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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:** **S in tropical speleothems as proxy of volcanic explosivity and tool for refined geochronology: a Micro XRFand micro XANES investigation.**	**Experiment number**: EC445
Beamline: ID 21	**Date of experiment**: from: 15 July 2009 to: 20 July 2009	**Date of report**: 12- August 2009
Shifts: 15	**Local contact(s)**: VINCENT DE ANDRADE	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Silvia Frisia & *Michael Griffiths, The University of Newcastle, NSW AUSTRALIA
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Preliminary Report:

3 shifts (15th July 8 AM to 23:00) were used for alignment. We started the experiment at about 24:00 of the 15th.
Energy was shifted from 2.48 to 3 KeV, as all S was sulphate.
A few problems with iodet, but not critical.
We analysed the following samples: KRUM 3; LR06; SV1; Christmas Island 1

Sample KRUM 3. India (Himalayas).

Sample perfectly polished. Even if aragonite and relatively porous, counts were good.
Optimum pixel dwell time 500 ms, dsps S, Cl, Sr, Na, Oxy, Al
As was detected (L lines), which needs to be addressed with a specific experiment. It is interesting because the catchment feeds Bangla Desh river systems (which are known for As load)
Interval: 2.5 micrometers
2 long parallel scans; 8 short parallel scans at the top, 1 map.
Results: S decreases in the past 100 years. This was unexpected, as we expected it to rise due to anthropogenic emissions. Also, several S peaks present for the past 400 years. We need to check the exact date for correlation with known volcanic eruptions.
Presence of As, and Sr cycles would require experiments at ID22 to determine the chemical cycles as related to weather pattern.

Sample LR-06 Flores, Indonesia

8 scans and 7 maps, centered at 12,000 years ago and past 400 years

Pixel dwell time from 200 to 500 ms, dps: S, P, As, Si, Cl, Oxy.
Interval from 5 to 2.5 micrometers.
Results: no evident geochemical cycles. S decreases in the past 100 years as in KRUM 3. Hence, there is a trend in the Tropics which is opposite to that observed in the N Hemisphere. Needs to be addressed in a paper (Griffiths & Breitenbach in preparation). Also, S is not in layers, but as aligned 5 micrometer-wide "particles". This result sheds new light on the "incorporation" of S in speleothems. S as sulphate can be in layers (Frisia et al., 2005 after experiments at ID21), particles (this experiment) or in the calcite lattice (this experiment, see below). This result is important for the interpretation of volcanic activity proxy data (Frisia, Borsato, Breitenbach, Griffiths & De Andrade in preparation).
The presence of As, which turned out to be related to As present in the host rock, needs further exploration, due to the important issue of As incorporation in calcite (see Alexandratos et al., 2007). Micro X-ray fluorescence at ID 22 would be needed prior to EXAFS spectroscopy.
The behaviour of trace elements across the global climate change occurred between 12,000 and 11,500 years ago, is marked by a slow increase in S and Cl. This is preliminary interpreted as due to sea level rise. We will carry out S isotope ratio analyses (with SHRIMPIII) to test the hypothesis.

Sample SV 1 - Italy

Same settings as for KRUM and LR-06
11 scans and 1 map. Dps: S, Cl, P, Sr, Si, Oxy.
The sample was used for comparison of the S behaviour in the same time span (12,000 to 11,500 years ago) in a temperate, NH region and the Tropics (S Hemisphere, Flores).
The N Hemisphere specimen shows a more dramatic response to global climate change with respect to LR-06 (Tropics). P increases abruptly between the "dry" and "wet" portions of the stalagmite. Sr appears to do the same. Si, by contrast, shows peaks (detrital?) during the "dry" phase. Excellent data for palaeoclimate interpretation. Sr would need to be further investigated at ID22. Comparison with LA ICP MS traverses highlights that micro XRF (in this case at ID 21) reveals the abrupt transition (across 5 micrometers), whwreas ICP-MS shows a gradual transition. Data generated during experiment EC 445 are critical for speleothem-based palaeoclimate reconstructions. We, however, need more work prior to publication: 1) Sr isotope analyses (ongoing at Melbourne). Reproducibility of Sr behaviour across climate transitions, possibly with nano-XRF, on all the transitions identified by SV samples (glacial to interglacial). Reproducibility of P behaviour (ID 21 again).

Christmas Island, Australia (Tropics)

Same settings as for the previous specimens.
8 scans, 2 maps. Dps: S, Cl, Mg, Sr, P, Al.
This turned out to be an incredible specimen. Most important has been the observation of distribution of P in maps. P occurs around the calcite crystals, and it is NOT in the lattice. We know from NMR that P is present as phosphate phases. This is the FIRST time when P (phosphate) relationships with calcite in natural speleothems has been observed, with all the implications regarding its significance as environmental proxy. We can now compare P behaviour in this tropical specimen with our previous results on the Alpine Grotta di Ernesto obtained at ID 21. It is very clear from maps that P has an inhibiting action on growth.
Also, a very important result is the observation of S in maps, which is incorporated in the lattice. Also, S (as in Flores and KRUM) does not show increase in the past 100 years. S peaks are present in the past 400 years. These will be investigated through S isotope ratio analyses at SHRIMP .
The lattice of this calcite is probably distorted and XRD analyses are ongoing. This specific sample would need to be more thoroughly investigated for heavier trace elements which may contribute to lattice ditortion.

Report compiled by: Silvia Frisia