A

Scientific Report

on

The Functionality of Iron Minerals in Environmental Processes (FIMIN)

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Submitted by

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Purpose of the visit

The FIMIN 2010 was aimed to improve our understanding about the functionality of iron minerals and to be acquainted with different instrumental applications for the quantitative and qualitative characterization of different Fe minerals that occur in the natural environment as well as those that are prepared in the laboratory.

Work performed:

FIMIN workshop started on May 26th 2010 for 14 days until 8th June 2010 with an introductory series of presentation of all participants about their research work and the methods employed and their expected outcome from this workshop. The next day was a one-day field trip to one of the farmlands of the Viking in Roskilde in Denmark, which was leaded by Prof. Christian Bender Koch (University of Copenhagen, Department of Basic Sciences and Environment/Soil and Environmental Chemistry) and Prof. Bo Thamdrup (Institute of Biology, University of Southern Denmark). Prof. Koch started with a brief description about that area and the geochemistry of the land. Later we took sediment samples from a creek, which is continuously flowing from an iron rich lake nearby using a piston sampler. The ferrous content of the pore water sample was measured onsite using ferrozine estimation. Different strata of the soil near to the lake was taken vertically to see the changes in the predominant terminal electron acceptors like $Fe(III)$, $Mn(IV)$, SO_4^{2-}, CH_4 (redox potential) at different depths.

The lecture series and practical sessions started on the next day with Mössbauer spectrum data interpretation. The technique of Mössbauer spectroscopy is widely used in mineralogy to examine the valence state of iron, which is found in nature as Fe^0 (metal), Fe^{2+}, and Fe^{3+}, as well as the type of coordination polyhedron occupied by iron atoms (trigonal, tetrahedral, octahedral, etc.). Mössbauer spectroscopy is also used to assist in the identification of Fe oxide phases based on their magnetic properties. Prof. Koch had given us an introduction about the basics and the sample preparation for Mössbauer analysis. He explained us how does it works, and what it is used for. Samples that had been brought by the participants were measured on these days after calibrating the instrument using 12-micron thickness α-iron foil. Data analysis and interpretation were been performed using software called m-fit and proceeded with fitting the spectrum of the unknown samples against the calibration standard.

After the Mössbauer studies, we moved to the Centre for Electron Nanoscopy (CEN) at Danish technical University, Lyngby, Denmark and started with a short introduction about the history, equipments and facilities available at CEN by Prof. Rafal Dunin-Borkowski (CEN). Prof.Mihaly Posfai (Department of Earth and Environmental Sciences, University of Pannonia) did a presentation about electron microscopy.

Further, there were lectures about scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution- transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction studies, electron tomography, and electron holography. Demonstrations of each instrument also had been done after each session corresponding to the lectures about each instrument. Detailed description of the sample preparation for each instrument was also discussed by the in-charges of the instruments. We did the sample preparation for various samples for SEM and TEM.

Lectures about environmental magnetism was given by Prof. Ann Hirt from Institute for Geophysics, ETH, Zurich She started with the introductory lectures about different types of magnetisms, and further moved onto the different ways for measuring the magnetism of environmental samples such as magnetic susceptibility, induced remanent magnetization (IRM's), anhysteretic remanent magnetizations (ARM's) etc.

Prof. Ian Snowball from the Paleomagnetic and Mineral Magnetic Laboratory in Centre for quaternary sciences, Lund University showed us the different ways for measuring both natural and artificially induced magnetizations. Demonstrations for superconducting rock magnetometer which has automatic alternating field demagnetization coils (max. 250 mT) with an inbuilt direct current coil for producing anhysteretic remanent magnetizations (ARM's), an in-house built magnetic susceptibility core conveyor coupled to a surface scanner and KLY-2 Kappa bridge for measuring the temperature dependence of magnetic susceptibility were also done.

Induced remanent magnetization was measured for two samples that have been already analyzed by Mössbauer spectroscopy using an alternating gradient magnetometer by measuring room temperature magnetic hysteresis properties and time dependent magnetizations.

Results

Mössbauer spectroscopy

A Mössbauer spectrum is a plot of the transmission of the γ-rays against the velocity of the source; movement of the source (^{57}Co) ensures that the nuclear environments of the absorber and the source will match at certain velocities (i.e. at certain energies). If a static magnetic field acts on the resonant nuclei, the six allowed transitions takes place that gives rise to a 6-line spectrum (sextet). In the absence of the magnetic field, it gives either one (singlet) or two (doublet) absorption maxima. The spectra is interpreted using the magnetic hyperfine field (B_{hf} in Tesla) which provide information about the valence and

magnetic properties of the compound, isomer shift (δ) which is the displacement of the spectrum expressed as the velocity of the source (mms^{-1}) to counteract with the displacement and quadrapole splitting which provide information about the site distortion when an electric field acts on the nucleus.

Data analysis and interpretation has been done for four iron minerals synthesized in the laboratory such as 2 line ferrihydrite, 6-line ferrihydrite, goethite and hematite. Mössbauer analysis was performed at room temperature with 512 numbers of channels in the memory and a velocity increment of 0.09203mm/s/channel using a constant acceleration spectrometer and a source of ^{57}Co in Rh. The spectrometer was calibrated using a 12.5 μm foil of alpha Fe at room temperature and all isomer shifts are given with respect to that of a-Fe at room temperature. Pearson chi squared (χ^2) fitting function is used to test the fitting and the value of χ^2 should not exceed greater than 1; as relaxation is possible in certain cases.

Sample.1- This sample was goethite synthesized in the laboratory according to the protocol of Schwertmann and Cornell (2000). The Mössbauer spectra (fig.1) displayed a characteristic asymmetric broadened line of sextet. It might be due the distribution of the B_{hf} (magnetic hyperfine field) owing to the poor crystallinity of the samples. The isomer shift of 0.37 mms^{-1} and a quadrapole splitting of -0.26 mms^{-1} confirmed that the sample was goethite when compared with the RT spectrum data of iron oxides according to Schwertmann and Cornell (2003).
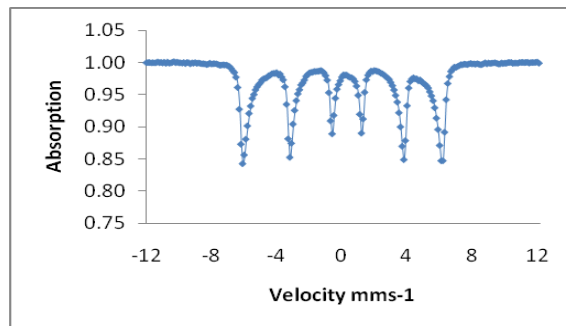

Fig.1. Mössbauer spectra for sample 1(Goethite) at 298 K

Sample 2- This was expected to be hematite (fig.2). After fitting with m-fit program, Mössbauer parameters with a B_{hf} of 51.7 T, isomer shift of 0.375 mms^{-1} and a quadrapole splitting of 0.2 mms^{-1} confirmed the sample is hematite as it has a sextet at room temperature. As the spectrum fits symmetrically it was also clear that it has bigger particles as the smaller particles often leads to shifts in uncertainties in the spectrum. The spectrum was less sensitive to impurities and poor crystalline effects

than that of goethite because hematite has a high Néel temperature. The sextet spectra revealed that it was well crystalline. Full hyperfine six-line pattern is shown only by samples of a large particle size. As the particle size is unknown, SEM and X-ray diffraction measurements were recommended.
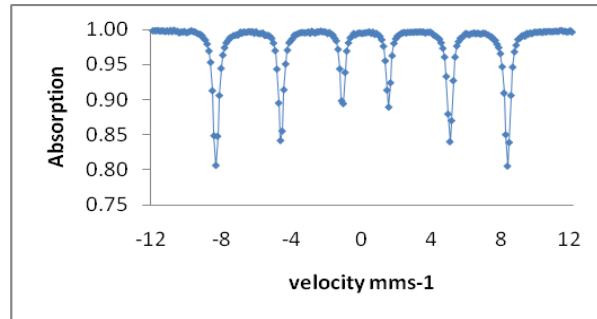
Fig.2 Mössbauer spectra for sample 2(Hematite) at 298 K

Sample 3- At room temperature, Mössbauer spectra of this sample has a doublet (fig 3) showing the hyperfine parameters with isomer shift of 0.34 mms^{-1}, a value that is typical for octahedrally coordinated high spin Fe^{3+} and a quadrapole splitting of 1.4 mms^{-1}. As it is not a straight forward interpretation of the mineral from the parameters obtained using the RT parameters for the iron oxides from Schwertmann and Cornell (2003), it should be more relevant to look into the different phases present in the sample by referring to the already reported data of allowed ^{57}Fe quadrapole splitting-isomer shift combinations for different valence states and coordination from Murad and Cashion (2004). It was shown that the sample consists of a mixture of [4] Fe^{3+}, [5] Fe^{3+}, and [6] Fe^{3+}.
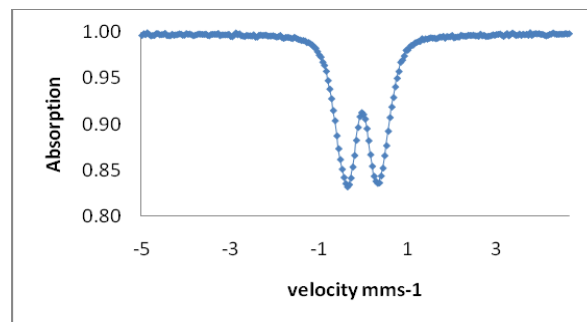
Fig.3 Mössbauer spectra for sample 3(2-Line Ferrihydrite) at 298 K

So with the sample 3 , 2-Line ferrihydrite as expected, the spectra showed that there can be mismatches in the lattice structure.

Sample 4- The magnetic hyperfine field parameters are 0.35 mms^{-1} as isomer shift and 1.3 mms^{-1} as quadrapole splitting for a doublet (fig.4). As there was no comparible results from the defined parameters for iron oxides, valence states and coordination number of the phases present were studied. This sample also shown to be a mixture of.Fe in different coordination such as [4] Fe^{3+}, [5] Fe^{3+}, and [6] Fe^{3+} than as 6-line ferrihydrite as expected.
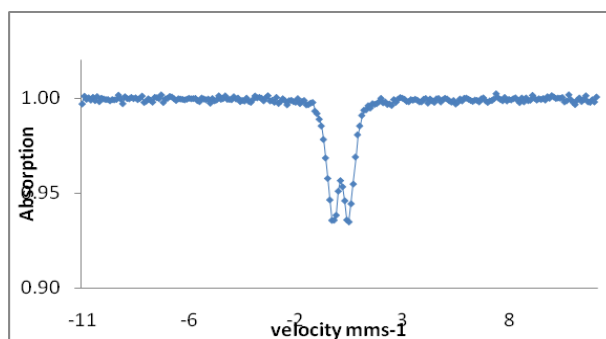

Fig.4 Mössbauer spectra for sample 4(6-Line Ferrihydrite) at 298 K

Mössbauer spectra analysis of synthetic and natural ferrihydrites varies considerably due to the variation in the crystallinity. The magnetic ordering takes place at a range of different temperatures between 70 K and 130 K rather than a sharp transition and it is complete between 45 K and 10 K(schwertmann and Cornell 2003).So inorder to get a sharp spectral line for both the samples 3 and 4, it is recommended to go to a low temperature (4.2 K) Mössbauer spectroscopic measurement.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy can obtain physical and chemical information about the surface of any sample -large or small - and often without any preparation. The magnification goes from 50 times right up to over 1 million times with a best resolution of less than 2 nm. The vacuum modes provide possibilities for examining a wide range of materials including biological specimens without destructing the sample. Besides imaging, areas and distances or particle sizes also can be measured. The electrons striking the sample produce three types of signal: Secondary-and back scattered electrons and X-rays. Different detectors make it possible to detect these signals. The backscattered electrons give the elemental composition and the X-ray signal gives the total chemical analysis or the position of any single element in the sample.

The FEGSEM is a scanning electron microscope with a Field Emission Gun (FEG) that gives a high resolution giving the possibilities to examine many different types of samples under vacuum, in gas or water vapor. The microscope can operate in as well high- and low vacuum as in environmental mode

Scanning electron microscopy of sample 3(fig.5), 2-line ferrihydrite (as expected) reveals that the sample contains nanoparticles which is unable to see separately even at 1 um scale .It confirmed that a better way of sample preparation has to be done for nanoparticles than using a common method of preparation.
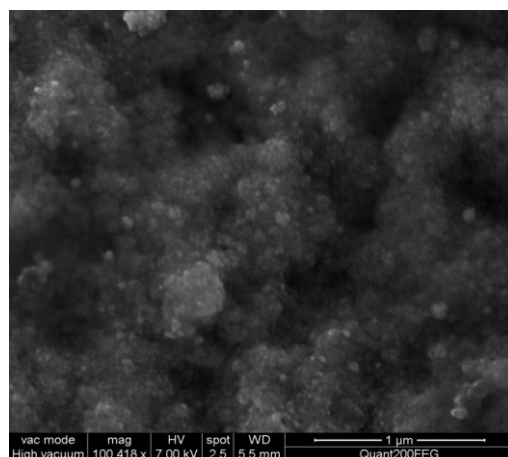

Fig.5, SEM image of sample 3 (2-Line Ferrihydrite) at high vacuum mode showing the aggregates of nanoparticles at a of magnification of 10^5 times.

Future Collaboration

Future collaboration is foreseen with the University of Copenhagen, Denmark for studying the structure and crystallinity of various Fe (III) species present and Fe (II)/Fe (III) species formed in the sediments by Mössbauer spectroscopy.

References

1. Cornell, R.M and Schwertmann, U (2003). The iron oxides: structure, properties, reactions, occurrences and uses. Wiley VCH.
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3. Schwertmann, U and Cornell, R.M (2000). Iron oxides in the laboratory. 2nd ed. Wiley-VCH, Weinheim, Germany.