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Multiple length scales characterization of morphologically perfectly preserved Triassic lycophytes spores after HP-LT metamorphism

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Carbonaceous material (CM) is widespread in metasedimentary rocks and mostly derives from the conversion of organic matter during diagenetic and metamorphic processes. In rocks that have undergone temperature higher than 300˚C, CM is generally slightly graphitized and has generally lost all textural information relative to its biogenicity. However such information is essential to track the evolution of life through geological times, especially in the early Earth. In this study, we present observations of metasedimentary rocks exhibiting lycophyte megaspores with an unusually and perfectly preserved morphology that have been submitted to a high-pressure, low-temperature metamorphism (∼360˚C, ∼12 kbars). These spores were found in argillaceous Triassic limestones from the La Vanoise massif (Western Alps, France). The combination of Raman microspectroscopy (RM), Scanning Electron Microscopy (SEM), Scanning Transmission X-ray Microscopy (STXM) and Transmission Electronic Microscopy (TEM) allowed us to characterise at multiple length scales both the organic material present in the megaspore walls, as well as the surrounding minerals, mostly (pure) calcium carbonates.

Using SEM and RM, we evidenced the systematic occurrence of a (Fe-Mg)-enriched calcite layer at the interface between megaspore walls and the matrix calcium carbonates. Moreover, high spatial (∼25 nm) and energy (∼0.1 eV) resolution near-edge x-ray absorption fine structure spectroscopy (NEXAFS) were obtained at the C K-edge by STXM and showed a strong textural interaction between carbonates and OM within the spore wall as well as the presence of two different types of OC. These different observations were substantiated by TEM showing the presence of slightly graphitized OC in the inner region of the megaspore wall versus porous and amorphous-like OC in the outer region. TEM also confirmed, at the nm scale, the presence of a (Fe-Mg)-rich carbonate crown along the megaspore wall with a different chemistry from that of the Ca-rich carbonates from the matrix. All these results will be discussed in the light of the structure of spore walls in modern analogues of megaspores.