

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: Spectromicroscopy studies of adsorbed and mineral forms of sulphur	Experiment number: ME-1267
Beamline: ID 21	Date of experiment: From: 6.4.2006 to: 11.4.2006	Date of report: 28.8.2006
Shifts: 15	Local contact(s): Dr. Murielle Salomé	<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 *Nora Tyufekchieva, Lehrstuhl für Bodenkunde, Technische Universitaet Muenchen		

Report:

In acidic soils, sulphate can be retained by adsorption to pedogenic minerals such as Al and Fe oxyhydroxides and by precipitation of Al or Fe (oxy) hydroxy sulphate minerals, such as jurbanite, basaluminite, alunite, or jarosite (e.g. Nordstrom, 1982). However, the contribution of precipitation and adsorption processes to the physico-chemical retention of sulphate in acid soils with different chemical environment is still unclear and a matter of an ongoing scientific debate (e.g. Wolt et al., 1992; Delfosse et al., 2005). Since both processes are different with respect to (i) their kinetics, (ii) the presence or absence of a SO_4^{2-} retention capacity limit, and (iii) the reversibility of the formation reaction, a correct assessment of the S retention capacity of a soil and a reliable prediction of soil S pool changes under changing environmental conditions requires knowledge about the form in which S is retained in a soil.

Sulphate adsorption occurs on the surfaces of various soil minerals, such as ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4 \text{H}_2\text{O}$), goethite ($\alpha\text{-FeOOH}$), hematite (Fe_2O_3) and gibbsite ($\alpha\text{-Al(OH)}_3$). In contrast to pure, well-crystallized Al and Fe hydroxy sulphate minerals which can be identified by XRD, particularly Al hydroxy sulphate minerals precipitated in soils are often amorphous, and closely associated to other minerals. Thus a direct proof of their existence in soils is almost impossible. In most studies, the presence of Al and Fe hydroxy sulphate minerals in soil environments was concluded on the basis of the ionic composition of the soil solution, using thermodynamic considerations (Nordstrom, 1982), or by comparing the amount of SO_4^{2-} that can be mobilized from the soil with different extractants which had been tested for their ability to dissolve Al hydroxy sulphate minerals (Prietzel and Hirsch, 1998; Delfosse et al., 2005). Hesterberg et al. (1999) showed that phosphate adsorbed to Al and Fe oxyhydroxides can be distinguished from phosphate minerals and precipitated phosphate by P K-edge XANES. Since sulfate and phosphate both are oxyanions and behave similarly in soil systems, it was hypothesized that also sulfate adsorbed to Al and Fe oxyhydroxides in soils could be distinguished from precipitated sulfate by S K-edge XANES.

The S K-edge XANES spectra of different sulfate salts (Fig. 1a) all show one or two distinct post-edge peaks in the 2490-2500 eV region in addition to the white-line at 2482 eV which is indicative for the S(VI) in sulfate. The white-line signal in these compounds generally is about 3 to 4 times stronger than the post-edge signal. The same is true for the Al hydroxy sulfates alunite and basaluminite, and the Fe hydroxy sulfates jarosite and schwertmannite (Fig. 1b). In contrast sulfate adsorbed to gibbsite, goethite, ferrihydrite, and hematite shows only very weak post-edge features, with the signal intensity being less than 10% of that of the white-line peak (Fig. 1c). An investigation of subsoil (B) horizons of various German forest soils with different parent materials and different levels of atmospheric S deposition (Fig. 1d) showed that the sulfate in most soils was adsorbed rather than precipitated sulfate. Precipitated CaSO_4 was detected in the Kyffhäuser soil, whose bedrock is pure gypsum, and in a grain in the soil Eichstätt. For the acid soils Selb, Alzenau, and Waldidylle, which all have been subject to high atmospheric S deposition in recent decades, the sulfate obviously is entirely adsorbed, and Al hydroxy sulfates are not present. Our results show that S K-edge XANES allows to identify adsorbed and precipitated sulfate in soils.

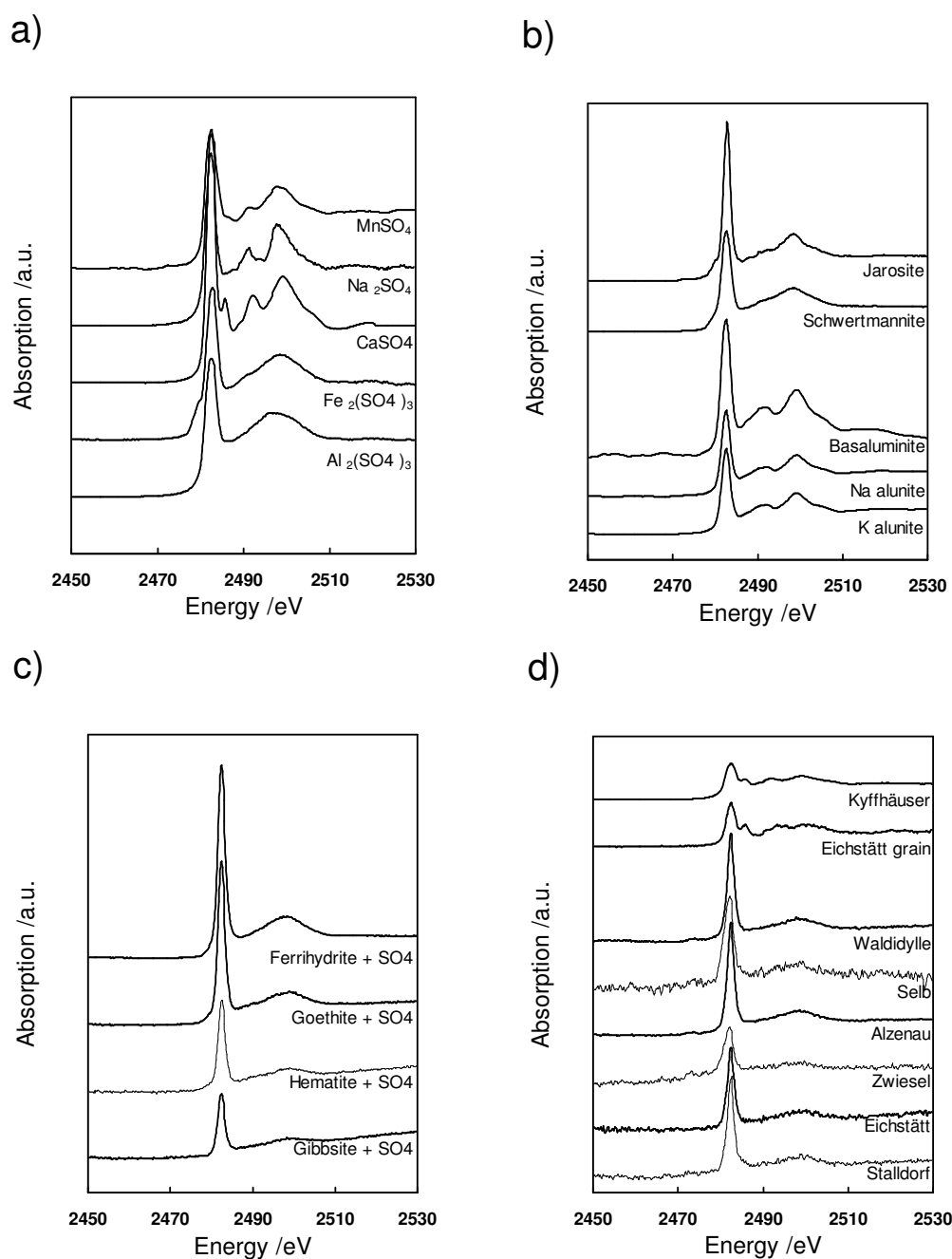


Figure 1: S K-edge spectra of (a) sulfate salts, (b) Al and Fe hydroxy sulfates, (c) sulfate adsorbed to Al and Fe oxyhydroxides, and (d) B and C horizons of soils with different parent material and S deposition.