**SEARCHING FOR EXTRATERRESTRIAL AMINO ACIDS IN A CONTAMINATED METEORITE: AMINO ACID ANALYSES OF THE ÇANAKKALE L6 CHONDRITE** A. S. Burton[1], J. E. Elsila[2], D. P. Glavin[2], J. P. Dworkin[2], and C. Y. Ornek[3], H. H. Esenoglu[4,5], O. Unsalan[6], B. Ozturk[7], [1]Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX, USA (aaron.burton@nasa.gov), [2]Solar System Exploration Divison, NASA Goddard Space Flight Center, [3]Environmental Engineering Department and Marine Sciences and Management Institute, Istanbul University, Istanbul, Turkey, [4]Department of Astronomy and Sapce Sciences, Istanbul University, Istanbul, Turkey, [5]Tubitak National Observatory, Antalya, Turkey, [6]Physics Department, Istanbul University, Istanbul, Turkey, [7]Astronomy and Sciences Department, Istanbul University, Istanbul, Turkey.

**Introduction:** Amino acids can serve as important markers of cosmochemistry, as their abundances and isomeric and isotopic compositions have been found to vary predictably with changes in parent body chemistry and alteration processes [1-3]. Amino acids are also of astrobiological interest because they are essential for life on Earth. Analyses of a range of meteorites, including all groups of carbonaceous chondrites, along with H, R, and LL chondrites, ureilites, and a martian shergottite, have revealed that amino acids of plausible extraterrestrial origin can be formed in and persist after a wide range of parent body conditions [5-8]. However, amino acid analyses of L6 chondrites to date [9, 10] have not provided evidence for indigenous amino acids. In the present study, we performed amino acid analysis on larger samples of a different L6 chondite, Çanakkale, to determine whether or not trace levels of indigenous amino acids could be found. The Çanakkale meteor was an observed fall in late July, 1964, near Çanakkale, Turkey [4]. The meteorite samples (1.36 and 1.09 g) analyzed in this study were allocated by C. Y. Ornek, along with a soil sample (1.5 g) collected near the Çanakkale recovery site.

**Methods for sample processing and analysis:** Sample processing for amino acid analyses was performed as described in depth elsewhere [11], and is briefly described here. Procedural blank samples and a soil sample (1.5 g) were processed in parallel with a crushed meteorite sample (1.36 g and 1.09 g, respectively). The soil and meteorite samples were crushed with a mortar and pestle and placed in individual ampoules with 4 mL water. The ampoules were sealed, and placed in an oven at 100 ºC for 24 h. For each sample, the supernatant was removed, divided in two equal aliquots, and dried down in separate vials. One aliquot of each sample was set aside for the analysis of free amino acids. The other aliquot was subjected to acid vapor hydrolysis (6N HCl) at 150 ºC for 3 h, to convert amino acid precursors to free amino acids (total amino acids = free + acid-labile). The samples were then purified by cation-exchange chromatography (BioRad AG50W X-8 resin) and eluted with aqueous ammonia (2M). The samples were dried down under vacuum, brought up in water. Aliquots of the sample were derivatized immediately prior to analysis by OPA/NAC derivation. The data presented herein are reported from analyses by liquid chromatography-UV fluorescence/time of flight mass spectrometry [11]. Compound specific isotopic data were obtained by gas chromatography-combustion isotope ratio mass spectrometry [3].

| Amino acid | Çanakkale 1 | Çanakkale 2 | soil |
|---|---|---|---|
| D-aspartic acid | 1.1 | 1.2 | 0.8 |
| L-aspartic acid | 3.9 | 4.3 | 2.9 |
| D-glutamic acid | 1.2 | 1.3 | 0.8 |
| L-glutamic acid | 8.5 | 8.5 | 4.7 |
| D-serine | 2.6 | 2.8 | 0.2 |
| L-serine | 8.6 | 8.5 | 1.5 |
| glycine | 63 | 67 | 9.7 |
| β-alanine | 2.4 | 2.9 | 1.3 |
| D-alanine | 1.6 | 1.0 | 1.2 |
| L-alanine | 5.5 | 4.9 | 6.7 |
| γ-amino-*n*-butyric acid | 1.1 | 1.1 | 1.6 |
| D,L-β-aminoisobutyric acid* | 0.7 | 0.8 | <0.01 |
| D,L-β-amino-*n*-butyric acid* | 0.6 | 0.7 | <0.01 |
| α-aminoisobutyric acid* | 0.4 | 0.4 | <0.01 |
| D,L -α-amino-*n*-butyric acid | 0.1 | 0.04 | 0.02 |

Table 1. Amino acid abundances (nmol/g) in Çanakkale meteorite and soil samples. The '*' denotes the amino acids observed in the meteorite samples but not in the soil or blank samples.

**Results:** We searched for a broad suite of two- to six-carbon amino acids in the Çanakkale meteorite and soil samples. The most abundant amino acids were those common in terrestrial biology (Table 1), including glycine and L-proteinogenic amino acids including aspartic acid, glutamic acid, serine and alanine. In order to further investigate the origins of these compounds, we performed compound-specific $\delta^{13}C$ measurements on the most abundant of these compounds (Table 2). The $\delta^{13}C$ values obtained for these biological amino acids are similar for amino acids extracted from the Çanakkale meteorite and soil samples, and range from 0 to -25‰, values that are consistent with a terrestrial origin [12, 13]. Interestingly, however, there are several amino acids that are much lower in abundance in the meteorite (<1 nmol/g) that do not appear in the soil sample or our procedural blanks (Figure 1). These include the four-carbon amino acids α-aminoisobutyric acid, D,L-β-amino-*n*-butyric acid, and D,L-β-aminoisobutyric acid. There are also a large suite of five-carbon amino acid isomers that are present in the Çanakkale meteorite that are not found in either the soil or procedural blank samples (data not shown). Unfortunately, these four- and five-carbon amino acids were not sufficiently abundant to permit compound-specific stable isotope measurements to be performed. Nevertheless, their absence in the soil and procedural blank samples argues against terrestrial contamination as their source.

| Amino Acid | Meteorite $\delta^{13}C$ (‰ VPDB) | Soil $\delta^{13}C$ (‰ VPDB) |
|---|---|---|
| L-alanine | -11 ± 3 | -16 ± 3 |
| D-alanine | Not determined | -18 ± 5 |
| L-valine | 0 ± 2 | -6 ± 2 |
| Glycine | -18 ± 2 | -4 ± 3 |
| D-aspartic acid | Not determined | -20 ± 5 |
| L-aspartic acid | -12 (single measurement) | -23 ± 2 |
| D-serine | -10 ± 9 | n.d. |
| L-serine | -2 ± 2 | -8 ± 1 |

Table 2. Compound specific stable isotope measurements for amino acids in the Çanakkale meteorite and soil sample.

**Discussion:** L chondrites comprise a large portion of the meteorites in collections on the modern Earth, both in terms of number (as of January 12th, 2016, more than 18,000 of the 52,000 entries in the meteoritical bulletin database are classified as L chondrites), as well as mass. Though the relative infall rates of different meteorite types has changed since the late heavy bombardment, it is plausible that L chondrite-like material was still significantly represented. Therefore, the discovery of even low levels of indigenous amino acids in L chondrites on a per gram basis could represent a significant source of amino acids when extrapolated across such a large mass of L chondrite material that was likely to have been delivered to the early Earth.

We are currently analyzing additional L6 chondrites that have experienced significantly less terrestrial contamination in order to more definitively address whether or not the amino acids we have observed here are indigenous. This work also highlights the power of compound specific organic measurements, which in this case allowed the detection of plausibly indigenous amino acids even in the presence of terrestrial contamination. Of equal importance is the availability of witness materials and procedural blanks, which enable indigenous compounds to be differentiaed from indigenous ones.

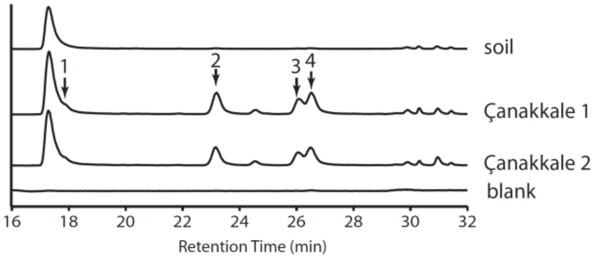


Figure 1. Extracted ion chromatograms of the four-carbon amino acids observed in the Çanakkale meteorite and soil samples. Labeled compounds are present int the Çanakkale meteorite but were not found in the soil or blank samples. 1 = D,L-β-aminoisobutyric acid, 2 and 3 = D- and L-β-amino-*n*-butyric acid, and 4 = α-aminoisobutyric acid.

**Conclusion:** Relatively large (> 1g) Samples of the Çanakkale L6 meteorite were analyzed for amino acids. Although contamination from terrestrial amino acids was observed, there were several amino acids that were present in the Çanakkale samples that were not observed in a terrestrial soil sample that was collected nearby nor were they found in procedural blanks during lab processing. It is plausible that these amino acids are extraterrestrial in origin, though this conclusion would be strengthened by finding similar amino acids suites in L6 chondrites that were not contaminated. Even at trace levels, the large mass of L6 chondrite material delivered to the Earth suggest that L chondrites could have been a significant source of amino acids for Earth and other planets in the solar system.

**References:** [1] Burton A. S. et al 2012 *Chem. Soc. Rev.* 41, 5459-5472. [2] Glavin D. P. et al. 2010 *Met. Plan. Sci.* 45, 1948-1972. [3] Elsila J. E. et al. (2012) *Met. Plan. Sci.* 47, 1517-1536. [4] Unsalan O. et al. (2012) *Spec. Act. A* 92, 250-255. [5] Burton A. S. et al. (2015) *Met. Plan. Sci.* 50, 470-482. [6] Callahan M. P. et al. (2013) *Met. Plan. Sci.* 48, 786-795. [7] Burton A. S. et al. (2012) *Met. Plan. Sci.* 47, 374-386. [8] Burton A. S. et al. (2011) *Met. Plan. Sci.* 46, 1703-1712. [9] Martins Z. et al. (2007) *Met. Plan. Sci.* 42, 1581-1595. [10] Jenniskens P. et al. (2014) *Met. Plan. Sci.* 49, 1388-1425. [11] Glavin D. P. et al. (2006) *Met. Plan. Sci.* 41, 889-902. [12] Burton A. S. (2014) *Met. Plan. Sci.* 49, 2074-2086. [13] Scott J. H. et al. (2006) *Astrobiology* 6, 867-880.