



Characterisation of organic inclusions in stalagmites using laser-ablation-micropyrolysis gas chromatography–mass spectrometry



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ABSTRACT

Laser-micropyrolysis gas chromatography–mass spectrometry (La-Py-GC–MS) allows the analysis of small targeted areas of organic material. In this proof of concept study a novel application of the technique is demonstrated. Three types of organic matter preserved in speleothems were analysed: dissolved organic matter within the calcite crystal matrix; detrital organic inclusions; and lithified guano derived from birds and bats. The results indicate that there is significant heterogeneity within each sample type, with guano samples having the highest variability. However, there are also distinctive La-Py-GC–MS products that allow separation of the sample types geochemically. These include the chain length distribution within the longer chain *n*-alkanes (>C₂₀), with the guano sample having a dominance of chain lengths below C₂₇, whilst the other two sample types are dominated by *n*-alkanes of C₂₇ and above. The detrital inclusion sample has a higher relative abundance of pyrrole and methylpyrroles. A homologous series of longer chain alkylbenzenes is seen only in the guano samples.

Our preliminary data indicate that fingerprints of La-Py-GC–MS analyses may be useful to provide information on organic matter preserved in speleothems, but more work is required to extend the technique to lower organic content samples, and to fully test the application in a larger dataset of preserved organic matter types.

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1. Introduction

Laser-micropyrolysis gas chromatography–mass spectrometry (La-Py-GC–MS) can yield geochemical information from laser spots as small as ~20 μm spot size, and thus provides the ability to provide reasonably detailed analyses of heterogeneous pyrolysable organic matter at resolutions similar to that of microscopy [27]. In general, La-Py-GC–MS has been demonstrated to provide similar data to flash pyrolysis, but at the 10 s of microns scale [52], and multiple applications have been developed, especially within organic rich rocks. These include the analysis of individual macerals, so as to ascertain the chemistry specific to each maceral type [26,44,28,30], the characterisation of solid bitumens at the

molecular level [30,41], the analysis of lignins [31], and the analysis of microfossils, such as Tasmanites algae [28,29], acritarchs [4,5], chitinozoans [34] and pollen [1]. Oil-bearing fluid inclusions have also been analysed by La-Py-GC–MS [28,53], although sensitivity and power of the laser tends to lead to some laser artefacts that make comparison with other bulk analytical methods difficult [25]. Use of a pulsed femtosecond laser has allowed single oil inclusions to be analysed successfully [46]. Outside of geology, La-Py-GC–MS has also found use in forensic studies such as analysis of paint flakes [3,39]. A recent study comparing La-Py-GC–MS to Curie point pyrolysis GC–MS (CP-Py-GC–MS) concluded that there were several advantages pertaining to the use of laser pyrolysis, including the provision for smaller sample sizes and good spatial analytical control [2], but that the higher (estimated as >1000 °C) and unquantified temperature applied in laser pyrolysis will affect compound distributions. They therefore concluded that the nature of the organic matter was important in assessing the suitability of pyrolysis techniques, with more mature organic matter better suited to laser work [2].

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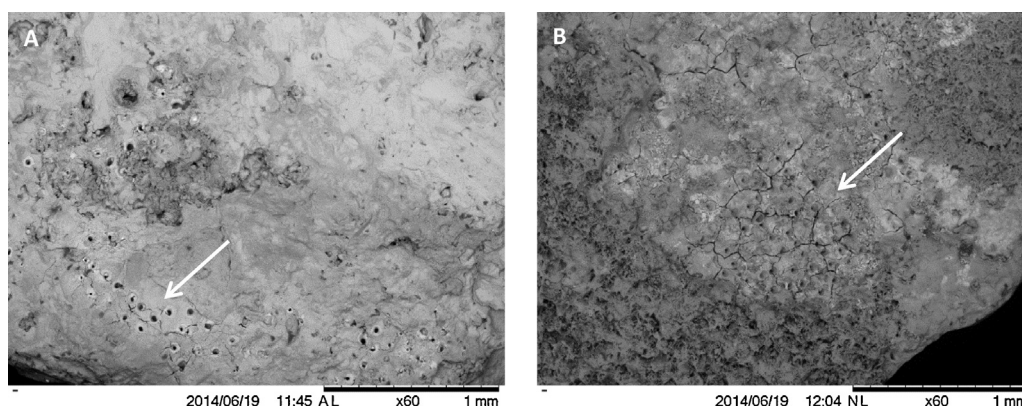


Fig. 1. SEM images showing laser ablation holes (indicated with arrow) in (a) a detrital inclusion in Bero-1, and (b) the lithified guano of HV-1.

Here, a laser pyrolysis instrument with an Nd-YAG infrared laser was used to characterise organic matter preserved within speleothems. The analysis of organic matter in speleothems is a subject of increasing research interest as it potentially provides new palaeoenvironmental records focused on vegetation change [50,14,17,36], soil dynamics [50,19,36], and temperature [51,13,20]. However, the focus on biomarkers extractable by wet chemistry from the carbonate means that most research to date has required relatively large sample sizes of calcite (1–100 g) ([50,14,51,13,36]), compared to established inorganic geochemical proxies. Selected techniques published to date allow analysis of less than 1 g of calcite: thermochemolysis of lignin (0.5 g; [12,16]); one study of lipid biomarkers in an American stalagmite (0.3–0.5 g; [40]) amino acid analysis (25–120 mg, [35,15]); high performance liquid chromatography analysis of short chain fatty acids (0.5–3.5 g, [21]); and liquid chromatography–isotope ratio mass spectrometry (LC–IRMS) analysis of bulk organic isotopes (0.2 g; [18,19]). Of these, only LC–IRMS of bulk $\delta^{13}\text{C}$ has so far been fully applied in a multi-proxy palaeoenvironmental reconstruction [19]. The need for larger calcite samples significantly limits the temporal resolution of the time-series recovered, and often excludes the possibility of analysing individual organic inclusions or layers resulting from biofilms or airborne, water-lain, or faunal detrital input. Alternative techniques such as continuous fluorescence analysis have met with good success in providing high resolution records of certain forms of dissolved organic matter (e.g. [7,8,37,9,38,10]), but are limited in the amount of molecular detail that can currently be recovered. The development of new analytical techniques that can be applied at a high sample resolution and with minimal wet chemical preparation is therefore desirable.

In this paper, the La-Py-GC-MS technique was applied to three speleothem samples with contrasting organic contents: (i) soil-derived dissolved organic matter distributed within the crystalline calcite; (ii) detrital or in-situ particulate organic matter; and (iii) lithified guano of a known faunal origin. Comparison of these samples and consideration of the characteristic chemical differences provides an initial insight into the potential utility of the La-Py-GC-MS technique, and possible future applications in speleothem geochemistry.

2. Materials and methods

2.1. Samples

Three speleothem samples were analysed in this preliminary study to represent three preserved organic matter types. The first is an Australian stalagmite (370 FS03) of Plio-Pleistocene age from the Nullarbor Plain, Australia. This sample has a black colouration hypothesised to be due to a high proportion of humic acids

entrapped in the crystalline structure [22]. Due to this abnormal organic content, it is the only speleothem analysed where it was possible to pyrolyse the calcite using the La-Py-GC-MS instrument as currently configured. The second sample is from an Ethiopian stalagmite (Bero-1) from the Mechara region of Ethiopia, which formed between 10 ka and present in an open cave, recessed into a cliff-face [6]. It contains laminae of visible detrital organic matter, which may have been deposited by water, or due to the relatively open nature of the cave, possibly by air or faunal input. The third sample (HV-1) is a crust of lithified guano incorporated into a Peruvian stalagmite from Cueva de las Lechuzas in Peruvian Amazonia, and is believed to be Holocene in age (H. Vonhof pers comm.). Based on modern accumulations in the area, the guano is derived from a mixture of bats and oilbirds, which both live in the cave.

A sample section approximately 5 mm × 5 mm was removed from each speleothem, centring on visible organic inclusions in the case of Bero-1 and HV-1 guano. Prior to analysis, the sample blocks were cleaned in dichloromethane to remove surface contamination. Samples were thermally desorbed in the pyrolysis chamber of the instrument (see Section 2.2) at 100 °C for 10 min prior to analysis to reduce desorption artefacts, although the latter were found to be significant only for the guano samples. To minimise these artefacts, piece 2 of the guano was thermally extracted offline at 200 °C, and held at 100 °C in an oven overnight prior to analysis.

2.2. Analytical methods

A detailed description of the instrument and methodology can be found elsewhere [27,28,11,1,39]. Briefly, a continuous wave laser (Laser Applications 9500, Nd:YAG laser, $\lambda = 1064$ nm) was tightly focused onto selected areas of the sample through an Olympus BPX60M microscope equipped with reflected light illumination and using long distance working objectives (20X/0.4 and 50X/0.5). The sample was located in a purpose-built pyrolysis chamber (100–110 °C, 100 mL helium flow) which was interfaced to a GC-MS system (Hewlett Packard 6890 GC interfaced to a 5973 mass selective detector, electron energy 70 eV) via a gas inlet system designed for maximum transfer efficiency of the gaseous products. The products of the pyrolysis process were cryogenically trapped in a coiled nickel loop using a liquid nitrogen bath. After trapping the products, a 6 port transfer valve was rotated to transfer 1 mL/min helium through the trap and the contents were then desorbed by heating to 320 °C. The products were cryo-focused again in a loop of GC column immersed in a liquid nitrogen bath. The full scan GC-MS analysis (m/z 50–550) of the pyrolysates was performed on a DB-5MS column (J&W, 60 m, 0.25 mm I.D., 0.25 μm film thickness) with helium as carrier gas with constant pressure of 25 psi. The GC oven was programmed for an initial temperature of 40 °C (2 min hold) followed by heating at 4 °C/min to 310 °C (30 min hold).

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