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Abiotic formation of organic biomorphs under diagenetic conditions

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Supplementary Information

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Methods

Experimental procedure

Pure powder of yeast RNA and α-quartz (Sigma-Aldrich) were used for the present experiments. 100 mg of RNA and 200 mg of α-quartz were mixed within 5 mL of pure bi-distilled water and introduced in a PTFE reactor (Parr) filled by pure argon (> 99.99 %) in a glove box. These reactors were placed in a MEMMERT UN30 oven at 200 °C for 20 days. The soluble fraction of the experimental residues was extracted by centrifugation and the remaining solid fraction was then washed 3 times with pure bi-distilled water and dried overnight in an oven at 50 °C before characterisation.

SEM, FIB & STEM

Scanning electron microscopy (SEM) investigations were performed on powders deposited on carbon tape using a SEM-FEG ZEISS ULTRA 55 (IMPMC, Paris) equipped with a Bruker EDS QUANTAX detector (Bruker Corporation, Houston, TX, USA). Images shown here (secondary electrons) were collected using an acceleration voltage below 2 kV, thereby preventing irradiation damages. Electron dispersive X-ray spectroscopy (EDXS) maps were collected on powders coated with 5 nm of platinum using an acceleration voltage of 10 kV. Focused ion beam (FIB) foils were extracted from organic biomorphs never exposed to high acceleration voltage using an FEI Strata DB 235 (IEMN, Lille, France). Milling at low gallium ion currents allowed minimising common artefacts including local gallium implantation, mixing of components, redeposition of the sputtered material on the sample surface and significant changes in the speciation of carbon-based polymers (Bernard *et al.*, 2009; Schiffbauer and Xiao, 2009). Transmission electron microscopy in scanning mode (STEM) was performed on the FIB foils using a Thermofisher Titan Themis 300 microscope operated at 300 keV (CCM – Lille, France).

Size distribution

The area of a thousand of biomorphs was measured on SEM images using the ImageJ elliptical selection tool. The equivalent diameter of each biomorph was estimated such as $d_{eq} = 2\sqrt{(Area/\pi)}$ (Rouillard *et al.*, 2018).

EA-IRMS

Total carbon and nitrogen contents and C and N isotopic compositions were determined using a Flash 2000 Thermo CHNSO elemental analyser coupled to a Thermo Fisher DeltaV Advantage IRMA (MNHN SSMIM, Paris). Experimental residues were primarily flash combusted at 1020 °C in the oxidation column of the EA (chromium oxide, cobaltous oxide, quartz wool). Oxidation products were then carried by a stream of helium (100 mL/min) through the reduction column (copper, quartz wool) at 650 °C and water was removed from the resulting gases through a magnesium perchlorate filter. The CO_2 and N_2 were then separated in a chromatographic column heated at 40 °C, passed through a thermal conductivity detector (1000 µV) where elemental compositions were measured, and carried into the source of the IRMS where the isotope ratios were measured. Alanine was used as standard for both elemental and isotopic analyses and for uncertainties.

XRD

X-Ray diffraction (XRD) patterns were acquired using a BRUKER D2 PHASER diffractometer (IMPMC, Paris) operating at 30 kV and 10 mA with a Cu anode ($K\alpha_{1,2}$ at 1.54 Å). Analyses were performed on finely ground powders deposited on a silicium sample holder. The angular range in 2θ was 5-70° with a step size of 0.03° and with a counting time of 3 s per step.

NMR & FTIR

Cross polarisation ^{13}C nuclear magnetic resonance (NMR) experiments were performed with a magic-angle spinning probe 1H/X at 14000 kHz using a BRUKER AVANCE III 500 MHz (IMPC, Paris) operating at 125.77 MHz. Chemical shifts were calibrated using the carboxyl signal of adamantane (38.52 ppm). NMR data were acquired with a contact time of 1 ms and a recycle delay of 1.5 s. Note that this configuration only provides qualitative information, especially as the possible presence of radical species may be responsible for quenching of signals. Fourier-transform infrared (FTIR) spectra were recorded in the 400-4000 cm^{-1} range with a 4 cm^{-1} resolution using a Nicolet 6700 FTIR spectrometer fitted with a KBr beamsplitter and a DTGS-KBr detector. The powder spectra were obtained under ambient conditions by averaging 200 scans obtained in attenuated total reflectance (ATR) geometry using a Specac Quest ATR device fitted with a diamond internal reflection element.

STXM-based XANES

Scanning transmission X-ray microscopy (STXM) analyses were performed on FIB foils to document both the carbon and nitrogen speciation of the biomorphs using the HERMES STXM beamline at the synchrotron SOLEIL (Saint-Aubin, France - Belkhou *et al.*, 2015; Swaraj *et al.*, 2017). Energy calibration was done using the well-resolved 3p Rydberg peak of gaseous CO_2 at 294.96 eV for the C K-edge, and using the $1s \rightarrow \pi^*$ photoabsorption resonance of gaseous N_2 at 400.8 eV for the N K-edge. X-ray absorption near edge structure (XANES) hypercube data (stacks) were collected with a spatial resolution of 35 nm at energy increments of 1 eV over the 250-450 eV region and at energy increments of 0.1 eV over the carbon (270–340 eV) and the nitrogen (390–450 eV) absorption ranges with a dwell time of less than 1 ms per pixel to prevent irradiation damage (Wang *et al.*, 2009). Stack alignments and extraction of XANES spectra were done using the aXis2000 software. Normalisation of data was done using the QUANTORXS freeware (Le Guillou *et al.*, 2018).

Supplementary Figure

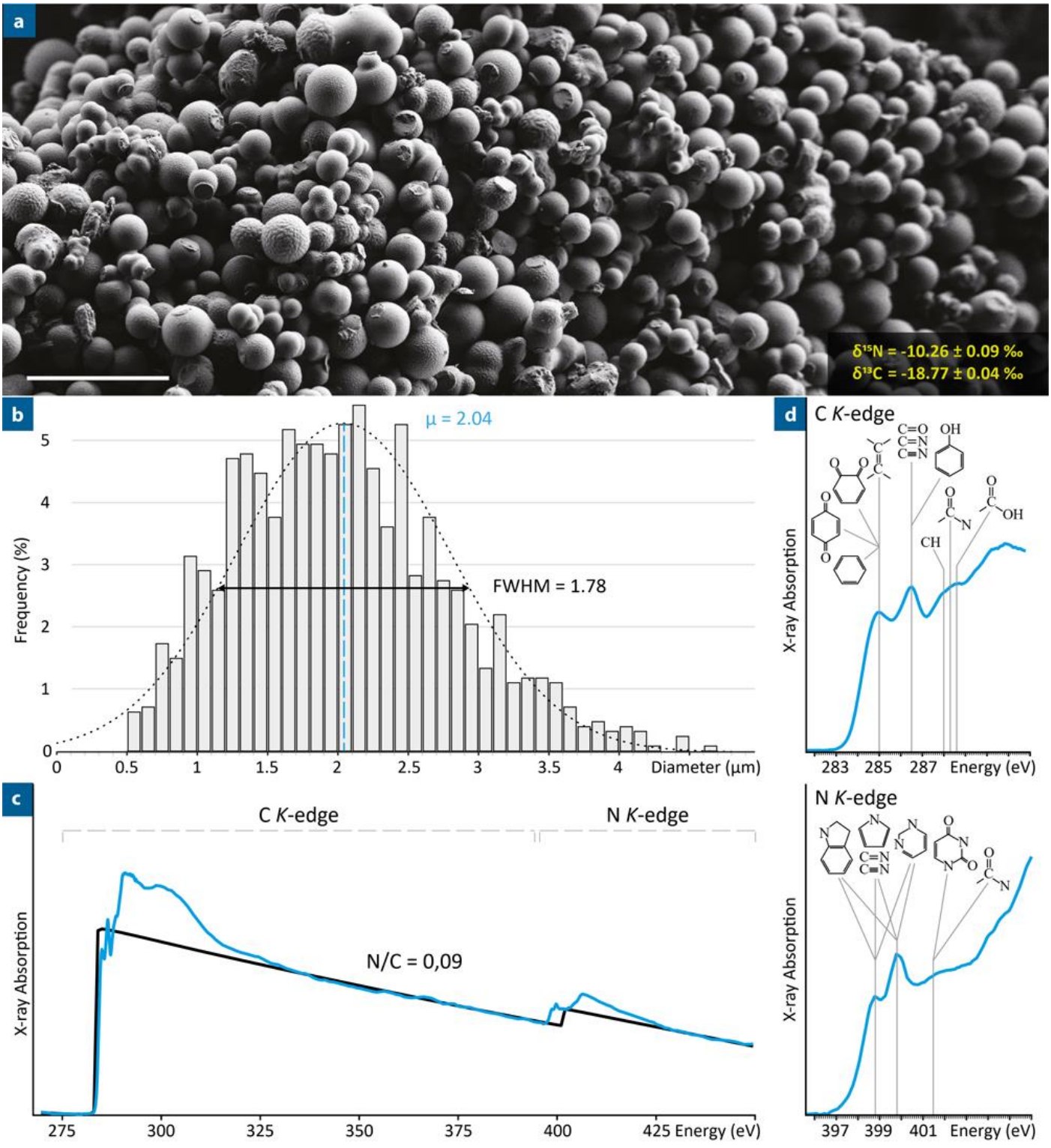

Figure S-1 Results of the quartz-free control experiment. **(a)** SEM image (secondary electrons) of the organic biomorphs produced in the absence of quartz. Their $\delta^{13}C$ and $\delta^{15}N$ are indicated in yellow. Scale bar: 10 µm. **(b)** Bar chart showing the size distribution of the spheroidal organic biomorphs produced in the absence of quartz (FWHM: full width at half maximum). **(c)** X-ray absorption spectrum of the spheroidal organic biomorphs produced in the absence of quartz and their corresponding N/C value. **(d)** C- and N-XANES spectra of the spheroidal organic biomorphs produced in the absence of quartz

Supplementary Information References

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