PRESERVATION POTENTIAL OF MOLECULAR BIOSIGNATURES IN THE MARTIAN SUBSURFACE. A. D. Bravenec1, G. D. Bromiley1, W. Montgomery2, C. R. Cousins3, C. R. Ward4, and T. J. Ward4, 1School of GeoSciences, Grant Institute, University of Edinburgh, King’s Buildings, Edinburgh, UK, EH9 3FE (A.D.Bravenec@sms.ed.ac.uk), 2Department of Earth Science and Engineering, Imperial College London, UK, SW7 2AZ, 3School of Earth and Environmental Sciences, University of St Andrews, Irvine Building, North Street, St Andrews, Fife, UK, KY16 9AL, 4Department of Chemistry and Biochemistry, Keck Center for Instrumental and Biochemical Comparative Archaeology, Millsaps College, Jackson, MS, USA, 39210.

Introduction: If molecular biotic evidence does exist on Mars, it is likely preserved within or below the crust where it would be protected from surface radiation and photolytic decomposition [1, 2]. Extended UV exposure is expected to result in the eventual destruction of surface organics and diagnostic biomarkers [3]. Oxidative degradation presents another barrier to biosignature preservation. A highly oxidizing layer is thought to exist at the Martian surface, penetrating the regolith to a depth of 0.5–1 mm, with a mildly oxidizing layer occurring from 1.5–200 m [4]. Diffusion models suggest an unoxidized layer occurs below a depth of 200 m [4, 5]. Thus subsurface biosignatures are potentially less prone to oxidative degradation.

Molecular biosignatures may have an advantage over morphological biosignatures (e.g. microfossils) in the subsurface environment. For instance, while micromorphology can potentially distinguish biotic from abiotic carbonates [6], carbonates experience significant loss of primary microfabric and destruction of fossil evidence due to pervasive recrystallization during diagenesis [7]. Molecular biosignatures may become increasingly important indicators of life under such subsurface conditions.

Experimental studies of the interactions between bio-organics and minerals under conditions simulating the harsh Martian environment provide key insights into possible prebiotic processes and the search for life. Additionally, assessing the evolution of organic molecules in subsurface environments has significant implications for evaluating plausible scenarios for the origins of life. Despite protection from UV and oxidative degradation, buried biosignatures may undergo diagenetic processes that decrease the concentration of organic matter, as well as other degradation mechanisms as a result of elevated temperatures, pressures, and mineral-organic interactions [8, 9]. The aim of this study is to experimentally determine whether biosignatures of life can survive burial, metamorphism, and diagenetic events at various Martian metamorphic facies. A drill is planned in the forthcoming ExoMars mission to access such subsurface environments. Results of this study will inform future in-situ searches for life on Mars as well as the interpretation of organic analyses from past missions.

Experimental Methods: To test the preservation potential of various biosignatures, we subjected organic-rich carbonate samples to temperature and pressure conditions representative of different metamorphic facies (Fig. 1). Experiments were conducted in a piston-cylinder press and in a high temperature furnace, reaching up to 15 kbar and 550 °C. An endolithic and microbe-rich natural calcite (calcium carbonate with minor amounts of magnesium) deposited from a CO2-rich hot spring served as the starting material.

Organic Analysis: Pyrolysis gas chromatography-mass spectrometry (Py-GC-MS) and solvent extracted GC-MS data was obtained for the untreated and treated samples. Pyrolysis accesses both the soluble and insoluble organic matter contained within the whole rock, while liquid extraction allows for separation of fractions based on polarity and derivatizations to increase targeted sensitivity. Comparisons of the material before and following the experiments reveal how the overall organic profile and specific biosignatures respond to temperature, pressure, and experimental duration. Total-ion chromatogram (TIC), extracted-ion chromatogram (XIC), and selected-ion monitoring (SIM) modes were used for analysis, where SIM affords far greater sensitivity and TIC is used for general characterization.
Results and Discussion: Artificial thermal matura-
tion experiments conducted at ambient pressure and
atmosphere conditions demonstrate a strong influence
on organic degradation. Minimal differences appear
between the untreated sample and the sample heated
for 2 hours at 110 °C, while the experiments at 300,
410, and 550 °C reveal severe degradation of the or-
ganic profile. For the sample treated at 410 °C, the
combined alkanes + alkenes + aromatic portion drasti-
cally increased at early retention times, while the com-
ounds in this fraction found at greater retention times
decreased dramatically (Fig. 2). This implies that such
early eluting compounds are degradation products. In
comparison, the degradation patterns of certain bi-
omarkers (e.g., hopanes and steranes) suggest a higher
preservation potential.

High-pressure experiments. A number of expe-
riments conducted at high pressures demonstrate improved
preservation of organics compared to ambient pressure.
The high pressure experiments compare different pres-
sure and temperature regimes at varied time durations
to better constrain degradation kinetics. For the 8 kbar
experiments, the experiment conducted at 300 °C
demonstrates significant retention of the original
organic profile, while the sample held at 550 °C for 5
days shows severe degradation (Fig. 3), in both the
overall organic profile and in respect to specific
biomarkers. Similar to the ambient pressure experi-
ments, certain classes of more complex biosignatures
remain resistant and amenable to detection following
pressure treatment.

Future Work: Our ongoing research will expand
this topic to the following: 1) the influence of different
mineral matrices on biosignature preservation, 2) the
influence of lower pressure regimes, especially in a
dynamic fluid/brine environment as shown in Fig. 4,
3) the influence of oxidation gradients in the shallow
subsurface, and 5) an examination of the intracrystal-
line versus the free portion of organics.