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Abiotic formation of organic biomorphs under diagenetic conditions

I. Criouet¹, J.-C. Viennet¹, P. Jacquemot^{1,2}, M. Jaber², S. Bernard^{1*}



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Abstract



The most ancient fossil record contains fundamentally important information on both the diversity and disparity of ancient life. Yet this ancient record is not that easy to decode, due to difficulties mainly pertaining to the impact of the geological history. Thus, the convergence of multiple lines of evidence is seen as necessary to build a robust demonstration of the biogenicity of putative traces of life. Yet, we experimentally show here that abiotic organic cell-like microstructures meeting all the criteria of biogenicity may form in cherts under classical conditions of diagenesis. These organic biomorphs produced from a mixture of RNA and quartz in water exposed to temperature and pressure conditions (200 °C, ~15 bars) exhibit morphological, chemical and isotopic signatures typical of organic microfossils. The results of this study exemplify the pitfalls that Archean palaeontologists may encounter when searching for traces of life in ancient rocks.

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Letter

We still do not know when, where and how life started to exist on Earth. As the unique source of direct information about past life, the ancient fossil record may provide answers. Yet, although the ancient fossil record may contain fundamentally important ‘bio-geochemical’ signals, its quality is far from perfect, making it not that easy to decode (Brasier *et al.*, 2006; Javaux, 2019). Archean palaeontology only relies on degraded signals difficult to interpret, as illustrated by the number of controversies having so far hindered the search for the most ancient traces of life on Earth (Schopf, 1975; Javaux, 2019).

A main difficulty is the lack of a univocal criterion to rely on when discussing the biogenicity of putative remains of life in ancient rocks: neither the carbon isotopic compositions nor the morphologies should be seen as unambiguous biosignatures (Craig, 1954; Horita, 2005; Cosmidis and Templeton, 2016; Garcia-Ruiz *et al.*, 2020). In fact, mineral biomorphs may easily be produced experimentally *via* self-assembly processes (Garcia-Ruiz *et al.*, 2003) and may exhibit high levels of complexity (Garcia-Ruiz *et al.*, 2009; Noorduyn *et al.*, 2013; Rouillard *et al.*, 2018). Worse still, Cosmidis and Templeton (2016) recently demonstrated that carbon-sulfur biomorphs could also be produced.

Chemical information may help to identify remains of life (Benzerara *et al.*, 2006; Bernard *et al.*, 2007; Alleon *et al.*, 2018; Loron *et al.*, 2019), but abiotic processes may lead to the formation of disordered carbonaceous materials difficult to distinguish from biogenic ones (Pasteris and Wopenka, 2003; De Gregorio *et al.*, 2011). Collectively, because none of the criteria commonly

used to discuss biogenicity are sufficient in themselves, many authors have emphasised the need for gathering multiple lines of evidence to demonstrate convincingly the biological origin of any putative remain of life in ancient cherts (*e.g.*, Westall, 2005; Wacey, 2009; Bernard and Papineau, 2014; Javaux, 2019). Yet, as illustrated by the present study, purely abiotic microstructures may fulfill not only a couple but many (if not all) of the commonly used criteria of biogenicity, *i.e.* morphological, chemical and isotopic criteria, even the most conservative ones (*cf.* below).

Here, we exposed RNA (*i.e.* the most emblematic organic molecule of the prebiotic RNA World; Higgs and Lehman, 2015) to thermal conditions typical of diagenesis (200 °C), in pure bi-distilled water under an autogenic pressure of 15 bars, in the presence of quartz (*i.e.* the main mineral of Archean cherts; Perry and Leticariu, 2007) and under an argon atmosphere for 20 days. We conducted additional experiments under the same conditions with RNA in the absence of quartz and with quartz in the absence of RNA to serve as controls. The water insoluble experimental residues were characterised using X-ray diffraction (XRD), isotopic ratio mass spectrometry (IRMS), solid-state ¹³C cross polarization magic-angle spinning nuclear magnetic resonance (¹³C CP MAS NMR) and Fourier transform infrared (FTIR) spectroscopies. Additional characterisation was conducted using advanced microscopy and spectroscopy tools including scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDXS), scanning transmission electron microscopy (STEM) and scanning transmission X-ray microscopy (STXM) coupled with X-ray absorption near edge structure (XANES) spectroscopy.

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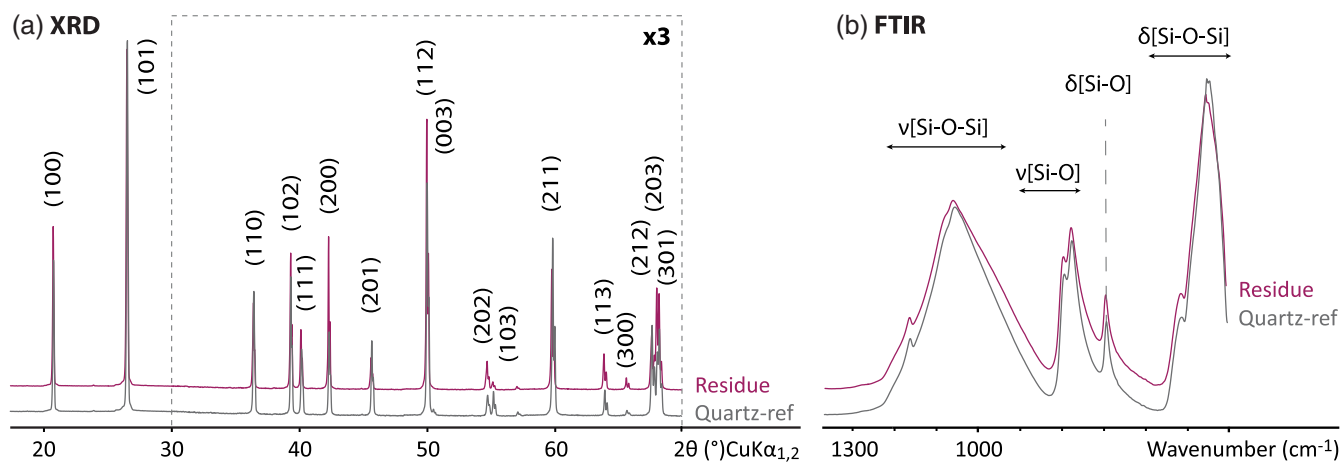


Figure 1 XRD and FTIR results. (a) Powder XRD patterns of the experimental residue (α -quartz + RNA + H₂O at 200 °C, 15 bars, 20 days) and of the α -quartz reference (intensity increased $\times 3$ from 30 to 70° 2 θ). (b) ATR-FTIR spectra of the experimental residue (α -quartz + RNA + H₂O at 200 °C, 15 bars, 20 days) and of the α -quartz reference.

Quartz was relatively unaffected by the experimental conditions. The main peaks of the XRD pattern of the experimental residue are those of α -quartz (*i.e.* 4.47 Å (100), 3.40 Å (101) and 2.57 Å (110); Fig. 1a). Likewise, the FTIR spectrum of the residue exhibits absorption bands typical of α -quartz (Fig. 1b): Si-O-Si and Si-O bending vibrations at 455 cm⁻¹, 514 cm⁻¹ and 694 cm⁻¹, Si-O stretching vibrations at 775 and 794 cm⁻¹ and Si-O-Si stretching vibrations at 1052 and 1160 cm⁻¹ (Fig. 1b; Anbalagan *et al.*, 2010). Nevertheless, SEM images reveal the presence of dissolution pits at the surface of quartz grains, indicating that a certain fraction of quartz dissolved during the experiment (Fig. 2a).

Most importantly, SEM images show the presence, at the surface of the quartz grains, of newly formed spheroidal carbonaceous microstructures (Fig. 2), resembling micro-organisms such as *Staphylococcus* or *Thermococcales* (Fig. 2i,j). Arranged in clusters, these spheroidal organic biomorphs exhibit a rather restricted range of diameters of about ~0.5 to ~5 μm ($\mu = 2.03 \mu\text{m}$; Fig. 2c). Most display a rough surface resembling the ultra-structure of living cells, and many are connected together as if they were microbes encompassing cell division (Fig. 2). These spheroidal organic biomorphs exhibit N/C values of 0.1 (*vs.* 0.4 for RNA), $\delta^{13}\text{C}$ values of $-19.35 \pm 0.04 \text{‰}$ (*vs.* $-22.62 \pm 0.04 \text{‰}$ for RNA) and $\delta^{15}\text{N}$ values of $-9.95 \pm 0.09 \text{‰}$ (*vs.* $-12.11 \pm 0.09 \text{‰}$ for RNA), *i.e.* values not that different from those expected for organic microfossils (*e.g.*, Craig, 1954; Mojzsis *et al.*, 1996; Horita, 2005).

While the NMR spectrum of RNA is dominated by the signals of ribose (between 60 and 105 ppm) and nucleobases (between 140 and 170 ppm), the NMR spectrum of these spheroidal organic biomorphs indicates the presence of aliphatic, aromatic and heterocyclic carbons (signals from 0 to 50 ppm, 100 to 130, and 130 to 150 ppm respectively) and amide and ketone groups (features at ~170 and 200 ppm) (Fig. 3a; Jacquemot *et al.*, 2019). This is in line with the FTIR spectrum showing C-H bending vibrations at 1367 cm⁻¹, aromatic C=C stretching vibrations at 1442 cm⁻¹ and CH₃/CH₂ stretching vibrations from 2850 to 2980 cm⁻¹ (Fig. 3b). The additional features at 1594 cm⁻¹ and 1675 cm⁻¹ highlight the presence of N-H bonds in amides or amines, as well as C=N bonds in imines or C=O bonds in ketones (Fig. 3b; Li *et al.*, 2014; Bernard *et al.*, 2015).

In contrast to RNA which C-XANES spectrum exhibits a number of well defined absorption features attributed to

nucleobases and ribose (Fig. 4; Viennet *et al.*, 2019, 2020), the spheroidal organic biomorphs display a XANES spectrum with large features attributed to (hetero)quinones and olefinic or aromatic carbons (284.8–285.5 eV), imines, nitriles, ketones and/or phenols (286.4 eV) and amide groups (288.2 eV) (Fig. 4; Le Guillou *et al.*, 2018), *i.e.* a spectrum not that different from those expected for microfossils. The N-XANES spectrum confirms the presence of imine/nitrile (peaks at 398.3 and 399.4 eV) and amide functions (feature at 401.5 eV) (Fig. 4; Alleon *et al.*, 2017). Control experiments revealed that the presence of quartz has no influence on the properties of the produced spheroidal organic biomorphs (Fig. S-1).

By analogy with the production of hydrothermal carbon spheres (a.k.a. hydrochars), it can be assumed that the formation of these spheroidal organic biomorphs resulted from a cascade of reactions involving hydrolysis, dehydration, aromatisation and condensation (LaMer, 1952; Sevilla and Fuentes, 2009a,b). The entire process should not be seen as a suite of consecutive reactions, but rather as a parallel network of different reaction paths (Funke and Ziegler, 2010; Hu *et al.*, 2010). The hydrolysis of RNA likely produced organic acids having accelerated dehydration and fragmentation processes (*i.e.* ring opening and bond breaking), forming soluble by-products such as furfural-like compounds (Sevilla and Fuentes, 2009a,b). These by-products likely underwent aromatisation and condensation (possibly *via* intermolecular dehydration), leading to the production of aromatic clusters (Sevilla and Fuentes, 2009a,b). Burst nucleation processes likely took place when the concentration of aromatic clusters reached the critical supersaturation point, the nuclei growing by diffusion to the surface of the chemical species present in the solution, eventually forming the spheroidal organic biomorphs (Sevilla and Fuentes, 2009a,b). According to the LaMer model (LaMer, 1952), the structure of these spheroidal organic biomorphs should be composed of an aromatic-rich hydrophobic core and a hydrophilic surface containing a larger concentration of reactive oxygen-rich functional groups, as observed for hydrochars (Baccile *et al.*, 2009; Sevilla and Fuentes, 2009a,b; Higgins *et al.*, 2020). Yet, spatially resolved STXM investigations reveal that the spheroidal organic biomorphs produced here are quite homogeneous chemically, at least at the submicrometre scale, with rather equivalent concentrations of aromatic, ketone and amide groups inside their core and at their surface.

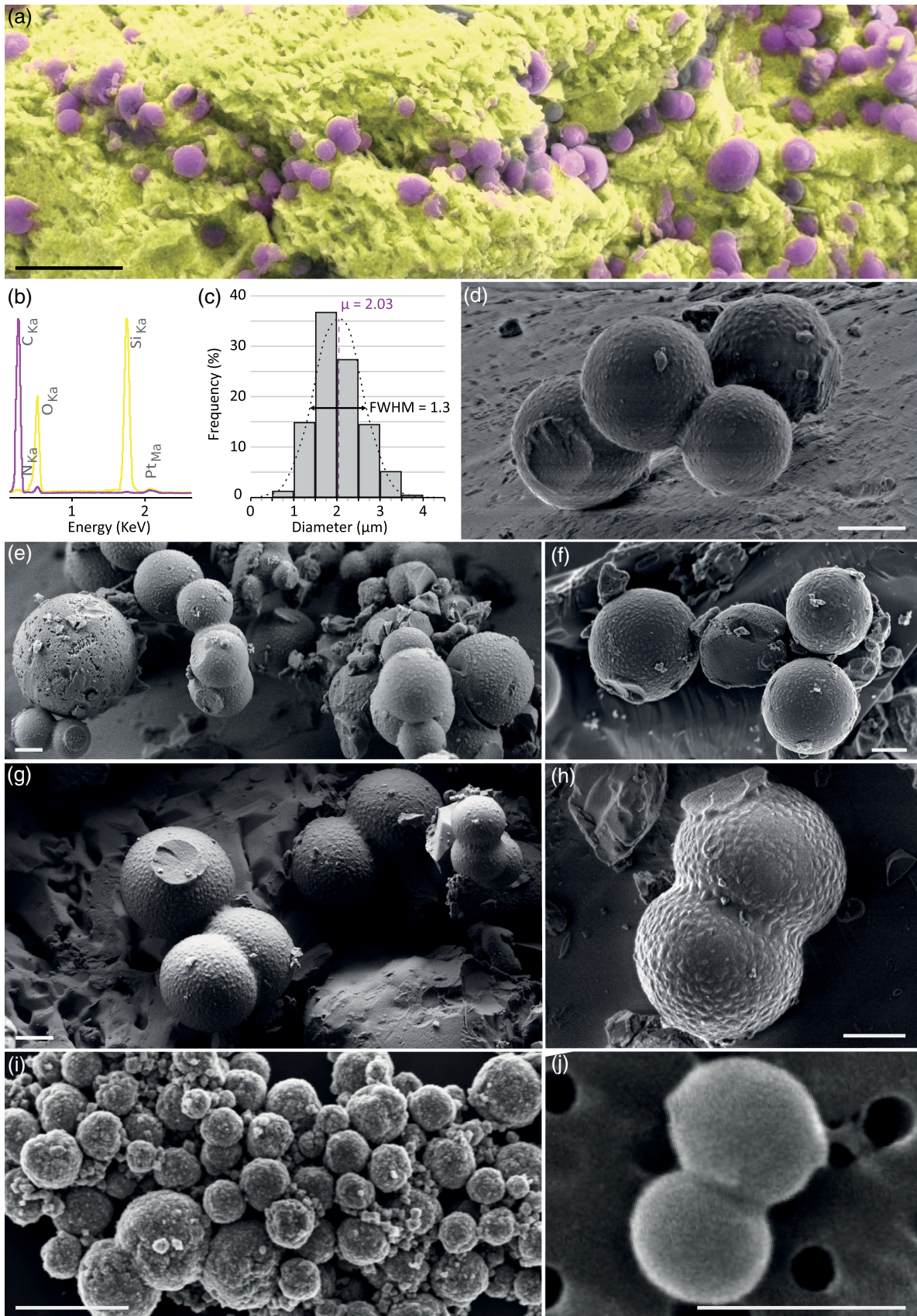


Figure 2 SEM investigations of the experimental residue (α -quartz + RNA + H₂O at 200 °C, 15 bars, 20 days). (a) EDX map of the residue and (b) corresponding EDX spectra. Quartz appears in yellow and the spheroidal organic biomorphs appear in purple. (c) Bar chart showing the size distribution of the spheroidal organic biomorphs produced during the experiments (FWHM: full width at half maximum). (e-h) SEM images (secondary electrons) of the spheroidal organic biomorphs produced during the experiments. (f, g) SEM images (secondary electrons) of *Thermococcus prieurii* cells (courtesy of Aurore Gorlas). Scale bars: (a) 10 μ m, (d-j) 1 μ m.

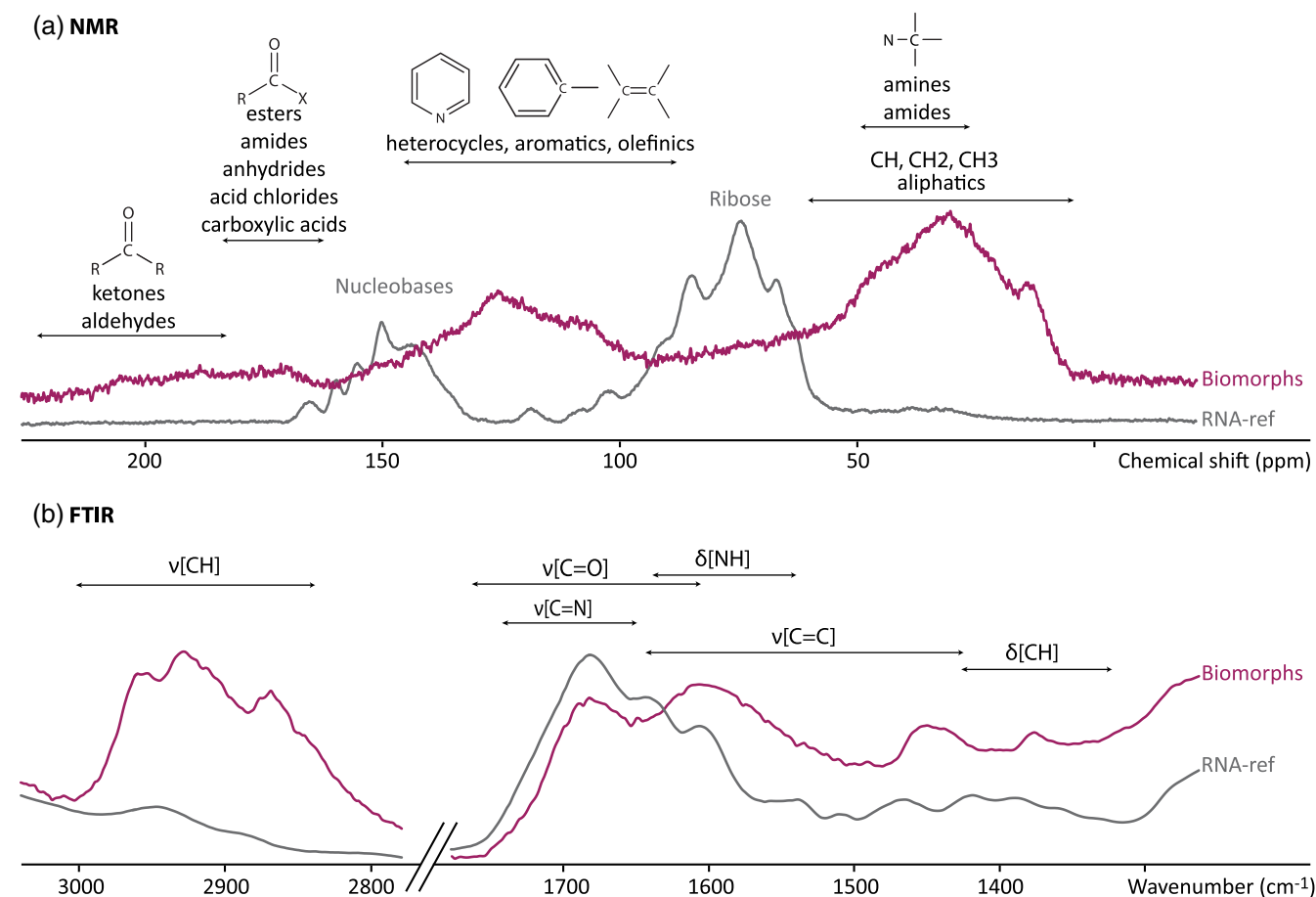


Figure 3 Solid state ^{13}C NMR and ATR-FTIR results. **(a)** Solid state ^{13}C CP MAS NMR spectra of the experimental residue (α -quartz + RNA + H_2O at 200 °C, 15 bars, 20 days) and of the RNA reference. Spectra are normalised to the quantity of carbon. **(b)** ATR-FTIR spectra of the experimental residue (α -quartz + RNA + H_2O at 200 °C, 15 bars, 20 days) and of the RNA reference. Spectra are normalised to the total carbon content. Note that the intensity of the signals were increased $\times 3$ for clarity from ~ 3035 to ~ 2775 cm^{-1} .

Collectively, in contrast to mobile hydrocarbon microspheres that can be encountered in the geological record (Wanger *et al.*, 2012), the spheroidal organic biomorphs produced here exhibit all the morphological and geochemical features typical of organic microfossils (size, morphology, ultra-structure, chemistry, isotopic signatures). Worse still, it has been shown that, if exposed to pressure and temperature conditions typical of the geological history undergone by ancient cherts, such spheroidal organic biomorphs may evolve into double shell hollow spheres (Hu *et al.*, 2010; Li *et al.*, 2016). In other words, because they meet all the criteria commonly used to discuss biogenicity, even the most conservative ones (Brasier *et al.*, 2006), the abiotic spheroidal organic biomorphs described here would logically be recognised as truly biogenic organic microfossils if they were found in ancient cherts.

The results of the present study exemplify the pitfalls that Archean palaeontologists may encounter when searching for traces of life in ancient rocks (*e.g.*, Schopf, 1975; Javaux, 2019). It is clear that if new strategies are not adopted, ambiguities and controversies will persist. Advanced spatially resolved spectroscopy techniques may provide some clues regarding the molecular structure of putative organic microfossils (*e.g.*, Brasier *et al.*, 2015; Alleen and Summons, 2019), but this is not sufficient. Because unambiguously determining the exact nature of putative organic microfossils requires information on their original chemical nature, only laboratory experiments

may provide the necessary constraints to eventually decode the most ancient fossil record (*e.g.*, Javaux, 2019).

Author Contributions

IC, PJ and SB designed the present study. IC and PJ performed the NMR analyses. IC, PJ and SB performed the SEM analyses. IC and JCV performed the EA-IRMS analyses, the XRD analyses and the FTIR analyses. IC, JCV and SB performed the STXM analyses. All authors contributed to the interpretation of the data and discussed their implications. IC, JVC and SB wrote the manuscript, with critical inputs from PJ and MJ.

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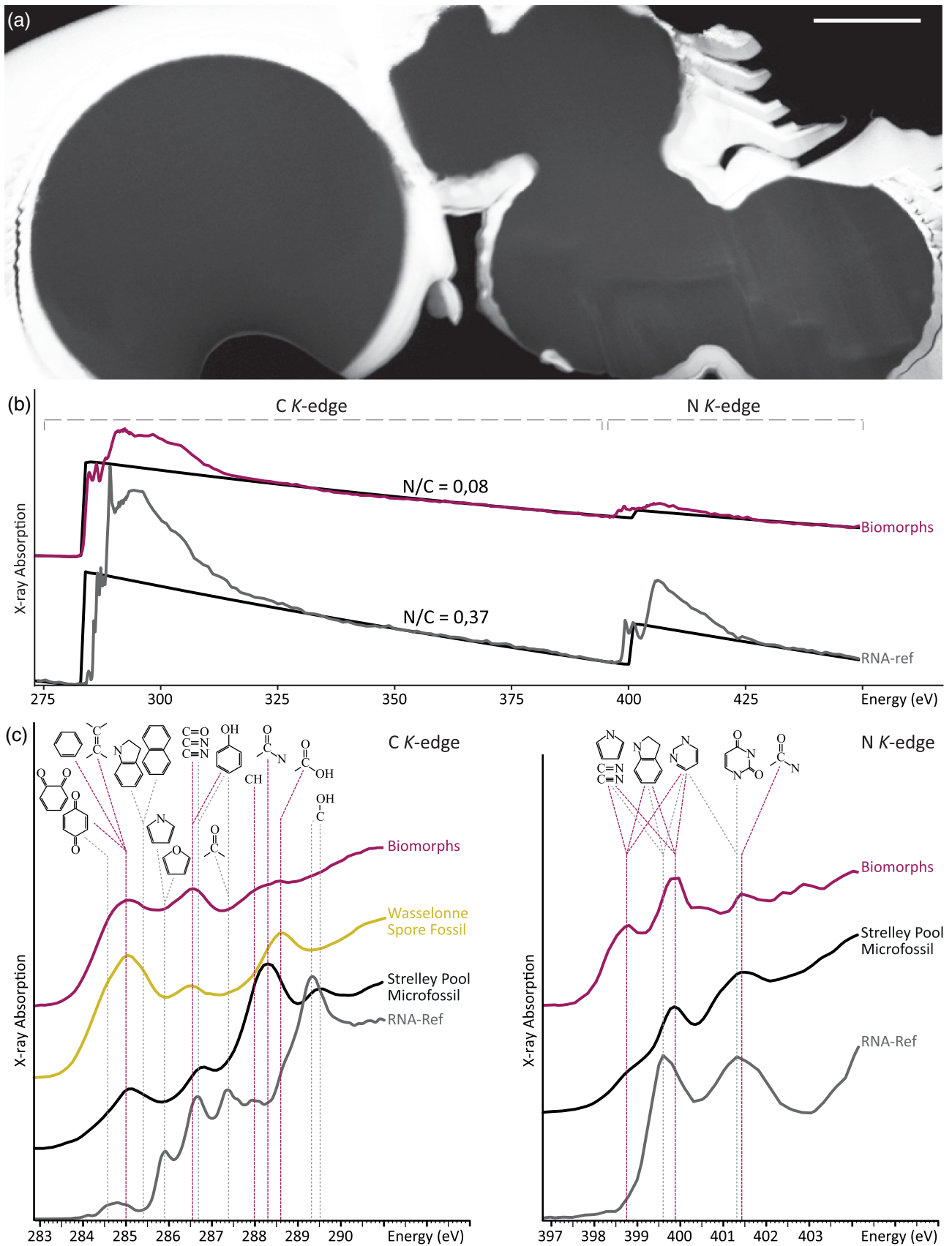


Figure 4 STEM and STXM-XANES results. **(a)** Transmission electron microscopy image (STEM mode) of the FIB section extracted from spheroidal organic biomorphs. Scale bar: 1 μm . **(b)** X-Ray absorption spectra of the organic biomorphs and of the RNA reference, with their corresponding N/C values. **(c)** C- and N-XANES spectra of the organic biomorphs and of the RNA reference compared to spectra of organic microfossils from Waselonne (Bernard *et al.*, 2009) and Strelley Pool (Alleon *et al.*, 2018). All spectra are normalised to C and N quantities.

at SOLEIL. The SEM facility at IMPMC is supported by Region Ile de France grant SESAME Number I-07-593/R, INSU-CNRS, INP-CNRS and UPMC-Paris 6, and by the Agence Nationale de la Recherche (ANR) grant number ANR-07-BLAN-0124-01. The TEM facility at the CCM (Lille University) is supported by the Chevreul Institute, the European FEDER, and Région Nord-Pas-de-Calais. The HERMES beamline (SOLEIL) is supported by the CNRS, the CEA, the Region Ile de France, the Departmental Council of Essonne and the Region Centre.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2102>.



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References

- ANBALAGAN, G., PRABAKARAN, A., GUNASEKARAN, S. (2010) Spectroscopic characterization of Indian standard sand. *Journal of Applied Spectroscopy* 77, 86–94.
- ALLEON, J., BERNARD, S., LE GUILLOU, C., DAVAL, D., SKOURI-PANET, F., KUGA, M., ROBERT, F. (2017) Organic molecular heterogeneities can withstand diagenesis. *Scientific Reports* 7, 1508.
- ALLEON, J., BERNARD, S., LE GUILLOU, C., BEYSSAC, O., SUGITANI, K., ROBERT, F. (2018) Chemical nature of the 3.4 Ga Strelley Pool microfossils. *Geochemical Perspectives Letters* 7, 37–42.
- ALLEON, J., SUMMONS, R.E. (2019) Organic geochemical approaches to understanding early life. *Free Radical Biology and Medicine* 140, 103–112.
- BACCILE, N., LAURENT, G., BABONNEAU, F., FAYON, F., TITRICI, M.-M., ANTONIETTI, M. (2009) Structural Characterization of Hydrothermal Carbon Spheres by Advanced Solid-State MAS ¹³C NMR Investigations. *The Journal of Physical Chemistry C* 113, 9644–9654.
- BENZERARA, K., MENGUY, N., LOPEZ-GARCIA, P., YOON, T.-H., KAZMIERCZAK, J., TYLISZCZAK, T., GUYOT, F., BROWN, G.E. (2006) Nanoscale detection of organic signatures in carbonate microbialites. *Proceedings of the National Academy of Sciences* 103, 9440–9445.
- BERNARD, S., PAPINEAU, D. (2014) Graphitic Carbons and Biosignatures. *Elements* 10, 435–440.
- BERNARD, S., BENZERARA, K., BEYSSAC, O., MENGUY, N., GUYOT, F., BROWN, G., GOFFE, B. (2007) Exceptional preservation of fossil plant spores in high-pressure metamorphic rocks. *Earth and Planetary Science Letters* 262, 257–272.
- BERNARD, S., BENZERARA, K., BEYSSAC, O., BROWN, G.E., STAMM, L.G., DURINGER, P. (2009) Ultrastructural and chemical study of modern and fossil sporoderms by Scanning Transmission X-ray Microscopy (STXM). *Review of Palaeobotany and Palynology* 156, 248–261.
- BERNARD, S., BENZERARA, K., BEYSSAC, O., BALAN, E., BROWN JR., G.E. (2015) Evolution of the macromolecular structure of sporopollenin during thermal degradation. *Heliyon* 1, e00034.
- BRASIER, M., MCLOUGHLIN, N., GREEN, O., WACEY, D. (2006) A fresh look at the fossil evidence for early Archaean cellular life. *Philosophical Transactions of the Royal Society B: Biological Sciences* 361, 887–902.
- BRASIER, M.D., ANTCLIFFE, J., SAUNDERS, M., WACEY, D. (2015) Changing the picture of Earth's earliest fossils (3.5–1.9 Ga) with new approaches and new discoveries. *Proceedings of the National Academy of Sciences* 112, 4859–4864.
- COSMIDIS, J., TEMPLETON, A.S. (2016) Self-Assembly of biomorphic carbon/sulfur microstructures in sulfidic environments. *Nature Communications* 7, 12812.
- CRAIG, H. (1954) Geochemical implications of the isotopic composition of carbon in ancient rocks. *Geochimica et Cosmochimica Acta* 6, 186–196.
- DE GREGORIO, B.T., SHARP, T.G., RUSHDI, A.I., SIMONEIT, B.R.T. (2011) Bugs or Gunk? Nanoscale Methods for Assessing the Biogenicity of Ancient Microfossils and Organic Matter. In: GOLDING, S.D., GLIKSON, M. (Eds.) *Earliest Life on Earth: Habitats, Environments and Methods of Detection*. Springer Netherlands, Dordrecht, 239–289.
- FUNKE, A., ZIEGLER, F. (2010) Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels, Bioproducts and Biorefining* 4, 160–177.
- GARCIA-RUIZ, J.M., HYDE, S.T., CARNERUP, A.M., CHRISTY, A.G., VAN KRANENDONK, M.J., WELHAM, N.J. (2003) Self-Assembled Silica-Carbonate Structures and Detection of Ancient Microfossils. *Science* 302, 1194–1197.
- GARCIA-RUIZ, J.M., MELERO-GARCIA, E., HYDE, S.T. (2009) Morphogenesis of Self-Assembled Nanocrystalline Materials of Barium Carbonate and Silica. *Science* 323, 362–365.
- GARCIA-RUIZ, J.M., VAN ZUILEN, M.A., BACH, W. (2020) Mineral self-organization on a lifeless planet. *Physics of Life Reviews* 34–35, 62–82.
- HIGGINS, L.J.R., BROWN, A.P., HARRINGTON, J.P., ROSS, A.B., KAULICH, B., MISHRA, B. (2020) Evidence for a core-shell structure of hydrothermal carbon. *Carbon* 161, 423–431.
- HIGGS, P.G., LEHMAN, N. (2015) The RNA World: molecular cooperation at the origins of life. *Nature Reviews Genetics* 16, 7–17.
- HORITA, J. (2005) Some perspectives on isotope biosignatures for early life. *Chemical Geology* 218, 171–186.
- HU, B., WANG, K., WU, L., YU, S.-H., ANTONIETTI, M., TITRICI, M.-M. (2010) Engineering Carbon Materials from the Hydrothermal Carbonization Process of Biomass. *Advanced Materials* 22, 813–828.
- JACQUEMOT, P., VIENNET, J.C., BERNARD, S., LE GUILLOU, C., RIGAUD, B., DELBES, L., GEORGELIN, T., JABER, M. (2019) The degradation of organic compounds impacts the crystallization of clay minerals and vice versa. *Scientific Reports* 9, 20251.
- JAVAU, E.J. (2019) Challenges in evidencing the earliest traces of life. *Nature* 572, 451–460.
- LAMER, V.K. (1952) Nucleation in Phase Transitions. *Industrial & Engineering Chemistry* 44, 1270–1277.
- LE GUILLOU, C., BERNARD, S., DE LA PENA, F., LE BRECH, Y. (2018) XANES-Based Quantification of Carbon Functional Group Concentrations. *Analytical Chemistry* 90, 8379–8386.
- LI, J., BERNARD, S., BENZERARA, K., BEYSSAC, O., ALLARD, T., COSMIDIS, J., MOUSSOU, J. (2014) Impact of biomineralization on the preservation of microorganisms during fossilization: An experimental perspective. *Earth and Planetary Science Letters* 400, 113–122.
- LI, S., PASC, A., FIERRO, V., CELZARD, A. (2016) Hollow carbon spheres, synthesis and applications – a review. *Journal of Materials Chemistry A* 4, 12686–12713.
- LORON, C.C., FRANÇOIS, C., RAINBIRD, R.H., TURNER, E.C., BORENSTAJN, S., JAVAU, E.J. (2019) Early fungi from the Proterozoic era in Arctic Canada. *Nature* 570, 232–235.
- MOJZSIS, S.J., ARRHENIUS, G., MCKEEGAN, K.D., HARRISON, T.M., NUTMAN, A.P., FRIEND, C.R.L. (1996) Evidence for life on Earth before 3,800 million years ago. *Nature* 384, 55–59.
- NOORDUIN, W.L., GRINTHAL, A., MAHADEVAN, L., AIZENBERG, J. (2013) Rationally Designed Complex, Hierarchical Microarchitectures. *Science* 340, 832–837.
- PASTERIS, J.D., WOPENKA, B. (2003) Necessary, but Not Sufficient: Raman Identification of Disordered Carbon as a Signature of Ancient Life. *Astrobiology* 3, 727–738.
- PERRY, E.C., LEFTICARIU, L. (2007) Formation and Geochemistry of Precambrian Cherts. *Treatise on Geochemistry* 7, 1–21.
- ROUILLARD, J., GARCIA-RUIZ, J.-M., GONG, J., VAN ZUILEN, M.A. (2018) A morphogram for silica-witherite biomorphs and its application to microfossil identification in the early earth rock record. *Geobiology* 16, 279–296.
- SCHOPF, J.W. (1975) Precambrian Paleobiology: Problems and Perspectives. *Annual Review of Earth and Planetary Sciences* 3, 213–249.
- SEVILLA, M., FUERTES, A.B. (2009a) Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides. *Chemistry – A European Journal* 15, 4195–4203.



- SEVILLA, M., FUERTES, A.B. (2009b) The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon* 47, 2281–2289.
- VIENNET, J.-C., BERNARD, S., LE GUILLOU, C., JACQUEMOT, P., BALAN, E., DELBES, L., RIGAUD, B., GEORGELIN, T., JABER, M. (2019) Experimental clues for detecting biosignatures on Mars. *Geochemical Perspectives Letters* 12, 28–33.
- VIENNET, J.-C., BERNARD, S., LE GUILLOU, C., JACQUEMOT, P., DELBES, L., BALAN, E., JABER, M. (2020) Influence of the nature of the gas phase on the degradation of RNA during fossilization processes. *Applied Clay Science* 191, 105616.
- WACEY, D. (Ed.) (2009) *Early Life on Earth*. Springer Netherlands, Dordrecht.
- WANGER, G., MOSER, D., HAY, M., MYNENI, S., ONSTOTT, T.C., SOUTHAM, G. (2012) Mobile hydrocarbon microspheres from >2-billion-year-old carbon-bearing seams in the South African deep subsurface. *Geobiology* 10, 496–505.
- WESTALL, F. (2005) Early Life on Earth: The Ancient Fossil Record. In: EHRENFREUND, P., IRVINE, W.M., OWEN, T., BECKER, L., BLANK, J., BRUCATO, J.R., COLANGELI, L., DERENNE, S., DUTREY, A., DESPOIS, D., LAZCANO, A., ROBERT, F. (Eds.) *Astrobiology: Future Perspectives*. Springer Netherlands, Dordrecht, 287–316.