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Abiotic chemically oscillating reactions make patterns in deep-sea ferromanganese nodules

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Supplementary Information

The Supplementary Information includes:

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1. Materials and Methods

a. Deep-sea specimen collection

Samples were collected from five different cruises using the human-operated submersibles *Jiaolong*, *Shenhaiyongshi* and *Fendouzhe*, each equipped with robotic manipulators and mechanical push-core devices. All photos of FMN shown in this work were collected from the samples listed in Table S-1, which lists the samples studied, GPS coordinates, and collection methods. Samples were frozen at -20 ºC onboard and immediately after collection. Prior to cutting, samples were thawed in air, dried at 50 ºC in a drying oven, and cast in epoxy.

Table S-1 List of Fe-Mn specimens studied in this work.

Sample number	*GPS coordinates*	Sample description and collection method*
JL181YB14	139.32448°E 16.80884°N	Ferromanganese nodules buried in pushcore sediments (14cm depth)
JL181YBS	139.32448°E 16.80884°N	Ferromanganese nodule at the surface of pushcore sediments
JLBC01 (JL box 1)	139.5373°E 16.7761°N	Ferromanganese nodules collected by the box core sampler during the Shenhaiyihao (Jiaolong) 2021 cruise
SQW37	113.5514°E 18.6991°N	Ferromanganese nodule collected by the HOV Shenhaiyongshi
SY165G1-3	112.8010°E 17.4245°N	Carbonate sediments with micro-FMN collected by the HOV Shenhaiyongshi
JL190	129.592488°E 17.042148°N	Ferromanganese crust collected by the HOV Jiaolong

Sample number	*GPS coordinates*	Sample description and collection method*
SY207	140.32586°E 11.61118°N	Ferromanganese crust collected by the HOV Shenhaiyongshi
SY303	141.68942°E 11.78027°N	Ferromanganese crust collected by the HOV Shenhaiyongshi
SY314	141.25467°E 12.78377°N	Ferromanganese crust collected by the HOV Shenhaiyongshi
FDZ187-NO4	106.1892°E 36.0597°S	Ferromanganese nodule collected by the HOV Fendouzhe

* HOV is human operated vehicle

b. Optical and electron microscopy

Thin sections were prepared according to standard techniques and were 30 microns in thickness and finished with 0.25 mm Al_2O_3 polishing powder in water. Slabs were prepared by mounting FMN specimens in epoxy with 24 hours curing period inside a vacuum jar, followed by cutting with a dicing saw and polishing with SiC paper down to 4000 grit size. Petrographic observations were done by polarizing microscopy and scanning electron microscopy. Polarizing microscopy imaging was performed in reflected light, plane polarised light and cross-polarised light on polished slabs and thin sections. Objectives used were 5x, 10x, 20x, 50x, and 100x. SEM imaging was performed on one Au-coated thin section (*SY165G1-3*) with an Apreo C SEM from Thermo Scientific using a 15 kV and 50 pA primary beam, whereas energy-dispersive spectroscopic analyses were performed with a 15 kV beam at 0.20 nA.

c. Micro-Raman spectroscopy

Micro-Raman was performed with a α300 WITec micro-Raman system located at the Institute of Deep-Sea Science and Engineering of the Chinese Academy of Sciences in Sanya, Hainan. A 532 nm laser was used at low power, between 0.5 and 2 mW, to minimize possible laser-heating alteration of FMN specimens and of the organic matter they contain. A 50 mm diameter optic fiber was used to collect inelastically scattered photons from the specimen and transmit them to the spectrometer. A 600 lines/mm grating was used to generate spectra with a bandwidth of about 4000 cm^{-1} and 4 cm^{-1} of spectral resolution. Hyperspectral images with spatial resolution between 1 and 3 pixels per micron were collected from the opaque specimen surface, or within 0.5 mm depth from the surface where possible, however, no organic contamination was detected in any analysis. Some analyses showed the distinct spectrum of the embedding epoxy with a characteristic strong broad peak between around 2900 and 3000 cm^{-1}, a strong narrow peak around 3070 cm^{-1} and a forest of weak to medium peaks between about 750 and 1600 cm^{-1}. Only cosmic ray reduction was applied to correct the raw Raman spectral data (filter size 2, dynamic factor 8). Because the fluorescence was deemed to contain information about organic matter, no background subtraction was applied to the spectra. Average Raman spectra shown represent reproducible averages of several hundred spectra for the stromatolite column and intercolumnar space.

d. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a Versa Probe 4 (ULVAC-PHI, inc., Japan) at the Deep-sea Science and Technology core facility of the Chinese Academy of Sciences in located Yazhou city, Hainan. The system was operated with the SmartSoft-VP 3.3.1.1 software. The operating vacuum was around 5×10^{-6} Pa while the X-ray source (monochromatic Al Ka) had an energy of 1486 eV and a power of 25 W. The beam spot size was about 100 µm in diameter, and the analysis mode was FAT. In survey mode, the energy bandwidth was 1400 eV, the energy resolution was 0.8 eV, and the time per step was 50 ms. For higher resolution spectra at selected edges, the scanned mode was used, also with a time per step of 50 ms, and the Table S-2 below shows the analytical parameters for each edge.

XPS data was corrected and processed according to standard techniques and using the XPSPEAK41 software. Modelled peaks were generated using Gaussian-Lorenz functions. This work was accomplished by the Theoretical and Computational Chemistry Team from Scientific Compass, Shiyanjia Lab (www.shiyanjia.com).

Table S-2 XPS scanning parameters

Edge	Energy bandwidth	Energy resolution
N1S	392-410eV	0.125 eV step
C1S	279-297eV	0.100 eV step
O1S	523-543eV	0.100 eV step
Mn2p	53-93eV	0.125 eV step
Mn3S	632-672eV	0.125 eV step
Fe2p	700-740eV	0.125 eV step

e. Chemically oscillating reaction experiments

All photos of COR shown in this work were collected for this work from experimental solutions listed in Table S-3. The COR experiments were performed under uncontrolled standard conditions inside 10 cm diameter glass Petri dishes using the following solutions:

Table S-3 Reactant solutions prepared for COR experiments

Solution	Compound formula	Compound name	Concentration	Volume added
A1	$NaBrO_3$ and H_2SO_4	Sodium bromate and sulphuric acid	[1 M] and [0.33 M]	6 ml
B1	$C_3H_4O_4$	Malonic acid	[1 M]	1 ml
C1	NaBr	Sodium bromide	[1 M]	0.5 ml
Ferroin	$Fe(C_{12}H_8N_2)_3SO_4$	Phenanthroline ferrous sulfate	[0.025 M]	1 ml
B2	$C_5H_6O_5$	α-Ketoglutarate	[1 M]	1 ml
D2	$KMnO_4$	Potassium permanganate	[0.1 M]	1 ml
E2	$MnSO_4$	Manganese sulphate	[0.1 M]	1 ml

COR experiments were performed with the following procedure: The first three solutions (A1, B1, and C1) were mixed until the yellow colour disappeared, which took approximately two minutes of gentle stirring in a fume hood. This step is when the most bromine gas (Br_2) is released, perceptible from its characteristic odour. The ferroin solution is then added and the mixture is stirred again, which spontaneously begins to exhibit heterogeneous blue to orange colour changes. Once well mixed and with a homogeneous orange colour, the solution is left still. After a few seconds, randomly localised blue oxidation spots begin to appear in the solution and start to diffuse radially with seconds time scales. Oscillations are displayed by colour gradients from darkest blue to lightest orange in each radially diffusing circular wave, followed by another circular blue wave starting to radially diffuse in the same central oxidation spot. These blue-coloured chemical waves, presumably composed of reaction products such as ferric iron and bromomalonic acid, form visibly contrasting chemical waves that can appear as perfect to irregular circularly concentric rings. These periodically oscillate as the colour gradients change over second to minutes times scales. For the modified COR, solution B2 was added after the addition of ferroin, and D2 and E2 were also added after the ferroin.

Experiments were performed on the laboratory benchtop, after the degassing of bromine gas in a fume hood. Outside the fume hood, vibrations and air currents caused by the fume hood are minimised, which avoids disturbances in pattern formation. A white LED light board was used to visualise the characteristic COR patterns

in transmitted light and to collect videos of experiments using a CCD camera. Each reaction lasts between about 30 and 45 minutes, until the Petri dish is filled completely with the blue colour in classical COR or green colour in the COR with added manganese compounds (Fig. S-2). Bubbles of CO_2 attached to the Petri dish by surface tension become more numerous. The number of reaction resets (i.e. stirring after the Petri dish solution has become blue returns it to an orange colour) and the concentration and volume of reactants affect the overall duration of each experiment. Usually, several resets are possible with a single mixed COR solution

Supplementary Figures

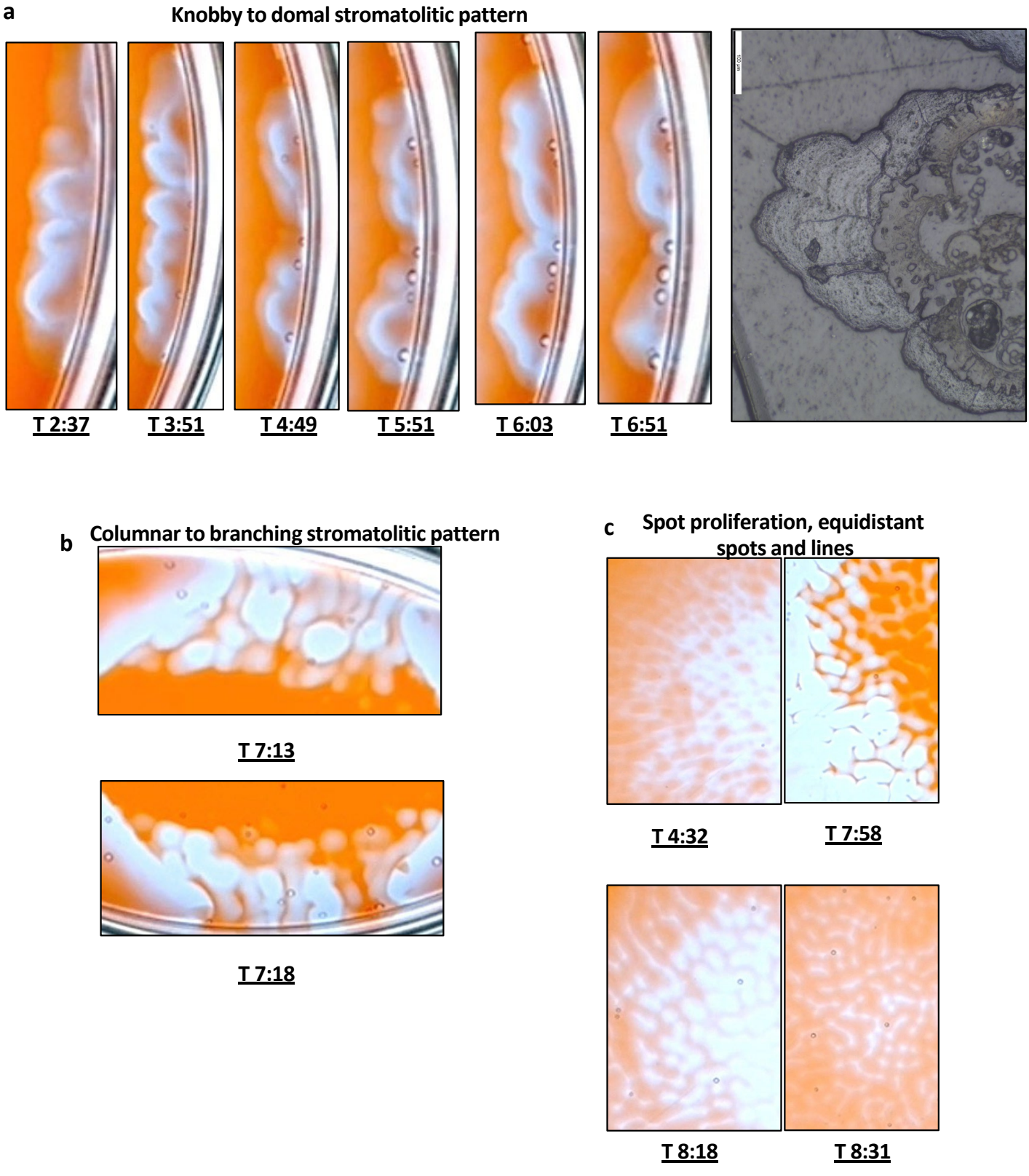

Figure S-1 Detailed COR experiments with manganese compounds compared to patterns in FMN. Examples of **(a)** time evolution of finely laminated knobby to domal stromatolitic patterns, compared to a similar pattern of domal stromatolite in FMN, **(b)** columnar to branching stromatolitic patterns, **(c)** spot proliferation that form equidistant spots and lines, when the spots join….

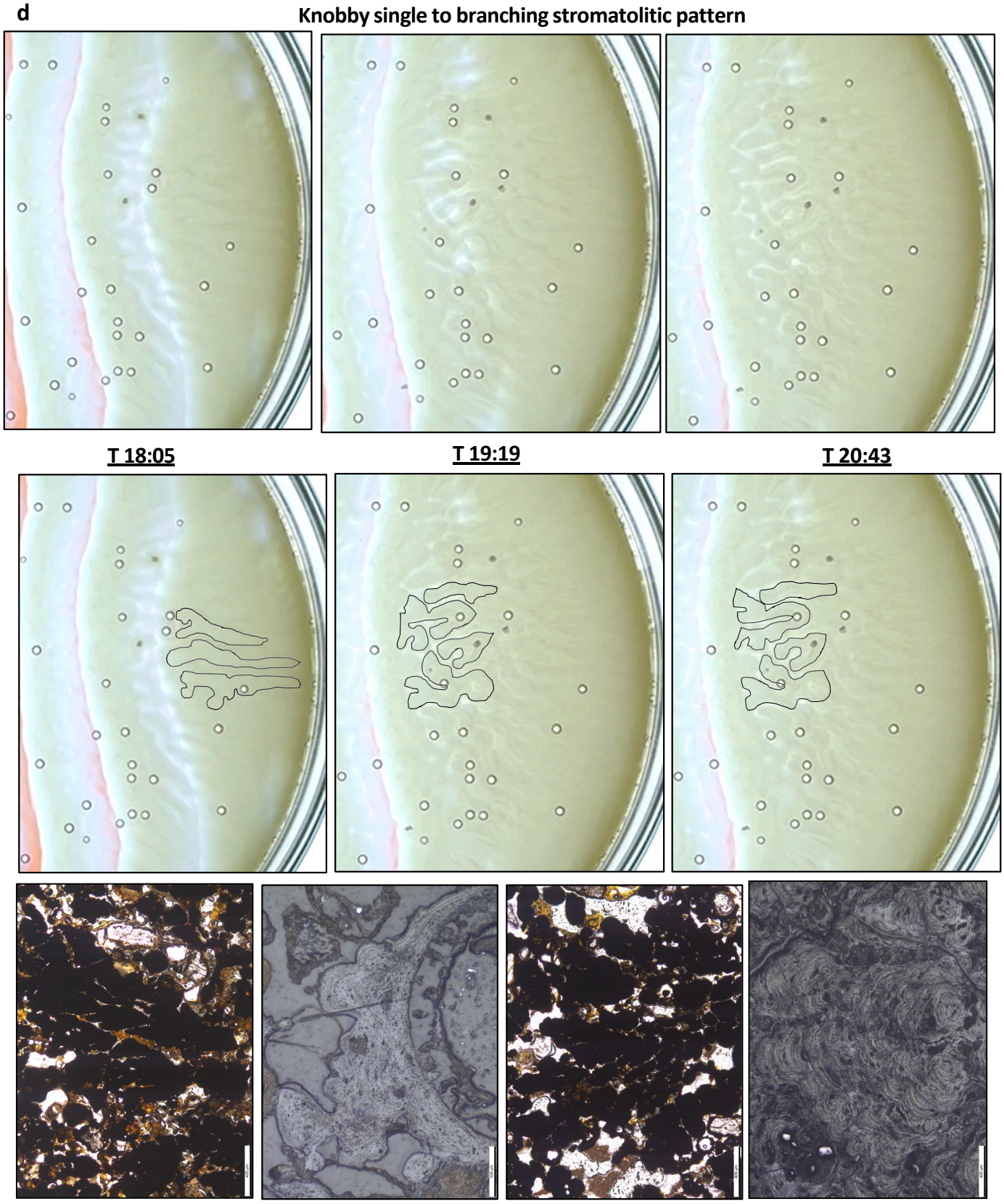

Figure S-1 *continued* **(d)** knobby single or bifurcate columnar stromatolitic patterns, with interpretive sketched contour lines, and compared to similar stromatolitic patterns in FMN…

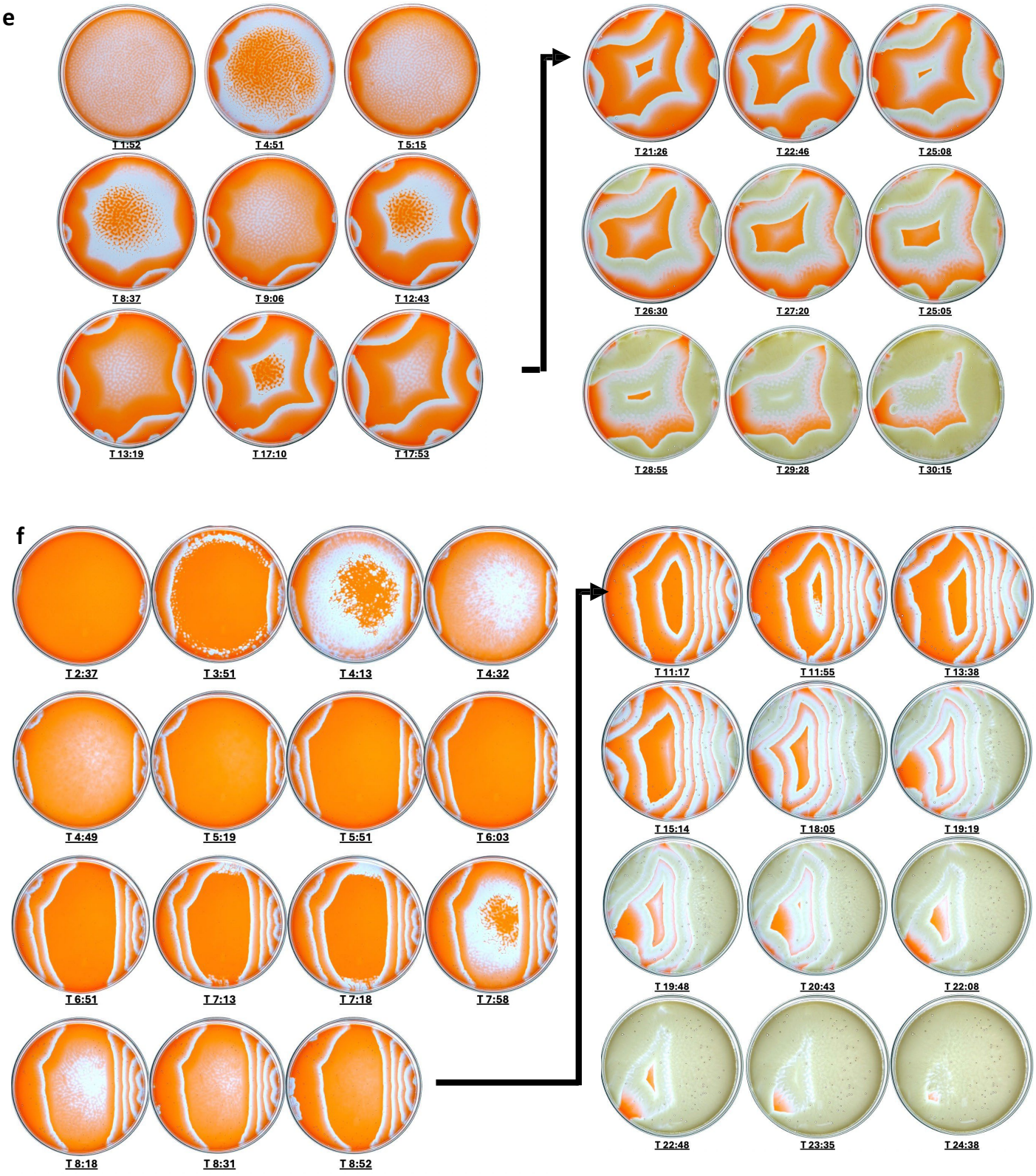

Figure S-1 *continued* **(e-f)** time series for two selected COR experiments that produced stromatolitic patterns, triggered by surface tension from the Petri dish edge. Other similar experiments [e.g., Fig. 2-d] produce stromatolitic patterns from oxidation spots diffusing radially outwards. All Petri dishes are 10 cm in diameter.

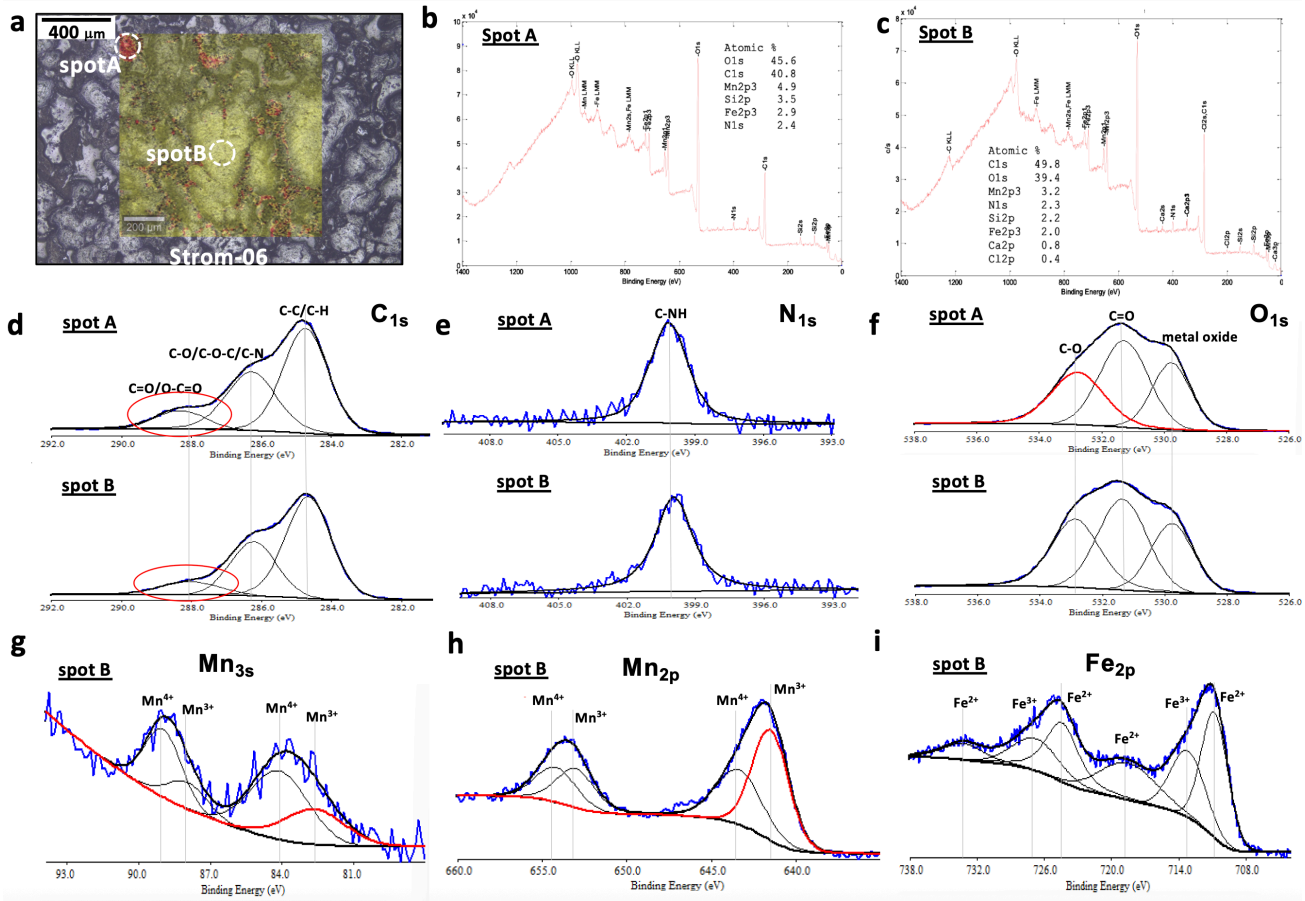

Figure S-2 X-ray photoelectron spectra of organic matter and metal oxides in FMN (*SY314*). **(a)** Approximate location of two XPS analytical spots (where spot A is in the intercolumnar space and spot B is in the stromatolite column) shown on Raman image semi-transparency overlain on reflected light image [see Fig. (1f-g)]. **(b-c)** Survey mode spectra of the two analytical spots showing identified peaks and compositional tables. **(d-f)** XPS spectra of spot A (top) and spot B (bottom) in the C_{1s}, N_{1s}, and O_{1s} regions. Identified peak assignments include: 284.7 eV for C-C/C-H bonds; 286.2 eV to 286.3 eV for C-O/C-O-C/C-N bonds, and 288.0 to 288.3 eV for C=O/O-C=O bonds; 400.0 eV to 400.1 eV for C-NH bonds; 529.8 eV for metal oxide bonds; 531.2 eV to 531.3 eV for C=O bonds; and 532.8 eV to 532.9 eV for C-O bonds. The red ellipse in (d) shows a noteworthy difference for the carboxyl (O-C=O) peak. **(g-i)** XPS spectra of spot B in the Mn_{3s}, Mn_{2p}, and Fe_{2p} regions. Identified peak assignments include: 82.6 eV, 88.0 eV, 641.5 eV, and 653.0 eV for Mn^{3+}; 84.1 eV, 89.0 eV, 643.4 eV, and 654.2 eV for Mn^{4+}; 710.8 eV, 718.5 eV, 724.7 eV, and 733.2 eV for Fe^{2+}; 713.2 eV and 726.8 eV for Fe^{3+}.