ORIGIN-DIAGNOSTIC PATTERNS IN LIPID DISTRIBUTIONS: STRATEGIES FOR LIFE DETECTION. D.K. Buckner[1,2,3], M.J. Anderson[3,4], S. Wisnosky[4,5], W. Alvarado[3,6], A.J. Williams[1], M.B. Wilhelm[3]; [1]University of Florida (bucknerd@ufl.edu), [2]Blue Marble Space Institute for Science, [3]NASA Ames Research Center, [4]Millennium Engineering and Integration, Co., [5]University of Miami, [6]University of Chicago

Introduction: Lipids are key molecular targets in the search for life. Lipids (e.g. fatty acids and ether-linked acyclic hydrocarbons) form the membranes ubiquitous to Terran life and likely putative extraterrestrial organisms: cellular life requires encapsulation [1]. Simple lipids are also synthesized abiotically and comprise >60% of soluble organics in meteorites [2]. Distributions of structural features (e.g., chain length, unsaturations, branching) in fatty acid and acyclic hydrocarbon samples can provide origin-diagnostic information (i.e. biotic vs. abiotic) [3,4]. Lipids are geologically robust (~Gyr lifetimes). The longevity of some hydrocarbons [5] is the same as the age of sediments laid down during Mars' most habitable surface epochs [6,7], making these lipids some of the most logical, accessible [5,8] potential indicators of past life.

To infer biogenicity or its absence in extraterrestrial lipid samples, we reviewed and statistically analyzed studies on terrestrial and meteoritic fatty acids and acyclic hydrocarbons. Results reveal trends in lipid detection methods and multiple origin-diagnostic patterns in distributions of molecular features in samples that signal biotic vs. abiotic synthesis [3,4]. Findings highlight the utility of lipids as astrobiological targets and provide guidance on *in situ* detection methods.

Methods: Data on sample processing + analytical techniques and structural elements (i.e., **Table 1**) was collated from studies of fatty acids and acyclic hydrocarbons in meteorites and terrestrial samples of varying age, from globe-spanning locales (Mars analog focus). Fatty acid studies include 893 terrestrial samples (114 papers), 58 meteorite samples (22 papers). Acyclic hydrocarbon studies include 592 terrestrial samples (100 papers), 31 meteorite samples (13 papers). Datasets were populated with study data and statistical analyses performed to elucidate trends.

	Feature	Distribution within sample
Fatty acids, acyclic hydrocarbons	Chain length	Min & max chain length
		Dominant (i.e., most abundant) molecule
	Unsaturations	Presence of unsaturations y/n
		Max # unsaturations in a single chain
		Dominant unsaturated molecule
	Branching	Presence of branching y/n
		Min & max chain length with a branch
		Max # branches in a single molecule
		Max branch length
		Dominant branched molecule

Table 1. *Data parameters collected from reviewed studies: structural elements (i.e., "Feature") & distribution in each sample of terrestrial & meteorite lipids.*

Results: Trends were identified in sample processing and analytical techniques and origin-diagnostic patterns in distributions of molecular features.

Trends in Lipid Extraction & Analytical Techniques. Solvent-based techniques are most commonly used to extract lipids from geologic samples, varying by solvent choice, apparatus, temperature, pressure, ultrasonic energy, leveraged in ~83.1% (1308/1574) of samples. Gas chromatography-mass spectrometry (GC-MS) is most frequently used to identify molecules, in ~88.8% (1397/1574) of samples.

Fatty Acid Distributions. In terrestrial samples, fatty acids are 4 - 34 carbons long, with a min length of 14 reported in ~43.8% (391/893) of samples and max length of 18 in ~21.1% (188/893); the dominant fatty acid is most frequently $C_{16:0}$. In meteorites, fatty acids are 1 - 12 carbons long, with a min length of 2 in ~51.7% (30/58) of samples and max length of 10 in 50.0% (29/58); $C_{2:0}$ is most frequently dominant.

Terrestrial studies report unsaturated fatty acids with 1 - 6 double bonds in ~77.5% (692/893) of samples, and the dominant unsaturated fatty acid is most frequently $C_{18:1}$. Meteorite studies rarely report unsaturated fatty acids, in 2/58 samples, with $C_{4:1}$ in both.

Branched fatty acids are reported in ~62.9% (562/893) of terrestrial samples; they contain 6 - 32 carbons in the main chain (**Fig 1a**), 1 - 5 branches per molecule, and individual branches are all one carbon long. Branch positions most often occur from the middle of the main chain to the terminal end opposite the carboxyl (**Fig 1b**); iso and anteiso configurations are favored. Anteiso-$C_{15:0}$ is most frequently the dominant molecule. Branched fatty acids are reported in ~79.3%

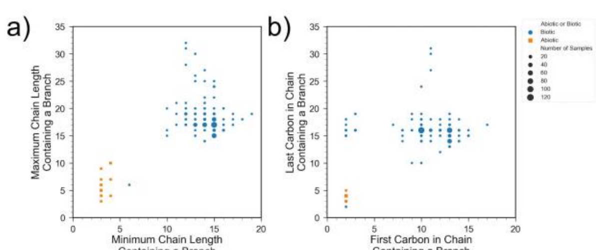

Fig 1. *(a) Min & max main chain lengths of fatty acids with branches for 551 terrestrial (blue/circle) & 46 meteoritic (orange/square) samples. (b) First & last branch position in the main chain for 529 terrestrial (blue/circle) & 40 meteorite (orange/square) samples.*

(46/58) of meteorite samples; they contain 3 - 10 carbons in the main chain (**Fig 1a**), 1 or 2 branches extend off the main chain, and individual branches are 1 - 3 carbons long. Branching begins at the first position (i.e., 2Me) relative the carboxyl in all samples, but can extend to later positions (**Fig 1b**). The dominant molecule is most frequently 2Me-$C_{3:0}$ (i.e., iso-$C_{3:0}$).

Distributions of Acyclic Hydrocarbons. In terrestrial samples, acyclic hydrocarbons are 4 - 46 carbons long (**Fig 2**), with a min length of 15 in ~16.9% (100/592) of samples and a max of 33 in ~14.9% (88/592); the dominant fatty acid is most frequently $C_{27:0}$ or $C_{17:0}$. In meteorites, acyclic hydrocarbons are 1 - 31 carbons long (**Fig 2**), with a min length of 1 in ~22.6% (7/31) of samples and a max of 26 in ~16.1% (5/31); most frequently C_1 or $C_{10:0}$ is dominant.

Terrestrial studies report alkenes with 1 - 7 double bonds in ~16.0% (95/592) of samples. The dominant alkene is most frequently an isoprenoid. Meteorite studies report alkenes in (9/31) of samples; the dominant alkene is reported in 2 samples and is $C_{2:1}$ in both.

Branched acyclic hydrocarbons in terrestrial samples contain 4 - 41 carbons in the main chain, 1 - 8 branches per molecule, and individual branches are 1 - 6 carbons long. Isoprenoid configurations are favored as the dominant in ~76.5% (310/405) of samples where structures are resolved. Consequently, branching begins at the 2Me position for the majority of samples, extending down the chain with even spacing between branches. Meteorite samples frequently contain many branched acyclic hydrocarbons (16/31 samples), but structures are rarely resolved (5/16 samples), appearing as an unresolved complex mixture (UCM) of many highly branched moieties. Indigenous isoprenoids are not reported in the meteorite studies in our analysis.

Discussion: From this analysis, we identify numerous origin-diagnostic patterns in distributions of fatty acid and acyclic hydrocarbon structural elements indicating biogenicity or abiogenicity. Biotically-

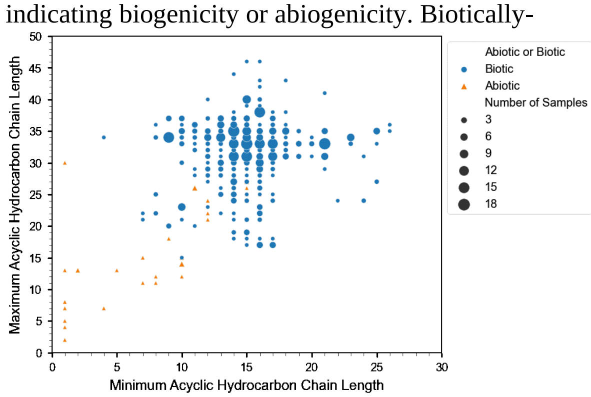

Fig 2. *Min and max acyclic hydrocarbon chain lengths reported in 592 terrestrial (blue/circle) and 30 meteorite (orange/triangle) samples.*

synthesized fatty acids are characterized by longer chain lengths, frequent mono- and polyunsaturations, monomethyl branching at specific positions from the mid-chain to terminal end in the main chain, and preference for iso and anteiso configurations. Abiotically-synthesized fatty acids are shorter, rarely unsaturated, with abundant random branching that occupies any position in the main chain. Biotically-synthesized acyclic hydrocarbons are long-chained, often unsaturated, and display distinct patterns in branching, with frequent and abundant isoprenoids that are decidedly non-random in structure. Abiotically-synthesized acyclic hydrocarbon distributions are less constrained due to limited samples, but tend towards shorter chains, rare unsaturations, no discernable patterns in branching or preferences for specific isomers, UCM, and lack isoprenoids. For both lipid classes, biotic samples display multiple non-random distributions of independent structural features, along with preferences for specific chain lengths and configurations out of many possible.

Conclusion: Understanding the range of origin-diagnostic features and patterns that infer biogenicity or abiogenicity in terrestrial and meteoritic lipids is a critical step in the search for life [4,5]. Although lipid biomarker structures are well-known and widely studied within terrestrial [1,5] and meteoritic [2] organic geochemistry, our approach provides a framework to support organics detection and interpretation. Each examined structural element could independently indicate synthesis, providing multiple chances to infer biogenicity from a single Martian lipid sample. Our findings highlight the utility of lipids as important molecular targets for astrobiology applications. While extraterrestrial life may utilize suites of biochemicals partially different from Terran life, understanding the ranges of features and molecular windows that contain origin-diagnostic information in terrestrial lipids can provide guidance on approaches for organics-based life detection on other planets. Our results also show various parameters (e.g., solubility, polarity, molecular weight) informing instrument requirements for characterizing lipids *in situ* [8] on Mars and Icy Moons.

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