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THE SEARCH FOR AND IDENTIFICATION OF AMINO ACIDS, NUCLEOBASES AND NUCLEOSIDES IN SAMPLES RETURNED FROM MARS

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INTRODUCTION:

The Mars Sample Return mission will provide us with a unique source of material from our solar system; material which could advance our knowledge of the processes of chemical evolution.

As McKay (1) and others have pointed out, on Mars, geological investigations based on the Viking datasets have shown that primordial Mars was in many biologically important ways similar to the primordial Earth; the presence of surface liquid water, moderate surface temperatures, and atmosphere of carbon dioxide and nitrogen, and high geothermal heat flow. Indeed, it would seem that conditions on Earth and Mars were fundamentally similar during the first one billion years or so. As has been pointed out (1), Mars may well contain the best preserved record of the events that transpired on the early planets.

Examination of that early record will involve searching for many things, from microfossils to isotopic abundance data.

We propose an investigation of the returned Mars samples for biologically important organic compounds, with emphases on amino acids, the purine and pyrimidine bases, and nucleosides.

EXPERIMENTAL:

A. Sample extraction

Extraction of these molecules from the returned samples will be performed using the hydrothermal extraction technique described by Cheng and Ponnamperuma (2).

A one to five gram sample of finely divided sample will be placed in a pyrex glass extraction tube, 3 ml of ultrapure water will be added per gram of sample, the tube sealed with a hydrogen-oxygen torch, shaken well, then placed in a 165^{o} oven for 1 hour. All samples processing procedures will be conducted in a clean room.

At the end of this period the tube will be centrifuged and the supernatant removed for analysis. Portions of the extract will be analyzed for amino acids, nucleobases and nucleosides.

B. Analysis of sample extracts

Capillary gas chromatography-mass spectrometry, reversed-phase liquid chromatography, affinity chromatography and capillary GC using chiral phases will all be utilized in these studies. Figure 1 illustrates the separation of amino acid enantiomers by chiral phase capillary GC. Each number on the figure denotes enantiomers of an amino acid (from: Abe, I., in Amino Acid Analysis by Gas Chromatography, Zumwalt, R., Kuo, K. C., and Gehrke, C. W., eds., CRC Press Inc., 1987).

For analysis of the extract for free amino acids or amino acids present in a bound or peptidic form, aliquots will be analyzed by capillary GC/MS both before and after hydrolysis with 6N hydrochloric acid. The extracts will be derivatized to the N-trifluoracetyl n-butyl esters or N-heptafluorobutyryl isobutyl esters and examined for the presence of amino acids by GC/MS.

Establishment of the presence of amino acids would then lead to the next logical step, which would be the use of chiral stationary GC phases to determine the enantiomeric composition of the amino acids present, and thus potentially establish their biotic or abiotic origin.

This investigation will utilize chiral stationary phases such as Chirasil-Val which resolves the enantiomers of amino acids. Bayer *et al.* (3) have recently provided an excellent review of recent progress in separation of amino acid entiomers using chiral polysiloxanes.

Successful examination of the returned Mars samples for the presence of indigenous amino acids and the determination of their enantiomeric composition will obviously require rigorous exclusion of terrestrial contamination, and our study of the returned lunar samples provides considerable background on matters ranging from sample acquisition, processing and handling to evaluation of the purity of reagents and glassware used. Figure 2 illustrates the levels of contamination present in a single fingerprint (4).

Analysis of the returned Mars samples for amino acids, therefore, will require both the use of the best analytical techniques available and the design of experiments in such a way as to avoid contamination and yield the maximum amount of information.

Confirmational analyses for amino acids would include ion-exchange and reversed-phase liquid chromatographic analyses; for example, analyses comparable to our IEC analyses of Apollo 17 samples (Figure 3, references 5-7).

For analyses of the returned Mars samples for nucleobases and nucleosides, affinity and reversed-phase liquid chromatography would be utilized. Figure 4 demonstrates our separation of ribo- and deoxyribonucleosides by RPLC, and Figure 5 shows our separation of some 37 major and modified ribonucleosides. This technology, coupled with scanning UV detection for identification, presents a powerful tool for nucleobase and nucleoside analysis. Mass spectrometric analysis of these compounds would confirm their presence in samples returned from Mars.

SAMPLE TYPES AND QUANTITY:

It is requested that the main samples consist of core samples. The core samples should be taken at up to 5 m in depth. The samples should consist of 20-25 g from each total core sample. The core sample should be subsampled at 10 different depths with 2 g for each subsample. The samples should be protected from extreme heat and radiation, and maintained in a nitrogen atmosphere or atmosphere similar to that of Mars. It is essential that the sample containers be ultraclean, and that the samples be protected from terrestrial contamination.

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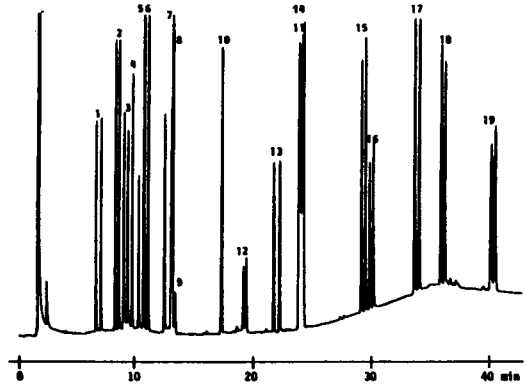


Figure 1.

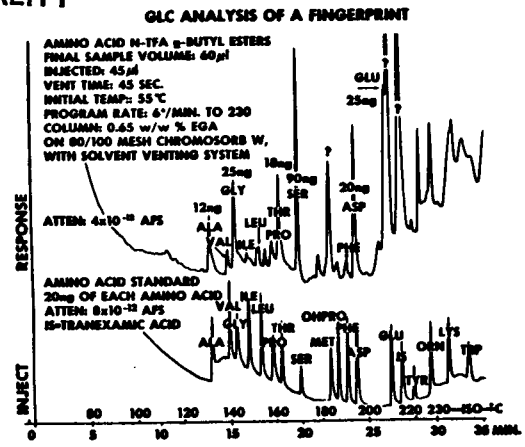
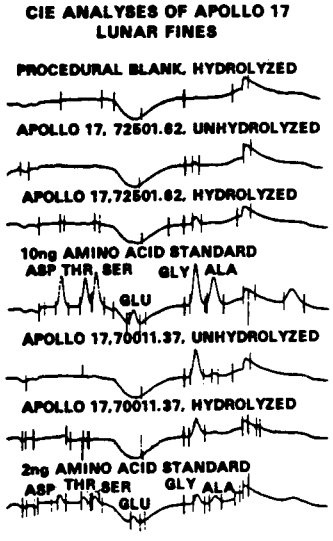


Figure 2.



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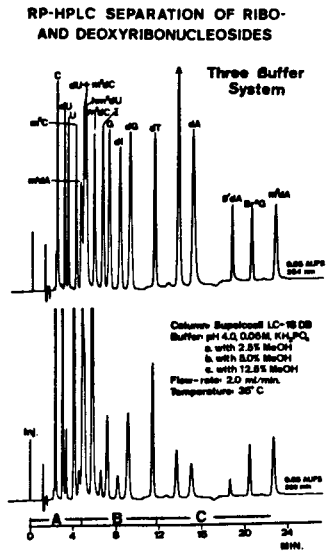

Figure 4.

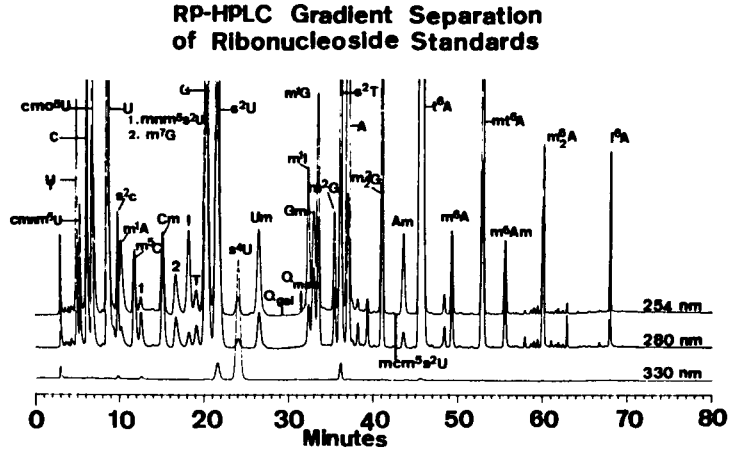

Figure 5.