THE ABUNDANCE AND ENANTIOMERIC COMPOSITION OF AMINO ACIDS IN THE SUTTER'S MILL CARBONACEOUS CHONDRITE.

D. P. Glavin[1], A. S. Burton[1,2], J. E. Elsila[1], J. P. Dworkin[1], Q. -Z. Yin[3], and P. Jenniskens[4,5]. [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, daniel.p.glavin@nasa.gov, [2]Catholic University of America, Greenbelt, MD 20771, [3]University of California Davis, Davis, CA 95616, [4]SETI Institute, Mountain View, CA 94043, [5]NASA Ames Research Center, Mountain View, CA 94035.

Introduction: On the morning of April 22, 2012, a ~2 to 4 meter sized near-Earth asteroid fell over the Sierra Nevada mountains in California and CM chondrties landed over a wide area near Sutter's Mill in El Dorado County. Two days later, one of us (PJ) found a 4 g piece of the asteroid, designated SM2, on pavement in the parking lot of Henningsen-Lotus Park and collected the meteorite in aluminum foil [1]. When found, the meteorite had been crushed by car tire into four cm-sized and several smaller fragments, no longer protected by a glassy fusion crust. They were not touched by human hands, but were exposed to the ambient environment before collection and to human breath afterwards. Several additional meteorites were later collected by NASA Ames led volunteer search teams and by local residents, and a Sutter's Mill meteorite consortium was established [2].

Here we report on the abundance and enantiomeric compositions of amino acids in an HCl-hydrolyzed, hot-water extract of SM2, which was recovered on April 24, 2012 prior to the heavy rains April 24-25, and two other fragments SM12 and SM51 that were recovered post-rain on April 29 and May 2, respectively [2]. Fully crusted SM12 was collected in aluminum foil, while SM51 was found by a local resident. Soil samples were collected at the SM12 and SM51 sites.

Methods: The abundance, distribution and enantiomeric compositions of the two- to six-carbon aliphatic amino acids found in these samples were measured by ultra performance liquid chromatography fluorescence detection and time of flight mass spectrometry (UPLC-FD/ToF-MS) coupled with *o*-phthaldialdehyde/*N*-acetyl-L-cysteine (OPA/NAC) derivatization [3]. As a control, a crushed serpentine sample that had been heated at 550°C for 24 h in air was processed in parallel. For comparison, a similar sized sample of the Murchison CM2 carbonaceous chondrite from the Smithsonian National Museum of Natural History (USNM 6650) and a terrestrial soil sample from the fall site of the SM51 meteorite fragment were also analyzed using the same protocols.

Results and Discussion: Analysis of the Sutter's Mill meteorite water extracts by UPLC-FD/ToF-MS indicated the presence of several C_2 to C_6 amino acids well above blank levels (Fig. 1). Only trace levels (< 10 ppb) of glycine, β-alanine, and L-alanine were present in the serpentine blank which indicates that minimal amino acid contamination of the meteorite samples occurred during the processing procedure. However, we cannot rule out the possibility that the Sutter's Mill meteorite samples were contaminated by terrestrial amino acids during atmospheric entry, from the landing site itself, and/or during collection and curation. In contrast to the Murchison meteorite which has a complex distribution of amino acids with a total C_2 to C_5 amino acid abundance of ~14,000 parts-per-billion (ppb) [3], the three Sutter's Mill meteorite fragments analyzed have a much simpler amino acid distribution with lower total amino acid abundances ranging from ~660 ppb to 9,500 ppb (Table 1).

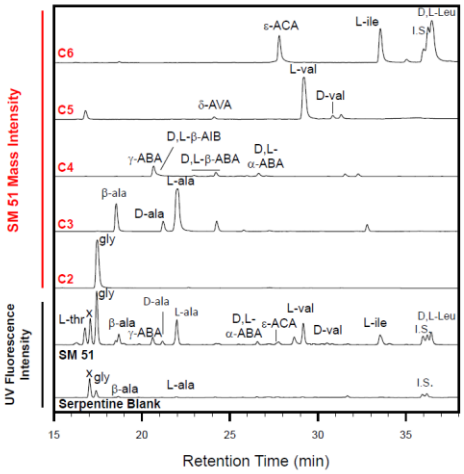

Figure 1. The 15- to 38-min. region of the liquid chromatography with fluorescence detection and time of flight mass spectrometry chromatograms of the serpentine procedural blank and the Sutter's Mill (SM51) meteorite HCl-hydrolyzed, hot-water extracts. The mass traces correspond to the OPA/NAC derivatives of the C_2 to C_6 amino acids. Abbreviations: gly, glycine; thr, threonine; ala, alanine; ABA, amino-*n*-butyric acid; ε-ACA, ε-amino-*n*-caproic acid; val, valine; leu, leucine; δ-AVA, δ-aminovaleric acid; AIB, aminoisobutyric acid; X, unidentified desalting artifact; and I.S., internal D,L-norleucine standard used to estimate amino acid desalting recoveries.

Based on the higher total amino acid abundances in SM51 compared to SM2 and SM12 and the fact that SM51 was exposed to the terrestrial environment longer than the other two meteorites, it is possible that SM51 experienced a greater degree of terrestrial amino acid contamination. The low D/L enantiomeric ratios of several proteinogenic amino acids in the Sutter Mill meteorite samples compared to Murchison (Table 1), and similarly low D/L values measured in soil collected from the SM51 meteorite landing site (Table 1) also suggest a significant amount of terrestrial protein amino acid contamination of Sutter's Mill. However, it is worth noting that the most 'pristine' meteorite sample (SM2) collected before the heavy rains, has higher D/L protein amino acid ratios than SM12 and SM51 (Table 1). This could mean that SM2 contains and indigenous component of these protein amino acids. Carbon isotopic measurements of these common protein amino acids will be required to establish if there is an extraterrestrial component. Other non-protein amino acids that are rare on Earth, yet commonly found in other CM meteorites including Murchison such as α-aminoisobutyric acid (α-AIB) and isovaline [3], were not detected in Sutter's Mill. However, traces of D,L-β-AIB (~ 2 to 4 ppb) were detected in all three Sutter's Mill meteorite fragments and could be extraterrestrial in origin (Table 1). β-AIB was not detected in the terrestrial soil sample above the 1 ppb level (Table 1).

Table 1. Comparison of the total abundances and enantiomeric (D/L) ratios of selected amino acids in the Sutter's Mill and Murchison CM carbonaceous chondrites and a terrestrial soil sample.

	SM2[a]	**SM12[b]**	**SM51[b]**	**Soil[bc]**	**Murchison[d]**
Amino Acid Abundances					
Total C_2 to C_5-amino acids[†]	~660 (ppb)	~1,400 (ppb)	~9,500 (ppb)	~790 (ppm)	~14,000 (ppb)
D+L-aspartic acid	85 ± 10	154 ± 22	1432 ± 162	127 ± 32	152 ± 31
D+L-glutamic acid	141 ± 11	477 ± 27	2890 ± 904	107 ± 17	700 ± 86
Glycine	170 ± 20	222 ± 57	960 ± 229	130 ± 17	1995 ± 122
D+L-alanine	54 ± 23	124 ± 16	814 ± 166	141 ± 34	1282 ± 90
β-alanine	45 ± 16	47 ± 4	182 ± 29	20 ± 4	1419 ± 157
γ-ABA	6 ± 3	39 ± 31	617 ± 179	11 ± 2	1460 ± 213
D+L-β-AIB[e]	~2 [f]	~2 [f]	~4 [f]	< 0.001	343 ± 102[g]
D+L-valine	37 ± 11	123 ± 16	881 ± 178	83 ± 8	126 ± 43
Enantiomeric Ratios					
(D/L) asp	0.44	0.26	0.27	0.24	0.91
(D/L) glu	0.26	0.17	0.19	0.26	0.96
(D/L) ala	0.54	0.16	0.14	0.16	0.95
(D/L) val	< 0.35	0.17	0.06	0.09	0.95

[a] Data from [2]. [b] Data from this study. [c] Terrestrial soil sample collected from the SM51 meteorite fall site. [d] Data from [3]. [e] Enantiomers could not be separated under the chromatographic conditions. [f] Tentatively identified above blank levels. [g] Data from [4]. Errors in the abundances are based on the standard deviation of the average value of three separate measurements. Propagated errors for D/L ratios ranged from ± 0.01 to 0.09. [†] Total includes all C_2 - C_5 acyclic amino alkanoic acids including several not listed in the Table.

The higher relative abundances of the non-protein amino acids β-alanine (BALA) and γ-amino-*n*-butyric acid (GABA) in Sutter's Mill compared to the terrestrial soil (Figure 2), and the fact that BALA and GABA are present mostly in the free form (~ 60 to 95%) in SM51 compared to only ~30 to 40% free BALA and GABA in the terrestrial soil, suggests that these and possibly other *n*-ω-amino acids could be indigenous to the meteorite, possibly formed at elevated temperatures by Fischer-Tropsch Type (FTT) reactions as previously suggested for CV and CO type carbonaceous chondrites [5].

The low abundances of *n*-ω-amino acids, as well as β-AIB in the Sutter's Mill meteorite compared to other CM meteorites such as Murchison (Table 1) is consistent with mineralogical evidence and Raman measurements of macromolecular carbon that at least some parts of the Sutter's Mill meteorite parent body experienced extensive aqueous and/or thermal alteration at temperatures above ~150°C [2]. These Sutter's Mill results are also consistent with recent laboratory experiments demonstrating that *n*-alkyl-α-amino acids will rapidly decompose to CO_2 and NH_3 by decarboxylation and deamination when heated to temperatures above 150ºC in the presence of water and minerals [6].

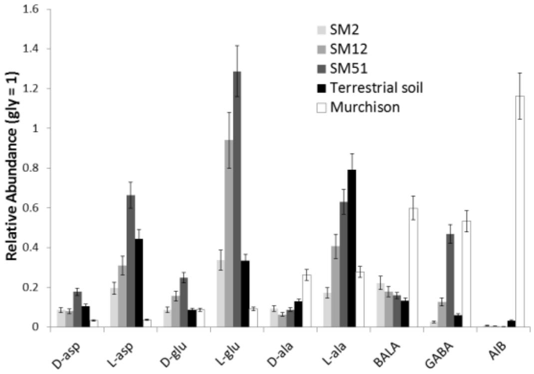

Figure 2. The relative molar abundances (glycine = 1) of several amino acids in the Sutter's Mill meteorite (SM2, SM12, and SM51) compared to the Murchison meteorite (USNM 6650) and a terrestrial soil sample collected from the SM51 meteorite fall site.

Future asteroid sample return missions are needed to return 'pristine' fragments of carbonaceous material that have experienced only limited exposure to organics from the terrestrial environment. OSIRIS-REx, NASA's first asteroid sample return mission launching in 2016, will travel to a near-Earth carbonaceous asteroid (1999 RQ36), study it in detail, and return at least 60 grams of pristine regolith to Earth in 2023 [7].

References: [1] Jenniskens, P. et al. (2012) *Meteorit. Bull.*, *46*, 1. [2] Jenniskens, P. et al. (2012) *Science*, *338*, 1583-1587. [3] Glavin, D. P. et al. (2010) *MAPS*, *45*, 1948-1972. [4] Ehrenfreund, P. et al. (2001) *PNAS 98*, 2138-2141. [5] Burton, A. S. et al. (2012) *MAPS*, *47*, 374-386. [6] McCollom, T. et al. (2012) *GCA*, in press. [7] Lauretta, D. S. et al. (2012) *LPS XLIII*, Abstract#2491.

Acknowledgments: We appreciate the rapid recovery of the Sutter's Mill meteorite made possible by the local communities of Lotus, Coloma, Pilot Hill, and Grass Valley and the NASA Ames coordinated search efforts supported by the NASA Lunar Science Institute. The authors would like to thank R. Patrinellis for collecting the soil sample from the SM51 fall location and G. Cooper for preparation of the SM2 and SM12 meteorite fragments. DPG, JPD and JEE acknowledge funding support from the NASA Astrobiology Institute and the Goddard Center for Astrobiology, and the NASA Cosmochemistry and Astrobiology: Exobiology and Evolutionary Biology Programs.