

## ■ Metamorphic evolution of carbonate-hosted microbial biosignatures

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### ■ Supplementary Information

The Supplementary Information includes:

- Methods
- Figures S-1 to S-5

### *Methods*

#### Experimental HPHT conditions

Individual samples were exposed to HPHT conditions for 24 hours using a Depths of the Earth QUICKpress™ piston-cylinder press at the Geophysical Laboratory, Carnegie Institute of Washington, USA. For a review on experimental petrology, including an overview of the piston cylinder apparatus, see Holloway and Wood, (1988). The samples were sealed by welding in gold capsules. The assembly consisted of a barium carbonate outer sleeve wrapped in lead foil enveloping a pyrex sleeve containing the graphite furnace and crushable MgO components. The welded gold capsules were hosted within MgO sleeves and MgO powder was pressed into the spaces to ensure static pressure conditions. Note, while external pressure conditions applied were static, the heterogeneous nature of natural material mean that internally, uniform compaction during static compression cannot be expected, and is an important aspect of replicating natural systems. Temperature was measured using a type-S thermocouple and monitored and maintained using a Eurotherm control. Six HPHT conditions were selected based on their representation of metamorphic PT-space (Fig. S-1c). These were three experiments at 500 MPa: (i) 500 MPa, 200 °C; (ii) 500 MPa, 350 °C; (iii) 500 MPa, 500 °C; and three experiments at 800 MPa: (iv) 800 MPa, 300 °C; (v) 800 MPa, 425 °C; (vi) 800 MPa, 550 °C. Of these, an additional duplicate run of the 500 MPa, 350 °C experiment was conducted for additional analysis of an acid-etched, unpolished surface. Experiments ran for 24 hours, after which they were quenched by shutting off the power to the press while maintaining pressure until the sample reached room temperature. For subsequent analysis, each experimental charge and the positive controls were rough-polished on one side using alumina polishing powder to reveal a sample surface, before being mounted in epoxy resin and polished using alumina polishing powder. Polished starting material samples and experiment charges were first analysed by Raman spectroscopy, followed by SEM analysis. The duplicate 500 MPa, 350 °C experimental sample and an additional starting material sample were etched on the sample surface to remove a surface layer of carbonate, revealing organic and siliceous sample components for SEM imaging. Samples were etched with 10 % HCl for 30 minutes, rinsed in DI water, then air-dried. These samples were not polished so to preserve the natural structures revealed by the etching process.

#### Raman Spectroscopy

Polished samples were analysed using a WITec Alpha500 Confocal Raman spectrometer at CNRS, CBM, Orléans, France. For this, a

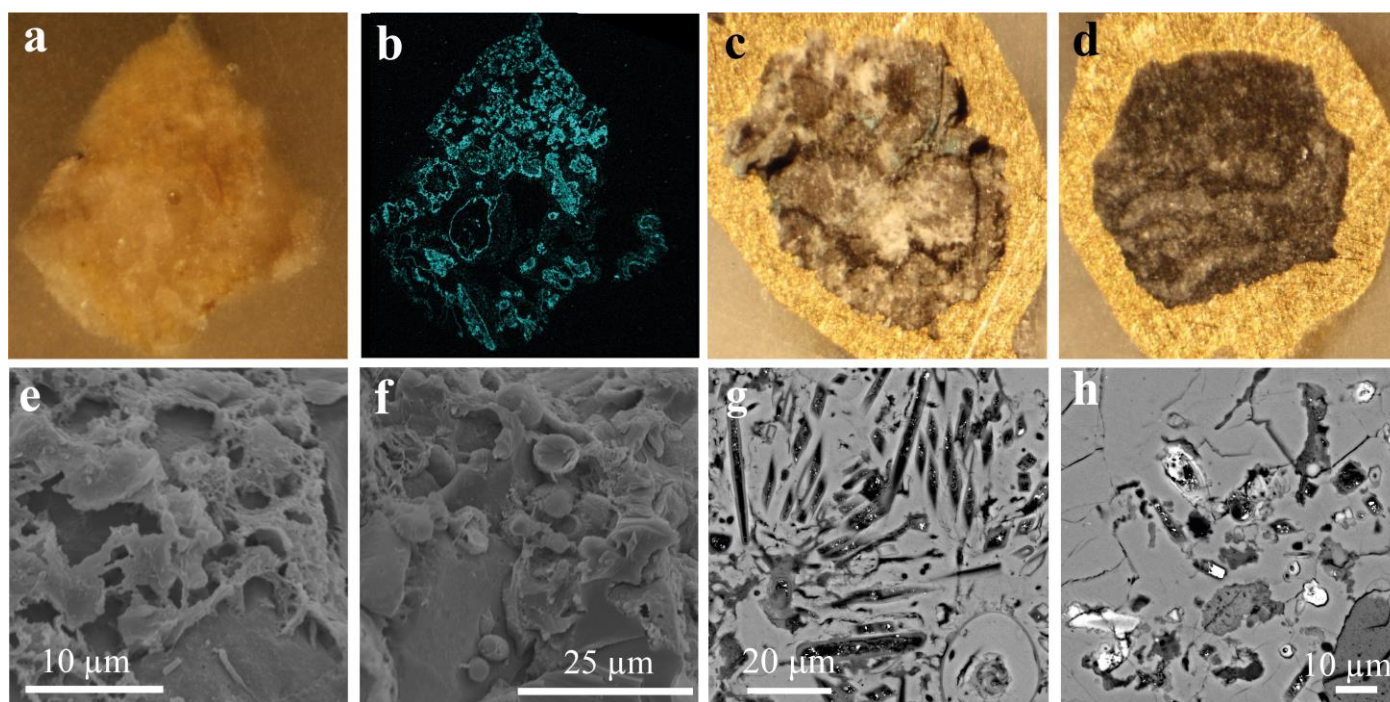


Nd:YAG frequency doubled green laser (wavelength 532 nm) was used. Initial transmitted light observation of the sample was performed and images of target areas captured. Maps were acquired using a Nikon E Plan 50x objective with a numerical aperture N.A. = 0.75. The corresponding diameter of the laser spot was thus approximately 850 nm ( $d = 1.22 \cdot \lambda / \text{N.A.}$ ). The grating used was a 600 g/mm associated with a spectral resolution of approximately  $3.8 \text{ cm}^{-1}$ . Raman imaging was conducted by scanning the samples over areas ranging from  $80 \times 80 \mu\text{m}^2$  and  $600 \times 600 \mu\text{m}^2$ . Maps were acquired during continuous scans whereby the sample is continuously moved below the laser. The exposure time is thus dependent of the spot size, the scan size, the resolution of the map and the integration time (more details can be found in Foucher *et al.*, 2017). Power was tuned in order to prevent burning of sample materials, which was determined by visual inspection before and after data acquisition. The collected imaging data were then analysed using Witec proprietary software (Witec Project). False-colour compositional maps were produced using the peak area over the baseline. For low P T samples, masks were created to select only pixels associated with satisfactory signal to noise ratio for the carbonaceous matter (low background level and high G band intensity), and the corresponding spectra were averaged. For higher P T samples, the signal to noise was good enough to obtain the average spectrum from the full maps.

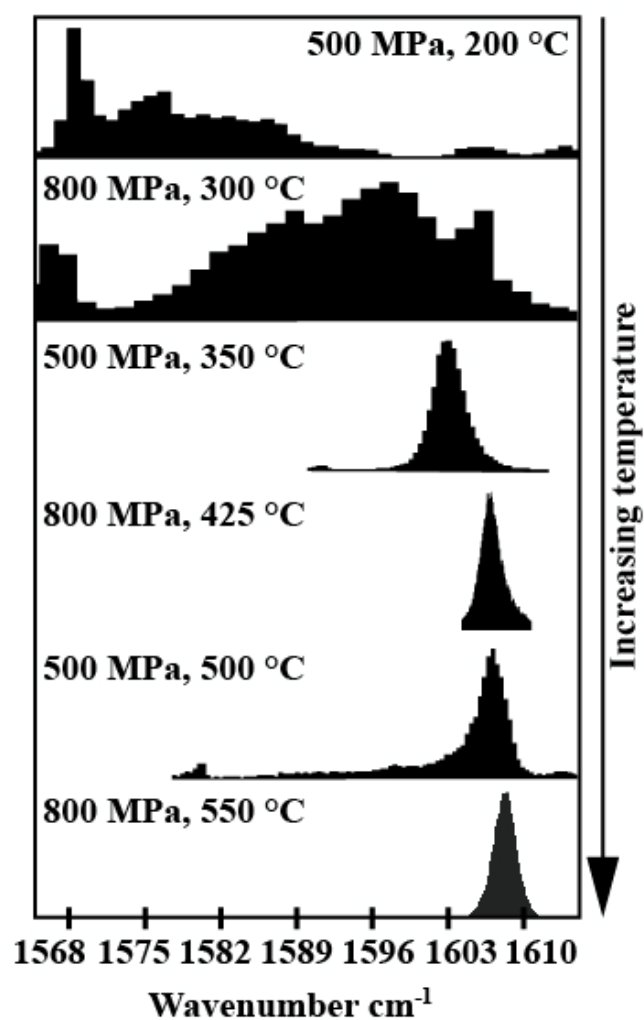
### Field Emission Gun-Scanning Electron Microscope analysis

Following Raman spectral mapping, experimental and starting material samples were carbon coated and analysed using a Field Emission Gun Scanning Electron Microscope (FEG-SEM) at the University of Edinburgh, UK, with elemental quantification achieved via Energy Dispersive System (EDS) analysis. An accelerating voltage of 20 KeV and working distance of 7 mm was used.

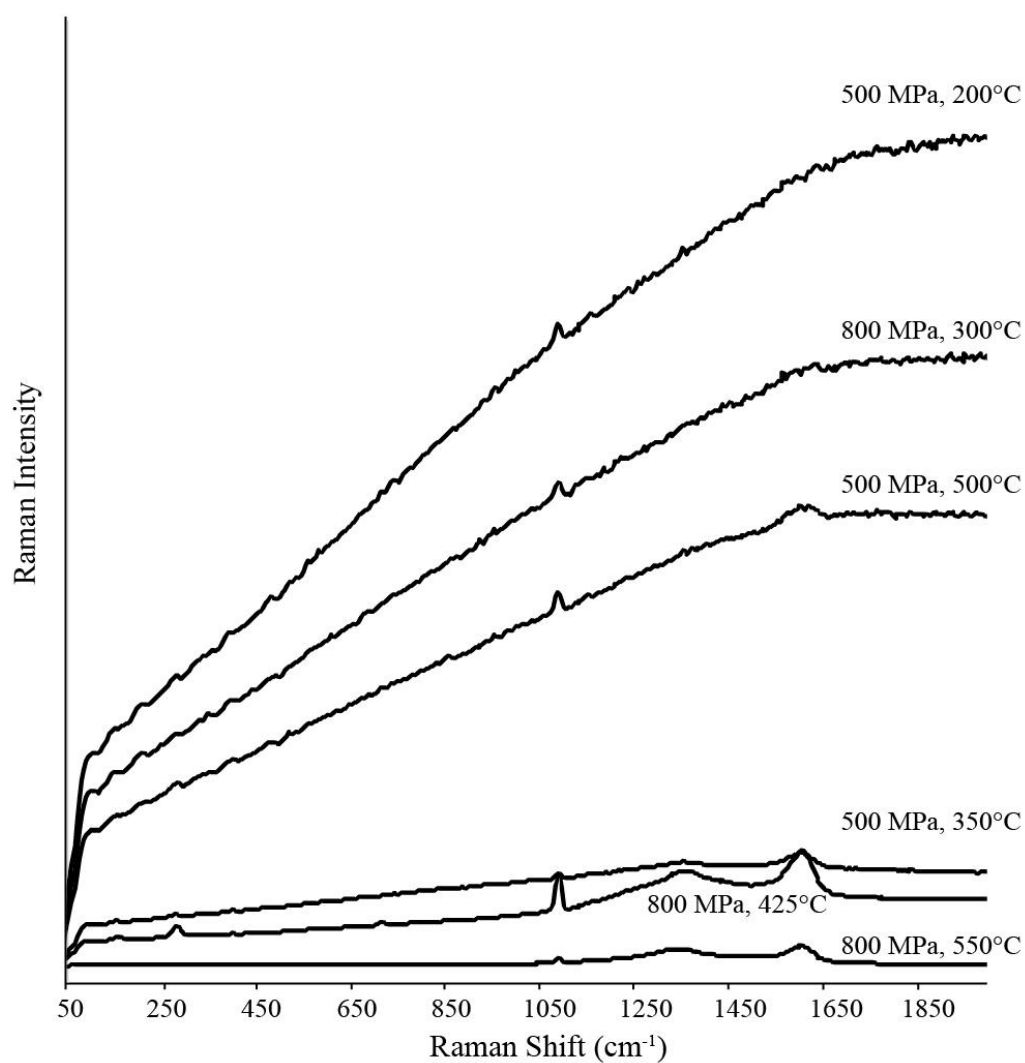
### Supplementary Figures



**Figure S-1** Reflected light microscope images (**a, c, d**) of exposed polished surfaces (all approximately 2-3 mm across) of (**a**) starting material (**c**) 800 MPa, 300 °C experiment; and (**d**) 800 MPa, 425 °C experiment, where dark organic matter can be seen forming a defined fabric within the light grey calcite matrix, a feature absent from the starting material. (**b**) EDS elemental map of Si (cyan) of the exposed surface in (**a**); SEM images (**e-f**) of the acid-etched duplicate 500 MPa, 350 °C experiment showing (**e**) silicified filament structures and (**f**) intact coccoidal structures; and (**g-h**) SEM image showing intact (**g**) and partially-degraded (**h**) diatom frustule structures in the starting material and at 800 MPa, 300 °C, respectively.

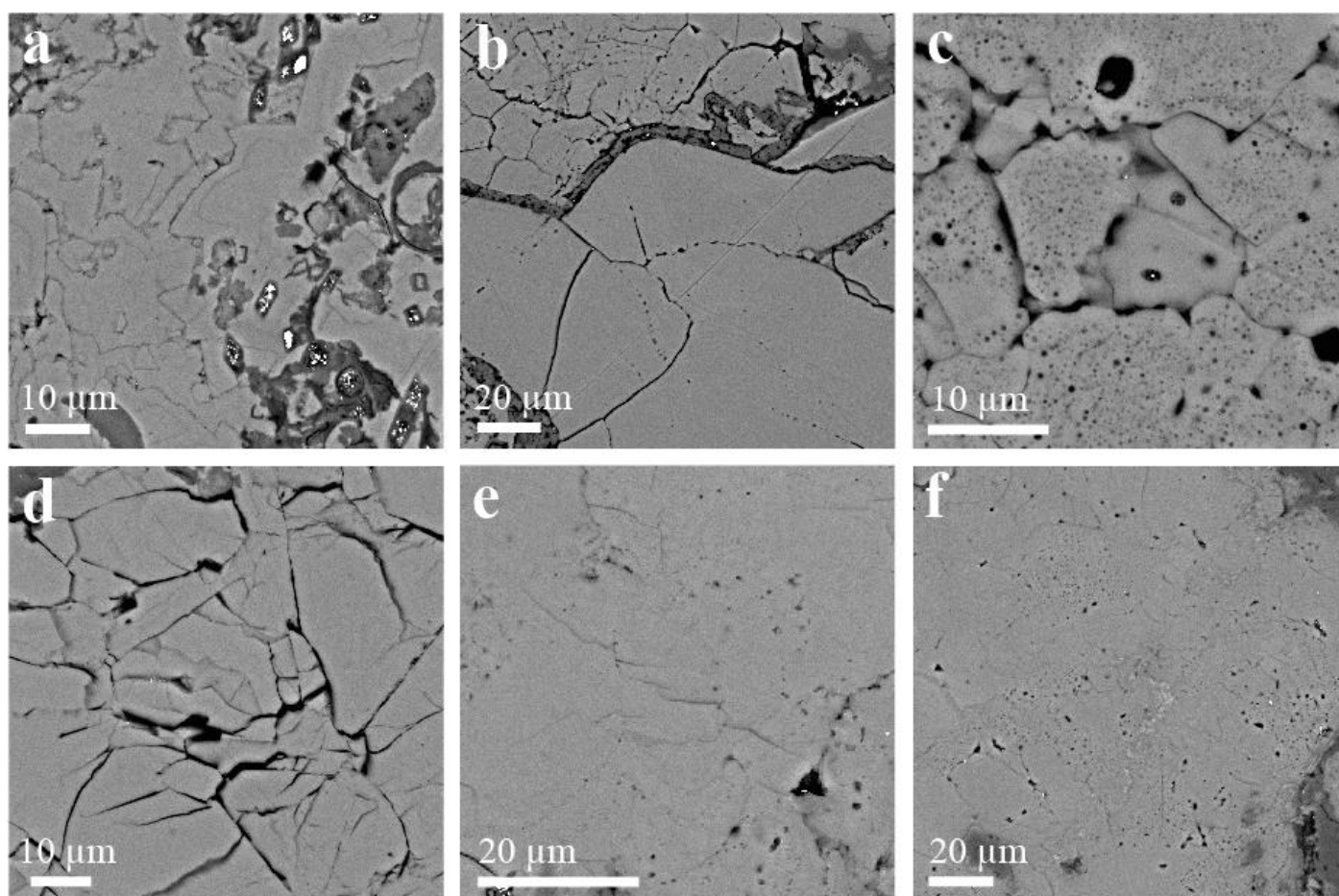


**Figure S-2** Pixel histograms of the G band peak centre across the six experiments, in order of increasing temperature.

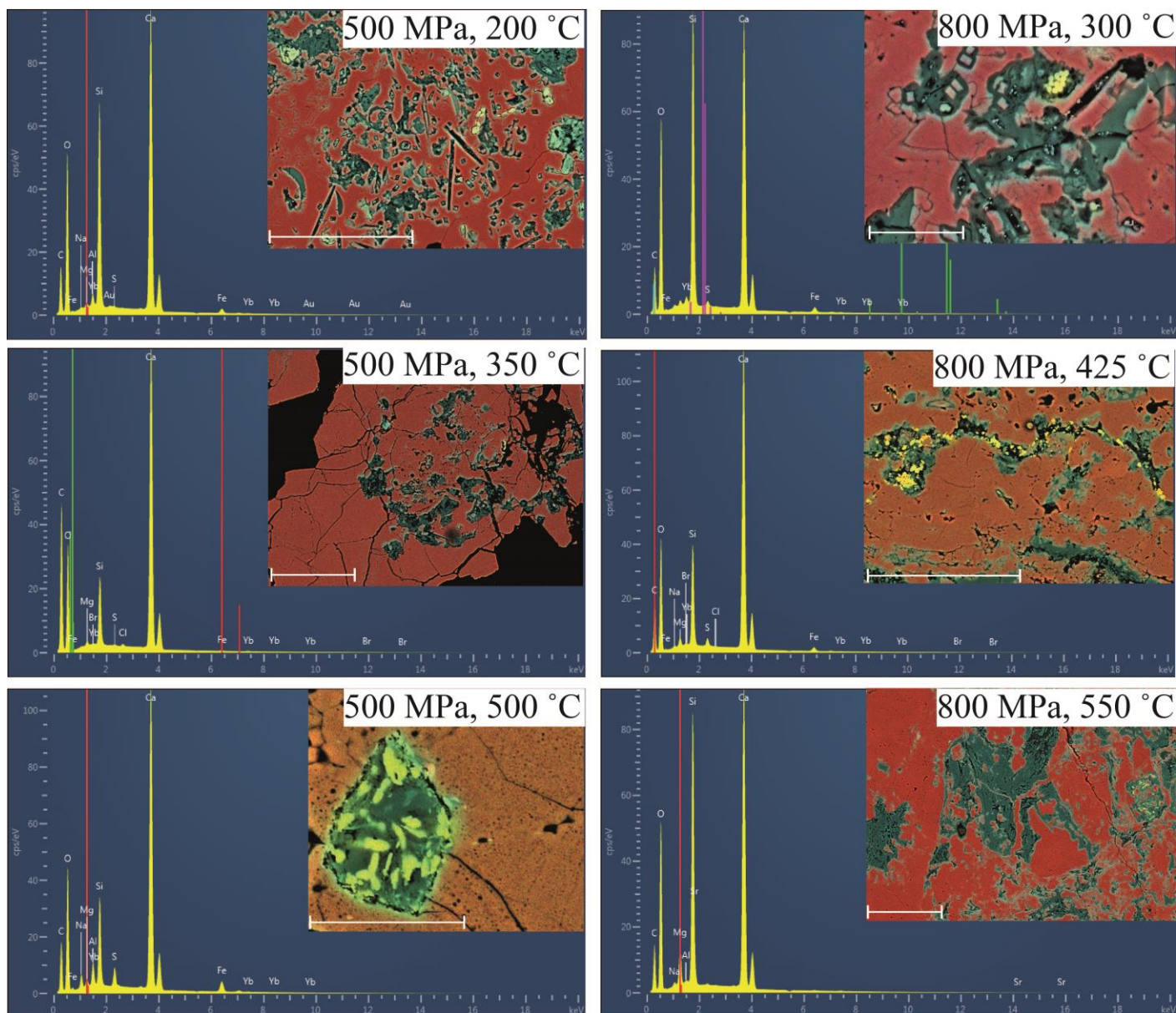


**Figure S-3** Raman spectra for the six experimental conditions before background fluorescence is removed. Note that for the starting material, very high fluorescence masked all Raman signals, and so is not included here.





**Figure S-4** SEM images of experimental samples showing (a) 500 MPa, 200 °C with no degassing or fracturing; (b) fracturing and minor degassing at 500 MPa, 350 °C; (c) fracturing and extensive degassing at 500 MPa, 500 °C; (d) fracturing but no degassing at 800 MPa, 300 °C, (e) 800 MPa, 425 °C with minor degassing and no fracturing; and (f) recrystallisation of the calcite matrix and minor degassing at 800 MPa, 550 °C.



**Figure S-5** EDS spectra measured from the example mapped regions depicted within the manuscript. Scale bar = 100  $\mu\text{m}$ , with the exception of 500 MPa, 500  $^{\circ}\text{C}$  and 800 MPa, 300  $^{\circ}\text{C}$ , which are 25  $\mu\text{m}$ .

### Supplementary Information References

- Foucher, F., Guimbretière, G., Borst, N., Westall, F. (2017) Petrographical and Mineralogical Applications of Raman Mapping. In: Maaz, K. (Ed.) *Raman Spectroscopy and Applications*. IntechOpen.
- Holloway, J.R., Wood, B.J. (1988) *Simulating the Earth: Experimental Geochemistry*. Unwin Hyman Inc, London, pp. 1-196.