



## **In-situ structural and chemical characterisation of biogenic organic matter in 2.72 Ga stromatolites, Tumbiana Formation, Western Australia**

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The Pilbara Drilling Project collected rocks from the Tumbiana formation (2.719 Ga, Fortescue Group), in which organic carbon isotope values indicative of the presence of methanotrophic prokaryotes have been reported. The drilled rocks consist mainly of a section of black shales, stromatolitic carbonates and volcanic tuffs deposited in shallow (marine or lacustrine) water.

High spatial and spectral resolution techniques were used to investigate the composition and relationship with the host mineralogy of the carbonaceous matter (CM) preserved in two representative stromatolitic samples. The first one (sample 1) consists of the core of a m-scale stromatolite characterized by mm-scale periodic layering composed of variably silicified micritic carbonates and mud layers. The mud layers are composed of silica, pyrite, chlorite, K-sericite, anatase and apatite. The second sample (sample 2) consists of an aggregate of tiny stromatolites (mm) interdigitated with mudstone and fine-grained tuffaceous layers a few mm thick and several cm long. The core of sample 2 shows the same textural and mineralogical characteristics as the large specimen, although at a much smaller scale. Bulk carbon stable isotope of sample 1 shows  $\delta^{13}\text{C}_{\text{org}}$  value of -49.1 per mil reflecting microbial assimilation of methane (C. Thomazo, this volume).

Scanning Electron Microscopy (SEM) analysis coupled with micro-Raman spectroscopy revealed that the CM is preferentially located in the mud layers in both samples. Raman analysis indicates a polyaromatic structure with grafted aliphatic chains of undetermined length, but does not demonstrate the biogenicity. Raman spectra de-

convolution indicates that the CM experienced low grade, zeolite facies metamorphism ( $T < 200^{\circ}\text{C}$ ). Fourier Transform Infrared spectroscopy (FTIR) analysis of sample 1 revealed the occurrence of organic functional groups including short aliphatic chains and C-N (amine or amide) functions. This demonstrates that nitrogen is an important organic component of the CM. Carbon K-edge XANES spectroscopy using synchrotron Scanning Transmission X-Ray Microscopy (STXM) technique revealed the carboxylic function and confirmed the occurrence of aliphatic carbon, thus providing further support for a biologic origin of the organic matter investigated.

The structure and mineral distribution are reminiscent of modern stromatolites. If the communities involved in stromatolites building were the same as today, pyrite would be the bacterial sulphate reduction (BSR) product in this system. Pressure solution during sediment burial has driven the remobilization of organic matter on a local scale within stromatolites, erasing its link with the original mineralogy. Current investigations aim at finding the origin of the organic matter in such banded structures.