



Late Neogene speleothems from the Nullarbor: a micro XRF investigation of the role of sea level changes influence on pre-Glacial mode climates for the Australian continent

Experiment number:
EC-794

Beamline: ID-21	Date of experiment: from: 04/07/11 08:00 to: 08/07/11 08:00	Date of report: 28/08/11 <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Murielle Salome	

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Aim of the proposal was to characterise the chemical nature of thin layers which marked changes in fabrics within Late Miocene to Pliocene (7 to 3 MA) stalagmites formed in caves of the Nullarbor Plain (S Australia) to identify phreatic conditions and bacterial-related processes.

Experimental technique(s) used, measurement strategy

Setting: 7/8 multibunch mode, Current 199 mA, Monochromator Si (111), Beam Size 2 μ m. Energy 2.45 to 2.53 KeV, then 2.9 KeV. Monochromator calibration on reference material CaSO₄.

- 1) We carried out X-ray absorption near-edge spectrometry across the absorption K-edge of S on double polished specimens with banding which was clearly visible under the optical system of the beamline. This allowed us to obtain excellent control of data points. S in stalagmite layers marking fabric changes is present exclusively as highly oxidised S-sulphate. Subsequently, we tested S-speciation by XANES on a phreatic continental carbonate where we identified bacterial (?) filaments by SEM. The test was conducted on subglacial calcite crust from Antarctica. XANES spectra clearly revealed the presence of both S-aminoacid and S-sulphate with different distribution according to fabrics.
- 2) Once we were confident about the absence of reduced S-species in the Nullarbor stalagmites, we set the exciting energy of the microprobe at 2.9 keV and focused on the analysis of distribution of environmentally critical trace elements and. Batchfitting and correction for flux revealed the presence of Na, Mg, Al, Si, P, S, Cl. We obtained 15 chemical maps in the allocated shifts. Four long maps (about 1000 micrometers x 700 micrometers with pixel dwelling time ca. 80 mS) were carried out at night shifts.

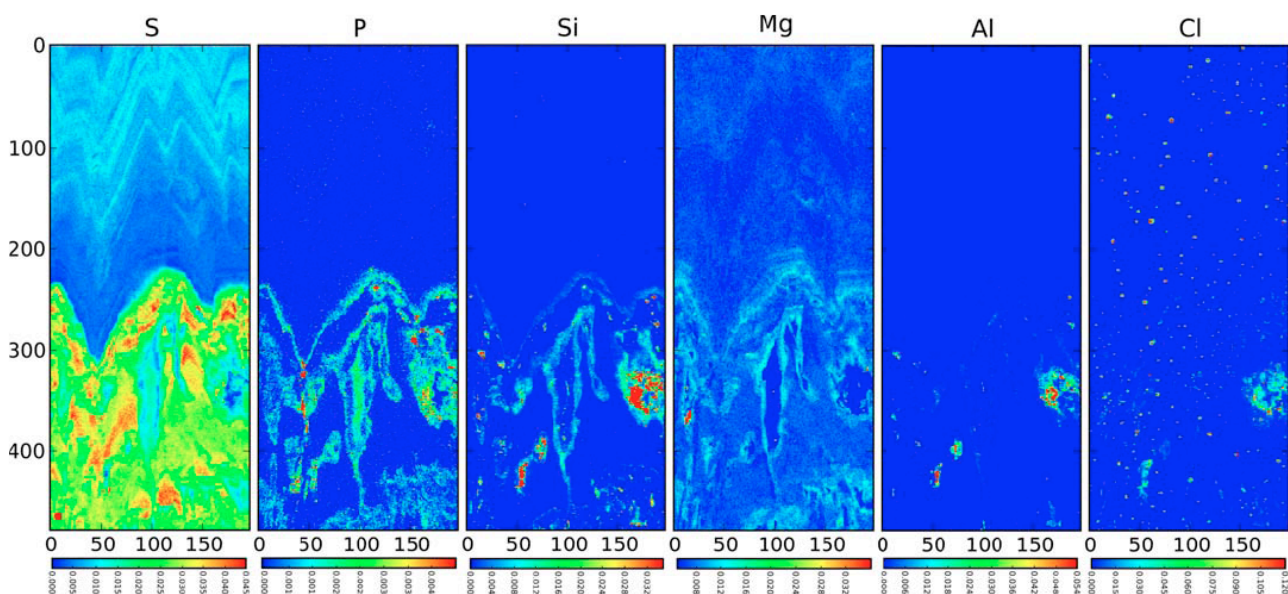
Results

In-situ XANES spectra of Pliocene cave carbonates show main peak at 2.481 KeV indicative of highly oxidised S-sulphate and, consequently, formation of the thin, white layers in oxidised vadose environments.

All spectra show a minor peak at 2.4785 which is probably due to photoreduction. A 22 Kyr old subglacial carbonates show a major peak at 2.4817 KeV in the matrix, and minor peak at 2.473 which can be ascribed to S-aminoacid (see for example Dauphin et al., 2003) at the boundary between detrital particles and calcite matrix. This is the first robust indication that organic molecules are present at ice-bedrock boundary during glacial maxima in Antarctica.

Chemical maps of Nullarbor speleothem layers reveal microstructures otherwise not visible by optical and electron microscopy or LA-ICP-MS mapping. Elements such as S and P highlight crystal terminations, dissolution phenomena and provide important information on pH changes during deposition. We obtained excellent chemical maps, and we selected the following two examples for this report which illustrate the most typical results obtained through EC 794.

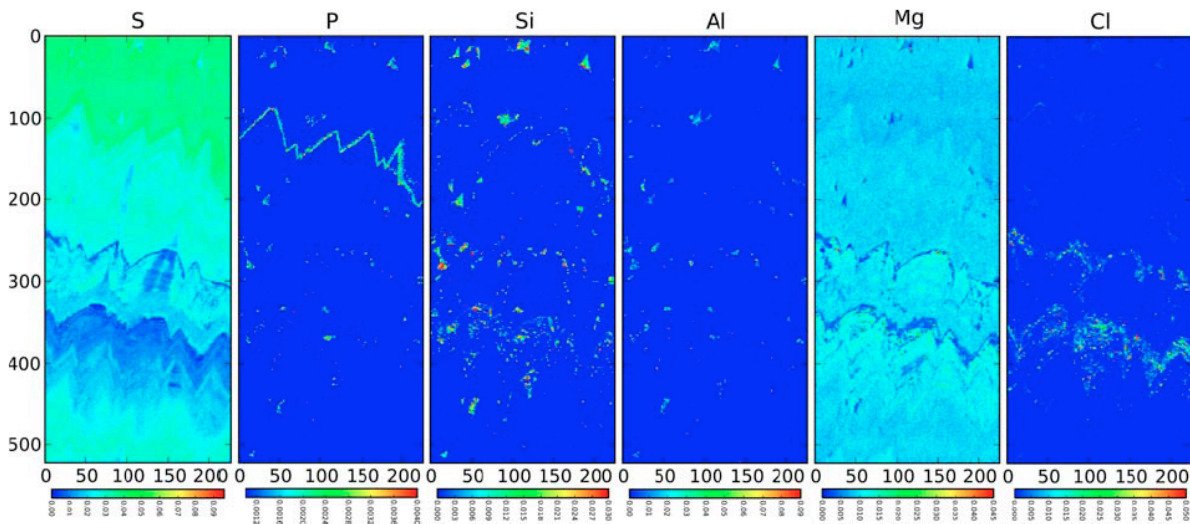
1 - Sample Null 645_MO1t – “Wet” Mid Pliocene : Map generated between a distinctive passage between white layer and dark-brown crystalline layer marking the cessation of stalagmite growth. Chemical mapping clearly shows that crystal tips in the white layer underwent dissolution at micrometer scale. S-sulphate enrichment in the white layer is indicative pH relatively lower than in the top brown layer, consistent with the dissolution. P increases toward the tip of crystals and lines cavities. We suspect that P in the Nullarbor speleothems is the marker for microbial films, whereas S is related to inorganic sulphate precipitation in dry periods. Maps also show Si associated with Cl in P-rich “pockets”. This association is typical of evaporative conditions. Chemical mapping allows, therefore, a new interpretation of the climate significance of Nullarbor stalagmites: during the “wet Pliocene” there were dry phases when the dripwater pH shifted to more alkaline conditions. Exposure to mixture with saline waters favored microbial colonization of the speleothems. The presence of Br, detected at ID22, provides robustness to our inference that the parent water in the final stages of stalagmite deposition was modified groundwater.



Map Null 645_MO1#3: h= 390 μm; z= 480 μm, pixel size= 2 μm, dwell time 0.08s.

Sample Null FS04 Mid Pliocene.

Map generated across a distinct white layer in the stalagmite. S-sulphate defines crystal terminations and highlights dissolution features. P highlights pristine crystal terminations and caps the S-rich layer. Again, P and S do not show the same distribution. Note the association of Si and Cl, indicative of dry setting. In this case, however, there is no relationship with P. We, thus, tentatively infer that P is the only element clearly related to microbial activity. Most other elements are related to inorganic processes.



Map Null FS04#4: $h = 450 \mu\text{m}$; $z = 900 \mu\text{m}$, pixel size = $2 \mu\text{m}$, dwell time 0.08s.

Final Remarks

We believe that the results obtained through 9 shifts at EC 749 allow for a re-interpretation of the current favored hypothesis of “perennial El Nino conditions” for the Mid-Pliocene. Data indicate that, at least in S Australia, climate was punctuated by dry periods comparable to today’s conditions. This evidence provides robustness to a current debate of climate variability during the Mid Pliocene, a period believed to be a possible analog for our future. We are writing a research paper on the basis of the results obtained at ID21. Critically, we found that S species mapping at high resolution provides valuable information on microbial processes, pH and parent water chemistry and is unequivocally a new environmental proxy in continental carbonate-based studies. We, therefore, would like in the near future to investigate the S-speciation in subglacial calcites from Antarctica and the Alps to gain insight on subglacial processes and investigate environments otherwise inaccessible to our research.