ORGANIC RECORDS OF LIFE ON MARS: THE KINETICS OF LIPID DEGRADATION IN CIRCUMNEUTRAL IRON-RICH DEPOSITS. J. S. W. Tan[1] and M. A. Sephton[1], [1]Imperial College London, London, SW7 2AZ, UK (jonathan.tan12@imperial.ac.uk).

Introduction: The successful search for life on Mars is dependent on the careful consideration of rocks that reflect deposition in environments that are likely to have supported life. Iron-rich, aqueous environments provide habitable niches on Mars due to the availability of dissolved Fe(II) that can drive both aerobic and anaerobic microbial metabolism [1]. Low temperature, circumneutral, iron-rich aqueous environments have recently been the subject of significant interest due to observations made by the Mars Science Laboratory (MSL) rover Curiosity that suggest the presence of a circumneutral, low salinity, possibly redox-stratified iron-rich lacustrine environment that existed between 3.8 – 3.1 Ga at Gale Crater [2,3]. The primary iron mineral found in these Martian deposits is ferrihydrite ($Fe_5HO_8 \cdot 4\ H_2O$).

It is thus necessary to determine the degradation reactions, mechanisms, and organic matter-mineral interactions associated with biomarker preservation in ferrihydrite, especially with respect to the processes and fluxes associated with the post-burial effects of diagenesis. Recent geochemical work has focused on using hydrous pyrolysis to expound on the post-burial effects of diagenesis on the degradation of specific organic compounds, especially with respect to Mars-analogue geochemical environments [4].

Field Work and Methods: Samples were collected from ocherous, highly amorphous, ferrihydrite flocs precipitated by iron-oxidizing bacteria (FeOB) in a circumneutral iron-rich groundwater system. SEM imaging revealed that the flocs were composed of filamentous sheaths that were identified as characteristic biostructures of *Leptothrix ochracea*, a chemolithoautotrophic FeOB.

In addition to natural samples, synthetic ferrihydrite was made to test the effects of artificial maturation on ferrihydrite in the absence of organic matter. The synthesized ferrihydrite was analyzed by powder XRD to ensure that the products were amorphous and analogous to the mineral content of the natural ferrihydrite.

Natural mixtures of the stream sediments and their associated microbial populations and remains prepared at high (suffix H) and low (suffix L) water-to-rock ratios. The samples were subjected to hydrous pyrolysis at 200, 240, and 280 °C for 72 hours. Lipids in each sample were extracted ultrasonically, derivatized, and analysed on a gas chromatography-mass spectrometer (GC-MS).

The kinetic parameters of these organic degradation reactions, including any additional effects promoted by the interactions between the organic matter and the mineral matrix, were derived from the results of hydrous pyrolysis using the integrated form of the first-order reaction rate and Arrhenius equations [5].

Lipid Analysis: The solvent extracts of the unmatured ferrihydrite were found to be composed primarily of fatty acids, including saturated, unsaturated and terminally branched species (Figure 1), consistent with their high abundance in bacterial cell membrane phospholipids [7]. Saturated fatty acids were observed to be the most resistant, surviving pyrolysis at 280 °C while retaining a biogenic even-over-odd predominance (EOP) pattern in carbon-chain lengths, consistent with previous hydrous pyrolysis studies [4].

Samples artificially matured at high water-to-rock ratio samples (NFH) were found to have greater lipid abundances than the corresponding low water-to-rock ratio samples (NFL), but at the latest stages of diagenesis, a majority of lipids were lost regardless of the degree of water activity.

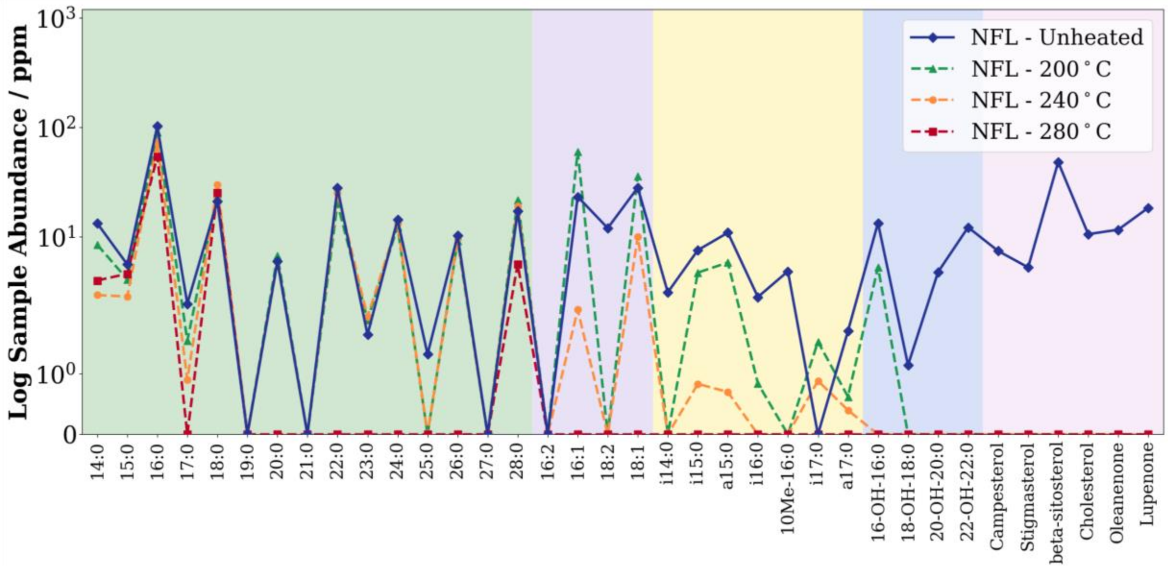
Organic Matter-Mineral interactions: The organic matter-mineral interactions in these iron-rich environments are found to be strongly controlled by the changes in the mineralogy of the iron substrate. As temperature increases, lipids are desorbed from the surface of the ferrihydrite substrate, with peak desorption occurring when ferrihydrite transforms into magnetite, and the surface area of the crystalline iron oxide cannot retain all sorbed material.

At the same time, presence of organic matter was found to influence the transformation products of ferrihydrite; synthetic, organic-poor ferrihydrite transformed into hematite, while natural, organic-rich ferrihydrite inhibited this process and instead transformed into magnetite at higher temperatures.

Kinetic Parameter Modelling: The kinetic behavior of the lipid degradation reaction can be approximated by a pseudo first-order reaction, and was modelled as such. The model data suggest that all lipids expected to be completely oxidized on thousand year timescales, regardless of water availability or iron oxide mineralogy.

Discussion: Our experiments indicate that should any organic matter preserved in circumneutral ferrihydrite-rich environments would take the form of saturated fatty acids that still retain biogenic EOP patterns.

Figure 1: Representative lipid profiles in both matured and unmatured natural circumneutral iron-rich stream samples at different temperatures. This graph shows that biogenic EOP patterns are preserved even in the later stages of diagenesis, most of the lipids are destroyed following simulated diagenesis in these iron-rich environments.



However, the kinetics of organic degradation in these environments suggest that that iron-dominated environments are poor targets for solvent extraction-based life detection techniques on Mars. Comparisons to our previous work show that circumneutral iron-rich deposits are less favorable for the preservation of solvent-extractable organic matter compared to other iron-rich deposits, such as acid streams (Table 1).

Our experiments also indicate that magnetite and maghemite derived from the reduction of ferrihydrite could be potential mineralogical biomarkers. These minerals may be formed at elevated temperatures in the presence of water and a reductant such as organic matter. While these minerals would contain little diagnostic information about the organic matter, there may be other biogenic signatures associated with the deposit, such as structural biomarkers formed by iron encrustations or insoluble macromolecular organic compounds such as kerogen. However, it must be emphasized that magnetite found in association with ferrihydrite can be formed via a variety of geochemical pathways that do not require an organic matter reductant.

Conclusions: We find that some samples that reflect habitable conditions on Mars can inhibit the preservation of Martian organic matter when exposed to geological storage over billions of years. Sample selection strategies must therefore consider the pre-, syn- and post-burial histories of habitable conditions on Mars and the balance between the production of biomass and the long-term preservation of organic biomarkers over geological time.

Table 1: Preservation potential of various Mars-analogue environments as derived from the kinetics of artificial maturation.

Mars-Analogue Environment	Key Minerals	Preservation Potential (ka)
Iron-rich acid deposit	Jarosite, Goethite, Quartz	21.9 – 114.0
Iron-rich acid deposit with clay component	Jarosite, Goethite, Kaolinite, Quartz	0.2 – 1.4
Iron-rich circumneutral deposit	Ferrihydrite	0.7 – 0.8

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