Amino Acid chiral recognition using X-Ray Diffraction of thin films D. Dragoi, J. Kulleck, I. Kanik and L. W. Beegle. Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, Ca 91109, ddragoi@cco.caltech.edu, James.G.Kulleck@jpl.nasa.gov, Luther.Beegle@jpl.nasa.gov, ikanik@pop.jpl.nasa.gov,

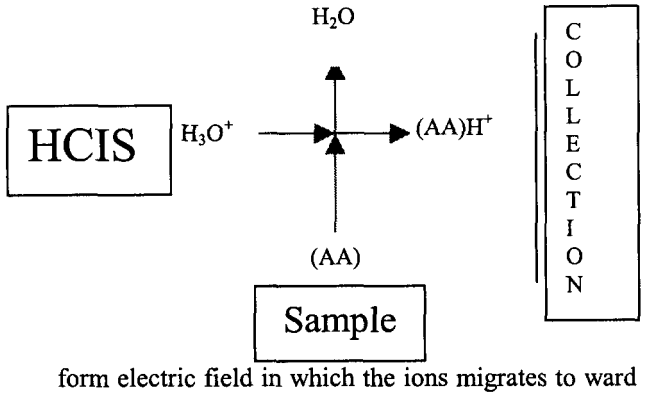
The astrobiological search for life, both extinct and extant, on other solar system bodies will take place via several planned lander missions to Mars Europa and Titian. The detection and identification of organic molecules that have been associated with life is a major technical achievement. Terrestrial life utilizes organic molecules, such as amino acids, as its basic building block. Natural process can create amino acids, as is demonstrated by their detection in meteoritic material. In this process, the organic molecules are created roughly in a even mixture of D and L forms. Biological process, however, can utilize almost uniquely one form or the other. In terrestrial biology only the L form is common in biological processes. If life existed else where in the D form it be concluded that life had evolutionary beginning on that body. Detection of an entomeric excess of L over D would also be a powerful sign that life had existed on that body at one time.

We have begun a series of experiments to extract organic molecules from rock and soil samples utilizing both direct heating and laser desorption. Our intended goal is to be able to collect only organic molecules on a collector plate. If this apparatus is operated over time it will act as an organic molecule concentrator, which should aid in the identification of molecules which may exist in exceedingly rare qualities on the Martian surface and sub surface.

We have designed, constructed and characterized a new high-pressure (5 Torr, representing the Martian atmospheric pressure) hollow cathode ionization source (HCIS) that can be utilized as an ionizer in a wide variety of mass analyzers [1]. It is able to function under ambient Martian atmospheric conditions without modification. The ionizer produces a stream of H_3O^+ ions from pure water vapor (H_2O) introduced into the ionizer from a small liquid water container. These ions react with air-borne samples and ionize organic species present via proton-transfer-reaction (PTR) without ionizing the atmospheric components. The constituents of the Martian atmosphere and most non-organic species present on the surface will not react with H_3O^+ as they have lower proton affinities than H_2O [1], while organic species tend to have higher affinities then H_2O

To facilitate the ionization of target molecules through the PTR process, a beam of (H_3O^+ ions, generated by the HCS (see Fig.2), are extracted into a reaction chamber. In our system the reaction chamber consists of 8 concentric rings having different electrical potential applied to them. This creates a near uniform electric field in which the ions migrates to ward the collection plate. At the 5 torr pressure this allows for the dissociation of H_2 clusters as well as a long path length for the PTR to take place.

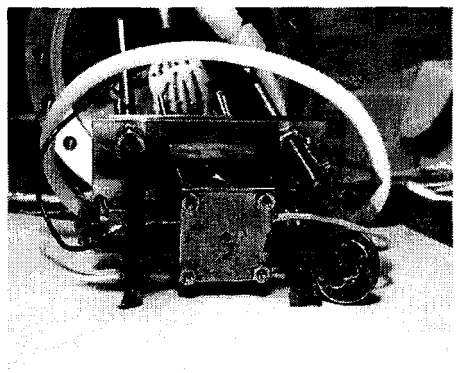
Fig.1 A schematic of the PTR ionization process. The HCIS creates H_3O^+ which reacts with amino acids (AA) released from a sample via heating. The ion and the molecule collide causing the H^+ to transfer from the AA which is then collected on a plate.



X-Ray Diffraction of Organics

It was determined that upon collection, the samples would be analyzed via HPLC or ESI/IMS and/or XRD to determine if structural changes have occurred on the organics in question. In order to do this analysis, the sample holder had to be removed, the sample collected weighed (to determine efficiency of the process) and sample extracted from the holder. To look at the samples first using laboratory X-Ray diffraction reduced the complexity. A thin D and L-

Fig.2 Photograph of the Hollow Cathode Ionization Source capable of producing the H_3O^+ reactant ion.



phenylalanine powder layer crystallized in slow evaporation process, using ultrapure water, spectrophotometric grade, is deposited on a low x-ray scatter membrane in order to increase x-ray S/N ratio and minimize the background. A standard laboratory x-ray analysis consists on using a monochromatic x-ray beam directed to the surface of the specimen that makes an angle θ with the incident beam fixed in direction and an x-ray detector collects the scattered x-rays at an angle 2θ. Both detector and specimen are coupled while the detector is moving around the sample and collect the diffracted x-rays that contains information about type of atoms and their periodic distribution in space, usually limited to the crystal unit cell. In order to get a complete x-ray diffraction pattern, which is a plot of x-ray diffracted, counts per seconds unit, versus 2θ in degrees, a θ/2θ scan is performed using a computer controlled goniometer. Most used commercial instruments these days is Siemens D500 x-ray diffractometer with Cu-Kα radiation and well aligned specimen holder. At JPL we used an updated version of Siemens D500 which has a Kevex semiconductor x-ray detector, a rotating holder for specimen to remove the preferred orientation effect, and automatically controlled using MDI software.

Fig.3 shows an example of the diffraction pattern for two specimens, D and L phenylalanine, fresh crystallized in pure water within same conditions. For raw phenylalanine D and L enantiomers produced by Sigma-Aldrich company [5], , the x-ray diffraction pattern coincides, as we expected, so no differences can be observed. However, for fresh crystallized specimens of D and L form, a difference can be evidenced. We will study this effect farther using different 'ph' solutions for crystallization. Comparing difraction patterns for L and D fresh crystallized phenylalanine in pure water, Fig.3, we observed shift-sin peak position, and differences in peaks intensity. These differences are due to specific interactions of D and L phenylalanine molecules with water molecules. The x-ray diffraction pattern for D and L form shown in Fig.3 reflects new structural configurations such as rotation, slight deformation and/or translation of the phenylalanine molecule inside the unit cell. In some cases, the structure includes a molecule of water that alter the diffraction patter too. Structural solution for freshly crystallized phenylalanine can be found using Rietveld refinement technique, which is a fairly mature method for determining crystal structure from powder diffraction.

This method has been demonstrated to work for some protein structures by Von Dreele [4].

Acknowledgment:

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References: [1] Beegle L.W. et al. (2001) *LPSC 32nd Abstract #2139.* [2] Beegle L.W. et al. (2001) *J. of Mass Spec, submitted.* [3] Asbury G.R. (1999) Ph.D. Thesis, Washington State University. [4] Asbury, G.R. and Hill, H.H. (2000) Anal. Chem.72, 580-584. [4] Von Dreele R.B. (2000) DXC 49th , [5] Sigma-Aldrich, Missouri, USA.

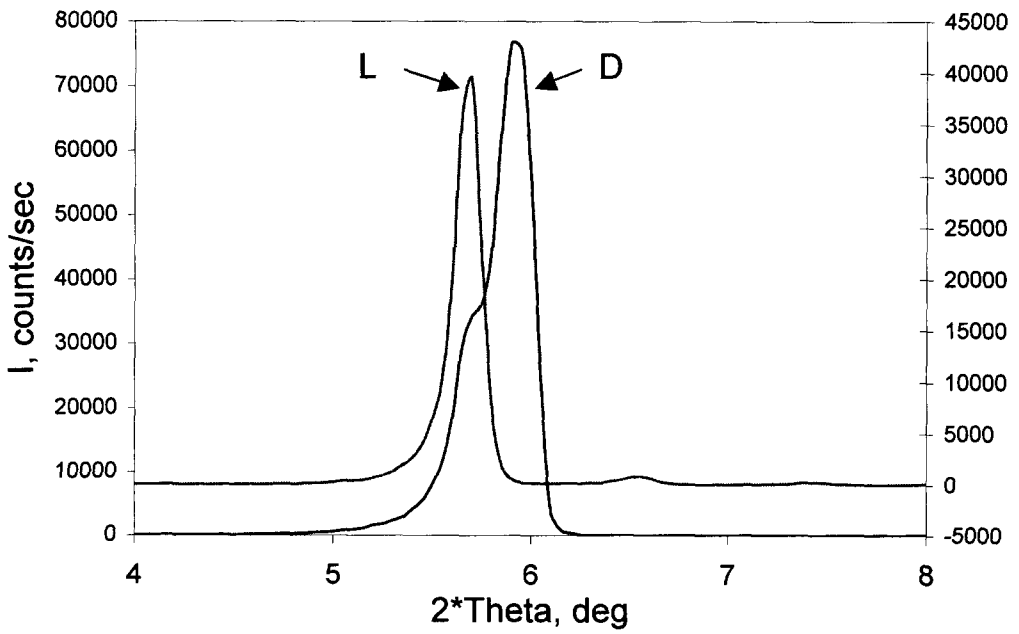

Fig.3 Two x-ray diffraction patterns for phenylalanine using fresh crystallized specimens of D and L enantiomers.