DETECTION OF CARBONACEOUS MATERIAL IN FOSSIL MARINE MICROBIALITES BY RAMAN SPECTROSCOPY (LÁNCARA FORMATION, LOWER CAMBRIAN, CANTABRIAN MOUNTAINS, SPAIN).

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Introduction: Marine carbonate lithofacies formed 512 My ago (lower Cambrian, Stage 4) in tidal plains in a mixed carbonate platform – where sedimentation was strongly influenced by tides and storms – have been analyzed. The carbonate sedimentation was produced by enzymatically controlled mineralization [1] through the epibenthonic fauna such poriferans (Archaeocyaths –extinct taxa), echinoderms and molluscs, as well as by induced biomineralization by benthonic microbial communities (BMC). The lithofacies correspond to high energy deposits like bioclastic pelletoidal limestones and oncolitic facies and low energy deposits like fenestral limestones and microbialites. Microbia-lites are mineral deposits formed through trapping and binding of detrital sediment as well as the locus of the mineral precipitation of BMC [2]. Microbial activity favoured characteristic macrostructures like digitate thrombolites [3] and spongiostromata oncolites (related with cyanobacteria coatings) and microstructures like microbial peloids, crusts and clotted microfabrics [4].

Raman spectroscopy has been used to differentiate the main carbonate minerals and to detect the presence of carbonaceous material in enzymatically controlled minerals (skeletal elements), microbially induced biominerals and abiotically precipated cements. Different macro and microestructures (thrombolites, oncolites, fenestral bindstones, microbial crusts and microbial peloids) have been analyzed in the microbialites.

On studing carbonaceous material it is known that the two crystalline forms of carbon, diamon and graphite, are characteried by two Raman bands at 1386 (D band) and 1595 cm^{-1} (G band), respectively. The Raman parameters of these bands are very sensitive to structural disturbances by electronic configuration sp^2-sp^3 changes in the carbon bands (C-C) and consequently their presence are use to estimate the structural properties of the carbonaceous material. In particular, the intensity ratio between the G and D bands has been shown to be indicative of the crystallinity degree of the material. This can provide intersesting information about the thermodicamical processes of crystallization.

Materials and methods: The Raman experiments were performed on thin sections using a high resolution Raman spectrometer LABRAM HR 800UV from Horiba-Jobin & Yvon Spex, equipped with an Olympus BX41 microscope and a XYZ-axis motorized stage. A x100 objective and backscattering configuration were used for Raman spectra acquisition. A 632.8 nm HeNe laser were used as excitation probe. The nominal laser power on the samples was 1mW and the irradiance was about 100 $kWcm^{-2}$. The spectral window was [200-3800] cm^{-1}, the integration time was [5-60] s and 2 accumulations were used as acquisition parameters. All this results in an spectral resolution higher than 1 cm^{-1}.

Results and discussion: Skeletal remains (Archaeocyaths and hyolithids) are composed of $CaCO_3$ and show weak bands of disorganized carbonaceous material. Microbial macro- and microstructures show important changes in compositon. A Raman profile along a columar thrombolite shows compositional variations between microsparitic calcite ($CaCO_3$) and dolomicrospar $(CaMgCO_3)_2$ and presence of carbonaceous material. Intercolumn space is filled by microbial peloids ($CaCO_3$) with low intensity vibrational bands characteristic of the disorganized carbonaceous materials. However, thrombolites, fenestral bindstones and microbial microsparitic crusts in close localities are solely composed of calcite and carbonaceous material displaying well differentiated D and G bands. The Spongiostromata oncolites related with cyanobacteria do not show rests of carbonaceous material. Microbial peloids are dolomitized and preserve low cristalinity carbonaceous material. The precipitation sequence of calcite cements in cavities shows two distinct phases: an early marine cementantion phase with signatures of disorganized carbonaceous material and a later burial cementation phase abiotically precipitated.

Conclusions: Raman spectroscopy is shown to be a powerfull technique to analyze the presence of carbonaceous material in fossil marine microbialities as well as to give insight into the thermodinamical crystallization processes occurring in the Cambrian samples.

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