THE FATE OF ANCIENT MACROMOLECULES ON MARS: ARTIFICIAL MATURATION OF IRON AND SULFUR-RICH MARS ANALOGUES. J. S. W. Tan[1], S. H. Royle, and M. A. Sephton[1], [1]Imperial College London, London, SW7 2AZ, UK (jonathan.tan12@imperial.ac.uk).

Introduction: Any past life on Mars would have left behind organic fossils that, if preserved, could be recognized as diagnostic evidence for life at the present day [1]. For effective preservation, these remains must have avoided the harsh radiation flux at the martian surface, survived geological storage for billions of years, and remained detectable within its geochemical environment by analytical instrument suites used on Mars today, such as thermal extraction techniques.

In order to remain distinguishable from abiotic carbon, molecular organic biosignatures must be shielded from the harsh radiation flux at the Martian surface and its deleterious effect on organic matter. One mechanism that promotes such preservation is burial, which raises questions about how organic biomarkers are influenced by the post-burial effects of diagenesis.

Acidic iron- and sulfur-rich streams are appropriate analogues for the late Noachian and early Hesperian periods of martian history, when Mars exhibited extensive habitable environments [2]. Previous work has shown that solvent-extractable organic matter is unlikely to be preserved over geological timescales in these environments [3]. However, insoluble macromolecular material, i.e. kerogens, are more refractory and thus may still be detectable at the present day.

In this study, we investigate the detectability of macromolecular organic material by pyrolysis-gas chromatography-mass spectrometry (py-GC-MS) in acidic iron- and sulfur-rich stream samples that have been artificially matured using hydrous pyrolysis.

Field Work and Methods: Samples were extracted in cylindrical cores from two acidic iron- and sulfur-rich streams from Dorset, UK [3]. The first acid stream was located in St. Oswald's Bay (clay poor sulfur stream), exhibiting sediments containing iron oxyhydroxides (goethite) and minor iron sulfates (jarosite) in an acidic environment with waters of pH 3.5. The second acid stream was present at Stair Hole (clay-rich sulfur stream), and possessed a weaker flow and higher pH than observed in St. Oswald's Bay. The clay-rich sulfur stream contained 36 wt% of illite and kaolinite as revealed by X-ray diffraction analysis.

Laboratory Simulation of Diagenesis: The sulfur stream samples were artificially matured using hydrous pyrolysis, a well-known technique conventionally used to artificially mature organic matter-rich samples in the laboratory, and also used to simulate the effects of diagenesis on biomarkers [4,5]. We had previously used this procedure to investigate the effects of post-burial diagenesis on Mars-analogue samples [3].

Natural mixtures of the stream sediments and their associated microbial populations and remains were prepared and subjected to hydrous pyrolysis at 200, 240, and 280 °C for 72 hours. The samples where then solvent-extracted to ensure that all organic material detected during py-GC-MS was derived from to insoluble macromolecular material.

Alkali/Acid Leaching and py-GC-MS: As a means to remove iron sulfate and iron (oxy)hydroxide minerals that have been shown to interfere with organic matter detection during py-GC-MS analysis [6], a subset of each sample was treated with a strong alkali, followed by a strong acid.

5 – 10 mg of matured, unmatured, leached and unleached samples was pyrolyzed in a CDS Analytical 2000 Pyroprobe in a helium atmosphere and heated with a ramp rate of 20 °C ms^{-1} to 650 °C and held for 15 s. Separation and identification of the pyrolysis products was conducted by a gas chromatography–mass spectrometer (GC-MS).

Consequences of post-burial diagenesis on macromolecular material: It was found that macromolecular organic matter can survive the artificial maturation process. Between the early and late stages of simulated diagenesis, there is only a slight decrease in the organic response and diversity of both clay-rich and clay-poor samples. The lack of degradation associated with diagenesis is consistent with the refractory nature of macromolecular organic matter in terrestrial environments.

Diagenesis can also result in the production of new compounds; thiophenes are observed in the matured clay-rich samples, while they are absent in the unmatured clay-rich samples. These thiophenes are likely produced during abiotic incorporation of sulfur during diagenesis [7].

Influence of mineralogy on organic matter detectability via py-GC-MS: Consistent with previous studies, if jarosite and goethite are present in the sulfur stream environment, they interfere with the py-GC-MS detection of organic compounds in these samples [6].

We find that the presence of clay minerals reduced the obfuscating effect of the oxidizing minerals by providing non-deleterious adsorption sites. Clays are known to have catalytic effects on adsorbed organic matter; unlike iron phases, however, the catalytic effects of clay do not result in the same degree of transformation of organic matter.

However, if the samples are treated with a simple alkali and acid leaching process that removes oxidizing minerals such as iron sulfates, oxides, and oxyhydroxides, the sulfur stream samples exhibit much greater organic responses during py-GC-MS in terms of both abundance and diversity of organic compounds, such as the detection of hopanes in all leached samples (Figure 1).

Conclusions: Our results suggest that macromolecular kerogens can be preserved over billions of years of geological storage while still retaining diagnostic organic information, even in environments that do not support the preservation of solvent-extractable organic matter. The organic material stored within these environments can be detected with thermal extraction strategies, such as py-GC-MS.

However, oxidizing minerals such as jarosite and goethite pose a significant barrier to detection. These minerals severely reduce organic responses due to the release of oxygen during thermal decomposition, as well as the catalytic transformation of adsorbed organic matter during surface reactions. Clays reduce the deleterious effect of jarosite and goethite during flash pyrolysis experiments by providing a competing, non-deleterious adsorption site for organic matter.

Should any oxidizing minerals be removed from the sample via simple preparative steps such as alkali and acid leaching, a significant amount of potentially diagnostic biogenic organic matter can be detected.

References: [1] Summons, R.E., et al., (2011). *Astrobiology 11*, 157–181. [2] Fernández-Remolar, D.C., et al., (2005). *Earth Planet. Sci. Lett. 240*, 149–167. [3] Tan, J., Sephton, M. A., (2019) *Astrobiology 20*. [4] Lewan, M.D., (1985) *Philos. Trans. R. Soc. London. Ser. A, Math. Phys. Sci. 315*, 123–134. [5] Koopmans, M.P., et al., (1995) *Org. Geochem. 23*, 583–596. [6] Lewis et al., (2018). *Astrobiology 18*.

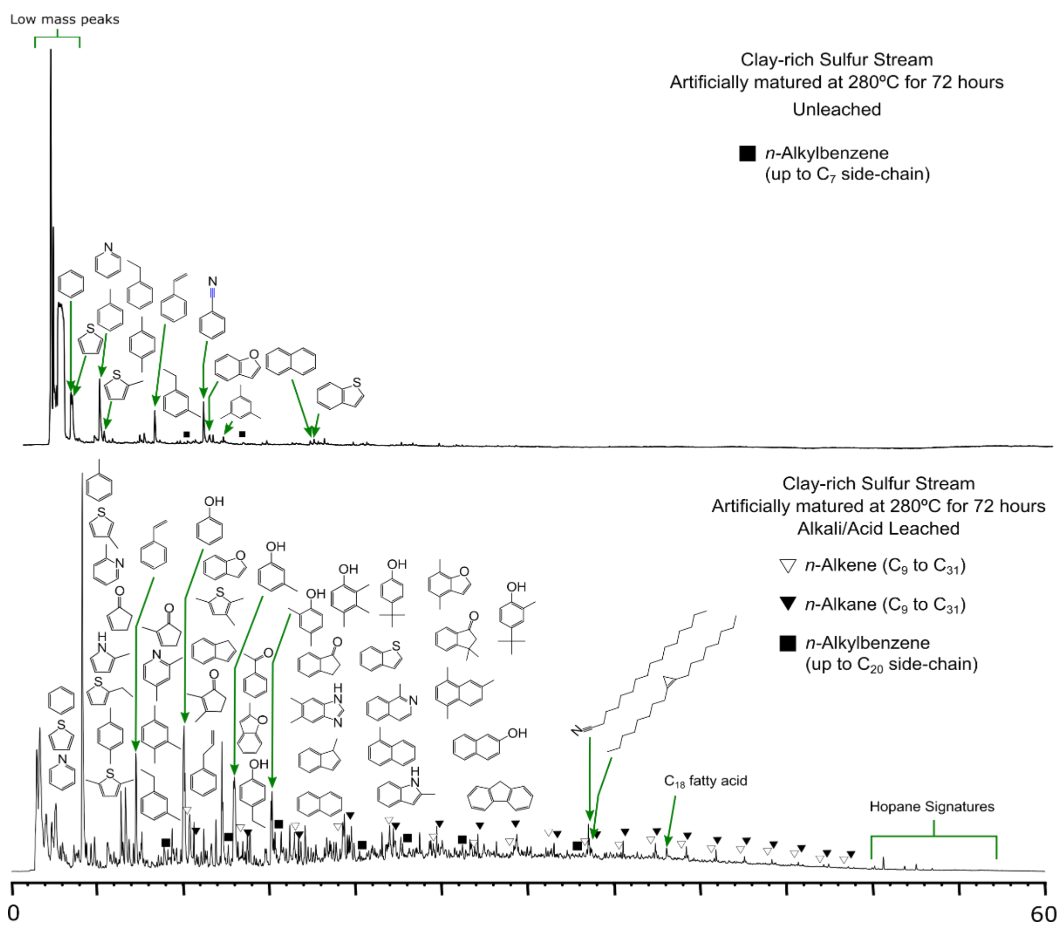

Figure 1: Total ion current (TIC) chromatograms of artificially matured samples from an acidic, iron- and sulfur-rich stream deposit. These particular chromatograms illustrate the differences between the organic responses if the samples are not leached (top), and if the samples are leached with alkali/acid (bottom).