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A novel analytical pyrolysis technique for investigating the presence of N-bearing biopolymers in fossils and its potential applications in their molecular taphonomy in deep time

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The increase in reports of purported preservation of proteins[e.g. 1, 2] and chitin[e.g. 3, 4] in fossils from a range of geological ages, using a range of different methods, has rejuvenated the debate over the preservation potentials of such tissues (mostly composed of nitrogenous biopolymers) in deep time. Several studies had been previously published which suggested that the preservation of proteins in fossils from deep time was perhaps more widespread than previously thought [e.g. 5,6]. Subsequently, reports skeptical of the previous studies were published, citing concerns of false positives, misidentification of biosignals, and cross-contamination [e.g. 7]. However, the recent independent studies perhaps indicate that a re-assessment of the preservation and mechanisms of decay of these biopolymers may be pertinent, utilizing evidence from a broader variety of techniques.

Here we propose pyrolysis comprehensive two-dimensional gas chromatography/ time-of-flight mass spectrometry (Py-GC×GC-TOFMS) as one such method. We first analyze industrial standards of chitin and collagen, and a well-documented Jurassic melanin sample to identify characteristic pyrolytic products for each. We find that 3-acetamidofurans, 3-acetamidopyrones and their methylated homologues are characteristic pyrolytic markers for chitin, and substituted cyclic 2,5-diketopiperazines (2,5-DKPs) are characteristic for collagen, while concluding that it is difficult to assign characteristic products for melanin. We then analyze an Eocene mammal bone and Pliocene fungi and report the presence of the respective characteristic compounds in each. In the latter case, we opine that this method could be useful for chitin assignment in Pre-Cambrian samples. We conclude that this is a robust and independent technique which can be used to differentiate between N-bearing compounds in fossils, as well as potentially contribute towards understanding their taphonomy at the molecular level in deep time.

References

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