

**THE FUNCTIONALITY OF IRON MINERALS
IN ENVIRONMENTAL PROCESSES (FIMIN)**

Standing Committee for Life, Earth and Environmental
Sciences (LESC)



Introduction

The European Science Foundation (ESF) is an independent, non-governmental organisation, the members of which are 80 national funding agencies, research-performing agencies, academies and learned societies from 30 countries.

The strength of ESF lies in the influential membership and in its ability to bring together the different domains of European science in order to meet the challenges of the future.

Since its establishment in 1974, ESF, which has its headquarters in Strasbourg with offices in Brussels and Ostend, has assembled a host of organisations that span all disciplines of science, to create a common platform for cross-border cooperation in Europe.

ESF is dedicated to promote collaboration in scientific research, funding of research and science policy across Europe. Through its activities and instruments ESF has made major contributions to science in a global context. The ESF covers the following scientific domains:

- Humanities
- Life, Earth and Environmental Sciences
- Medical Sciences
- Physical and Engineering Sciences
- Social Sciences
- Marine Sciences
- Materials Science
- Nuclear Physics
- Polar Sciences
- Radio Astronomy
- Space Sciences

Iron is the fifth most abundant element in the Earth's crust. It occurs naturally as either ferrous or ferric iron and forms a wide variety of minerals, some of which are highly reactive towards environmental processes. Iron tends to coordinate with a large number of organic and inorganic ligands, and this in turn exerts a strong impact on its redox properties. The relevance of these properties with respect to a wide range of (bio)geochemical processes in aquatic systems has been addressed by various disciplines within the environmental, geochemical and biogeochemical sciences. Such processes are generally related to the surface properties and transformation reactions of iron minerals.

It is impossible to detail here all the major processes in which iron plays a principal role, but some of the environmentally most significant ones that are of direct relevance to this programme are listed below:

- Iron is an important metal cofactor in many redox active and regulatory proteins required for a diverse range of **metabolic processes**.
- Iron species serve as electron acceptors for heterotrophic bacterial growth (e. g. Fe(III) (oxyhydr)oxides) and as electron donors for chemoautotrophic (e. g. pyrite) and photoautotrophic **growth of bacteria and archaea**.
- Efficient iron metabolism is critical for life in many environments, where it is the **limiting nutrient** controlling many biogeochemical cycles.
- Iron is of importance to those interested in the **origin of life**, with iron minerals potentially serving as templates for prototype metabolic reactions, and potential electron donors or acceptors for early respiratory processes.
- Iron forms a wide number of minerals with varying surface reactivities that play a prominent role in **environmental chemistry**, including both natural processes (e.g. adsorption, abiotic reduction during sediment diagenesis) and anthropogenic activities such as water treatment and contaminant degradation in soils and ground water. Furthermore, weathering of iron minerals (particularly pyrite) may lead to severe environmental damage.
- The redox chemistry of iron during sediment diagenesis is strongly linked to the **global carbon and sulphur cycles** and may drive CO₂ storage in sediments. It has hence played an important role in governing the chemical state of the Earth's surface in both the modern environment and throughout geological time.

Our understanding of the chemical and biological fundamentals of surface processes and iron mineral transformation reactions is, however, still incomplete. Improvement in our knowledge of the function of this abundant element in biogeochemical cycles is therefore

Cover picture:

Acidic ground water discharge in southern Western Australia leads to precipitation of ferric iron sulfate minerals (Jarosite). Courtesy of S. Peiffer

Aims and Objectives

a goal in many scientific disciplines. Moreover, FIMIN will significantly contribute to obtaining a better understanding of processes that are crucial to human and societal development such as the supply of clean water, remediation of contaminated sites or the regulation of CO₂ emissions. It therefore appears that the time is ripe to formulate a cross-disciplinary approach to understanding the role of iron in the environment and to make the ensuing knowledge, expertise and relevant instrumentation available to researchers throughout Europe. This Research Networking Programme addresses this need through an intensive training and education programme.

The running period of the ESF Research Networking Programme FIMIN is four years from May 2009 to May 2013.



The FIMIN logo

FIMIN relies and builds on existing national and international projects and initiatives, such as those in which several members of the Steering Committee already participate. As these activities tend to have narrow and specific research goals they are often limited to a specific discipline, and all are restricted by a tight schedule. Therefore, the Research Networking Programme will allow scientists interested in evaluating the role and use of iron in the environment to adopt a truly **multidisciplinary approach** in Europe in order to address major open questions of global significance in this field.

The ultimate goal of the project is to **elucidate the functionality of iron minerals**. Cycling of electrons and matter through iron minerals is of relevance to contrasting disciplines in the environmental sciences, including geochemistry, biogeochemistry, microbiology, soil and hydrological sciences, and biotechnology. FIMIN therefore aims to:

- improve our understanding of the surface reactivity of iron minerals from a mechanistic point of view,
- understand the mechanisms and strategies that microorganisms adopt to cope with surface chemical constraints,
- integrate this knowledge into the modelling and quantification of electron fluxes in natural systems,
- develop sound strategies to make use of the functionality of iron minerals in (bio)technological applications.

In order to meet these goals FIMIN strive to integrate scientists working on a **variety of scales** (e.g. from molecular geochemistry, through reactor dimension and catchment size to the global scale), using **different methods** (e.g. spectroscopy, geochemical techniques, stable isotope techniques, molecular biology, microbiology, field techniques and modelling) and investigating **different environmental systems** (e.g. soils, sediments, waters and remediation systems). FIMIN will allow the science community in Europe to identify and to innovatively address cross-disciplinary research problems, the investigation of which is beyond the scope of individual isolated projects. Primarily, FIMIN will further promote and facilitate:

- (a) exchange of knowledge and materials (microbes, cultivation techniques, reference minerals or preparation procedures), and
- (b) access to and support of analytical equipment and potential study sites.

The following initiatives will serve to stimulate mutual learning within the programme:

- providing a platform for European researchers of different disciplines to promote and integrate various concepts and techniques related to the understanding of the functionality of iron in natural and anthropogenic processes,

- facilitating exchange of know-how and materials (microbes, cultivation techniques, reference minerals or preparation procedure),
- initiating new research activities that use state-of-the-art techniques and technologies for studying the role of iron in environmental (bio)geochemistry.
- providing means, including exchange visits, conferences, workshops, summer schools, common databases and an interactive webpage, for the development and promotion of common approaches for studying chemical and biological processes related to iron species in environmental systems,
- enabling access to and support with analytical equipment or interesting field sites,
- providing opportunities for training young investigators in the latest advances in relevant techniques, such as spectroscopy and molecular biology.

FIMIN will develop mainly along the following research themes:

Theme 1: The role of iron oxide surfaces in biogeochemistry

The surfaces of iron minerals are known to mediate a number of biogeochemical reactions. Adsorption of a reactive species can alter the coordination sphere of a surface-bound species through bond weakening, which is in many reactions mediated by electron transfer processes. As a consequence Fe^{2+} detaches and is being released into the solution. Recent findings suggest that Fe^{2+} interferes with the bulk mineral to generate new and potentially highly reactive mineral phases at the surface, the mechanisms of which are completely unknown. Understanding the role of Fe^{2+} at iron oxide surfaces is therefore a key to understanding the biogeochemistry of iron.

Based on the currently available experimental data and observations made both in well-defined systems and in the field, several knowledge gaps are evident regarding the nature and dynamics of electron transfer processes at iron mineral surfaces:

- The mineralogy of iron mineral phases formed from reduction of Fe(III) and oxidation of Fe(II) on minerals by various reactants are not well characterised.
- The geochemical controls on the mineral formation and evolution are not well understood.
- The natures of surface properties, how surface chemistry changes, transient intermediate phases, and steady-state endpoints are unknown.

^{57}Fe Mössbauer spectroscopy has turned out to be a powerful tool in studying these questions. It allows the direct observation of the chemical nature of ^{57}Fe atoms without disturbing the geochemical environment of the sample. Of all Fe isotopes, Mössbauer is sensitive only

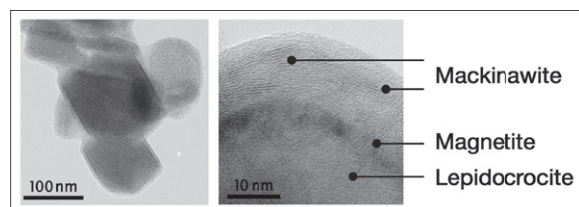


Figure 1. Transmission electron microscopy images of lepidocrocite after 2 hours of reaction with sulphide at pH 7. A layer has formed around the particles (left). Electron diffraction demonstrates that the phases formed on the surface are mackinawite (FeS) with some magnetite/maghemite (dark spots) between mackinawite and lepidocrocite. These images provide insight into the mechanisms and product formation of a surface reaction. They demonstrate that sulphide is rapidly bound to the surface of an iron oxide to form a new phase (Hellige, Pollok, and Peiffer, unpublished results, images taken by K. Pollok, Bavarian Geoinstitute, Bayreuth University).

to ^{57}Fe and invisible to other Fe isotopes. Mössbauer spectroscopy offers also other practical advantages including the preservation of wet, anoxic conditions and sensitivity to adsorbed, amorphous, and particulate Fe forms without any sample matrix effects.

Research Theme 1 supports activities aimed at unravelling biogeochemical processes at the mineral surfaces of iron oxide minerals.

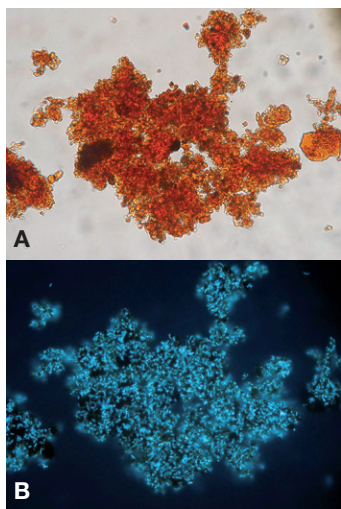


Figure 2. Microscope pictures of iron oxide aggregates retrieved from laboratory incubation experiments. Picture A shows iron oxide aggregates in bright field mode. In picture B, bacteria bacteria were stained with a dye and become visible in fluorescence mode. These pictures illustrate the intimate connection between iron minerals and microorganisms. (T. Behrends, Utrecht University, unpublished images)

Theme 2: Iron as a key redox species in microbiological processes

A connection between microbial activity and redox transformations of iron was postulated by C.G. Ehrenberg more than 170 years ago based on his microscopic studies of bog iron ores. However, only in the recent decades has the relevance of microbial transformations for the cycling of iron in nature become increasingly evident. Thanks to the development of new cultivation methods it became possible to isolate iron-oxidising or -reducing bacteria and to study their metabolic capabilities. Enormous progress in molecular biology provided new insight into the complex microbial ecology of microorganisms involved in iron cycling. However, this development is still ongoing and many questions regarding the microbial role in the iron cycle in natural environments still remain open. For example, the quantitative significance of microbial mediated iron transformations is still unclear because microbial processes often compete with abiotic reactions and their individual contributions are difficult to separate. It appears that many species use naturally occurring organic redox shuttles, e.g., humic acids for transfer of electrons to the iron oxide surface, the kinetics of which are not well understood nor are the thermodynamics. It appears that both the redox potential of the bulk mineral and also the particle size

regulate the extent of such mechanisms. Moreover, passivation of the surface by dissolved organic matter or inorganic species may interfere with electron shuttling processes. Also our understanding of the diversity of microorganisms contributing to iron transformations in natural environments is still in its infancy and linking microbial community structure with its functionality still needs to be resolved.

Identification of biogeochemical processes in sedimentary or soil samples can be performed by measuring stable isotopes ratios of Fe. Some of the largest fractionations in the isotopic composition of iron occur between oxidised and reduced forms. Because biochemistry involves changes in redox state, this fractionation process has been a major motivation for developing this isotopic system as a means for tracing biogeochemical phenomena. In environments that contain iron in both oxidation states, the oxidised form is generally enriched in the heavy isotopes at the order of several parts per mil (‰) at room temperature.

Research Theme 2 supports activities aimed at improving our knowledge about the role of microorganisms in the natural iron cycle.

Theme 3: Environmental biogeochemistry of iron

Iron oxide and oxyhydroxide minerals in the environment are important sorbents for many trace metals (e.g., Cu, Pb, Zn) and metalloids (As, Sb). They strongly influence trace element mobility, bioavailability, and cycling in terrestrial and aquatic systems. Due to its extremely large surface area, poorly crystalline Fe(III) minerals are of particular importance. For example, the schwertmannite, a ferric hydroxyl sulphate mineral that is commonly formed in environments affected by acid mine drainage, can retain significant fractions of the metals and metalloids released by sulphide oxidation in these systems.



Figure 3. Secondary Fe(III) minerals formed by oxidation of ferrous iron present in ground water discharging from a deposit of mining waste (Courtesy of L. Lövgren, University of Umeå).

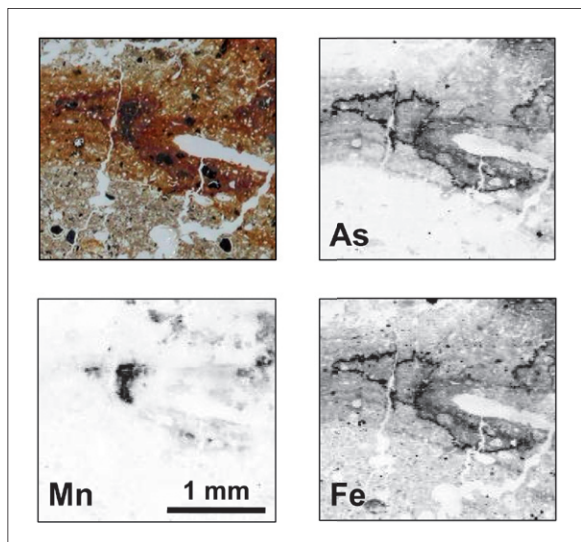


Figure 4. Distribution of As, Fe, and Mn around a root channel in a contaminated river floodplain soil (from Voegelin et al., 2007: *Geochim. Cosmochim. Acta* 71: 5804-5820). The light microscope image (upper left panel) shows the Fe-enriched zone around the root channel. Arsenic is closely associated with Fe near the root channel (upper and lower right panels). The highest concentrations are observed in a rim at some distance from the channel surface. A large Mn-concretion is located close to the root channel, but it is not enriched in As (lower left panel). In the element maps, dark grey tones indicate high concentrations and light grey tones low concentrations (Courtesy of R. Kretschmar).

Figure 4 illustrates the close association of arsenic with iron in a contaminated river floodplain soil. When the soil is oxic, arsenic is present mainly as As(V) sorbed to poorly crystalline Fe(III) hydroxides. Prolonged flooding, however, induces anoxic conditions favouring microbial reduction and dissolution of Fe(III) hydroxides, reduction of As(V) to As(III), and release of Fe(II) and As(III) into pore water. Understanding the processes governing the kinetics of microbial iron and arsenic reduction and release in soils and sediments are currently active research fields in environmental biogeochemistry.

Research Theme 3 supports activities aimed at understanding the role of iron (bio)geochemistry in the behaviour and cycling of essential or potentially toxic trace elements and metalloids in the environment.

Theme 4: Techniques to identify processes related to the biogeochemistry of iron

For assessing the functions of iron minerals in biogeochemical processes it is important to identify the mineral species and to understand its physical and chemical properties. Several iron oxide and oxyhydroxide, as well as sulphide species have similar structures and little

compositional differences. In addition, these minerals are typically nanocrystalline, making their proper characterisation difficult.

Several microscopic and spectroscopic techniques are available for characterising iron mineralogy and morphology. Atomic force microscopy may be used for observing structural changes of individual iron crystals during Fe redox reactions. Synchrotron-based spectroscopic techniques (e.g., XAFS, XANES) potentially offer highly resolved mineralogy information. Electron microscopy (SEM and TEM) provides imaging capabilities for evaluating changes in particle morphology and estimating particle sizes. Transmission electron microscopy is uniquely suitable for studying the properties of nanocrystalline iron minerals, since it includes a combination of imaging, diffraction, and spectroscopic techniques. In combination with high-resolution images, electron diffraction can be used for identifying the structures of the iron minerals. Energy-dispersive X-ray spectrometry and electron energy-loss spectroscopy are used for quantitative analyses of individual nanoparticles. Advanced TEM techniques include off-axis electron holography that can be used to quantitatively measure the magnetic moments and to study the magnetic microstructures of both individual particles and their assemblages.

Research Theme 4 supports activities aimed at disseminating existing knowledge on how to identify and characterise nanocrystalline iron minerals. In addition, we aim at developing new procedures and applying advanced TEM techniques for the study of magnetic properties and atomic-scale compositional and structural features of iron minerals.

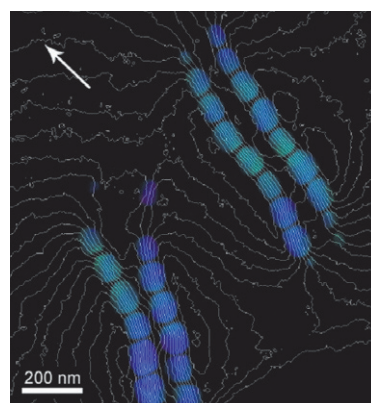


Figure 5. Magnetic phase contours measured using electron holography from two pairs of bacterial magnetite chains, after magnetising the sample parallel and antiparallel to the direction of the white arrow. The colours show the direction of the magnetic induction according to the colour wheel. The uniform blue colour and the parallel direction of the contours indicate that all crystals are magnetic single domains and are magnetised parallel to the chain axis (Courtesy of M. Pósfai, University of Pannonia).

Planned Activities

FIMIN will organise and/or support several activities addressing one or more of the above research themes:

- Several **scientific workshops** will be organised or supported for the four-year period, focusing on specific FIMIN research topics:
 - 25 May-9 June 2010, Lund, Sweden, Lyngby and Copenhagen, Denmark: Magnetic methods in biogeochemistry – from field to microscopy and Mössbauer spectroscopy
 - 7-11 August 2011, Tübingen, Germany: Advanced tools in environmental biogeochemistry – Opportunities and limitations
 - 2011, United Kingdom: Environmental iron microbiology
 - 2011/2012, Austria: The use of stable isotopes of Fe in environmental and biogeochemistry
- **Winter school** (7-11 March 2011, Cordoba, Spain): Iron in the environment: from nature to the laboratory
This five-day school is set up for junior researchers (PhD students, post-docs) who are interested in the nature and dynamics of iron and iron minerals in natural environments. It will deal with iron in soils, sediments, surface and ground water, and geological systems. Reviews on iron minerals and their environmental significance, as well as on the principles and the state-of-the-art of analytical techniques will be presented.
- Long- and short-term **exchange grants** are provided for researchers to visit institutions in other participating countries in order to foster the exchange of knowledge at the European level. Calls for grants are opened three times a year, with application deadlines on 1 October, 1 February and 1 June of each year.

All scientists actively focusing on any of the FIMIN research themes are encouraged to apply. Applications will be selected according to scientific excellence and in agreement with ESF priority rules (see 'Guidelines for Management of ESF Research Networking Programmes', www.esf.org/RNP-guidelines).

For more and up-to-date information please visit the FIMIN websites. Here you may subscribe to the FIMIN mailing list to keep informed about calls and events: www.fimin.eu and www.esf.org/fimin.

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