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Laser Raman micro-spectroscopy of Neoproterozoic - Early Palaeozoic organic-walled palynomorphs: palaeobiological interpretation

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Proterozoic and Palaeozoic organic walled microfossils (palynomorphs) comprise a wide range of organisms (e.g. , oceanic photosynthetic microplankton, microzooplankton, and microscopic spores from earliest land plants), which characterize important evolutionary events in Earth's biosphere. For example, the evolutionary patterns and abundance fluctuations of acritarchs in the sedimentary records have been put in relation with changes in ocean chemistry, global glaciations, the diversification of metazoans, and variations in atmospheric CO2 concentration. Palynomorphs also record the transition of life from water (freshwater algae) to land (earliest miospores). Classical morphological comparative analytical methods are limited to those cases in which direct comparisons with extant organisms are available, but in many instances the biological affinities of pre-Devonian palynomorphs remain unknown. Recently, new techniques based on microchemical analysis of individual organic-walled microfossils demonstrated their potential for elucidating the cellular anatomy, composition, and mode of preservation of microfossils, thus offering new insights into their palaeobiology. In this study Laser Raman micro-spectroscopy was applied to a range of exceptionally well-preserved palynomorphs of late Neoproterozoic to early Devonian age, in order to better characterize their chemical composition.

Raman spectra were successfully obtained from the studied palynomorphs; all showed characteristic bands attributable to C=C stretching for polycyclic aromatic compounds and contributions from CH2/CH3 bending. As in previously published MicroRaman spectra of organic-walled microfossils of varying age and state of preservation, the spectra reported here are characterized by two main lines at ∼1350 and ∼1600 cm-1 given by the so-called "D" (disordered) and "G" (graphitic) bands. These spectral features can be attributed to molecular subunits of interlinked aromatic hydrocarbons. It is important of notice that the position and shape of bands can vary between the species within the same sample, showing variability in the exact chemical composition depending on the species studied. For instance, the position of the main peak in the "D" region is placed at 1354 cm-1 in Navifusa majensis and Leiosphaeridia sp., whereas in Valeria lophostriata it is placed at 1375 cm-1. Similarly, the wavenumber of the "G" band is different, being 1600 cm-1 for the first two species and at 1577 cm-1 for Valeria lophostriata. Since these differences are taxon specific we suggest that they relate to the initial chemical and physical differences between the newly synthesised acritarch walls. The differences observed may be the preserved differences in chemistry of the biomacromolecules that comprised the original (not diagenetically modified) acritarch walls. Alternatively, the observed differences may only reflect result from differences between the original wall biomacromolecules, but no longer incorporate them since they have been entirely modified into geomacromolecules over time.