COMBINING MORPHOLOGICAL AND MOLECULAR BIOSIGNATURES IN PUTATIVE ICHNOFOSSILS AS A CASE STUDY FOR AN APPROACH TO LOCATING CANDIDATE MICROFOSSILS ON MARS

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Introduction

❖ At present, the surface of Mars appears to be devoid of life, but may have been habitable 3.5 billion years ago
❖Evidence for life on the surface of Mars may be in the form of bacterial fossils.
❖Structures that form through geological processes can be misidentified as fossilised bacteria.
❖ Metabolic processing imprints evidence of biological activity in the composition of high molecular weigh organic compounds called molecular biosignatures[1].
❖Linking fossil morphology with molecular biosignature could simultaneously provide two lines of evidence for a biological influence upon geological structures on Mars[2].
❖This can assist in the triaging of sample selection for casheing by Mars 2020 in preparation for the Mars sample return mission at the end of the decade[3].

Mars Analogue Morphological Biosignature

❖Ontong Java Plateau (OJP) sample Leg 192 1184A 13R core 145-148 interval was obtained from the Ocean Drilling Programme (ODP) (Fig 1 a-c) and served as our Mars analogue.

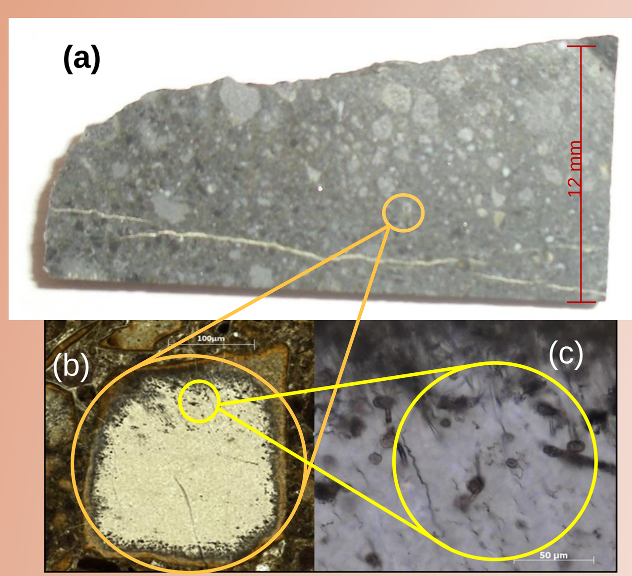

Fig 1: ***(a)*** *Photograph: Section through OJP sample showing glass clasts (**b**): Glass clast x20 **(c)** Microtubules x64*

❖A 30µm thin section was prepared and microtubular alteration textures within glass shards suggested to be ichnofossils were identified.
❖The three zones: A microtubule poor centre; a microtubule tubule rich perimeter and the surrounding matrix of cemented lapilli sized grains were assigned (Fig 2).

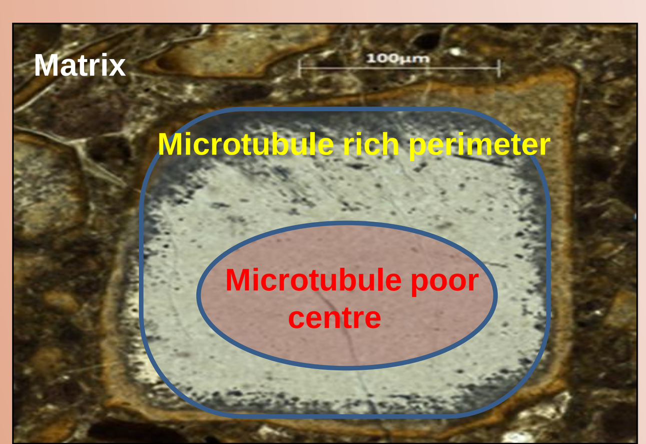

Fig 2: *A Basaltic glass shard showing zone where the morphological biosignature can be observed. Scale bar = 100 µm*

X-ray photoelectron spectroscopy (XPS)

❖XPS was used to investigate the distribution of organic material in the three zones
❖The sample was decontaminated using argon gas cluster sputter gun etching[4]

Fig 3: *A 30 X 30 grid was placed over a shard and XPS analysis was conducted in each cell. Scale bar = 1 mm*

❖Carbon and nitrogen was measured in each cell and assigned a 'heat map' colour based on concentration.
❖These were mapped to the grid in Fig 4.

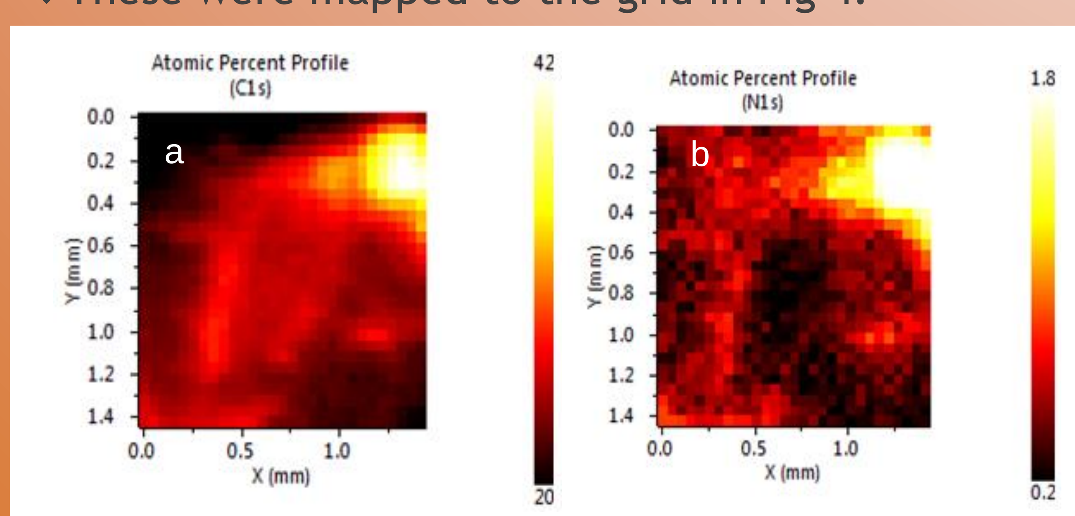

Fig 4: *Concentration distribution of (a) carbon and (b) nitrogen measured by XPS*

❖Carbon and Nitrogen did not clearly map to the microtubule rich region.

Time of Flight Secondary Ion Mass Spectrometry

❖NanoSIMS with a Bi^{++} was used obtain a high-resolution spectral image (Fig 5 a-d).

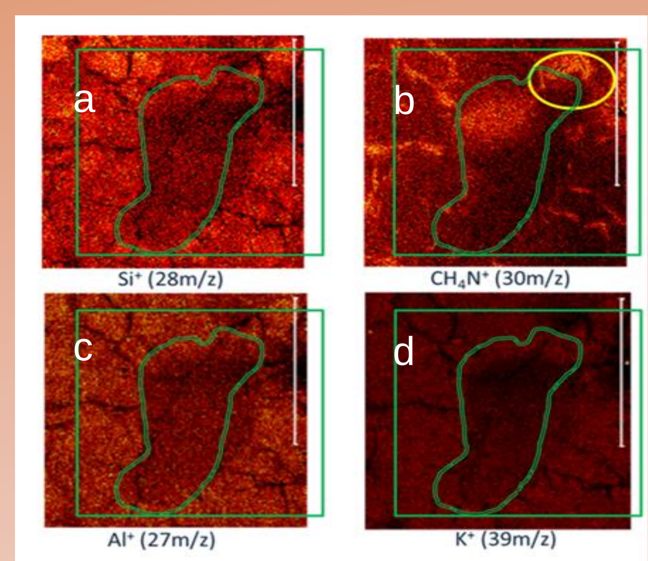

Fig 5 a-d: *NanoSIMS image, green outline within green box shows the perimeter of clast under analysis. Yellow ellipse shows the hot spot region observed in the XPS analysis(Fig 4). Scale bar = 1mm*

❖NanoSIMS provided excellent resolution (70 nm.pixel^{-1})
❖However, the largest mass fragment that was confidently identified was 30 u.
❖This was inadequate for the detection of the high molecular weight organic compounds that can serve as molecular biosignatures.

Gas Cluster Primary Ion Beam

❖Sample was analysed using a J105 ToF SIMS with an argon gas cluster primary beam[5].
❖ The gas cluster primary beam spreads the energy over a wider region, therefore causes less damage to high molecular weight organic compounds (Fig 6 a & b).

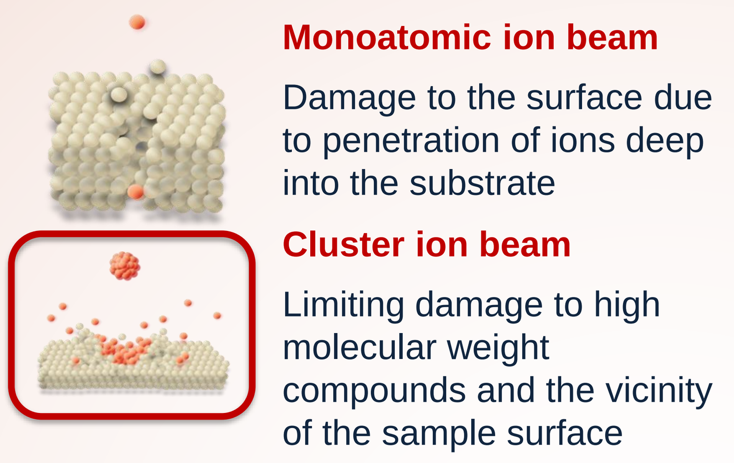

Fig 6: *Comparison of surface damage between **(a)** monoatomic and **(b)** gas cluster primary beams*

J105 total ion image

❖Due to the surface damage caused by the nanoSIMS primary beam, a new area was selected for the J105 analysis.

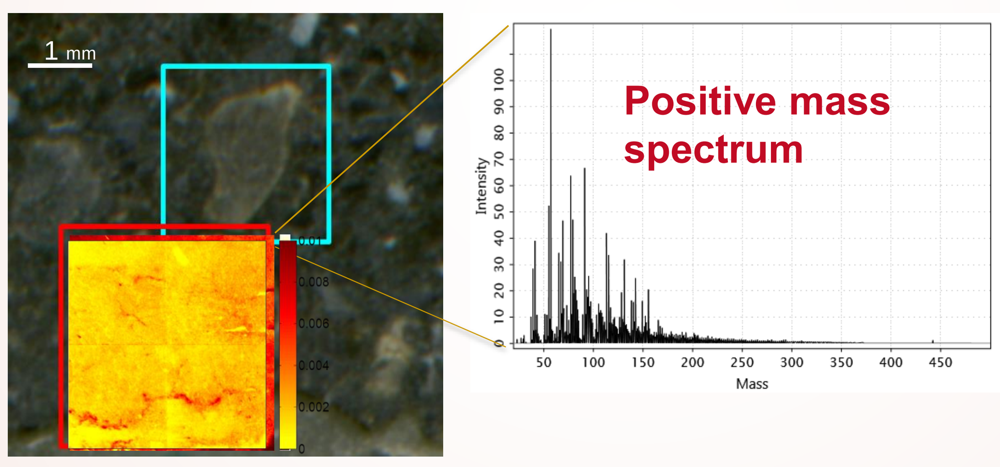

Fig 7: *Image generated by 4.2 million total ion spectra*

❖The J105 was able to detect organic compound with a higher molecular weights (Fig 7b).
❖However, the distribution of the organic material could not be decerned.

Principle Component Analysis (PCA)

❖PCA was used to highlight the difference between the mass spectra within the region of analysis.

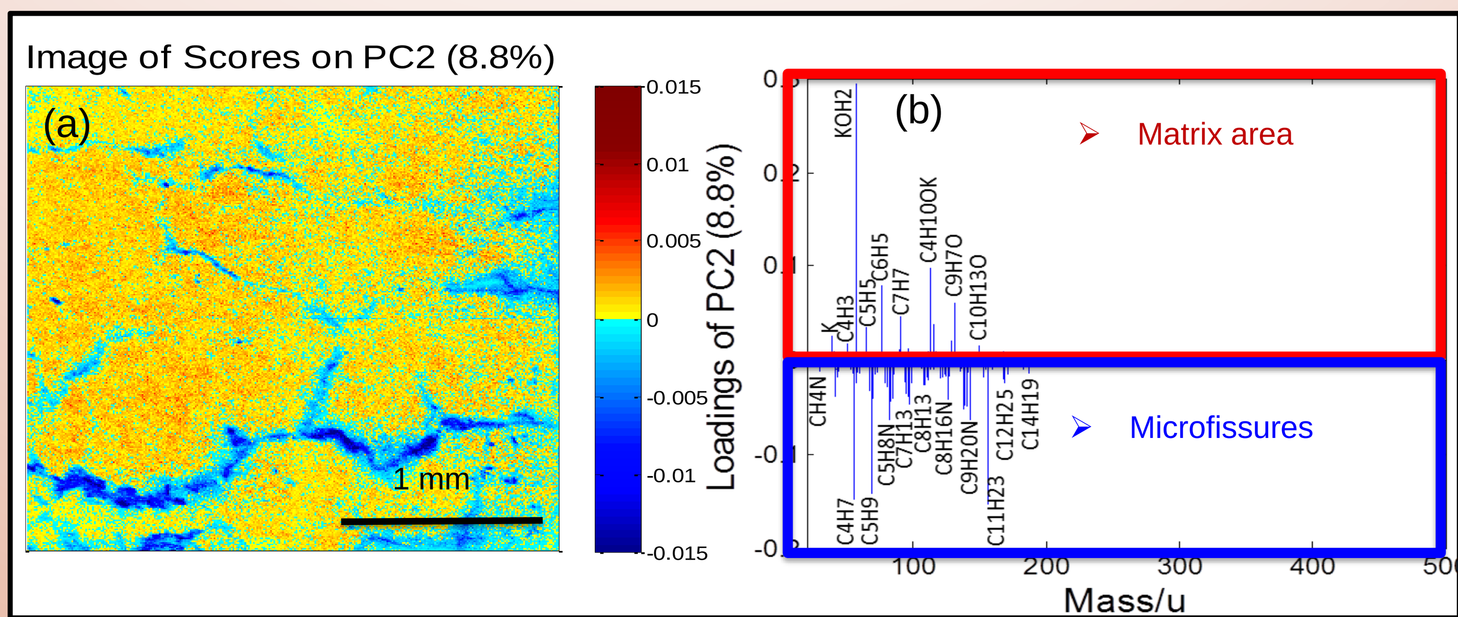

Fig 8 (a) *image of PCA scores* **(b)** *loading of the masses with impirical chemical assignments*

❖Two populations of organic material were detected.
❖These were heterogeneously distributed (Fig 8a).
❖Compounds that loaded positively with respect to the PCA and those that loaded negatively with respect to the principle component (Fig 8b).
❖The positively loaded organic compounds (red box) contained a high proportion of homoatomic aromatic compounds and the negatively loaded organic compounds (blue box) contained a high proportion of organic aromatic compounds with nitrogen substitutions[6].

Source of the Aromatic Compounds with N Substitutions

❖Organic nitrogen concentrated in voids and cracks in the matrix and around weathered perimeter of the glass shard.
❖Aromatic compounds with N substitutions are associated with decomposed chitin (Fig 9c).
❖Chitin is the structural biopolymer of fungus.
❖Microtubules are possibly the result of excavation by fungi in the submarine crust[7].

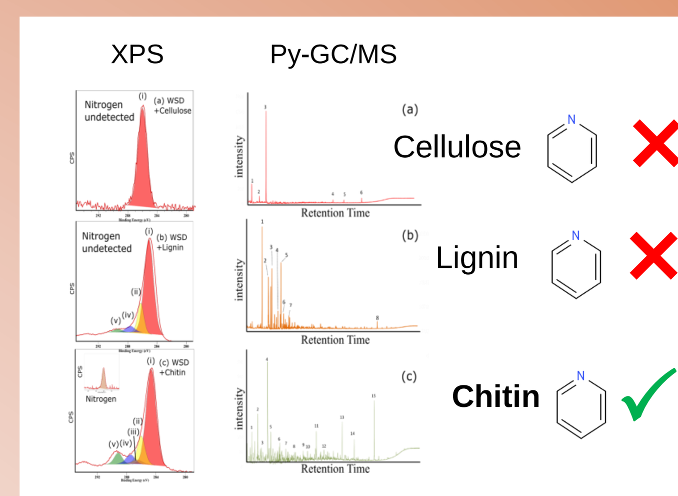

Fig 9: *Comparison of XPS and py-GC/MS spectra of different artificially decomposed plant and fungal structural biopolymers**(a)** cellulose **(b)** lignin **(c)** chitin[8]*

Conclusion

❖J105 can generate images based upon high molecular weight organic compound over 1.5× 1.5 mm area
❖J105 colocalised geomorphology with the composition the organic material.
❖Spectral imaging provides link between chemical and molecular information and the structures within geological samples at millimetre scale with micron scale resolution.
❖Assisting in determining the province of geological structures.

Follow on Work: Spectroscopic Imaging and analysis of More Mars Analogues

❖Confirming the biogenicity of terrestrial fossil structurers would assist in the visual identification of comparable structures on Mars, such as those in Fig 10a, which may be repositories of fossilised life.
❖The database of images and spectra would assist in the sample selection triage process by Mars 2020 in preparation for the sample Earth Return mission (Fig 10).

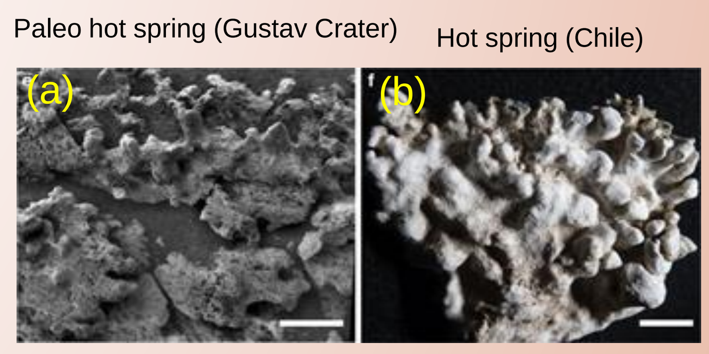

Fig 10 (a) *Eroded structures on the surface of Mars* **(b)** *Putative terrestrial analogue*

Scale bar = 1 cm. ***Credit:*** *Ruff and Farmer (2016)[9]*

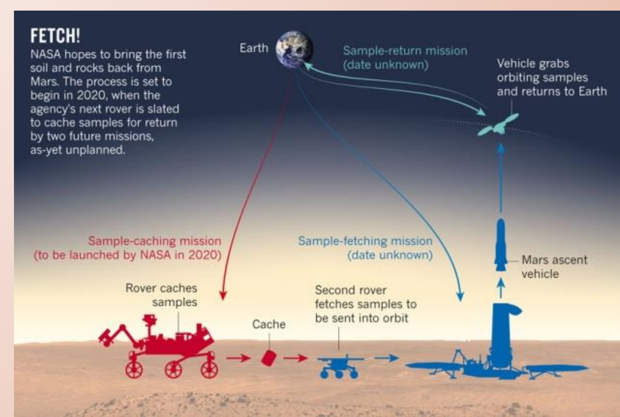

Fig 11 *Diagram of the robotic Mars Sample return mission.* **Credit:** NASA

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[8]Purvis *et al.*, (2020) *in review*
[9]Ruff & Farmer (2016) *Nature Comms.* 7

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