AMINO ACID ANALYSES OF THE ANTARCTIC CM2 METEORITES ALH 83100 AND LEW 90500 USING LIQUID CHROMATOGRAPHY-TIME OF FLIGHT-MASS SPECTROMETRY.

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Introduction: The investigation of organic compounds in primitive carbonaceous meteorites provides a record of the chemical processes that occurred in the early solar system. In particular, amino acids have been shown to be potential indicators in tracing the nature of carbonaceous chondrite parent bodies [1]. The delivery of amino acids by carbonaceous chondrites to the early Earth could have been any important source of the Earth's prebiotic organic inventory [2]. Over 80 different amino acids have been detected in the Murchison CM2 meteorite, most of them completely non-existent in the terrestrial biosphere [3].

We have optimized a new liquid chromatography-time of flight-mass spectrometry (LC-ToF-MS) technique coupled with OPA/NAC derivatization in order to detect amino acids in meteorite extracts by UV fluorescence and exact mass simultaneously. The detection limit of the LC-ToF-MS instrument for amino acids is at least 3 orders of magnitude lower than traditional GC-MS techniques.

Here we report on the first analyses of amino acids and their enantiomeric abundances in the CM2 carbonaceous meteorites ALH 83100, LEW 90500, and Murchison using this new LC-ToF-MS instrument configuration. Amino acid analyses of any kind for the CM meteorite ALH 83100 have not previously been reported.

Samples and Analytical Techniques: The Antarctic CM2 carbonaceous chondrites ALH 83100 (split 246, parent 26) and LEW 90500 (split 69, parent 1) were provided by the meteorite sample curator at the NASA Johnson Space Center. The CM2 meteorite Murchison (USNM 6650.2) was provided by the Smithsonian Museum of Natural History. The meteorite samples were crushed into a fine powder with an annealed (500°C overnight) mortar and pestle in a positive pressure (1-μm filtered air) clean room. Crushed serpentine (a hydrated magnesium silicate) that had been heated at 500°C for several hours was used as a procedural blank. In addition, a sterile nylon bag used to store the Antarctic meteorite samples after collection was also analyzed in parallel.

A portion of each sample (~50 to 200 mg) was sealed in a clean glass test tube with 1 ml of double-distilled water for 24 h in a heating block set at 100°C. The ampoules were cracked open and centrifuged to separate out the particulate from the water supernatant. One half of the water extract was transferred to a new test tube, dried under vacuum and desalted by using cation exchange resin (AG50W-X8, 100-200 mesh, Bio-Rad) prior to HPLC-FD and LC-ToF-MS analysis to determine the abundance of free amino acids associated with the bulk sample. The remaining water supernatant was transferred to a separate test tube, dried under vacuum, hydrolyzed under 6 M HCl vapor at 150°C for 3 h, desalted, and analyzed by using OPA/NAC derivatization and HPLC separation to determine bound amino acids in the bulk sample [4].

Results and Discussion: The HPLC-FD and LC-ToF-MS chromatograms of the 6 M HCl-hydrolyzed, hot water extracts of the CM2 meteorites ALH 83100, LEW 90500 and Murchison and the serpentine blank are shown in Figure 1. The distributions of amino acids in the LEW 90500 and Murchison meteorites were found to be nearly identical, which is consistent with previous analyses of these two meteorites [1, 5]. The most abundant amino acids detected in Murchison and LEW 90500 were α-aminoisobutyric acid (AIB) and isovaline (1,300 to 3,200 ppb). In contrast, ALH 83100 contained a much lower abundance of AIB (250 ppb) and isovaline (< 10 pp) compared to Murchison and LEW 90500. Therefore, if Strecker-cyanohydrin synthesis was the predominant pathway for the formation of amino acids on these CM meteorite parent bodies [1, 6], then ALH 83100 originated on a chemically distinct parent body that was depleted in acetone and 2-butanone required for the formation of AIB and isovaline by Strecker [1].

The most striking difference between ALH 83100 and the other CMs was the large unidentified peak (marked 'X' in Fig. 1) present in the hydrolyzed extract of ALH 83100 at a much higher concentration (~ 8,500 ppb) than detected in Murchison (240 ppb) and LEW 90500 (390 ppb). Peak X was only detected at very low concentrations (~ 150 ppb) in the water extract of ALH 83100 prior to acid hydrolysis, which indicated that compound X was present in predominantly bound or peptide form. A peak with a similar retention time was also detected by HPLC-FD in a previous analysis of the Antarctic Martian meteorites ALH 84001 and MIL 04436 [7, 8], however the mass of the compound was not determined.

Using HPLC-FD and LC-ToF-MS, we were able to identify compound X in ALH 83100 as ε-amino-n-caproic acid (EACA) based on the exact molecular mass (m/z = 393.15, ES+ mode) and UV fluorescence retention time of the OPA/NAC derivative (Fig. 1). A high concentration of EACA was also identified in the

acid hydrolyzed Nylon bag water extract. This result is not surprising since Nylon-6 is simply a peptide of EACA and upon acid hydrolysis will yield large quantities of free EACA.

Conclusions: We have demonstrated that LC-ToF-MS coupled with HPLC-FD detection is a very powerful tool for the detection of amino acids in meteorite extracts. Using this new analytical technique we were able to identify a total of 20 different amino acids and their enantiomers in the Antarctic CM meteorites ALH 83100 and LEW 90500, as well as the non-Antarctic CM Murchison. One amino acid that has previously been detected in the Antarctic Martian meteorites ALH 84001 and MIL 03346, but has eluted identification, was also detected in the Antarctic meteorites ALH 83100 and LEW 90500 and determined by LC-ToF-MS to be EACA. EACA is a likely amino acid contaminant derived from the nylon bag used to store the Antarctic meteorite samples. Fortunately, Nylon-6 leaches only trace levels of other amino acids, however future meteorite collection efforts in Antarctica should consider other types of sterile sam-ple storage bags such as Teflon or polyethylene as an alternative to Nylon-6.

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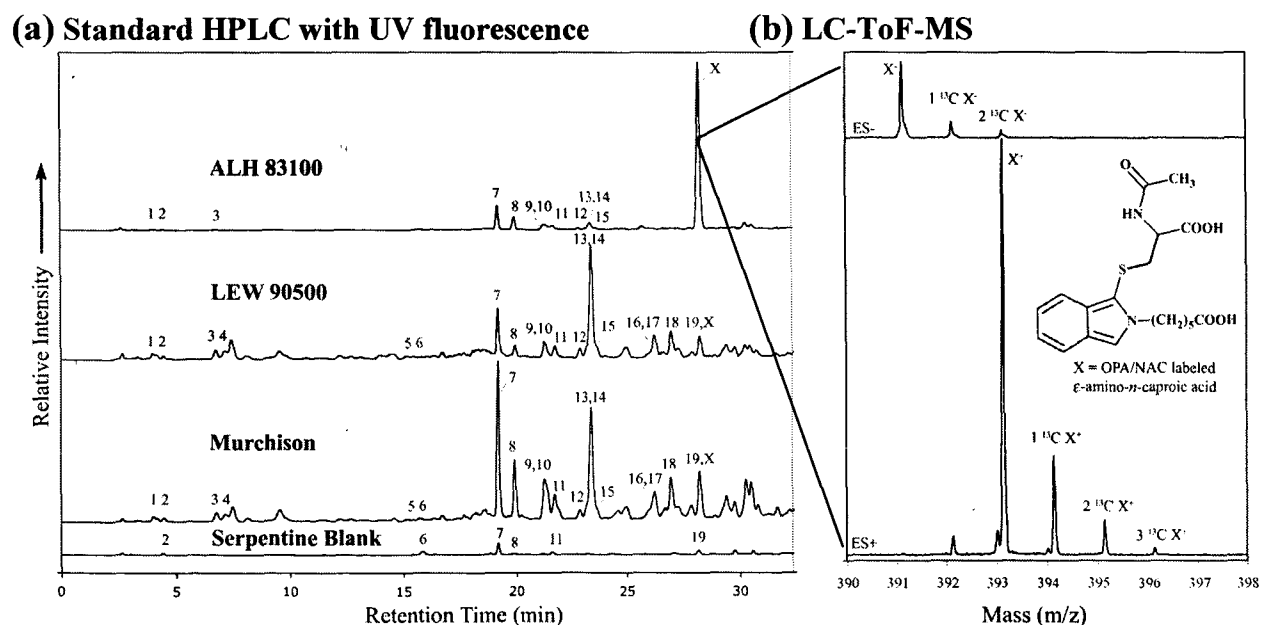
Figure 1. HPLC separation of OPA/NAC derivatives with simultaneous UV fluorescence and time of flight mass spectrometer (ToF-MS) detection of amino acids in the 6M HCl-hydrolyzed hot water extracts from the Antarctic CM2 carbonaceous chondrites ALH 83100 and LEW 90500, the CM2 meteorite Murchison, and a serpentine blank (a). The ToF-MS ion trace shows the exact mass of the OPA/NAC-ε-amino-n-caproic acid molecular ion as well as the mono-, di-, and tri-^{13}C species in both ES+ and ES- modes (b). The peaks were identified by comparison of the retention time and exact molecular mass to those in an amino acid standard run on the same day, as follows: 1, D-aspartic acid; 2, L-aspartic acid; 3, L-glutamic acid; 4, D-glutamic acid; 5, D-serine; 6, L-serine; 7, glycine; 8, β-alanine; 9, D-alanine; 10, γ-amino-n-butyric acid; 11, L-alanine; 12, D-β-amino-n-butyric acid; 13, α-aminoisobutyric acid (AIB); 14, D,L-β-AIB; 15, L-β-amino-n-butyric acid; 16, D,L-α-amino-n-butyric acid; 17, D-isovaline; 18, L-isovaline; 19, L-valine; and X, ε-amino-n-caproic acid (EACA).