



## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*<http://193.49.43.2:8080/smis/servlet/UserUtils?start>*

### ***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

Microspectroscopic speciation of iron in soils and soil particles

**Experiment****number:**

ME-944

<b>Beamline:</b> ID 21	<b>Date of experiment:</b> from: 18.2.2005                      to: 23.2.2005	<b>Date of report:</b> 31.8.2005
<b>Shifts:</b> 15	<b>Local contact(s):</b> Diane Eichert	<i>Received at ESRF:</i>

**Names and affiliations of applicants (\* indicates experimentalists):****\*Jörg Prietzel, Lehrstuhl für Bodenkunde, Technische Universitaet Muenchen****\*Jürgen Thieme, Institut für Röntgenphysik, Universitaet Goettingen****\*Karin Eusterhues, Lehrstuhl für Bodenkunde, Technische Universitaet Muenchen****Report:**

Various inorganic and organic Fe-bearing standard substances (Fe(II) and Fe (III) chloride, sulfate, oxalate, etc.), as well as common Fe-bearing minerals in soils and sediments (pyrite, ferrihydrite, goethite, hematite, lepidocrocite, etc.) were investigated with Fe-K edge XANES and X-ray microscopy to specify different natural Fe components. Dilute mixtures of soil typical Fe minerals (pyrite, ferrihydrite, goethite) were analyzed to address the question of whether these phases can be quantified by XANES. This was done by an evaluation of their pre-edge peak, i.e. either by assessing the pre-edge peak centroid energy or using Linear Combination Fitting (LCF).

In the majority of cases the general pre-edge-peak shapes of the Fe K-edge XANES spectra acquired for the standard substances were different and can therefore be used to identify unknown Fe phases in soil and sediment samples. The centroid energies of the pre-edge peaks of the standards were strongly related to their Fe oxidation state. The pre-edge peak centroid energy thus is a valuable parameter for a quick estimation of the Fe(II)/Fe(III) partitioning of an unknown sample. However, the study of the mineral mixtures showed that the relationship between the Fe(II)/Fe(III) ratio and the pre-edge peak centroid energy is not always linear (Fig. 1). In unknown mixtures only a rough assessment, but not a precise determination of the Fe(II)/Fe(III) ratio is possible on the sole basis of their pre-edge peak centroids.

Using Linear Combination Fitting (LCF) the Fe(II)/Fe(III) partitioning and the pyrite/ferrihydrite or pyrite/goethite ratio of mineral mixtures could be predicted with satisfactory accuracy (Table 1). However, LCF failed to correctly distinguish ferrihydrite from goethite. Nonetheless, Fe-K edge XANES combined with a pre-edge peak evaluation using LCF seems to be a powerful tool for a Fe speciation in soils and sediments.

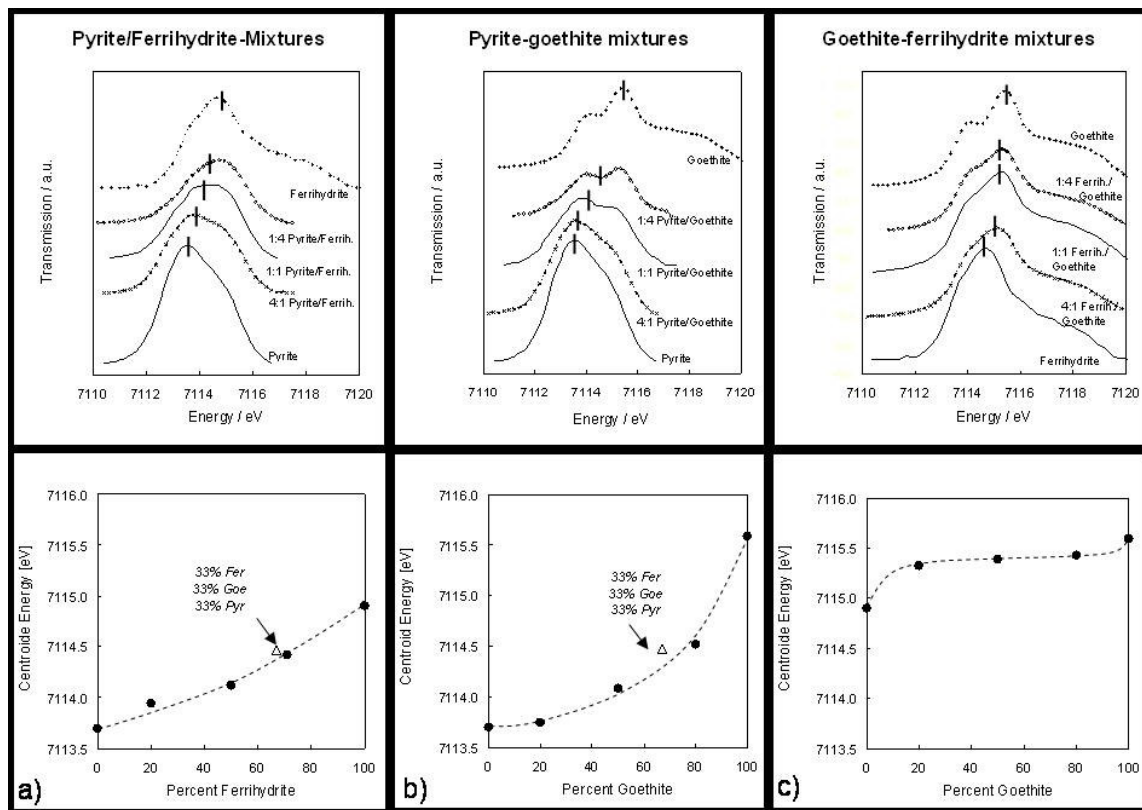


Figure 1: Pre-edge peak spectra for different mixtures of (a) pyrite and ferrihydrite, (b) pyrite and goethite, and (c) goethite and ferrihydrite. Pre-edge peak centroid energies are indicated with a solid bar.

Table 1: Fe(II)/Fe(III) ratios and mineral mixing ratios of defined mixtures of pyrite, ferrihydrite, and goethite estimated from their pre-edge peak centroid energies (CE) and calculated by Linear Combination Fitting (LCF), using the pre-edge peak spectra of the mineral mixtures and the pure minerals.

	Fe(II)/Fe tot	Fe(II)/Fe tot Calculated CE	Fe(II)/Fe tot Calculated LCF	Calculated (LCF) Percentage of		
				Pyrite	Ferrihydrite	Goethite
80% Pyrite / 20% Ferrihydrite	0.80	0.79	0.70	69.6 ± 1.0	25.7 ± 3.3	4.7 ± 3.1
50% Pyrite / 50% Ferrihydrite	0.50	0.65	0.47	46.5 ± 1.8	53.4 ± 5.8	0.0 ± 5.6
29% Pyrite / 71% Ferrihydrite	0.29	0.40	0.26	26.1 ± 2.4	70.9 ± 8.4	2.9 ± 7.9
80% Pyrite / 20% Goethite	0.80	0.97	0.86	85.9 ± 0.5	5.0 ± 1.6	9.2 ± 1.6
50% Pyrite / 50% Goethite	0.50	0.80	0.58	58.2 ± 1.1	5.7 ± 3.7	36.0 ± 3.4
20% Pyrite / 80% Goethite	0.20	0.57	0.31	30.9 ± 2.1	7.6 ± 7.2	61.6 ± 6.9
80% Goethite / 20% Ferrihydrite	0	NA	0	0.0 ± 0.0	23.1 ± 1.5	76.8 ± 1.6
50% Goethite / 50% Ferrihydrite	0	NA	0	0.0 ± 0.0	15.5 ± 1.3	84.6 ± 1.5
20% Goethite / 80% Ferrihydrite	0	NA	0	0.0 ± 0.0	39.9 ± 1.2	60.1 ± 1.4
33% Pyrite / 33% Ferrihydrite / 33% Goethite	0.33	0.50	0.28	28.7 ± 2.5	45.8 ± 7.9	25.4 ± 8.3