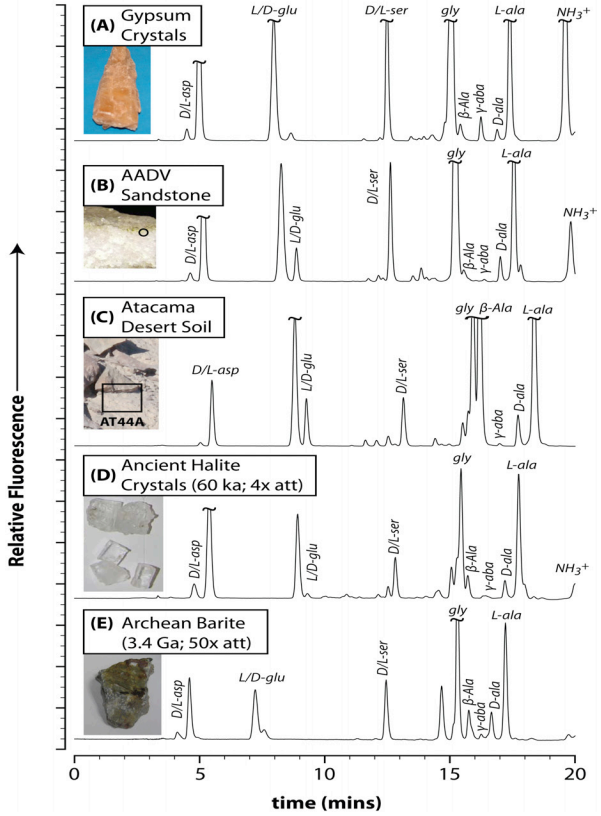
PRESERVATION OF NITROGENOUS ORGANIC COMPOUNDS IN TERRESTRIAL MARS ANALOG MINERALOGICAL ENVIRONMENTS – CASE STUDIES FOR ASTROBIOLOGY LANDING SITES ON MARS. A. D. Aubrey, NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109 (Andrew.D.Aubrey@jpl.nasa.gov).

Introduction: The search for biomolecules from an extinct or extant biota is a central focus of near future extraterrestrial exploration. Unlike morphological biomarkers, the detection of highly specific molecular compounds can offer unequivocal evidence of biological activity and is of primary importance to future life detection missions. Equally important to the detection of biomolecules is the ability to discriminate from any abiological synthetic products. The detection of amino acid distribution and chirality can discriminate between abiotic and biological sources through chirality measurements and provides a robust biochemical signature for evidence of life [1]. However, the stability of amino acids over geological timescales to destructive diagenetic pathways is a major concern. Here we evaluate concentrations and distributions of amino acids in geochemical Mars analog environments to help determine the most robust terrestrial environments for preservation of nitrogenous compounds. These distributions are evaluated with respect to identification of robust environments on the surface of Mars for the biosignature detection. The lifetimes of nitrogenous biomarkers likely extends to preservation potential for other organic compound classes. This study provides input to constrain landing site selection activities for future Mars astrobiological missions with respect to target chemical biomarker class and relative fitness of mineralogical environments for organic preservation.

Background: The strategy for the detection of extraterrestrial life shares similarity with the search for the earliest evidence of terrestrial life – major challenges include finding a rock record from early in a planet's history and detecting biosignatures that have not been destroyed over time by metamorphic or diagenetic processes. The most widely used strategies for detection of life in the Archean are the detection of morphological biosignatures [2] and carbon isotopic fractionation [3]. These methods lack the specificity for unequivocal life detection as morphological biosignatures are subject to structural interpretation without biochemical evidence and the latter lacks definition for Mars exploration due primarily to the lack of a widespread unfractionated carbon pool [4].

Amino acids are detected in high abundance in virtually every terrestrial environment, including Mars analog environments, due to their biological ubiquity (**Fig. 1A-D**). Amino acids have been defined as one high priority biomarker class for life detection in a recent ESA study [5] due to their ubiquity in terrestrial life and use of chirality as a powerful biogenic source indicator. Despite their high abundances in terrestrial environments, it is speculated that these and other molecular classes of nitrogenous compounds would not survive the timescales on Mars from an earlier aqueous epoch, *i.e.* survival over billions of years.

Fig. 1. HPLC-FD chromatograms of acid-hydrolyzed amino acid extracts after derivatization with *o*-phthaldialdehyde-N-acetyl-L-cysteine. (A) Modern bottom-growth gypsum crystal, Aerodrome Lake, Southwestern Australia; (B) Subsurface sandstone sample from Taylor Valley, Antarctica; (C) Gypsum-rich Atacama Desert surface soil, Yungay, Chile; (D) Halite Crystals from Saline Valley, CA (~60 ka); (E) Archean Barite sample (3.435 Ga). Amino acid distributions and chirality consistent with the presence of microbial life. Serine in the Archean barite sample and low D/L-ratios suggest that amino acids are more recent contaminants.



Amino acids have been detected in chert from the late Precambrian and claimed to be endogenous to these rocks [6]. These data do not reveal racemic amino acid abundances, which would be expected of endogenous amino acids that are hundreds of millions of years old due to the influence of racemization over geological timescales. The authors account for the presence of endogenous amino acids in chert samples despite low D/L-ratios due to very slow racemization kinetics in these geological samples. In another study,

the influence of contamination in ancient Isua supracrustal rocks (3.8 Ga) has been observed [7]. Recent analyses of an Australian Archean barite sample appears to confirm this observation (**Fig. 1E**), however the presence of several non-protein amino acids suggests long timescale diagenetic effects on ancient amino acids. Therefore, evaluation of the terrestrial Archean rock record for amino acid biosignatures carries with it the intrinsic difficulties associated with contamination.

Amino acids, most notably glycine and alanine, have been recovered from oil shale kerogens dated at ~4 Ma [8] and ~150 Ma [9] in previous studies. These data suggest that kerogen formed by diagenesis over millions of years can actually preserve primary amines in the rock record presumably as encapsulated proteins and cell wall material. Bulk nitrogen compounds have been observed to persist in ancient samples despite diagenesis over long timescales. Analyses of Archean aged samples for nitrogen has revealed elevated levels of ammonium in Isua supracrustal rocks [10]. Studies of kerogens in 3.5 Ga hydrothermal dykes likewise show significant concentrations of nitrogenous compounds [11].

There are multiple methods for organic preservation which can slow rates of organic diagenesis. One of these is mineral encapsulation/sequestration. This process is operational in evaporitic environments where encapsulation of organics during formation can allow for enhanced lifetimes of bioorganic materials. Another mechanism for bioorganic survival is by encapsulation within bacterial extrapolymeric secretions (EPSs) – amongst which stromatolites are classified. EPSs have been suggested as important targets for the detection of extraterrestrial microbial life [12] and these secretions have been determined to contain up to 35% protein by weight [13]. Rapid burial can also extend the lifetime of organics by sequestering organic material from terrestrial surface oxidation processes.

Organic Preservation on Mars: Contemporary Martian climate is extremely hospitable to organic preservation due to the prevailing cold and dry environmental condition, perhaps creating conditions where amino acids (and their chirality) could be preserved for billions of years [14]. These clement factors compete against destruction pathways, which are greatest at the surface of Mars, such as the influence of ionizing radiation [15], ultraviolet-radiation [16], and the presence of oxidants as components of the Mars regolith [17]. These studies support the premise that sampling at depth would be necessary for the detection of biosignatures due to harsh surface conditions. Thus, investigation of intact mineralogical facies that appear resistant to environmental weathering over time or have been buried for long timescales are the most attractive targets for the detection of biosignatures.

Conclusion: The most astrobiologically relevant landing sites for biosignature detection include those with mineral assemblages abundances that show capacity for preservation through organic encapsulation or long term burial. Regions with strong evaporitic mineral signatures, such as sulfates (gypsum/kieserite) or halite, are primary targets for biosignature detection because of their aqueous diagenetic formation pathways, high capacity for organic encapsulation during formation [18], and moderate resistance to weathering processes. Phyllosilicate regions on Mars are arguably the oldest exposed terrains on the Martian surface [19] and are thought to have been formed *via* aqueous activity over unaltered basalt under alkaline conditions when Mars may have been warm and wet. The preservation potential within phyllosilicate materials on Mars may have been increased due to deposition of sulfates (*i.e.* burial) over the Noachian terrain for much of their geological history.

This study supports the *"Follow the Nitrogen"* strategy [20] in the search for biomarkers on Mars and other planetary bodies. The biological importance of nitrogen has previously been suggested as a method of constraining the search for life on Mars [21], however specific nitrogenous organic compounds such as amino acids have the potential to detect unequivocal signs of life during future astrobiology missions. Highly sensitive technologies have been developed as flight instruments for the purposes of the detection of amino acids and other primary amines during future *in situ* investigations. We evaluate herein the suitability of amino acids as biomarkers for future life detection missions that may be present as remnants of extinct or extant life and their preservation potential on the surface of Mars.

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