.hydro.uni-bayreuth.de

Prof. Dieke Postma
Institute of Environment & Resources
Technical University of Denmark
Building 115
DK 2800 Kgs Lyngby
DENMARK
e-mail: djp@er.dtu.dk

Simon Poulton, Ph.D.
Associate research professor
Danish Center for Earth System Science
Institute of Biology
University of Southern Denmark
Campusvej 55
DK-5230 Odense M, Denmark.
e-mail: s.poulton@biology.sdu.dk

Dr. Kristina Straub,
Phone: +49-7531-882140
Fachbereich Biologie
Universität Konstanz
Universitaetsstr. 10

D-78457 Konstanz, Germany
e-mail: Kristina.Straub@uni-tuebingen.de

Prof. José Torrent
Escuela Técnica Superior de Ingenieros Agrónomos y Montes.
Universidad de Córdoba
Ed. Celestino Mutis.
Campus Rabanales.
Ctra N-IV Km 396 Apdo 3048
14080 Córdoba
Email: cr1tocaj@uco.es

Dr. Valentina Parfenova
Limnological Institute of Siberian Branch of the Russian Academy of Sciences
Laboratory of Aquatic Microbiology
664033, Irkutsk,
Ulan-Batorskaya, 3,
p.o Box 4199
Russia
e-mail: parf@lin.irk.ru

Dr. Katrin Wendt-Potthoff
UFZ Centre for Environmental Research
Department of Lake Research
Brueckstr. 3a
D-39114 Magdeburg
Tel ++49(391)8109-810
Fax ++49(391)8109-150)
katrin.wendt-potthoff@ufz.de

Jan Wiederhold
Institute of Terrestrial Ecology
ETH SGC Room D12
Grabenstrasse 3
CH-8952 Schlieren
Switzerland
email: wiederhold@env.eth.ch

5 Statistical Information

Gender: 7 female, 15 male

Nations (of institutes): Denmark 3, Germany 5, France 2, Israel 1, Italy 1, Netherlands 1, Russia 1, Spain 1, Sweden 1, Switzerland 3, United Kingdom 3

Age structure: (20 – 30) 1; (30-40) 9; (40-50) 7; (50-60) 5

Mean age 42 years