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ESRF

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.

ESRF	**Experiment title:** "Application of micro-XRF on alpine stalagmites for methodology and palaeoenvironment. "	**Experiment number**: ME-1272:
Beamline:	**Date of experiment**: from: 01/12/05 (8:00 am) to: 06/12/05 (8:00 am)	**Date of report**: 08/2006
Shifts:	**Local contact(s)**: Jean SUSINI	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

The following report includes discussions about :

1. General observations about our first run at the ESRF
2. The problems and solutions linked to the sample preparation
3. Results about FTIR spectroscopy and mapping
4. Results about X ray fluorescence
5. outlooks

1 General observations :

The aim of this experiment was to complete with high resolution element mapping, the petrographic and fluorescence spectroscopy analysis of two stalagmites from the Vercors Massif (SE, France). These two stalagmites (Cho9602 and Be99703) are of great interest for palaeoenvironemental reconstructions. The choice of these two stalagmites had been induced by the global knowledge acquired on these both samples for more than 5 years (U/Th ages, UV emission fluorescence, petrographic characterisation). in our laboratory with the physic laboratory of Lille (Phlam, UMR 8523).

We have obtained 15 shifts on ID 21 which allow the mapping of low molecular weight (MW) elements like Ca, Mg, Fe.

The project was too ambitious regarding the first spectrum. In fact, the very low concentrations of elements in the very concentrated calcite (CaCO3) matrix implied generally very long acquisition times which have required moving sample with the piezo electric translation gears. The result of this problem for detection implied to change our project.

Initially we wanted to scan or map some large part of the sample (about 5 to 10 mm). The time required for each point together with the limits of the sample translation with piezo implied to reduce our will. The time required for testing different sample at the energy of 3.95kev (to avoid the calcium very intense fluorescence) and at 7.2kev to scan the heavier element has spent a large part of our 15 shifts.
This experiment is positive :

- The next project will fit better with the possibility of the ID 21
- The low concentration of the elements (other that calcium) is interesting regarding publication of X ray fluorescence on stalagmites (e.g. works of S Frisia). The difference of our samples is assumed to be significant of a geological setting.
- This first run permits to understand how samples have to be prepared to be analyse by XRF and FTIR.

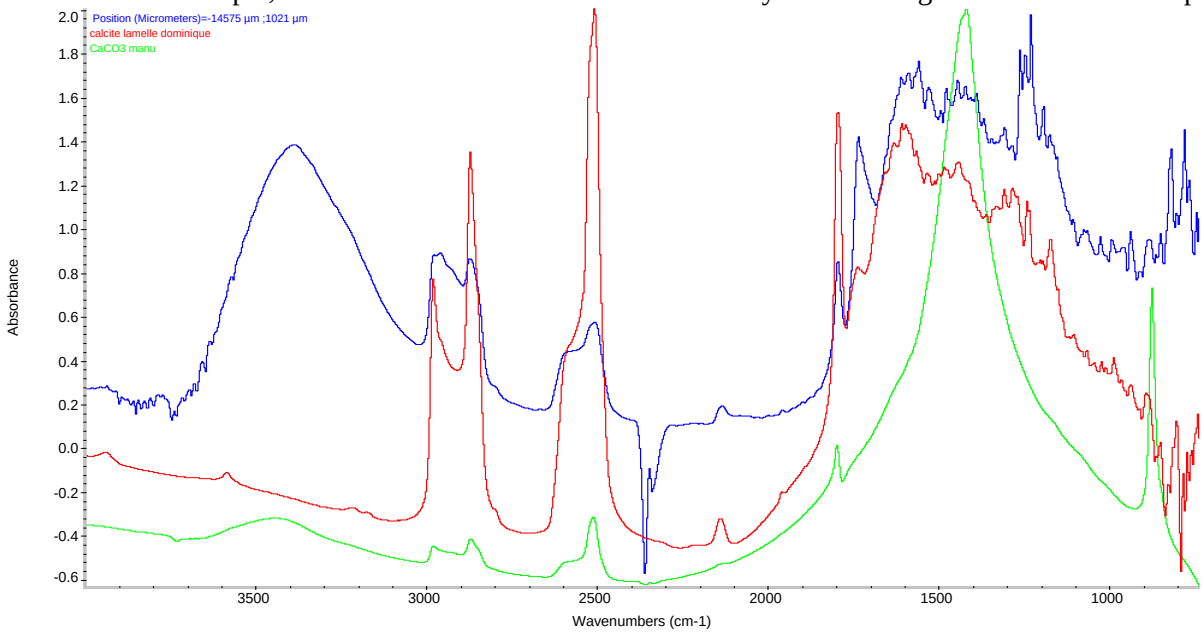
2 Sample preparation

We have test different method to take up the preparation of free thin sections of stalagmite with a thickness around 30 µm. We have prepared two free thin section for acquire FTIR and XRF map on a well laminated area around 400 µm *100µm. We didn't have enough time to acquire a well resolved XRF map of this area. We are convinced of the interest of coupling the inorganic high resolution mapping of XRF with the organic and inorganic mapping of FTIR at ID 21.

3 FTIR spectroscopy and mapping

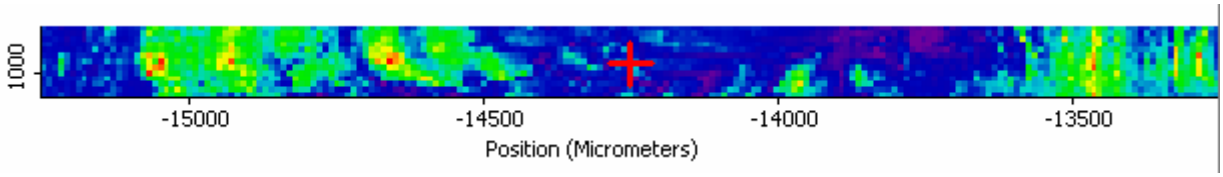
The analyses achieved with FTIR have led to :

1. The measurement of standard which have to be completed by organic matter standard. The figure below shows different calcite FTIR spectrum. The differencies are linked to the crystallisations : the blue line is a stalagmite natural sample, the red line is a natural thermal calcite crystal and the green line is a CaCO3 powder.

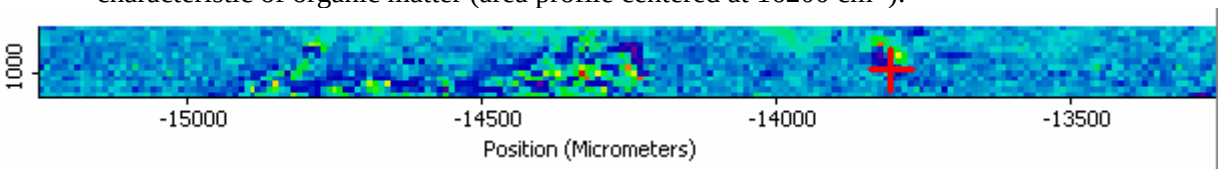


2. We present here the example of a the last sample which should be analyse with XRF and FTIR. The image below show the well laminated sample in the left and right part of the red rectangle area.

The map below shows the OH band of the COOH groups (area profile centered at 3400 cm^{-1}). The evolution of organic matter quality is very clear in the laminated part. It is the first time that a such change in the type of organic matter is shown in stalagmite lamination.



The interest of this map is increased by the following one which seems to correspond to the aromatic characteristic of organic matter (area profile centered at 16200 cm^{-1}).



If this characteristic was confirmed by further studies and analyses, it should indicate that while aromatic (condensed) organic matter supply is quite constant, a more fresh organic matter print the annual organic matter production in soils.

4 X ray fluorescence

Though X ray Fluorescence was the main interest of our experiment, this first run is difficult to use. In fact, maps and spectrum acquired are very noisy and very ambiguous. After processing with the software supplied by the ESRF and with matlab, we can't use these data. The only certainty is that our sample contain calcium but it is not a surprise.

5 outlooks

Before to complete the work on FTIR, we hope to acquire an interpretable XRF map for the well laminated sample presented above.

It is also evident that we need to acquire a better database of humic natural substances and a better knowledge of their relation with calcite.

These two developments have been proposed in two proposals in march 2006 and should be recombined in one proposal in September 2006.