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Sample handling and chemical extraction of chiral amino acids and other biomarkers from solid samples for the Mars Organic Analyzer (MOA)

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For future astrobiology experiments on Mars, one of the most challenging problems is the detection of biomarkers in soils and pulverized rock samples in which the compounds of interest are trapped within the solid matrix and are present at vanishingly low levels. The collection and the robotic preparation of these samples for chemical analysis without serious loss, degradation, decomposition or contamination of the target organic compounds represents a formidable task even under carefully controlled terrestrial laboratory conditions. We have addressed the issue of chemical extraction of amino acids, amines and polycyclic aromatic hydrocarbons (PAH's) using sublimation and liquid extraction methods. In this work, we present systematic studies of the use of sub-critical water extraction to isolate these target molecules using a variety of standardized laboratory formulated samples to quantify and characterize the extraction process and a series of field specimens taken from the Chilean Atacama Desert, the Mojave Desert and Panoche Creek area of the California Coastal Range. All results are compared to classical full acid hydrolysis sample preparation methods.

With sub-critical water extraction (SCWE), we flow 1 to 5 ml. of liquid water at temperatures ranging from 105 C to 250 C through a compressed pulverized solid sample (0.1 to 0.5 grams) at pressures of up to 1000 psia for controlled extraction times of 15 seconds to 5 minutes. The dielectric constant of liquid water is a strong function of temperature. At temperatures of 125 C and below, it is a strong polar liquid that read-

ily solvates polar molecules including amino acids, carboxylic acids and inorganic salts. As the temperature decreases the dielectric constant approaches that of hexane at 300 C, and liquid water behaves as a hot non-polar solvent, readily dissolving such non-polar compounds as polycyclic aromatic hydrocarbons. We have found that water from 150 C to 250 C readily hydrolyzes complex peptides releasing the component free amino acids. We will present quantitative results showing that at 150 C and 1000 psia, sub-critical water lyses a variety of spores mixed with test soils, releasing both dipicolinic acid and amino acids. We find racemization levels for l-amino acids extracted at 250 C for less than 5 minutes to be less than 3%. We will also present quantitative results showing the dependence of liquid water temperature, extraction time and solid-to-liquid volume ratios on the extraction efficiency for the capture of amino acids and PAH's. Finally, we will present engineering details of our Mars Astrobiology Probe (MAP) end-to-end field system for SCWE extraction, purification of the extract with sublimation, cold stage sample capture with fluorescamine and transfer to our micro-chip chiral amino acid analyzer using microzone capillary electrophoresis and laser induced fluorescent detection (see abstract EGU05-A-09649).