Detection of Trace Biomarkers in the Atacama Desert with a Novel *in situ* Organic Compound Analysis System

Alison M. Skelley[1], Andrew D. Aubrey[2], Peter Willis[3], Xenia Amashukeli[3], Adrian Ponce[3], Pascale Ehrenfreund[4], Frank J. Grunthaner[3], Jeffrey L. Bada[2] and Richard A. Mathies[1]

[1]Department of Chemistry, University of California, Berkeley, CA, 94720, USA; [2]Scripps Institution of Oceanography, University of California at San Diego, La Jolla, CA, 92093, USA; [3]Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena, CA, 91109, USA; [4]Astrobiology Laboratory, Leiden University, 2300 RA Leiden, The Netherlands

We have developed a suite of instruments consisting of subcritical water extraction (SCWE) and a sublimation system called the Mars Organic Detector or MOD for extraction of biomarker compounds from soil, together with a portable microchip capillary electrophoresis (CE) system for high sensitivity analysis of the fluorescently-labeled biomarker compounds. The CE instrument provides high resolution analysis of amino acid composition and chirality with ppb to part-per-trillion sensitivity (1). The CE instrument can also be used to analyze amines, di-amines, amino sugars and several of the nucleobases, nucleosides and nucleotides (2). Successful *in situ* Mars exploration requires the development of instrument suites advanced enough to operate in relevant field environments and the demonstration that they have the analytical capability and sensitivity to detect very low levels of biomarker compounds. We describe here the successful field trials of our approach in the Atacama Desert in Chile, an extremely dry, oxidized environment that is an excellent Mars analog site.

In June 2005 we selected Hill 3547 (S 24º 3.6423'; W 69º 5.2082'; elevation 3547') adjacent to the "Rock Garden" near the Yungay Field Station for study because it was relatively undisturbed by anthropomorphic activity (Figure 1). We performed detailed sampling at various sites with different topographies, slopes, and exposures (3). A subset of these samples was extracted in the field using the SCWE and the effluent from the extraction was directly labeled with fluorescamine and then analyzed on the portable CE microchip system. Samples taken from the exposed surface typically produced low levels (4-8 ppb) of amines and amino acids that were at the level of the blank solvent available to us in Chile. Samples taken from a shielded surface site or from areas of past water flows had 10-fold higher concentrations of amines and amino acids including especially valine, ala/ser and glycine (Figure 2). Chiral analysis of two of these samples gave D/L ratios of 0.4 for ala/ser. These data indicate that the identified amino acids are of biological origin. The partial racemization of these amino acids suggests that they may be ancient amino acids with ages in the range of 10^3 to 10^5 years, although we cannot rule out the possibility that they arise as components of cell walls from extant bacteria that are known to contain D/L ratios in a similar range. Post-field work analysis of the Atacama soil subset showed the average organic carbon and nitrogen to be 0.015% and 0.009%, respectively. One particularly interesting location, 'site 60', showed anomalously light stable carbon isotopes ($\delta^{13}C$ = -54 per mil) indicating microbial reworking of organic matter.

This work demonstrates the successful and robust operation of our instrument suite in the Atacama Desert. The instruments were subjected to over 30 °C temperature variations (~ 0ºC to 30 ºC) during a typical day of operation and the CE microchip system was used to perform 340 separate electrophoretic analyses on only 3 microchips over the course of one week. Our instrumental approach successfully detected trace levels of amino acids and organic amine biomarkers in one of the driest, most Mars-like environments on Earth. In addition, based on our chirality analysis we conclude that these organic deposits originated from terrestrial organisms and may have been deposited thousands of years ago. We will also report the results of further laboratory analyses of these samples designed to validate the field measurements of amino acid concentrations, their chiralities, to analyze for culturable bacteria, and to determine phospholipid fatty acid composition. The successful operation of our instrument suite in the Atacama Desert demonstrates both its technology readiness for *in situ* Mars exploration and its ability to detect the low ppt levels of biomarker compounds that may exist on Mars.

1. Skelley, A. M., Scherer, J. R., Aubrey, A. D., Grover, W. H., Ivester, R. H. C., Ehrenfreund, P., Grunthaner, F. J., Bada, J. L. & Mathies, R. A. (2005) *Proc. Natl. Acad. Sci. U.S.A.* **102,** 1041-1046.
2. Skelley, A. M., Cleaves, J. H., Bada, J. L. & Mathies, R. A. (2005)**,** Manuscript in preparation.
3. See http://astrobiology.berkeley.edu for additional details and pictures

Figure 1. Hill 3547 in the Atacama Desert, Chile that was selected for organic compound analysis.

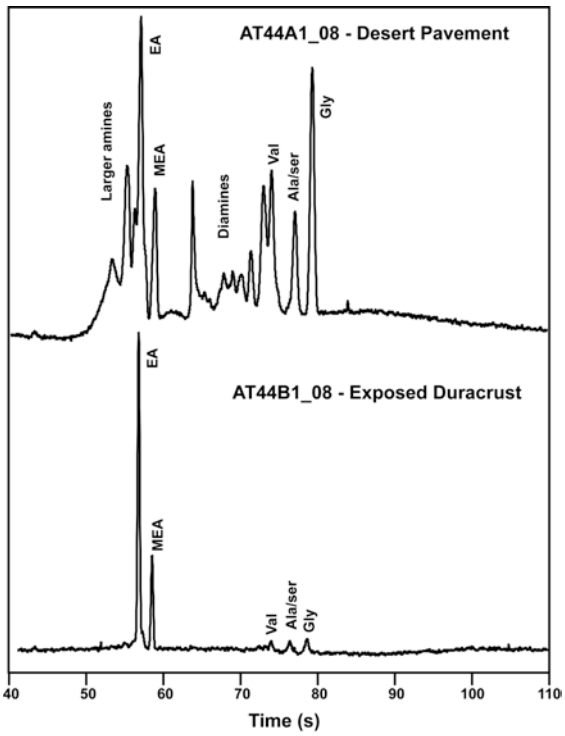

Figure 2. Comparison of organic analyses from the duracrust at Site 44. The exposed duracrust only contains amines and amino acids at the few ppb level of the solvent blank while the shielded desert pavement contains amino acids, diamines and amines at the 50 to 150 ppb levels.