



Experimental and geological approaches to elucidate chemical change in sporopollenin over geological time

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Sporopollenin is the primary biopolymer comprising the walls of sporomorphs (pollen and spores), both in extant material and found within the fossil record. Maturation processes associated with sedimentation and burial over geological timescales have long been considered to dramatically alter the chemical nature of organic material, most notably via oxidation.

Here we present experimental data derived from simulated maturation, analyses of Carboniferous fossil material, and modern-day material. Our data demonstrate the core structure of sporopollenin undergoes only minor chemical adjustments at lower grades of maturation, with the over-riding chemical signature remaining identifiable as that of sporopollenin, showing strong resemblance to modern material. This modern signature can, in specific cases be preserved in the geological record, demonstrated by the near-pristine chemical composition of megaspores preserved in cave deposits of Pennsylvanian age (Carboniferous, c. 310 Ma). Conversely, the labile component associated with sporopollenin is found to readily defunctionalise and repolymerise to generate a new polyalkyl macromolecule in situ. The labile component is shown to be held in position via ester linkages; a common chemical feature observed in extant sporopollenin.

This combined experimental and geological investigation provides insights into i) the preservation of chemical signatures within the fossil record, ii) considerations for sample preparation when undertaking chemical analysis of fossil sporomorphs, and iii) the long-term evolutionary stasis of sporopollenin, spanning geological time.