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1 **Abiotic synthesis of amino acids in the recesses of the oceanic lithosphere**

2

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5

6 **Abiotic hydrocarbons and carboxylic acids are known to be formed on Earth, notably**

7 **during the hydrothermal alteration of mantle rocks. Although the abiotic formation of**

8 **amino acids has been predicted both from experimental studies and thermodynamic**

9 **calculations, its occurrence has never been demonstrated in terrestrial settings. Using an**

10 **innovative multimodal approach combining high-resolution imaging techniques, we obtain**

11 **the first evidence for the occurrence of aromatic amino acids formed abiotically and**

12 **subsequently preserved at depth beneath the Atlantis massif (Mid-Atlantic Ridge). These**

13 **aromatic amino acids may have been formed through Friedel-Crafts reactions catalyzed by**

14 **an iron-rich saponite clay during a late alteration stage of the massif serpentinites.**

15 **Demonstrating the potential of fluid-rock interactions in the oceanic lithosphere to**

16 **generate amino acids abiotically gives credence to the hydrothermal theory for the origin of**

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17 **life, and may shed light on ancient metabolisms and the functioning of the present-day deep**
18 **biosphere.**

19

20 Abiotic synthesis of organic compounds by reduction of inorganic carbon species is
21 thermodynamically favored by the production of molecular hydrogen (H₂), which accompanies
22 serpentinization reactions¹. In these hydration reactions, the production of H₂ results from the
23 reduction of water coupled to the oxidation of the ferrous iron in olivine and pyroxene, the major
24 rock-forming minerals of the upper mantle¹⁻². Therefore, hydrothermal areas where active
25 serpentinization occurs are increasingly regarded as possible settings for the appearance of the
26 first building blocks of life and the emergence of primordial metabolisms³⁻⁴. In that perspective,
27 the discovery of the Lost City hydrothermal field hosted on the Atlantis Massif near the Mid-
28 Atlantic Ridge (MAR)⁵ deeply changed our vision of Earth habitability as it provides a modern
29 example of H₂-rich alkaline fluids generated at moderate temperatures (50-150°C), *i.e.* the most
30 favorable conditions for the appearance of life⁶.

31 During the last two decades, experimental studies and thermodynamic calculations
32 outlined the potential of serpentinization reactions to promote the abiotic formation of a diversity
33 of organic compounds, including some of direct interest to prebiotic chemistry such as the
34 protein-forming amino acids (Supplementary Table 1). However, reaction pathways for the
35 abiotic formation of amino acids under hydrothermal conditions are still not well constrained,
36 although several mechanisms have been proposed. Among the most commonly invoked
37 reactions, the Strecker synthesis produces amino acids (mostly aliphatic) from the reaction of
38 aldehydes or ketones with ammonia and cyanide. The overall reaction is thermodynamically

39 favored in hydrothermal environments and possibly catalyzed by metals and minerals
40 (Supplementary Table 1).

41 Geochemical and isotopic evidence demonstrates abiotic synthesis of only a restricted
42 number of low-molecular-weight organic compounds in hydrothermal systems associated with
43 serpentinization on Earth. These compounds include mainly methane, short-chain alkanes and
44 formate⁷. Although the presence of amino acids has been reported in hydrothermal vent fluids,
45 with concentrations reaching several hundreds to thousands of nanomoles, these amino acids
46 most likely derived from ecosystems hosted in the shallow oceanic crust⁸. Primordial amino
47 acids and other nitrogen-bearing organic compounds have generally been considered as
48 extraterrestrial in origin, and exogenously delivered to Earth by comets and asteroids⁹. These
49 organic nitrogen compounds would be inherited from the aqueous alteration of the chondrite
50 parent bodies or the asteroidal meteorites themselves, in a process resembling serpentinization as
51 it occurs on Earth¹⁰⁻¹¹. Although ref. (8) acknowledges that some of the amino acids detected at
52 the Lost City hydrothermal field could have been synthesized abiotically, the possibility that the
53 serpentinizing oceanic lithosphere could represent an efficient factory for nitrogen-bearing
54 organic compounds has been poorly assessed until now. The current approaches are indeed
55 mainly based on the analysis of fluids discharged at hydrothermal vents where, if abiotic
56 synthesis would occur, products are likely too diluted to be distinguished from background
57 biological contamination⁸.

58

59 **Serpentinite-hosted amino acids**

60 Our study focuses on a deeply serpentinized harzburgite recovered by drilling in the Atlantis
61 massif at a depth of 173.15 meters below sea floor (mbsf) during the IODP expedition 304 Leg

62 1309D¹². The Atlantis massif is a tectonically-exhumed dome (~16 km across and rising 4,267 m
63 above the seafloor) associated with an oceanic core complex located at the intersection between
64 the MAR and the Atlantis transform fault (30°8'N-42°8'W). The sample was selected based on
65 its elevated content in organic carbon determined by elemental analysis (*i.e.* 232 ppm)¹³. The
66 high-temperature (300-350°C)¹² hydrated paragenesis resembles that usually found in
67 serpentinized peridotites, with olivine being replaced by serpentine and magnetite exhibiting a
68 characteristic mesh texture (Extended Data Fig. 1). Yellow to brownish phases are frequently
69 found in the core of the mesh serpentine (Fig. 1a and Extended Data Fig. 1). These phases
70 correspond to Fe-rich serpentine and Fe-rich saponite enriched in organic carbon (Fig. 2 and
71 Extended Data Figs. 2 and 3f)¹⁴⁻¹⁵. They formed respectively during a second and third stage of
72 hydrothermal alteration occurring at lower temperature (<200°C for Fe-rich serpentine¹⁶ and
73 <100-150°C for saponite¹⁷) at the expense of the first generation of serpentine and of the olivine
74 kernels, some remnants of which can still be observed (Extended Data Fig. 1).

75 Synchrotron-coupled Deep-Ultra-Violet (S-DUV) microspectroscopy with excitation in
76 the range 250-310 nm revealed an intense UV-autofluorescence (Fig. 1 and Extended Data Fig.
77 4) where Fe-rich saponite was present (Fig. 2 and Extended Data Figs. 2-3). Full-field imaging of
78 the fluorescence collected in the 400-440 nm range following excitation at 275 nm showed a
79 heterogeneous spatial distribution of the strongest fluorescence intensities forming a tortuous
80 network within Fe-rich saponite (Fig. 1b). This is consistent with Scanning Electron Microscopy
81 (SEM) observations highlighting variable content in the organic carbon trapped in this mineral
82 phase (Figs. 2a-b). S-DUV autofluorescence was weaker in the Fe-rich serpentine compared to
83 the Fe-rich saponite and nearly absent in the adjacent mesh serpentine (Fig. 1). The fluorescence
84 signal collected between 300 and 550 nm after excitation at 275 nm was characterized by four

85 broad and overlapping bands respectively centered at 340 ± 6 , 358 ± 3 , 380 ± 3 and 403 ± 3 nm (Fig.
86 1 and Extended Data Fig. 4). These spectral features are indicative of the presence of tryptophan
87 to which the band at 358 nm can be assigned, and of indole, skatole, and hydroxyanthranilic acid
88 whose fluorescence spectra can be found in ref. (18). These three latter compounds may
89 correspond to products of either natural¹⁸ or UV-induced degradation¹⁹ of tryptophan, although
90 indole can also be an intermediate in the abiotic synthesis of tryptophan²⁰. The four organic
91 compounds were always spatially associated at comparable relative intensities (Extended Data
92 Fig. 4). In contrast to the fluorescence emission observed upon excitation at 275 nm, which is
93 close to the maximum absorption wavelength of tryptophan²¹, excitations at wavelengths of 250
94 and 310 nm did not lead to any other endogenous fluorescence emission (Fig. 1c). Whereas
95 protein-forming tryptophan in biological cells fluoresces at 335 nm after excitation at 275 nm
96 and does not produce significant signals at higher wavelengths (Fig. 1c)²¹, the UV-fluorescence
97 emission value obtained here for tryptophan agrees with the maximum of fluorescence emission
98 that arises when this amino acid is free (*i.e.* 360 nm)²¹, the spectral shift being due to
99 environment-related effects.

100 In agreement with S-DUV microspectroscopy, Time-of-Flight Secondary Ion Mass
101 Spectrometry (TOF-SIMS) imaging recorded in Fe-rich saponite revealed a systematic presence
102 of fragment ions characteristic of tryptophan (*e.g.* $C_9H_8N^+$; Figs. 3b-c and Extended Data Table
103 1)²². In addition to saponite/Fe-rich serpentine assemblages, tryptophan was also detected inside
104 saponite close to olivine kernels, although more spatially restricted and at lower fluorescence
105 intensities (Fig. 4). In all the areas where saponite and fragment ions characteristic of tryptophan
106 were both detected, TOF-SIMS analysis did not provide any evidence for the presence of
107 biomarkers, such as hopanoids, cholestane, pristane, squalane, lycopane or β -carotane²³⁻²⁵, which

108 are constituents of marine dissolved organic carbon¹³ or of deep microbial communities (Fig. 3d
109 and Extended Data Fig. 6).

110 The presence of N-bearing organic compounds in the Fe-rich saponite was confirmed by
111 Synchrotron-Fourier-Transform-Infrared microspectroscopy (S-FTIR) with vibrational modes
112 attributable to pyrrole and aromatic rings (at 1380 cm⁻¹ and 1460-1465 cm⁻¹), α -amines (in the
113 ranges 1460-1465 cm⁻¹ and 1550-1650 cm⁻¹) and carboxyl functional groups (at 1412 cm⁻¹ and
114 1728 cm⁻¹) (Extended Data Figs. 2b-c and Extended Data Table 2). The distribution of the
115 absorption bands resembles that observed for tryptophan²⁶, although with higher relative
116 proportions of primary amines and heterocycles and higher aliphaticity. Consequently, the broad
117 absorption band between 1550 and 1650 cm⁻¹ likely represents multiple overlapping bands from
118 different N-bearing heterocycles, as also observed by S-DUV microspectroscopy. Again, no
119 absorption bands were detected between 1627 and 1670 cm⁻¹ where the characteristic amide I
120 absorption band of protein secondary structures is observed²⁷.

121

122 **An abiotic origin for the amino acids**

123 The unique organic signatures derived from S-DUV, S-FTIR and TOF-SIMS measurements, all
124 preferentially associated with the Fe-rich saponite, are clearly different from those obtained
125 under comparable analytical conditions for microbial cells or biofilm-forming extracellular
126 polymeric substances (Figs. 1c and 3; Extended Data Figs. 2b and 6). The presence of microbes
127 or their remnants would have resulted in a spatially variable complex mixture of biopolymers, all
128 carrying diverse functional groups²⁸. In contrast, the organic material detected here corresponds
129 to low-molecular-weight compounds with TOF-SIMS $m/z < 350$ (Fig. 3d and Extended Data
130 Figs. 6). In addition, S-DUV, S-FTIR and TOF-SIMS analyses constantly display spectral

131 signatures that vary little from one micrometer to the other, all in favor of an abiotic origin for
132 the tryptophan. In agreement with this hypothesis, as observed by Transmission Electron
133 Microscopy (TEM), the Fe-rich saponite nanoporous network hosting the tryptophan signal is
134 too tiny to host or have hosted prokaryotic cells of a few micrometers (Figs. 4d and 5a-b and
135 Extended Data Figs. 3 and 5). The lack of amino acid characteristic signal in microfractures
136 related to the Fe-rich saponite claims in favor of the endogenicity of the detected tryptophan.

137 At the nanoscale, the C-enriched Fe-rich saponite displayed highly-variable texture and
138 porosity (Figs. 4d and 5a-b). At the interface between olivine crystals and mesh serpentine or Fe-
139 rich serpentine, *i.e.* where organic compounds displayed weak UV-fluorescence and TOF-SIMS
140 signals (Fig. 4), Fe-rich saponite lamellae are mainly subparallel although some sheet distortions
141 are visible (Fig. 4d and Extended Data Fig. 5). Where tryptophan was found at higher
142 concentrations in assemblages of Fe-rich saponite and Fe-rich serpentine (Figs. 1-3 and Extended
143 Data Figs. 2-4), TEM showed the presence of packed saponite sheets in face-face mode or edge-
144 face mode, forming a nanoporous house of cards structure (Figs. 5a-b). Such a state of structural
145 disorder is supported by the lack of absorption at 3415 cm^{-1} in the Fe-rich saponite S-FTIR
146 spectra, a band that theoretically corresponds to interlamellar water²⁹. Taken together, all these
147 observations suggest the formation of a reactive organoclay³⁰ during the late stages of aqueous
148 alteration of the Atlantis massif serpentinite.

149

150 **Abiotic Friedel-Crafts type synthesis**

151 Saponite, a tetrahedrally-charged trioctahedral smectite, is a well-known acid catalyst with high
152 adsorption, swelling and cation exchange capacities²⁹. These properties are widely used in the
153 industry for organic synthesis or for the reduction of inorganic nitrogen species²⁹⁻³⁰. Some

154 varieties of smectite, including saponite, were shown to promote the abiotic synthesis of
155 monocyclic as well as polycyclic aromatic hydrocarbons from methanol under hydrothermal
156 conditions (*i.e.* 300°C, 100 MPa)³¹. Smectite properties make possible the formation of pillared
157 structures out of their expandable silicate sheets by insertion, after exchange with interlayer
158 water, of ionic compounds and/or organic moieties acting as pillars propping apart the clay
159 sheets at increased interlayer distances (Fig. 5c), as observed by TEM (Fig. 4d). Further stacking
160 and distortion of the clay lamellae creates a network of interconnected nanopores with increased
161 surface area and reducing properties where organosynthesis can proceed and enhances interlayer
162 expansion (Figs. 5a-b and d)³⁰.

163 In the general structure of saponite, the octahedral sites are usually occupied by Mg²⁺
164 ions, while Al³⁺ ions substitute for Si in the tetrahedral sites. In the iron-bearing variety, both
165 Fe²⁺ and Fe³⁺ cations replace Mg²⁺ and Al³⁺ (Extended Data Tables 3 and 4), thus conserving the
166 negative charge of the silicate sheets and hence the cation exchange capacities while maintaining
167 the layered structure³². The presence of Fe³⁺ ions in the tetrahedral sheets (Extended Data Table
168 4) also enhances surface acidity and therefore the sorption and catalysis properties of saponite³².
169 The existence in the silicate sheet of Brønsted and Lewis acid sites to which aromatic and
170 heteroatomic compounds may sorb is suggested by the multiple absorption bands observed
171 between 1550 and 1650 cm⁻¹ on the Fe-rich saponite S-FTIR spectrum (Extended Data Fig.
172 2b)^{29,33}.

173 Due to their pillaring effect, enhanced sorption capacity and high reducible iron content,
174 Fe-smectites have been shown to be the most efficient solid catalyst for Friedel-Crafts
175 reactions³⁴. Friedel-Crafts-type reactions are the method of choice in the industry for the
176 alkylation of arenes and heteroarenes under the catalytic effect of Lewis or Brønsted acids, with

177 or without co-catalysts³⁵. In the present case, Friedel-Crafts-type reactions may therefore
178 represent an attractive explanation for the formation of aromatic amino acids such as tryptophan.
179 In the commonly-considered Strecker synthesis⁷, aliphatic amino acids are predominantly
180 formed (Supplementary Table 1) and additional reaction steps are subsequently required to form
181 aromatic amino acids. In contrast, starting from aromatic hydrocarbons or heteroaromatic
182 compounds to which substituents are added, Friedel-Crafts reactions may offer a more direct
183 route towards the formation of tryptophan at the acid sites of Fe-rich saponite, as demonstrated
184 experimentally through asymmetric alkylation of indole with various catalysts²⁰. Also in favor of
185 such a hypothesis is the considerable thermodynamic potential for the hydrothermal synthesis of
186 polycyclic aromatic hydrocarbons during serpentinization³⁶. (Poly)aromatic hydrocarbons may
187 hence be available as possible reactants in the shallow oceanic lithosphere.

188 We therefore propose that Friedel-Crafts reactions may be responsible for the formation
189 of abiotic aromatic amino acids during the hydrothermal alteration of oceanic peridotites, this
190 formation being catalyzed by Fe-rich saponite. Possible pathways could involve alkylation of
191 indole with pyruvate followed by amination, the abiotic synthesis of pyruvate under
192 hydrothermal conditions being demonstrated experimentally³⁷. In addition, as shown in Extended
193 Data Fig. 7 and Supplementary Information, chemical affinity calculations using concentrations
194 reported for the Lost City hydrothermal fluid endmember suggest that the abiotic formation of
195 indole, pyruvate and tryptophan from HCO_3^- , H_2 , and NH_3 is thermodynamically favorable under
196 the temperature, pH, and redox conditions prevailing in the Atlantis massif according to refs.
197 (38-39) (*i.e.* 100°C, pH = 8.5, $a_{\text{H}_2(\text{aq})} \sim 10^{-2}$ with $a_{\text{H}_2(\text{aq})}$, the activity of aqueous hydrogen). The
198 presence of NH_3 as the dominant form of nitrogen in the Atlantis massif is supported by
199 additional thermodynamic calculations (Extended Data Fig. 8) and the general recognition that

200 crustal nitrogen-reduction reactions operate during hydrothermal circulation, turning oceanic
201 nitrite and nitrate, and mantle N₂ into stable NH₃ and NH₄⁺, depending on pH⁴⁰⁻⁴¹.

202

203 **Implications**

204 The results reported above clearly indicate that clay-forming hydrothermal alteration of oceanic
205 rocks play a fundamental role in the synthesis and stabilization of such complex organic
206 compounds as aromatic amino acids. This may have far reaching implications for the carbon and
207 nitrogen cycles in the Earth system, as well as for the potential for prebiotic chemistry on Earth
208 and the deep biosphere.

209 Although little is known about the concentration of inorganic nitrogen species in the Lost
210 City hydrothermal fluids⁸, our discovery first implies that these fluids transport sufficient
211 nitrogen for the abiotic synthesis of N-bearing organic compounds. Second, our observations
212 may also extend the ranges of depths and temperatures beyond those generally considered as
213 compatible for the formation and preservation of organic molecules of prebiotic interest (*i.e.* in
214 the deep subsurface *vs* in hydrothermal vents). In a reduced rocky environment isolated from the
215 open ocean and atmosphere, sorptive mechanisms can additionally protect the clay-trapped
216 amino acids from hydrolysis⁴², as proposed for carbonaceous meteorites⁴³. Further petrological,
217 geochemical and thermodynamic investigations are however needed to better constrain the
218 conditions under which the Fe-rich saponite was formed in the Atlantis massif, saponite
219 precipitation occurring over a relatively large temperature range (*i.e.* 25-200°C)⁴⁴.

220 Nonetheless, saponite constitutes the main product of the alteration of basalts and
221 ultramafic rocks by silica-enriched hydrothermal fluids⁴⁴. Fe-rich saponite with its capability to
222 promote and preserve precursors of biopolymers, may have contributed to lay the foundations for

223 prebiotic synthesis when abundant ultramafic rocks formed the undifferentiated primeval
224 lithosphere covered by the large Hadean ocean⁴⁵. Although the diversity of amino acids possibly
225 synthesized in such a context need to be further explored, the scheme proposed here offers a
226 powerful mechanism to drive the synthesis of prebiotic compounds under realistic Archaean
227 conditions. Concentration and some forms of condensation, polymerization and further chemical
228 evolution are possible in the chemically-reducing nanopores formed by the Fe-rich saponite
229 sheets acting as a confined microreactor (Fig. 5). While tryptophan may not have served as a first
230 protein building block⁴⁶, amino acids are also known to serve as biochemical precursors, deemed
231 to catalyze the synthesis of sugars, aldehydes and nucleotide intermediates⁴⁷. If hyperalkaline
232 hydrothermal vent chimneys received a lot of attention for their vast network of
233 microcompartments walled by catalytic minerals, allowing the concentration of organic synthesis
234 products on the early Earth³, Fe-rich saponite with its tiny protective niches offers comparable
235 attractiveness. Its ion exchange capability drives chemical gradients and non-equilibrium
236 conditions while the silicate layers may play the interface role of cell membranes⁴⁸.

237 Finally, the possibility of abiotically-formed amino acids in the recesses of the oceanic
238 lithosphere has also important consequences for ancestral metabolisms and microbial life
239 strategies in the present-day deep biosphere. Both are strongly linked to the nature of compounds
240 that can be used as carbon and energy sources. Enlarging with amino acids the range of possible
241 abiotic organic compounds formed in the terrestrial crust offers an additional opportunity for
242 (organo)heterotrophy to operate in these deep environments⁴⁹. Anaerobic amino acid
243 fermentation, known as the Stickland reaction, involves amino acids, possibly of the same type,
244 serving both as electron donors and acceptors⁵⁰. Stickland reaction is a typical pathway of
245 anaerobic bacteria belonging to the Firmicutes phylum, which can be found in serpentinization

246 environments where electron acceptors are lacking⁴⁹. Whether abiotic amino acids may represent
247 valuable substrates for the ecosystems inhabiting serpentinites, and whether they have shaped
248 ancient microbial metabolisms or played a role in the emergence of a first form of biochemistry
249 on Earth remains to be addressed. Nevertheless, the new formation pathway proposed here
250 nurture the hydrothermal origin of life debate with an attractive alternative to the commonly
251 considered Strecker and Fischer-Tropsch-type reactions.

252

253 **Online Content** Methods, along with any additional Extended Data display items, are available
254 in the online version of the paper; references unique to these sections appear only in the online
255 paper.

256

257 **Data Availability** The data supporting the findings of this study are available within the paper,
258 its Extended Data and its Supplementary Information.

259

- 260 1. McCollom, T. M. & Seewald, J. S. Abiotic synthesis of organic compounds in deep-sea
261 hydrothermal environments. *Chem. Rev.* **107**, 382-401 (2007).
- 262 2. Mével, C. Serpentinization of abyssal peridotites at mid-ocean ridges. *C. R. Geosci.* **335**,
263 825-852 (2003).
- 264 3. Martin, W., Baross, J., Kelley, D. & Russell, M. J. Hydrothermal vents and the origin of life.
265 *Nat. Rev. Microbiol.* **6**, 805-814 (2008).
- 266 4. Sleep, N. H., Meibom, A., Fridriksson, Th., Coleman, R. G. & Bird, D. K. H₂-rich fluids
267 from serpentinization: geochemical and biotic implications. *Proc. Natl. Acad. Sci. U.S.A.*
268 **101**, 12818-12823 (2004).

- 269 5. Kelley, D. S. *et al.* An off-axis hydrothermal vent field near the Mid-Atlantic Ridge at 30° N.
270 *Nature* **412**, 145-149 (2001).
- 271 6. Russell, M. J. The alkaline solution to the emergence of life: energy, entropy and early
272 evolution. *Acta Biotheor.* **55**,133-179 (2007).
- 273 7. Konn, C., Charlou, J. L., Holm, N. G. & Mousis, O. The production of methane, hydrogen,
274 and organic compounds in ultramafic-hosted hydrothermal vents of the Mid-Atlantic Ridge.
275 *Astrobiology* **15**, 381-399 (2015).
- 276 8. Lang, S. Q., Früh-Green, G. L., Bernasconi, S. M. & Butterfield, D. A. Sources of organic
277 nitrogen at the serpentinite-hosted Lost City hydrothermal field. *Geobiology* **11**, 154-169
278 (2013).
- 279 9. Pizzarello, S., Williams, L. B., Lehman, J., Holland, G. P. & Yarger, J. L. Abundant
280 ammonia in primitive asteroids and the case for a possible exobiology. *Proc. Natl. Acad. Sci.*
281 *U.S.A.* **108**, 4303-4306 (2011).
- 282 10. Elsila, J. E. *et al.* Meteoritic amino acids: diversity in compositions reflects parent body
283 histories. *ACS Cent. Sci.* **2**, 370-379 (2016).
- 284 11. Elmaleh, A. *et al.* Formation and transformations of Fe-rich serpentines by asteroidal
285 aqueous alteration processes: A nanoscale study of the Murray chondrite. *Geochim.*
286 *Cosmochim. Acta* **158**, 162-178 (2015).
- 287 12. Blackman, D. K. *et al.* Drilling constraints on lithospheric accretion and evolution at Atlantis
288 Massif, Mid-Atlantic Ridge 30° N. *J. Geophys. Res.* **116**, B07103 (2011).
- 289 13. Delacour, A., Früh-Green, G. L., Bernasconi, S. M., Schaeffer, P. & Kelley, D. S. Carbon
290 geochemistry of serpentinites in the Lost City Hydrothermal System (30°N, MAR).
291 *Geochim. Cosmochim. Acta* **72**, 3681-3702 (2008).

- 292 14. Bisio, C. *et al.* Understanding physico-chemical properties of saponite synthetic clays.
293 *Microporous Mesoporous Mater.* **107**, 90-101 (2008).
- 294 15. Pisapia, C., Jamme, F., Duponchel, L. & Ménez, B. Tracking hidden organic carbon in rocks
295 using chemometrics and hyperspectral imaging. *Sci. Rep.* **8**, 2396 (2018).
- 296 16. Klein, F. *et al.* Magnetite in seafloor serpentinites- Some like it hot. *Geology* **42**, 135-138
297 (2014).
- 298 17. Nozaka, T., Fryer, P. & Andreani, M. Formation of clay minerals and exhumation of lower-
299 crustal rocks at Atlantis Massif, Mid-Atlantic Ridge. *Geochem. Geophys. Geosyst.* **9**, Q11005
300 (2008).
- 301 18. Determann, S., Lobbes, J. M., Reuter, R. & Rullkötter, J. Ultraviolet fluorescence excitation
302 and emission spectroscopy of marine algae and bacteria. *Mar. Chem.* **62**, 137-156 (1998).
- 303 19. Kumamoto, Y., Fujita, K., Smith, N. I. & Kawata, S. Deep-UV biological imaging by
304 lanthanide ion molecular protection. *Biomed. Opt. Express* **7**, 158-170 (2016).
- 305 20. Pavlov, N. *et al.* Asymmetric synthesis of β^2 -tryptophan analogues via Friedel-Crafts
306 alkylation of indoles with a chiral nitroacrylate. *J. Org. Chem.* **76**, 6116-6124 (2011).
- 307 21. Jamme, F. *et al.* Synchrotron UV fluorescence microscopy uncovers new probes in cells and
308 tissues. *Microsc. Microanal.* **16**, 507-514 (2010).
- 309 22. Sanni, O. D., Wagner, M. S., Briggs, D., Castner, D. G. & Vickerman, J. C. Classification of
310 adsorbed protein static ToF-SIMS spectra by principal component analysis and neural
311 networks. *Surf. Interface Anal.* **33**, 715-728 (2002).
- 312 23. Steele, A., Toporski, J. K. W., Avci, R., Guidry, S. & McKay, D. S. Time of flight secondary
313 ion mass spectrometry (ToFSIMS) of a number of hopanoids. *Org. Geochem.* **32**, 905-911
314 (2001).

- 315 24. Toporski, J. K. W. & Steele, A. Characterization of purified biomarker compounds using
316 time of flight-secondary ion mass spectrometry (ToF-SIMS). *Org. Geochem.* **35**, 793-811
317 (2004).
- 318 25. Siljeström, S. *et al.* Detection of organic biomarkers in crude oils using ToF-SIMS. *Org.*
319 *Geochem.* **40**, 135-143 (2009).
- 320 26. <http://webbook.nist.gov/cgi/cbook.cgi?ID=C73223&Type=IR-SPEC&Index=1>
- 321 27. Chiriboga, L. *et al.* Infrared spectroscopy of human tissue. I. Differentiation and maturation
322 of epithelial cells in the human cervix. *Biospectroscopy* **4**, 47-53 (1998).
- 323 28. Ménez, B., Pasini, V. & Brunelli, D. Life in the hydrated suboceanic mantle. *Nat. Geosci.* **5**,
324 133-137 (2012).
- 325 29. Kooli, F. & Jones, W. Characterization and catalytic properties of a saponite clay modified
326 by acid activation. *Clay Miner.* **32**, 633-643 (1997).
- 327 30. Molina, C. B., Casas, J. A., Pizarro, A. H. & Rodriguez, J. J. Pillared clays as green
328 chemistry catalysts: Application to wastewater treatment, in *Clay: Types, Properties and*
329 *Uses* (eds Humphrey, J. P. & Boyd, D. E.). Nova Science Publisher, New York, USA, 435-
330 474 (2011).
- 331 31. Williams, L. B. *et al.* Birth of biomolecules from the warm wet sheets of clays near spreading
332 centers, in *Earliest Life on Earth: Habitats, Environments and Methods of Detection* (eds
333 Golding, S. D. & Glikson, M.). Springer, Amsterdam, the Netherlands, 79-112 (2010).
- 334 32. Meunier, A., Petit, S., Cockell, C. S., El Albani, A. & Beaufort, D. The Fe-rich clay
335 microsystems in basalt-komatiite lavas: importance of Fe-smectites for pre-biotic molecule
336 catalysis during the Hadean eon. *Origins Life Evol. Biosphere* **40**, 253-273 (2010).

- 337 33. Belver, C., Bañares-Muñoz, M. A. & Vicente, M. A. Fe-saponite pillared and impregnated
338 catalysts I. Preparation and characterization. *Appl. Catal. B* **50**, 101-112 (2004).
- 339 34. Choudary, B. M., Kantam, M. L., Sateesh, M., Rao, K. K. & Santhi, P. L. Iron pillared clays
340 - efficient catalysts for Friedel-Crafts reactions. *Appl. Catal. A* **149**, 257-264 (1997).
- 341 35. Rueping, M. & Nachtsheim, B. J. A review of new developments in the Friedel-Crafts
342 alkylation - From green chemistry to asymmetric catalysis. *Beilstein J. Org. Chem.* **6**, No. 6
343 (2010).
- 344 36. Milesi, V., McCollom, T. M. & Guyot, F. Thermodynamic constraints on the formation of
345 condensed carbon from serpentinization fluids. *Geochim. Cosmochim. Acta* **189**, 391-403
346 (2016).
- 347 37. Cody, G. D. *et al.* Primordial carbonylated iron-sulfur compounds and the synthesis of
348 pyruvate. *Science* **289**, 1337-1340 (2000).
- 349 38. Seyfried, W. E. Jr., Pester, N. J., Tutolo, B. M. & Ding, K. The Lost City hydrothermal
350 system: Constraints imposed by vent fluid chemistry and reaction path models on subseafloor
351 heat and mass transfer processes. *Geochim. Cosmochim. Acta* **163**, 59-79 (2015).
- 352 39. Proskurowski, G., Lilley, M. D., Kelley, D. S. & Olson, E. J. Low temperature volatile
353 production at the Lost City Hydrothermal Field, evidence from a hydrogen stable isotope
354 geothermometer. *Chem. Geol.* **229**, 331-343 (2006).
- 355 40. Brandes, J. *et al.* Abiotic nitrogen reduction on the early Earth. *Nature* **395**, 365-368 (1998).
- 356 41. Schoonen, M. A. & Xu, Y. Nitrogen reduction under hydrothermal vent conditions:
357 implications for the prebiotic synthesis of C-H-O-N compounds. *Astrobiology* **1**, 133-142
358 (2001).

- 359 42. Salmon, V., Derenne, S., Lallier-Vergès, E., Largeau, C. & Beaudoin, B. Protection of
360 organic matter by mineral matrix in a Cenomanian black shale. *Org. Geochem.* **31**, 463-474
361 (2000).
- 362 43. Pearson, V. K. *et al.* Clay mineral-organic matter relationships in the early solar system.
363 *Meteorit. Planet. Sci.* **37**, 1829-1833 (2002).
- 364 44. Manuella, F. C., Carbone, S. & Barreca, G. Origin of saponite-rich clays in a fossil
365 serpentinite-hosted hydrothermal system in the crustal basement of the Hyblean Plateau
366 (Sicily, Italy). *Clays Clay Miner.* **60**, 18-31 (2012).
- 367 45. Arndt, N. T. & Nisbet, E. G. Processes on the young Earth and the habitats of early life.
368 *Annu. Rev. Earth Planet. Sci.* **40**, 521-549 (2012).
- 369 46. Granold, M., Hajieva, P., Toşa, M. I., Irimie, F.-D. & Moosmann, B. Modern diversification
370 of the amino acid repertoire driven by oxygen. *Proc. Natl. Acad. Sci. U. S. A.* **115**, 41-46
371 (2018).
- 372 47. Ruiz-Mirazo, K., Briones, C. & de la Escosura, A. Prebiotic systems chemistry: New
373 perspectives for the origins of life. *Chem. Rev.* **114**, 285-366 (2014).
- 374 48. Russell, M. J., Daniel, R. M., Hall, A. J. & Sherringham, J. A. A hydrothermally precipitated
375 catalytic iron sulphide membrane as a first step toward life. *J. Mol. Evol.* **39**, 231-243 (1994).
- 376 49. Schrenk, M. O., Brazelton, W. J. & Lang, S. Q. Serpentinization, carbon and deep life, in
377 *Carbon in Earth* (eds Hazen, R. M., Jones, A. P. & Baross J. A.). Mineralogical Society of
378 America, Chantilly, USA, Reviews in Mineralogy & Geochemistry, vol. **75**, 575-606 (2013).
- 379 50. Barker, H. A. Fermentation of nitrogenous compounds, in *The Bacteria. A Treatise on*
380 *Structure and Function* (eds Gunsalus, I. C. & Stanier, R. Y.). Academic Press, Cambridge,
381 Massachusetts, 151-207 (1961).
- 382

383 **Supplementary Information** including Methods is linked to the online version of the paper at
384 www.nature.com/nature.

385
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395
396 **Author Contributions** B.M., M.A., C.P. conceived the research. B.M., C.P., F.J., M.R., Q.P.V.,
397 A.B., M.A., and P.D. performed the experiments. L.R. performed the thermodynamic
398 calculations. B.M. wrote the manuscript. All authors contributed to the interpretation of the data
399 and commented on the drafts of the manuscript.

400
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407 **Figure Captions**

408

409 **Figure 1 | Endogenous UV-autofluorescence locally revealed by S-DUV imaging of a highly**
410 **altered mantle rock recovered at 173.15 mbsf from IODP Hole 304-1309D¹². UV-**
411 **fluorescence emerged from heteroatomic aromatic compounds shown to be spatially**
412 **restricted to a Fe-rich clay in which they are heterogeneously distributed. a**, Optical image
413 showing yellow to brownish phases identified as Fe-rich serpentine (Fe-Srp) and Fe-rich saponite
414 (Sap), hosted in a serpentinized harzburgite with olivine being replaced by magnetite (Mag) and
415 serpentine exhibiting a characteristic mesh texture (mesh Srp); the green arrow indicates sample
416 orientation. The light green square in **a** depicts the location of the full field S-DUV image
417 displayed in **b** and collected between 400 and 440 nm using excitation (λ_{exc}) at 275 nm. “a.u.”,
418 arbitrary unit. **c**, Fluorescence emission spectra collected with excitation wavelengths of 250,
419 275 and 310 nm at the location shown by an asterisk in **b**. The spectra collected at 250 and 310
420 nm do not show any significant UV-autofluorescence signal whereas the spectrum at 275 nm
421 displays fluorescence characteristic of indole at 340 ± 6 nm, tryptophan at 358 ± 3 nm, skatole at
422 380 ± 3 nm, and hydroxyanthranilic acid at 403 ± 3 nm¹⁸. Also shown are a fluorescence emission
423 spectrum collected at 275 nm in the Fe-rich serpentine and the typical emission spectrum of a
424 biological cell showing fluorescence maximum emission, mainly arising from protein-forming
425 tryptophan, shifted to 335 nm²¹. The orange area in **c** represents the fluorescence detection range
426 used in **b**. The blue box in **a** indicates the location where complementary S-FTIR measurements
427 were performed (Extended Data Fig. 2).

428

429 **Figure 2 | SEM images of the Fe-rich saponite enriched in organic carbon. a-b**, SEM-BSE
430 images collected at 15 kV on the mineral assemblage displayed in Figs. 1 and 3 and Extended
431 Data Fig. 1a with **b** being a close up view of the area indicated by the green box in **a**. The green
432 arrow indicates sample orientation; the orange dashed line and the associated arrow respectively
433 provide location and front face of the FIB foil milled for TEM observations (Figs. 5a-b and
434 Extended Data Fig. 3). Textures and differences in grey levels resulting from chemical contrasts
435 allow recognizing each mineral phase previously characterized by S-FTIR and electron
436 microprobe analysis, namely mesh serpentine (mesh Srp), Fe-rich serpentine (Fe-Srp) and Fe-
437 rich saponite (Sap). In particular, the characteristic platelets of saponite¹⁴ are well recognizable
438 in the SEM-SE image shown in **c** and collected at 3 kV accelerating voltage (location shown
439 with an asterisk in **a**); Fe-rich saponite presents distinct grey levels in **a** and **b** that relate to its
440 variable content in organic carbon, hence darkening its aspect when carbon is abundant.

441

442 **Figure 3 | The presence of tryptophan in the Fe-rich saponite was confirmed by TOF-SIMS**
443 **imaging with the colocalized collection of its characteristic fragment ions** (Extended Data
444 Table 1). **a**, TOF-SIMS ion image of mineral-derived Fe⁺ showing location of analysis with
445 respect to the mesh for the area displayed in Fig. 1a. The green arrow indicates sample
446 orientation. “TC”, total count. **b**, Molecular ion image (binning of 4) of the C₉H₈N⁺ fragment ion
447 at *m/z* 130.06 corresponding to the ion peak shown in **c**, which is characteristic of tryptophan²². It
448 reveals cluster-like accumulations within the Fe-rich saponite. **d**, TOF-SIMS spectrum (*m/z* 200-
449 600) reconstructed from the region displaying the highest count rates in **b**. It provides evidence
450 for the absence of common biomarkers²³⁻²⁵. Detailed spectra are provided in Extended Data Figs.
451 6a-n.

452

453 **Figure 4 | Systematic association of Fe-rich saponite with tryptophan.** **a**, Optical view of an
454 olivine (Ol) kernel in the mesh serpentine (mesh Srp) also shown in Extended Data Fig. 1b. The
455 green square indicates the position of the associated SEM-BSE images shown in **b** and **c** and
456 collected at 15 kV. **c**, Close up view of the area represented by the green box in **b**. The orange
457 dashed line and associated arrow in **b** respectively provide location and front face of the FIB foil
458 (Extended Data Fig. 5) milled for the TEM observations displayed in **d**. Textures and chemical
459 contrasts allow recognizing each mineral phase previously characterized by S-FTIR and electron
460 microprobe analysis, namely magnetite (Mag), Ol, mesh Srp, Fe-rich serpentine (Fe-Srp) and Fe-
461 rich saponite (Sap). **d**, TEM image showing the Fe-rich saponite layers to appear perpendicular
462 to the interface between the olivine kernel and the mesh serpentine with lizardite crystallites
463 appearing in black. The Fe-rich saponite lamellae are mainly subparallel although some sheet
464 distortions are visible. **e**, Associated S-DUV full field fluorescence images collected after
465 excitation (λ_{exc}) at 275 nm in the range 327-353, 370-410 and 412-438 nm. They show for all
466 these wavelengths, UV autofluorescence emission at the interface between olivine crystal and
467 serpentine where the Fe-rich saponite is located. **f**, TOF-SIMS ion image collected in the
468 $500 \times 500 \mu\text{m}^2$ area displayed in **a** and showing the distribution of the characteristic fragment ions
469 of tryptophan²² (Extended Data Table 1), hence confirming its presence close to the olivine
470 kernel. Evidence for the absence of common biomarkers²³⁻²⁵ can be found in the detailed spectra
471 provided in Extended Data Figs. 6o-v. The green arrows provide sample orientation.

472

473 **Figure 5 | Fe-rich saponite played the role of a catalyzing pillared-clay for the abiotic**
474 **synthesis of tryptophan.** **a-b**, TEM images collected on the ultrathin foil milled by FIB in the

475 area shown in Figs. 1-3 and Extended Data Figs. 2-4. The saponite (Sap) interfacing Fe-rich or
476 mesh-serpentine shows the presence of aggregates formed by packing of sheets opening
477 nanopores and suggests the occurrence of pillaring processes and a high reactivity of the clay. **c**,
478 Clay minerals possess negatively-charged silicate layers with cations in the interlayer space to
479 balance the charge. They all together allow sorption and exchanges of ions or organic moieties to
480 occur during water-clay interactions, hence propping apart clay layers at increased interlayer
481 distances, *i.e.* packing in face-face mode. **d**, Packing in face-face, edge-edge or edge-face mode
482 resulting in a house of card structure recognizable in **a** and **b**. The nanoporous structure
483 represents microreactors for the formation of tryptophan at the acid sites of the Fe-rich saponite.
484

486

487 **SUPPLEMENTARY INFORMATION**

488

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498

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501

502 **METHODS**

503

Sample preparation. Drilled rock samples were sawed with sterile ultrapure water in order to extract the inner core, free of possible post-sampling contamination. The saw was previously treated with 5% sodium hypochlorite, then rinsed twice with sterile ultrapure water. The inner core was then manipulated using clean pliers, thinned and polished manually on both faces (down to a thickness of tens of micrometers) with pure ethanol using silicon carbide polishing disks without any use of resin or glue. Samples were then sequentially analyzed using, by order of potential beam-induced damages and sample preparation constraints (*e.g.* metallic coating or sample milling), Synchrotron-Fourier-Transform-Infra-Red microscopy (S-FTIR), Synchrotron-coupled Deep-Ultra-Violet (S-DUV) microspectroscopy, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) imaging, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM).

514

Synchrotron-Fourier-Transform-Infrared microspectroscopy. S-FTIR hyperspectral imaging was performed at the SMIS beamline (SOLEIL synchrotron radiation facility, Saint Aubin, France)⁵¹ by taking advantage of the brightness of the bending magnet radiation and of the confocal geometry of the microscope objective⁵². The sensitivity of infrared microspectroscopy is on average 10^{-4} M (10^{-12} g of molecules)⁵¹. Data were acquired in transmission mode with a Nicplan microscope coupled to a Magna 550 FT-IR spectrometer (Thermo-Nicolet). The confocal aperture was set at $5 \times 5 \mu\text{m}^2$ using a $32\times$ infinity corrected Schwarzschild objective with a numerical aperture of 0.65 (Nicolet Refflachromat) and a matching $10\times$ condenser. The microscope is equipped with a motorized sample stage (repeatability $1 \mu\text{m}$) and a liquid nitrogen cooled mercury cadmium telluride detector (MCT-A; detector element size $250 \mu\text{m}$). The sample was deposited on a CaF_2 window without any treatment. Hyperspectral data cubes in which pixels correspond to individual S-FTIR spectra were collected in the $4000\text{-}800 \text{ cm}^{-1}$ mid-infrared range using a step size of $5 \mu\text{m}$. Acquisitions were carried out using 50 accumulations per spectrum/pixel with a spectral resolution set at 4 cm^{-1} . Spectrum analyses were first performed using OMNICTM software (Thermo Fisher Scientific) to obtain distribution maps of the aliphatic

527

529 CH₂/CH₃ stretching band area between 2800-3000 cm⁻¹ and then using an approach combining
530 Principal Component Analysis (PCA) and Multivariate Curve Resolution - Alternating Least
531 Squares (MCR-ALS) implemented on the Matlab[®] software and the PLS toolbox (Eigenvector
532 Research Inc.)¹⁵.

533 **Synchrotron-coupled Deep-Ultra-Violet microspectroscopy.** S-DUV microspectroscopy
534 allows imaging with a nanomolar sensitivity of aromatic, phenolic or unsaturated compounds
535 without any external fluorescent probes²¹. Fluorescence imaging was carried out at the DISCO
536 beamline (SOLEIL synchrotron radiation facility, Saint Aubin, France) where two
537 complementary full UV compatible microscopes are coupled to the monochromatized
538 synchrotron radiation continuously emitted from a bending magnet, which allows fluorescence
539 excitation down to 180 nm (from 250 to 310 nm in the present study) at a submicrometric spatial
540 resolution⁵³. The use of a synchrotron light as a UV source allows to precisely tune the excitation
541 light to the absorption of endogenous fluorochromes. Both microscopes, equipped with
542 motorized sample stages (repeatability μm), were used with a Zeiss Ultrafluar 40 \times (glycerine
543 immersion) objective. The sample was deposited on a quartz window without any treatment. In
544 order to localize fluorescent areas within serpentinites, a full field Zeiss Axio Observer Z-1
545 inverted microscope was first used. The fluorescent signal was collected by a PIXIS 1024 BUV
546 camera (Princeton Instruments) with bandpass filters at 327-353, 370-410, 412-438 and 400-440
547 nm (Semrock) and associated integration times of 120 s. Images were analyzed using the Fiji
548 software⁵⁴ and stitched by linear blending⁵⁵. Microspectrofluorescence emission spectra in the
549 range 285-550 nm were thereafter collected with a 70% C Peltier-cooled iDus CCD detector
550 (Andor) of 1024 \times 256 pixels with a 26 \times 26 μm pixel size on selected areas using a spectral
551 Olympus IX71 inverted microscope. Hyperspectral data cubes in which pixels correspond to
552 individual fluorescence spectra were collected on areas up to 100 \times 80 μm^2 in size with a 2 to 3
553 μm step size and 20 to 40 s acquisition time per spectrum/pixel. With the exception of manual
554 removal of spikes coming from cosmic rays, no filtering or treatment of the autofluorescence
555 spectra was conducted. Deconvoluted images of each individual fluorescent component were
556 then produced with the Labspec software (Jobin-Yvon, France) using Gaussian functions and 10
557 iterations.

558 **Time-of-Flight Secondary Ion Mass Spectrometry imaging.** TOF-SIMS imaging allows to
559 simultaneously detect inorganic and organic molecules on solid surfaces without extraction,
560 chemical preparation or derivatization. Experiments were conducted using a TOF-SIMS IV
561 reflectron-type mass spectrometer (IONTOF GmbH) located at the Institut de Chimie des
562 Substances Naturelles (CNRS, Gif-sur-Yvette, France)⁵⁶. The instrument is equipped with a
563 bismuth liquid metal ion gun delivering a pulsed Bi₃⁺ cluster ion beam. 25 keV primary ions
564 impacted the sample at an incidence angle of 45 $^\circ$ and a pulsed current of 0.1 pA. Emitted
565 secondary ions were accelerated to 2 keV (2 kV extraction) toward a field-free region and a
566 single stage reflectron (first-order compensation). Secondary ions ejected from the few upper
567 monolayers of the sample surface were post-accelerated to 10 keV before reaching the detector
568 made of a micro-channel plate, a scintillator and a photomultiplier. The ion column focusing
569 mode ensured a spatial resolution of 2-5 μm and a mass resolution of 5000 (full width half-
570 maximum) at m/z 500. A low-energy (\sim 20 eV) electron flood gun was used between two
571 successive primary ion pulses for charge compensation with minimum damage on the sample
572 surface. An optical camera located in the sample vacuum chamber aided location of the samples,
573 which were deposited on the sample holder without any treatment or adhesive. Ion images in
574 both negative and positive polarities were acquired in a raster pattern on areas of 500 \times 500 μm^2

575 and 256×256 pixels giving a pixel size of 1.95×1.95 μm². The images were recorded with a
576 primary ion fluence of 3.44 × 10¹¹ ions·cm⁻² (400 scans with cycle time of 100 μs). The
577 accumulated primary ion dose never exceeded 10¹² ions·cm⁻², which is below the static limit for
578 organic molecules⁵⁷. Data acquisition and processing were done using the SurfaceLab 6 software
579 (IONTOF GmbH). Spectra from the total analysis area or from selected regions of interest were
580 extracted. Internal mass calibration was performed using the low mass fragment ion signals of
581 H⁺, H₂⁺, H₃⁺, C⁺, CH₃⁺, and C₂H₃⁺ for the positive ion mode and C⁻, CH⁻, CH₂⁻, C₂⁻, C₃⁻, and
582 C₄H⁻ for the negative ion mode. Assignments of ion peaks were made according to the
583 instrument resolution, accuracy and the valence rule. The presence of tryptophan was
584 investigated through the identification and assignment of all required fragment ions that are
585 characteristic of this amino acid⁵⁸⁻⁶⁰. The absence of interferences was carefully checked for each
586 assigned peak and mass deviations relatively to the theoretical *m/z* values were calculated. They
587 all fall within admitted values for TOF-SIMS analyses (Extended Data Table 1). Image
588 reconstruction for selected fragment ions was carried out by integrating signal intensities at given
589 *m/z* values across the data set.

590 **Scanning Electron Microscopy.** SEM was performed at the Service Commun de Microscopie
591 Electronique à Balayage (UPMC, Paris, France) on Au-coated samples with a Zeiss SUPRA 55
592 VP field emission microscope operating at 3 to 15kV accelerating voltage at respectively low
593 and high currents (from 10 pA up to 1 nA). Images were collected using secondary electron (SE)
594 detectors (Everhart-Thornley and InLens for high and low voltage mode, respectively) and a
595 backscattered electron (BSE) detector (AsB). Images were further processed with the ImageJ
596 software⁶¹ for contrast and brightness adjustment.

597 **Focused Ion Beam (FIB) milling and Transmission Electron Microscopy.** As TEM requires
598 samples to be electron transparent, ultrathin foils (thickness < 100 nm) were milled using a Zeiss
599 NVision 40 cross beam microscope (CLYM, University of Lyon, France) which combines a high
600 resolution field emission SEM with a Seiko FIB column. The 10-15 nm thick Au layer
601 previously deposited for SEM observations prevented from amorphization of the subsurface.
602 Additionally, before excavation, milled volumes were protected by a FIB-induced 1-2 μm thick
603 carbon coating (Extended Data Figs. 3a-c and 5a-c) using a Ga⁺ beam, emitted by a Ga liquid
604 metal ion source operating at 30 kV accelerating voltage. To allow cross-sectional observations
605 at depth (Extended Data Figs. 3c-e and 5c-d), excavations were first made on one side of the
606 TEM foil location using ion beam current of decreasing intensities (13, 6.5, 3 nA and 700 pA).
607 Cross-sectional images were collected at 5 kV using a Secondary Electrons Secondary Ions
608 (SESI) detector and InLens detector for high and low voltage mode, respectively, and at 1.25 kV
609 using an Energy Selective Backscattered BSE detector. Elemental analyses were carried out with
610 an Oxford Instrument Energy Dispersive X-ray Spectrometer (EDS) (X-max 50 mm² silicon drift
611 detector). TEM sections were then extracted from the bulk sample following excavation of its
612 second side once a thickness of ~1-2 μm was reached. TEM sections were then fixed by C ion
613 beam deposition on a half copper TEM grid. Further thinning of the TEM foil to few tens of
614 nanometers was obtained with a glancing angle beam at low ion beam current (from 700 pA
615 down to 50 pA at 30 kV). They were finally cleaned for traces of Ga ion implantation by a
616 milling at 2 kV and 50 pA during 3-5 min on each side. TEM observations were then carried out
617 with a TOPCON operating at 200 kV (CLYM, University of Lyon, France). Images, further
618 processed with ImageJ software⁶¹ for contrast and brightness adjustment, have been collected at
619 a nanometric spatial resolution with a CCD Camera.

620 **Thermodynamic constraints on the abiotic synthesis of tryptophan at Lost City.** In order to
 621 evaluate the extent to which the temperature-pressure-composition conditions prevailing in the
 622 Lost City hydrothermal system are conducive to the abiotic synthesis of tryptophan and some of
 623 its possible precursors (indole and pyruvate) (Extended Data Fig. 7), the chemical affinities A_r of
 624 their formation reactions were computed at 100°C from the relation

$$A_r = RT \ln(K_r/Q_r)$$

625 where R and T stands for the gas constant and absolute temperature, respectively, Q_r is the
 626 reaction quotient, and K_r is the thermodynamic equilibrium constant. The reaction quotient is
 627 calculated from the relation
 628

$$Q_r = \prod_i a_i^{n_{i,r}}$$

629 where a_i represents the activity of the i^{th} species involved in the r^{th} reaction, and $n_{i,r}$ is the
 630 stoichiometric coefficient of the species in the reaction. Note that the chemical affinities
 631 computed below are mathematically equivalent to the opposite of the overall Gibbs energies ΔG_r
 632 computed by ref. (62) for the abiotic synthesis of amino acids in accord with
 633

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q_r$$

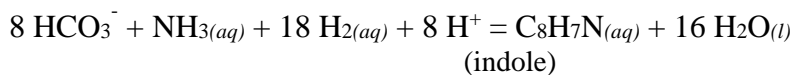
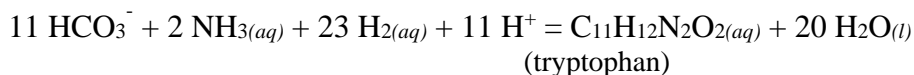
634 where ΔG_r° is the standard Gibbs energy of the abiotic synthesis reaction.
 635

636 In the absence of Helgeson-Kirkham-Flowers (HKF) parameters for aqueous indole and
 637 pyruvate, the values of the equilibrium constants at 100°C were estimated using the van't Hoff
 638 equation

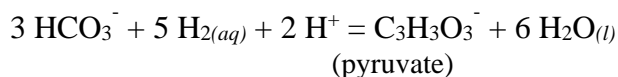
$$\log K_{373.15\text{K}} = \log K_{298.15\text{K}} + \frac{\Delta H_r^\circ}{RT} \left(\frac{1}{373.15} - \frac{1}{298.15} \right)$$

639 where ΔH_r° is the standard enthalpy of the reaction at 298.15 K. The equilibrium constants at
 640 25°C and 100°C have been carried out using standard Gibbs energies and enthalpies of formation
 641 taken from refs. (63-64) for the aqueous inorganic species and from ref. (65) for aqueous
 642 tryptophan, indole and pyruvate.
 643

644 Assuming a pH = 8.5 for a hypothetical Lost City fluid cooled to 100°C during its ascent
 645 towards the seafloor³⁸, the predominant inorganic carbon and nitrogen species are HCO_3^- and
 646 $\text{NH}_3(\text{aq})$ (Extended Data Fig. 8). Accordingly, the abiotic synthesis reactions have been written as



649 and



650 The reaction quotients were evaluated with activities for the aqueous species which approximate
 651 the concentrations reported for the Lost City hydrothermal fluids, *i.e.* $a_{\text{CO}_2(\text{aq})} = 10^{-2.54}$ (66),
 652 $a_{\text{H}_2(\text{aq})} \sim 10^{-2}$ (39), and $a_{\text{NH}_3(\text{aq})} \sim 10^{-6}$ (8). Nanomolar concentrations have been assumed for the
 653 organic compounds.
 654

655 The chemical affinities calculated for the abiotic synthesis of tryptophan, indole, and
 656 pyruvate are respectively 134.5 kJ·mol⁻¹, 193.48 kJ·mol⁻¹ and 43.07 kJ·mol⁻¹. The chemical
 657 affinity for the synthesis of tryptophan is significantly more favorable than that calculated by ref.
 658 (62) because of the higher concentration of H₂ in the Lost City fluids. The dependence of the
 659 chemical affinities of the reactions on the activity of aqueous H₂ can be deduced from Extended
 660
 661
 662

663 Data Fig. 7. It can be seen that the abiotic synthesis of tryptophan becomes favorable only for H₂
664 concentrations above $\sim 10^{-2.8} m$.

665

666 Supplemental References

- 667 51. Dumas, P. *et al.* Synchrotron infrared microscopy at the French Synchrotron Facility
668 SOLEIL. *Infrared Phys. Techn.* **49**, 152-160 (2006).
- 669 52. Jamme, F., Lagarde, B., Giuliani, A., Garcia, G. A. & Mercury, L. Synchrotron infrared
670 confocal microscope: Application to infrared 3D spectral imaging. *J. Phys.: Conf. Ser.* **425**,
671 142002 (2013).
- 672 53. Giuliani, A. *et al.* DISCO: a low-energy multipurpose beamline at synchrotron SOLEIL. *J.*
673 *Synchrotron Radiat.* **16**, 835-841 (2009).
- 674 54. Schindelin, J. *et al.* Fiji: an open-source platform for biological-image analysis. *Nat.*
675 *Methods* **9**, 676-682 (2012).
- 676 55. Preibisch, S., Saalfeld, S. & Tomancak, P. Globally optimal stitching of tiled 3D
677 microscopic image acquisitions. *Bioinformatics* **25**, 1463-1465 (2009).
- 678 56. Brunelle, A., Touboul, D. & Lapr evote, O. Biological tissue imaging with time-of-flight
679 secondary ion mass spectrometry and cluster ion sources. *J. Mass Spectrom.* **40**, 985-999
680 (2005).
- 681 57. Touboul, D., Kollmer, F., Niehuis, E., Brunelle, A. & Lapr evote, O. Improvement of
682 biological time-of-flight-secondary ion mass spectrometry imaging with a bismuth cluster
683 ion source. *J. Am. Soc. Mass Spectrom.* **16**, 1608-1618 (2005).
- 684 58. Mazel, V. *et al.* Identification of ritual blood in African artifacts using TOF-SIMS and
685 synchrotron radiation microspectroscopies. *Anal. Chem.* **79**, 9253-9260 (2007).
- 686 59. Cersoy, S., Richardin, P., Walter, P. & Brunelle, A. Cluster TOF-SIMS imaging of human
687 skin remains: analysis of a South-Andean mummy sample. *Mass Spectrom.* **47**, 338-346
688 (2012).
- 689 60. Farre, B. *et al.* Shell layers of the black-lip pearl oyster *Pinctada margaritifera*: matching
690 microstructure and composition. *Comp. Biochem. Physiol. B* **159**, 131-139 (2011).
- 691 61. Schneider, C. A., Rasband, W. S. & Eliceiri, K. W. NIH Image to ImageJ: 25 years of image
692 analysis. *Nat. Methods* **9**, 671-675 (2012).
- 693 62. Amend, J. P. & Shock, E. L. Energetics of amino acid synthesis in hydrothermal
694 ecosystems. *Science* **281**, 1659-1662 (1998).
- 695 63. Shock, E. L. & Helgeson, H. C. Calculation of the thermodynamic and transport properties
696 of aqueous species at high pressures and temperatures: Correlation algorithms for ionic
697 species and equation of state predictions to 5 kb and 1000 C. *Geochim. Cosmochim. Acta*
698 **52**, 2009-2036 (1988).
- 699 64. Shock, E. L., Helgeson, H. C. & Sverjensky, D. A. Calculation of the thermodynamic and
700 transport properties of aqueous species at high pressures and temperatures: Standard partial
701 molal properties of inorganic neutral species. *Geochim. Cosmochim. Acta* **53**, 2157-2183
702 (1989).

- 703 65. Tewari, Y. B. & Goldberg, R. N. An equilibrium and calorimetric investigation of the
704 hydrolysis of L-tryptophan to (indole + pyruvate + ammonia). *J. Solution Chem.* **23**, 167-
705 184 (1994).
- 706 66. Proskurowski, G. *et al.* Abiogenic hydrocarbon production at Lost City hydrothermal field.
707 *Science* **319**, 604-607 (2008).
- 708 67. Aubrey, A., Cleaves, H. & Bada, J. The role of submarine hydrothermal systems in the
709 synthesis of amino acids. *Origins Life Evol. Biosphere* **39**, 91-108 (2009).
- 710 68. Schulte, M. & Shock, E. Thermodynamics of Strecker synthesis in hydrothermal systems.
711 *Origins Life Evol. Biosphere* **25**, 161-173 (1995).
- 712 69. Lowe, C. U., Markham, R. & Rees, M. W. Synthesis of complex organic compounds from
713 stable precursors - formation of amino acids, amino acid polymers, fatty acids and purines
714 from ammonium cyanide. *Nature* **199**, 219-220 (1963).
- 715 70. Wolman, Y., Miller, S. L., Ibanez, J. & Oro, J. Formaldehyde and ammonia as precursors to
716 prebiotic amino acids. *Science* **174**, 1039-1041 (1971).
- 717 71. Fox, S. W. & Windsor, C. R. Synthesis of amino acids by heating of formaldehyde and
718 ammonia. *Science* **170**, 984-986 (1970).
- 719 72. Oro, J., Kimball, A., Fritz, R. & Master, F. Amino acid synthesis from formaldehyde and
720 hydroxylamine. *Arch. Biochem. Biophys.* **85**, 115-130 (1959).
- 721 73. Kamaluddin, Yanagawa, H. & Egami, F. Formation of molecules of biological interest from
722 formaldehyde and hydroxylamine in a modified sea medium. *J. Biochem.* **85**, 1503-1508
723 (1979).
- 724 74. Hatanaka, H. & Egami, F. The formation of amino acids and related oligomers from
725 formaldehyde and hydroxylamine in modified sea mediums related to prebiotic conditions.
726 *Bull. Chem. Soc. Japan* **50**, 1147-1156 (1977).
- 727 75. Hennet, R. J. C., Holm, N. G. & Engel, M. H. Abiotic synthesis of amino acids under
728 hydrothermal conditions and the origin of life - a perpetual phenomenon.
729 *Naturwissenschaften* **79**, 361-365 (1992).
- 730 76. Islam, M. N., Kaneko, T. & Kobayashi, K. Determination of amino acids formed in a
731 supercritical water flow reactor simulating submarine hydrothermal systems. *Anal. Sci.* **17**,
732 1631-1634 (2001).
- 733 77. Marshall, W. L. Hydrothermal synthesis of amino acids. *Geochim. Cosmochim. Acta* **58**,
734 2099-2106 (1994).
- 735 78. Yanagawa, H. & Kobayashi, K. An experimental approach to chemical evolution in
736 submarine hydrothermal systems. *Origins Life Evol. Biosphere* **22**, 147-159 (1992).
- 737 79. Huber, C. & Wächtershäuser, G. α -hydroxy and α -amino acids under possible Hadean,
738 volcanic origin-of-life conditions. *Science* **314**, 630-632 (2006).
- 739 80. Huber, C., Eisenreich, W. & Wächtershäuser, G. Synthesis of α -amino and α -hydroxy acids
740 under volcanic conditions: implications for the origin of life. *Tetrahedron Lett.* **51**, 1069-
741 1071 (2010).

- 742 81. Pajović, J. D. *et al.* Tryptophan-functionalized gold nanoparticles for deep UV imaging of
743 microbial cells. *Colloids Surf. B* **135**, 742-750 (2015).
- 744 82. Cao, X. & Fischer, G. Infrared spectral, structural, and conformational studies of
745 zwitterionic L-tryptophan. *J. Phys. Chem. A* **103**, 9995-10003 (1999).
- 746 83. Barth, A. The infrared absorption of amino acid side chains. *Prog. Biophys. Mol. Biol.* **74**,
747 141-173 (2000).
- 748 84. Baldermann, A. *et al.* The Fe-Mg saponite solid solution series: a hydrothermal synthesis
749 study. *Clay Miner.* **49**, 391-415 (2014).
- 750 85. Petit, S., Baron, F. & Decarreau, A. Synthesis of nontronite and other Fe-rich smectites: a
751 critical review. *Clay Miner.* **52**, 469-483 (2017).
- 752 86. Bakke, Ø. & Mostad, A. The structure and conformation of tryptophan in the crystal of the
753 pure racemic compound and the hydrogen oxalate. *Acta Chem. Scand. B* **34**, 559-570 (1980).
754

755 **Supplemental Table Legend**

756

757 **Supplementary Table 1 | Experimental and theoretical abiotic synthesis of amino acids at**
758 **conditions of hydrothermal systems.** Aromatic amino acids are highlighted in bold. In italic is
759 the experimental study with conditions that most resemble those of the Lost City subsurface⁶⁷.
760 Ala: alanine, β -Ala: beta-alanine, α -Abu: alpha-aminobutyric acid, γ -Abu: gamma-aminobutyric
761 acid, Aca: aminocaproic acid, Ava: aminovaleric acid, Arg: arginine, Asn: asparagine, Asp:
762 aspartic acid, Cys: cysteine, , Gln: glutamine; Glu: glutamic acid, Gly: glycine, His: histidine,
763 Ile: isoleucine, Ise: isoserine, Leu: leucine, Lys: lysine, Met: methionine, **Phe: phenylalanine**,
764 Pro: proline, Sar: Sarcosine, Ser: serine, Thr: threonine, **Trp: tryptophan**, **Tyr: tyrosine**, Val:
765 valine. TC and HE stand for thermodynamic calculations and analogical hydrothermal
766 experiments, respectively.

767 **Legends for Extended Data**

768

769 **Extended Data Table 1 | List of TOF-SIMS fragment ions potentially characteristic of**
770 **tryptophan** and detected in the region displaying the highest count rates in Fig. 3b. Only the
771 fragment ions $C_8H_7N^+$ and $C_9H_8N^+$ (in bold) are characteristic of this amino acid while the other
772 fragment ions can be shared with other amino acids²². Their small mass deviation from
773 theoretical m/z values and spatial colocation allow compound identification.

774

775 **Extended Data Table 2 | Assignment for the S-FTIR bands related to organic compounds**
776 **identified in the UV fluorescent saponite** (Extended Data Fig. 2). Contributions of the H-O-H
777 bending from interlayer water at 1627 cm^{-1} and of M-O-H vibration modes (with M indicating
778 any of the cations in the structure; e.g. Mg, Fe) may interfere in the range $1500\text{-}1680\text{ cm}^{-1}$ (ref.
779 15). Band assignments were taken from refs. (81-83).

780

781 **Extended Data Table 3 | Electron microprobe analyses (in wt.%) of the Fe-rich saponite**
782 **encountered in the serpentinized peridotite recovered by drilling at 173.15 mbsf in the**
783 **Atlantis massif**. Identification is supported by refs. (84-85). Associated mineral formulas are
784 presented in Extended Data Table 4. Analyses were acquired in punctual mode on carbon-coated
785 petrographic thin sections using the Cameca SX100 installed at Geosciences Montpellier
786 (France). Operating conditions were 20 keV and 10 nA.

787

788 **Extended Data Table 4 | Fe-rich saponite formulas and associated Fe^{3+} content calculated**
789 **from electron microprobe analyses shown in Extended Data Table 3.**

790

791 **Extended Data Figure 1 | Large optical views of the deeply serpentinized harzburgite**
792 **recovered by drilling the Atlantis massif (173.15 mbsf) during the IODP expedition 304 Leg**
793 **1309D**¹². Both photomicrographs are centered on the two areas described in the present study (in
794 Figs. 1-3 and 5 and in Extended Data Figs. 2 to 4 for **a** and Fig. 4 and Extended Data Fig. 5 for **b**,
795 respectively). The high-temperature hydrated paragenesis is composed of serpentine (mesh Srp)
796 and magnetite (Mag), both after olivine (Ol), and forming a characteristic mesh texture. Yellow
797 to brownish phases are frequently found in the core of the mesh serpentine. They correspond to
798 Fe-rich serpentine (Fe-Srp) and Fe-rich saponite (Sap), formed at lower temperature during
799 secondary and tertiary alteration reactions occurring at the expense of the mesh serpentine and
800 olivine kernels¹⁵, some remnants of which can still be observed. Hole figures an olivine crystal
801 removed during sample thinning and polishing. The green arrows indicate sample orientation.

802

803 **Extended Data Figure 2 | S-FTIR confirmed the presence of N-bearing organic compounds**
804 **in the Fe-rich saponite (Sap). a**, S-FTIR distribution maps of the aliphatic CH₂/CH₃ stretching
805 band area between 2800-3000 cm⁻¹ shown in **c** and collected in the area indicated by the blue box
806 in Fig. 1a. **b-c**, Associated S-FTIR spectra. The spectrum collected in the C-rich saponite (Fig. 2)
807 shows the presence of organic compounds with modes at (1) 1270 cm⁻¹ and 1285 cm⁻¹, (2) 1380
808 cm⁻¹, (3) 1412 cm⁻¹, (4) 1460-1465 cm⁻¹, (5) 1550-1650 cm⁻¹, and 1728 cm⁻¹ in **b** and 2855,
809 2871, 2924 and 2858 cm⁻¹ in **c**. Band assignments are compiled in Extended Data Table 2.
810 Contributions of the H-O-H bending from the saponite interlayer water at 1627 cm⁻¹ may
811 interfere¹⁵. Also shown are the S-FTIR spectra collected in the mesh serpentine (mesh Srp) and
812 the Fe-rich serpentine (Fe-Srp) both being nearly depleted in absorption bands related to organic

813 compounds. They show instead characteristic O-H stretching bands at 3570 and 3610 cm^{-1} and
814 M-O-H bending modes (with M indicating any of the cations in the hydrated silicate structure) in
815 the range 1500-1680 cm^{-1} . Dotted brown curves correspond to a mixture of saponite and
816 serpentine. Precise locations of analysis are indicated in **a** with the corresponding colored dots.
817 FTIR spectra of protein²⁷ and L-tryptophan²⁶ are shown for comparison. “o”, overtone-
818 combination bands; “v”, stretching; “ v_{as} ” and “ v_{s} ”, asymmetric and symmetric stretching,
819 respectively; “a.u.”, arbitrary unit.

820

821 **Extended Data Figure 3 | SEM image sequence illustrating FIB milling, which allowed to**
822 **visualize cross-sectionally the interfaces between the C-bearing Fe-rich saponite (Sap), the**
823 **Fe-rich serpentine (Fe-Srp), the mesh serpentine (mesh Srp) and the associated textures. a,**
824 SEM-SESI view at low magnification of the UV-fluorescent area depicted in Fig. 1 and
825 Extended Data Fig. 4; the white arrow points to the region where an ultrathin foil was milled for
826 TEM observations (Fig. 5a-b). The green arrow provides the orientation of the sample. **b,**
827 Enlarged SEM-SESI view of the region of interest coated with a carbon protective layer. The
828 orange arrow designates milling direction. **c,** SEM-BSE image showing the front face of the
829 milled section. **d-e,** Enlarged SEM-InLens views of the Fe-rich saponite displaying a nanoporous
830 texture with maximum pore size of less than 100 nm, in contrast with the compact Fe-rich
831 serpentine hosted in the mesh serpentine. Pores of the Fe-rich saponite are large enough to
832 support the presence of a 1.2 nm sized molecule such as tryptophan⁸⁶ (see also Figs. 5a-b for
833 associated TEM observations). **f,** Associated EDS spectra collected at 5 kV accelerating voltage.
834 “a.u.”, arbitrary unit.

835

836 **Extended Data Figure 4 | S-DUV spectral signature of the endogenous fluorescence**
837 **revealed in the Fe-rich saponite. a**, Full field S-DUV image displayed in Fig. 1 and collected
838 using an excitation wavelength (λ_{exc}) of 275 nm and a detection range of fluorescence emission
839 between 400 and 440 nm. **b**, Fluorescence emission spectra collected with excitation wavelength
840 of 275 nm summed from the hyperspectral datacube acquired in the area indicated by the orange
841 box in **a** (30 s/point, 2 μ m step). Fit of the S-DUV hyperspectral maps, performed using
842 Gaussian functions and 10 iterations, resolved 4 main contributions at 340 ± 6 , 358 ± 3 , 380 ± 3 and
843 403 ± 3 nm. **c**, Associated spatial distributions of fluorescence emissions at 340, 358, 380 and 403
844 nm. They revealed systematic colocalization of these 4 components. The green arrows indicate
845 sample orientation. “a.u.”, arbitrary unit.

846
847 **Extended Data Figure 5 | SEM image sequence illustrating FIB milling, which allowed to**
848 **visualize cross-sectionally the interfaces between the UV-fluorescent Fe-rich saponite (Sap),**
849 **the olivine kernel (Ol) and the mesh serpentine (mesh Srp). a**, SEM-SESI view at low
850 magnification of the UV-fluorescent area shown in Fig. 4; the white arrow points to the region of
851 interest where an ultrathin foil was milled for TEM observations (Fig. 4d). The green arrow
852 indicates the orientation of the sample. **b**, SEM-SESI view of the region of interest coated with a
853 carbon protective layer. The orange arrow designates the milling direction. **c**, SEM-SEI image
854 showing the FIB milled trench at the leading edge of the region of interest. **d**, SEM-BSE image
855 showing the front face of the milled section. Similarly to Extended Data Fig. 3, it revealed
856 marked textural contrasts between the mineral phases, the Fe-rich saponite presenting the highest
857 porosity.

858

859 **Extended Data Figure 6 | Enlarged views of the positive TOF-SIMS spectra collected in the**
860 **Fe-rich saponite. a-n**, Enlarged views of the positive TOF-SIMS spectrum from Fig. 3d
861 reconstructed from the region displaying the highest count rate. **i-n**, Selected close up views of
862 this TOF-SIMS spectrum showing regions where the peaks of fragment ions characteristic of
863 isoprenoids such as pristane ($C_{19}H_{40}$), squalane ($C_{30}H_{50}$) and lycopane ($C_{40}H_{56}$) along with
864 polycyclic compounds (cholestane, $C_{27}H_{48}$; β -carotane, $C_{40}H_{56}$ and hopanoids) should be found
865 if present²³⁻²⁵. These biomarkers were previously detected using gas chromatography in the bulk
866 rock¹³ but are not detected locally in our mineral assemblage. **o-v**, Enlarged views of the positive
867 TOF-SIMS spectra reconstructed from the region displaying the highest count rate in Fig. 4f. **a-c**
868 and **o-q** exhibit peaks of fragments ions characteristic of siloxane, a common plasticizer
869 contaminant. No significant peaks can be found in the 350-450 m/z regions (**d**, **e**, **r**, and **s**) where
870 the aliphatic fraction (including fragment ions from the sterane and hopane classes and from
871 alkanes and monocyclic alkanes) is expressed in positive TOF-SIMS spectra²³⁻²⁵.

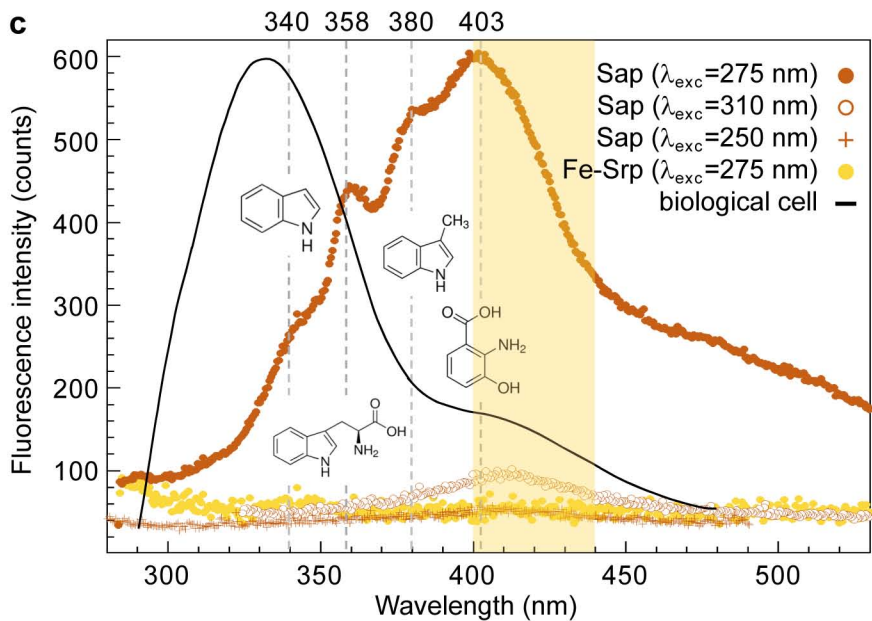
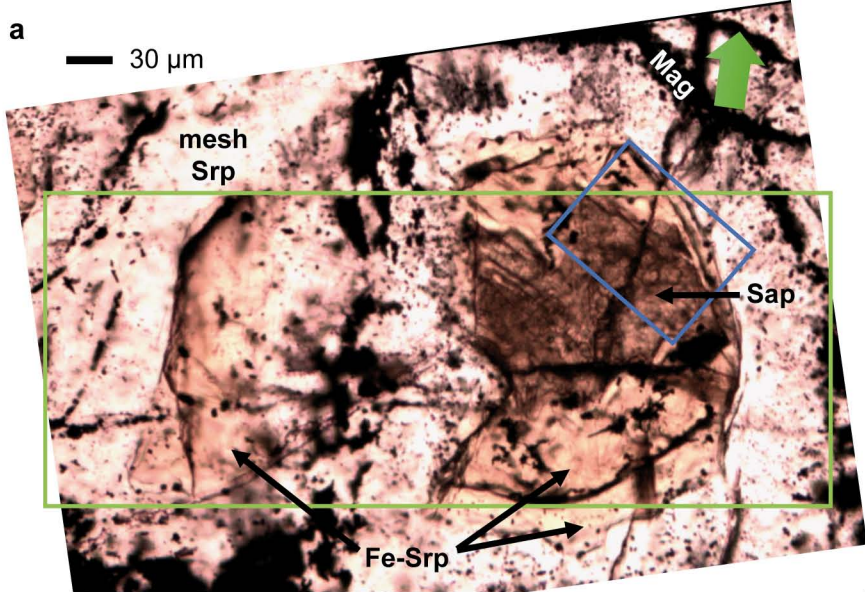
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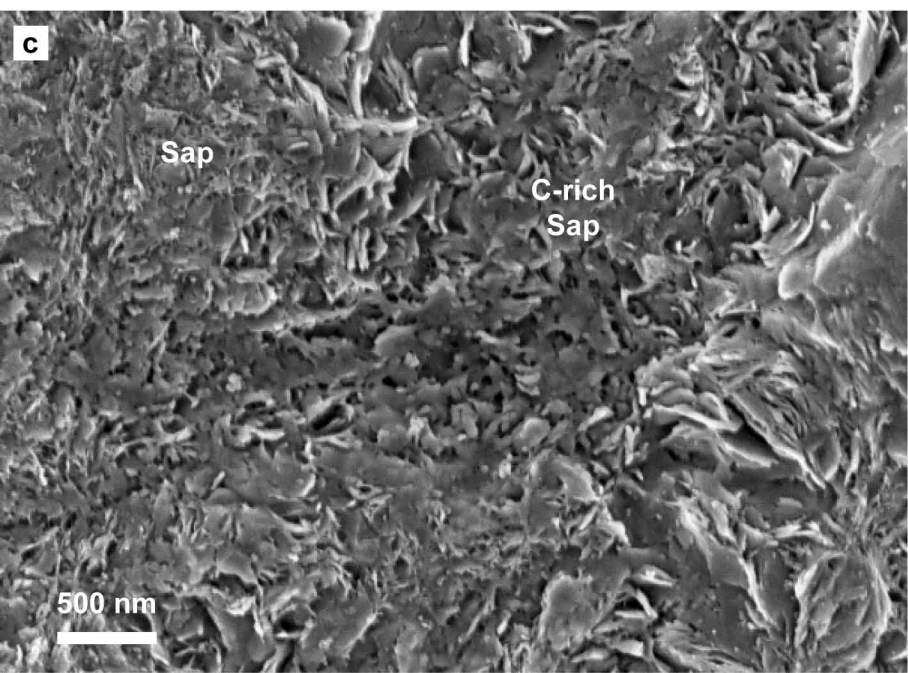
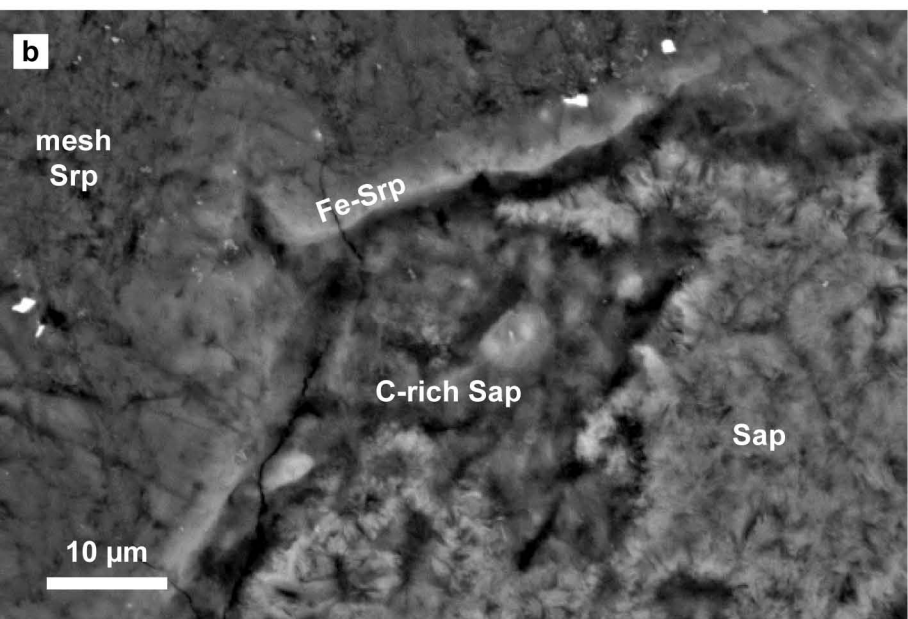
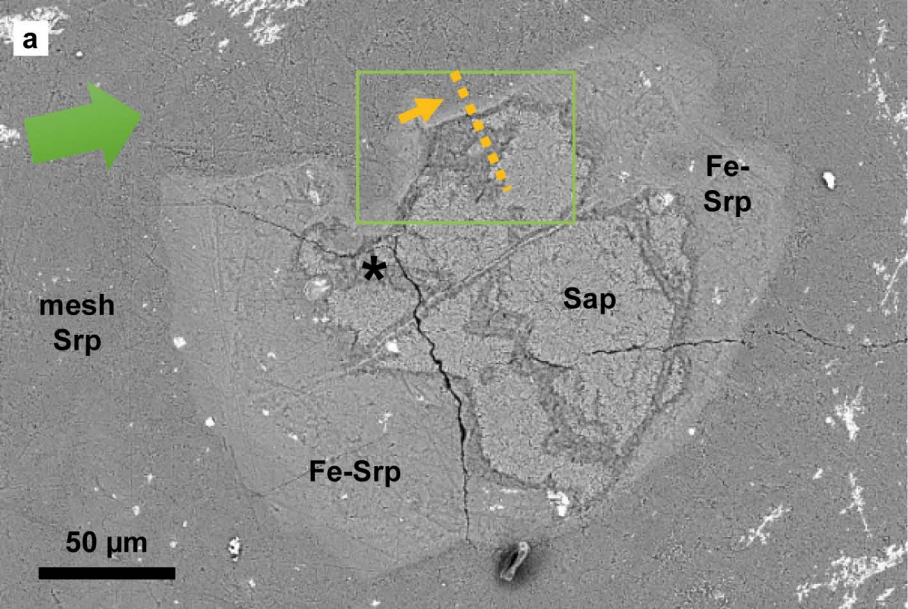
873 **Extended Data Figure 7 | Chemical affinity as a function of the logarithm of the activity of**
874 **aqueous dihydrogen ($H_{2(aq)}$) for the reactions corresponding to the abiotic synthesis of**
875 **pyruvate ($C_3H_3O_3^-$), indole (C_8H_7N), and tryptophan ($C_{11}H_{12}N_2O_2$)** (Supplementary
876 Information). The vertical lines indicate the range of H_2 activities reported for the moderate-
877 temperature fluids of the Lost City hydrothermal field³⁹.

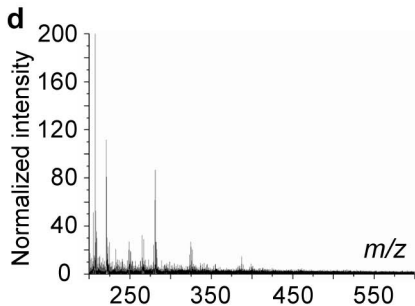
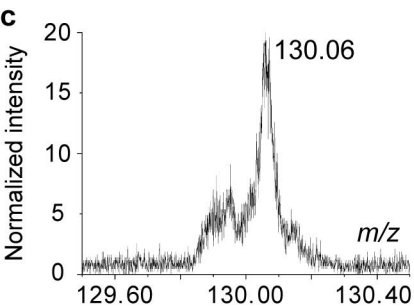
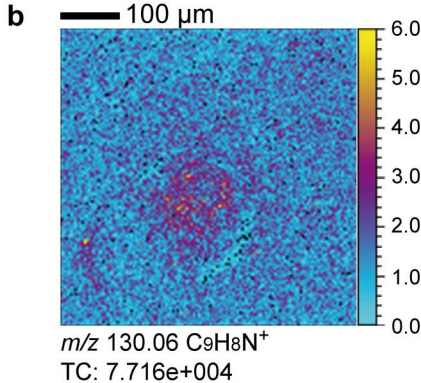
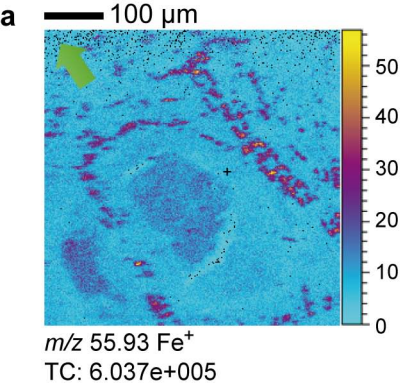
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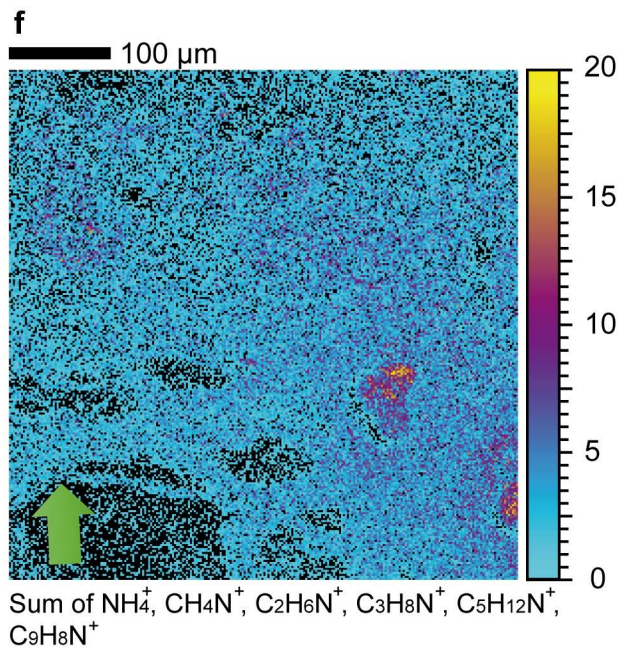
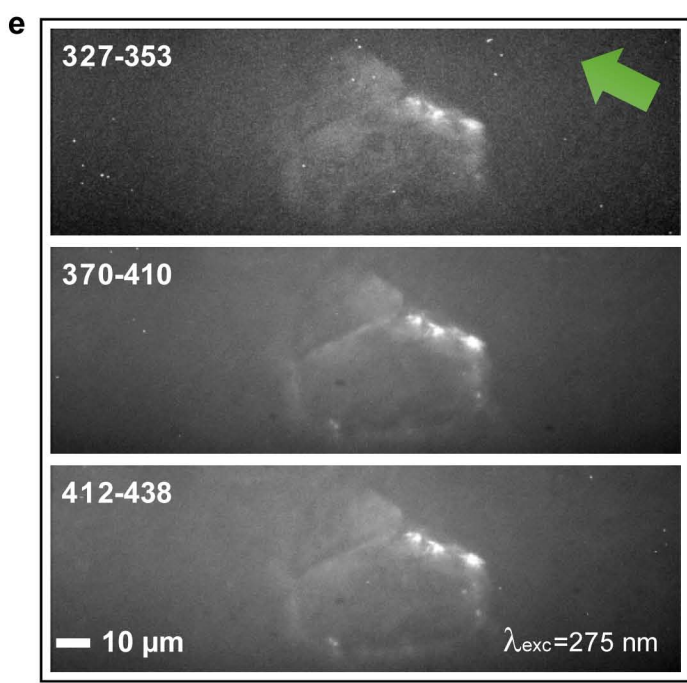
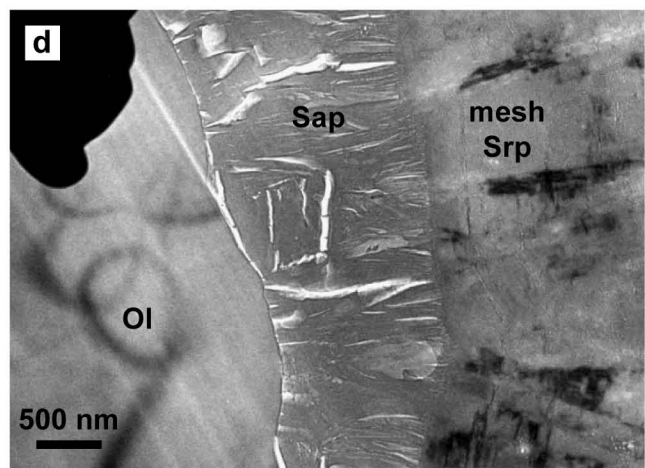
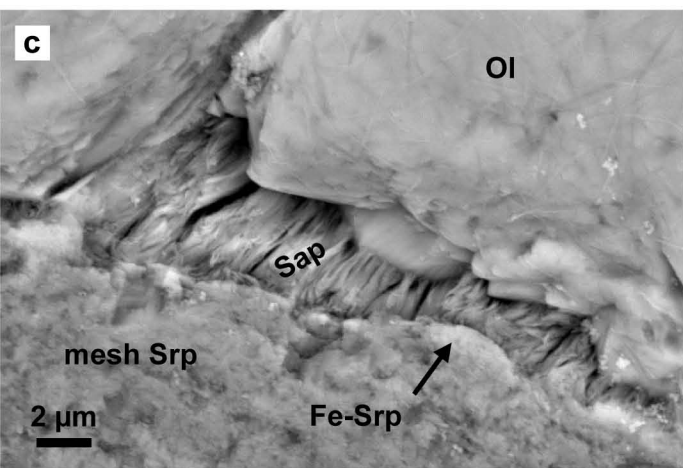
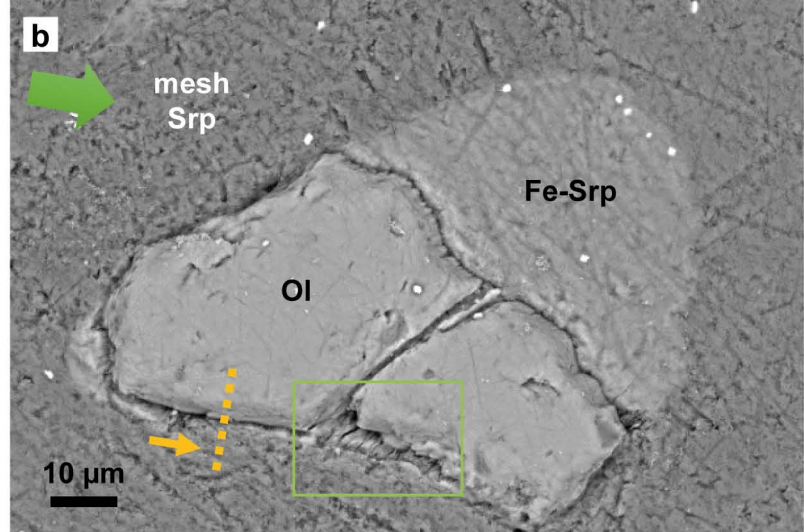
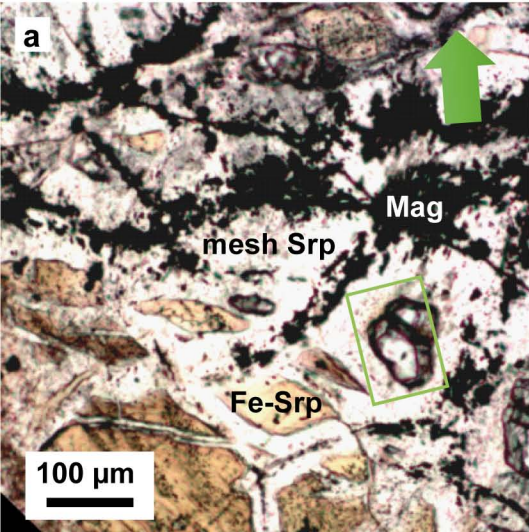
879 **Extended Data Figure 8 | Activity diagram of aqueous hydrogen ($H_{2(aq)}$) depicting, as a**
880 **function of pH, the fields of relative predominance of nitrogen species (*i.e.* ammonium,**
881 **NH_4^+ , aqueous ammonia, $NH_{3(aq)}$, and aqueous dinitrogen, $N_{2(aq)}$) at 200°C and 150 bar and**

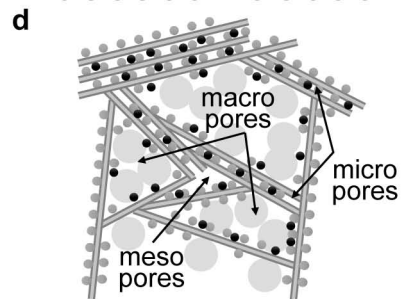
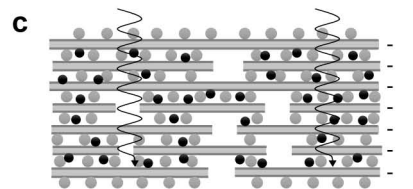
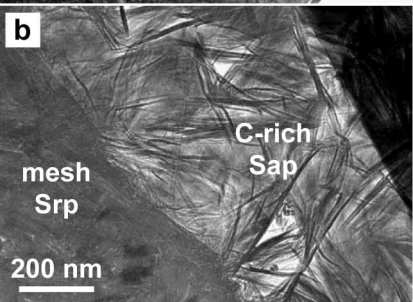
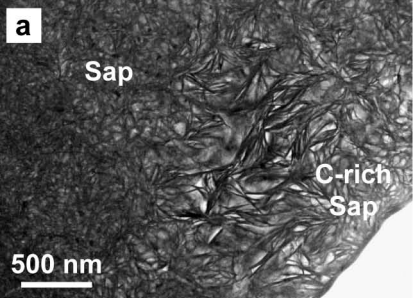
882 **considering a total nitrogen amount ($\sum N$) of $6 \cdot 10^{-6}$ M.** The limits between two predominance
883 fields have been drawn for equal activities of the nitrogen species. The dark blue star indicates
884 conditions encountered at depth in the Atlantis massif by considering a mean H_2 activity of 10.5
885 mM^{39} and a pH of 7.12 calculated with tremolite-chrysotile-diopside as the alteration assemblage
886 consistent with hydrothermal fluid composition³⁸. The activity of water was assumed equal to 1.
887 Diagram shows that $NH_{3(aq)}$ is thermodynamically favored at 200°C. QFM: quartz-fayalite-
888 magnetite mineral buffer.











- inorganic ions
- organic compounds
- tryptophan and its derivatives
- saponite sheet