Determination and quantification of fatty acids in speleothems and cave drip water using HPLC-ESI-IT/MS

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Cave drip water, speleothems and the proxies preserved within them have significant potential to record palaeoenvironmental changes in the regional vegetation [1]. The most common proxies measured in stalagmites are inorganic proxies, in particular oxygen isotopes [2]. More recently the importance of organic matter analyses in this field is examined. This study focuses on the research of lipid biomarkers. The lipids contained in stalagmites originate from the overlying soil and different plants, bacteria and fungi. Therefore different compositions of lipids may provide records of environmental changes [3].

In the following the development of a new method for the extraction of fatty acids (FA) from stalagmites and cave drip water and their measurement by HPLC-ESI-IT/MS (high performance liquid chromatography coupled to electrospray ion trap mass spectrometry) is presented. Five different FAs with chain lengths from C12 to C20 were applied as analytical standards. A mixture of these was used to optimize the separation by HPLC. The FAs were measured in negative polarity, so a time consuming derivatization of the analytes was not necessary. To simulate the extraction of the FAs several spiking experiments were performed. Solid phase extraction and liquid liquid extraction were used for the extraction procedure. Both methods were optimized and good reproducibilities with deviations below 10% were achieved. Quantitative analyses were accomplished and the limits of detection determined. As a proof of principle, first applications to the actual samples were successfully fulfilled. To testify the role of the FAs as palaeoclimate proxies further experiments will be performed.

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Sub-micrometer scale chemical mapping of complex monazites: the contribution of the NanoSIMS.

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Monazite [(Ce,La,Nd,Th)PO_4] is a very robust geochronometer which can record and preserve U-Th-Pb ages in various geological environments. For around ten years, monazite has also been increasingly studied because it is a key tracer for geological processes, especially fluid/rock interactions. Monazite grains often display variable chemical compositions at the grain scale and complex chemical zoning, sometimes correlated to age domains, reflecting the changes in physical and chemical parameters of the host rock. The development of *in situ* techniques (EMPA, LA-ICPMS, SHRIMP) enables the combined study of chemical and isotopic characteristics in the monazite at the scale of few μm. However, many recent studies show that: (1) it is not always possible to correlate age and chemical domains at these scales, (2) monazite often display very complex chemical zoning at infra μm scale and (3) TEM analyses show strong perturbations of the crystal lattice between 10 and 200 nm. In order to better understand the ages recorded by monazite it is necessary to obtain chemical informations at nm scale. In this context, the NanoSIMS appears to be the best suited tool.

We present here chemical elements (^{89}Y, ^{139}La, ^{208}Pb, ^{232}Th and ^{238}U) NanoSIMS images and analyses obtained in monazites studied in thin section or separates. ^{89}Y, ^{139}La, ^{208}Pb, ^{232}Th and ^{238}U ion images were obtained in monazite areas previously studied with EMPA and dated with LA-ICPMS. The NanoSIMS maps allow to characterise isotopically and chemically distinct domains that were not distinguishable on WDS X-ray maps. ^{208}Pb/^{232}Th maps derived from NanoSIMS images offer the possibility to correlate different age domains with the measured ^{208}Pb/^{232}Th ages obtained at larger scale (few μm) by LA-ICPMS.

These results are very promising for compositional and isotopic mapping with a highest spatial resolution in the monazite geochronometer.

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