

IMPLICATIONS OF THE PRESENCE OF SURFACE PERCHLORATE FOR *IN SITU* DETECTION OF ORGANIC COMPOUNDS DURING FUTURE MISSIONS. A. D. Aubrey¹, Eric T. Parker², F. J. Grunthaler¹ and J. L. Bada², ¹NASA Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (Andrew.D.Aubrey@jpl.nasa.gov; Frank.J.Grunthaler@jpl.nasa.gov), ²Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA (erictparker@gmail.com; jbada@ucsd.edu).

Introduction: One crucial discovery by the 2009 NASA Phoenix Lander was the detection of perchlorate at ~1% in the surface Martian regolith [1]. High concentrations of perchlorate may oxidize organics on Mars and be problematic during extraction of organics during future *in situ* investigations. High temperature pyrolytic extraction methods will likely result in catalytic degradation of organics [2] especially in the presence of oxidants or transition metals. If simulant studies reveal Martian soil chemistry to be incompatible with the survival of organics during pyrolytic extraction, then *in situ* instruments should utilize techniques that will not catalyze degradation during thermal volatilization (TV).

Atacama Desert soils are known to contain large abundances of perchlorate [3], most likely derived from atmospheric photochemical deposition [4]. Previous GCMS analysis of samples from the hyperarid core of the Atacama Desert reported no organics above ppb-levels and claimed that this hyperarid region represented the dry limit for microbial life [5]. Amino acids at ppb-levels are detectable in the majority of samples from this region using subcritical water extraction (SCWE). It is unknown whether amino acid abundances are impacted by the presence of surface soil oxidants such as perchlorate in the Atacama.

Discussion: Subcritical water extraction (SCWE) of amino acids has been successfully demonstrated on a variety of Atacama Desert soils (Fig 1) with high efficiencies compared to traditional quantification *via* acid hydrolysis. The characteristics of SCWE as a non-destructive and efficient extraction method is the reason it is the primary extraction step for the *Urey* organic detector [6] while it also may be integrated as a subsystem for other *in situ* instruments.

Amino acid distributions and enantiomeric ratios can be used to determine whether their source is extant microbial life or diagenetic products of extinct life. Atacama Desert subsurface samples (>5 cm depth) show much better preservation of microbial biosignatures, and this has been interpreted as enhanced organic preservation *via* shielding from harsh surface conditions (e.g. destruction by UV-radiation, fenton oxidation, free radicals). It is unknown whether degradation of organics by surface oxidants, such as perchlorate, act as leveling reactions in the Atacama Desert. In order to examine whether amino acid abundances and distributions are affected by perchlorate concentrations, [ClO₄⁻] is currently being measured by ion chromatography (IC) within these Atacama Desert

samples. Perchlorate concentrations are expected to be in low-ppm range due to levels observed in previous studies [3] and the extremely arid climate which enhances perchlorate deposition.

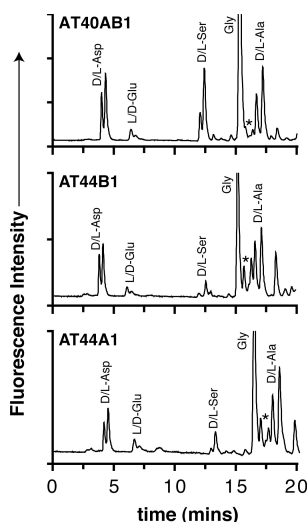


Fig 1. 0-20 minute HPLC chromatograms of subcritical water extracted Atacama Desert surface soil samples. Amino acids and their enantiomers are labeled while the asterisk represents the identification of two amino acid decarboxylation products, β -ala and γ -aba. These peaks are evidence of diagenetic processes in surface samples.

Conclusion: Results indicate that SCWE liberates amino acids from Atacama Desert soils quickly and efficiently despite the presence of perchlorate. Aqueous heating experiments at 100°C show minor differences in the rates of amino acid degradation over timescales of weeks, and therefore perchlorate should minimally effect SCWE at the short exposure times characteristic of these optimized extraction conditions [7]. Pyrolytic methods such as thermal volatilization (GCMS) may activate oxidants present in the Mars regolith and catalyze organic degradation [2] resulting in a false negative for organic compound detection. It may be necessary to adopt non-destructive techniques for organic extraction such as subcritical water extraction [7]. Although Mars analog locations such as the Atacama Desert show high abundances of perchlorate, it must be considered that Mars surface [ClO₄⁻] are approximately two orders of magnitude greater than terrestrial locations and these catalytic effects during TV would be more pronounced.

References: [1] Hecht M. et al. (2009) *Science*, in press. [2] Navarro-González R. et al. (2009) *Geophys. Res. Abs.*, 11, 1549. [3] Ericksen G. E. (1981) *USGS Prof. Pap.*, 1188, p37. [4] Bao H. and Gu B. (2004) *Environ. Sci. Technol.*, 38, 5073-5077. [5] Navarro-González R. et al. (2003) *Science*, 302, 1018-1021. [6] Aubrey A. D. et al. (2008) *Astrobiology*, 8, 583-595. [7] Amashukeli X. et al. (2007) *JGR*, 112, G04S16.