Contamination of meteorite samples with terrestrial amino acids

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Meteorites, the source of most extraterrestrial material, are believed to have provided a wide variety of proteinogenic amino acids (AA) according to Origin of Life researchers. The chemicals identified from fragments are listed, but, until recently, little or no effort has been dedicated to quantifying how much was due to terrestrial contamination, although contamination is considered to be inevitable.

In 2021, Glavin *et al.* analyzed three fragments from the Aguas Zarcas meteorite, which landed in Costa Rica in 2019 (*UA* samples, from the University of Arizona).[1] In addition, 10 g were extracted and ground to a powder from a single fragment of the Murchison meteorite, which had landed in Australia in 1969; individual portions (0.08 g and 1.0 g) were analyzed separately. The results, shown in table 1, provided insights about

Table 1. Nanomoles amino acid / g meteorite from Aguas Zarcas (UA) and Murchison (Mur.) meteorite fragments and soil samples from near the landing sites. Data extracted and reorganized from table 1 and 2 in Glavin *et al.* (2020).[1]

	Aguas Zarcas meteorite								**Murchison meteorite**					
Amino acid	**UA 2741 0.08 g [1,2]**		**UA 2741 0.5 g [1,3]**		**UA 2746 0.52 g [1,3]**		**UA soil [1,3]**		**Mur. 0.08 g[1,2]**		**Mur. 1 g [1,3]**		**Mur. soil [4]**	
	L	D	L	D	L	D	L	D	L	D	L	D	L	D
glycine	75		20		158		425		40		32		667	
alanine	18.4	3.7	3.5	1.6	38	17	213	74.3	3	2.2	8.2	8.3	356	47
glutamic acid	19.7	2.2	3.7	0.59	36	10.3	119	28	6.3	1.03	7.6	2.7	269	19
serine	18	3.4	1.5	0.3	6.6	1.9	91.3	16.9	3.5	0.13	0.6	0.4	199	15
threonine	14.8	0.01	28	0.2	56	0.7	107	4.2	2.21	0.02	0.32	0.17	0	0
aspartic acid	10.1	2.4	0.5	0.16	27	15.1	120	50	3	0.59	1.7	0.95	314	72
2-a-3-mba (valine isomer)	20.1	0.92	1.2	0.35	27	3.6	204	10	2.8	0.55	0.93	0.62	97	4
α-isovaline	5	4	3.5	2.8	3.9	2.9	0.1	0.1	11.8	10	11.5	9.5	0	0.1
α-aminoisobutyric acid (α-AIB)	4.6		5.6		52		1		11.4		10.4		0.1	
γ-amino-n-butyric acid + D,L-β-AIB	3.9		1.4		6		25.2		2.4		2		4.9	
β-alanine	3.4		0.9		10		26		6		16		8	
δ-5-apa	2.6		1		1.8		0.01		1.8		2.2		0	
γ-D,L-4-apa	2.1		0.8		0.7		0.01		2.9		0.9		0	
γ-D,L-4-a-2-mba	2.1		1		1.1		0.01		2.1		1.56		0	
D,L-α-amino-n-butyric acid	1.8		1.4		2.9		4		2		2.4		0.7	
β-3-a-3-mba	1.3		0.47		1		0.01		4.76		5.2		0	
α-norvaline (L-2-apa)	0.56	0.45	0.5	0.5	0.16	0.15	0.17	0.08	0.05	0.1	0.25	0.25	0	0
β-amino-n-butyric acid	0.26	0.33	0.19	0.19	0.3	0.34	0.6	0.48	1.6	1.8	1.2	1.2	0	6
β-3-a-2,2-dmpa	0.47	0.47	0.18		0.17		1		1.9		1.73		0	
ε-amino-n-caproic acid (EACA)	0.4		0.7		1.8		1.4		2.2		2.2		0	
γ-D,L-4-a-3-mba	0.31		0.06		0.04		0.01		0.42		0.07		0	
β-D,L-3-apa	0.27		0.6		0.9		0.5		2.7		2.5		0	
β-D,L-3-a-2-epa	0.1		0.1		0.1		0.1		0.3		0.3		0	
β-D,L- and allo-3-a-2-mba	0.04		0.8		1.4		0.01		0.29		0.3		0	

[1] Flame-sealed in a glass ampoule with water and extracted at 100°C for 24 h
[2] Hydrolysis using 6 M HCl at 150°C for 3 h
[3] Acid-hydrolysis under HCl vapour
[4] Unpublished analysis of soil 20–30 cm underground using LC-FD (high performance liquid chromatography with fluorescence detection) by Reid R. Keays from The University of Melbourne. Further details not provided.

Table 2. Based on data from table 1. The 'Total' columns sum the D- and L-enantiomers, and the 'Aver.' column is the average from the different samples from the same meteorite. The 'Prop.' column is the relative proportion compared to the total nmol of all AA.

	Aguas Zarcas meteorite											Murchinson meteorite								
	UA 2741 0.08 g[2]		UA 2741 0.5 g[3]		UA 2746 0.52 g			UA soil [1,3]			Mur. 0.08		Mur. 1 g			Mur. soil		
Amino acid	Total	Prop.	Total	Prop.	Total	Prop.	Aver.	Total	Prop.	Soil/ Aver.	Total	Prop.	Total	Prop.	Aver.	Total	Prop.	Soil/ Aver.
glycine	75	33.7%	20	23.7%	158	36.1%	84.3	425	27.9%	5.0	40	30.3%	32	23.5%	36.0	667	32.1%	18.5
alanine	22.1	9.92%	5.1	6.05%	55	12.6%	27.4	287	18.9%	10.5	5.2	3.94%	16.5	12.1%	10.9	403	19.4%	37.1
glutamic acid	21.9	9.83%	4.29	5.09%	46.3	10.6%	24.2	147	9.65%	6.1	7.33	5.56%	10.3	7.57%	8.8	288	13.9%	32.7
valine	21	9.44%	1.55	1.84%	30.6	6.99%	17.7	214	14.1%	12.1	3.35	2.54%	1.55	1.14%	2.5	101	4.86%	41.2
serine	21.4	9.61%	1.8	2.14%	8.5	1.94%	10.6	108	7.10%	10.2	3.63	2.75%	1	0.73%	2.3	214	10.3%	92.4
threonine	14.8	6.65%	28.2	33.5%	56.7	12.9%	33.2	111	7.30%	3.3	2.23	1.69%	0.49	0.36%	1.4	0	0.00%	—
aspartic acid	12.5	5.61%	0.66	0.78%	42.1	9.61%	18.4	170	11.2%	9.2	3.59	2.72%	2.65	1.95%	3.1	386	18.6%	123.7
Proteinogenic:	188.7	84.7%	61.6	73.1%	397	90.7%	215.8	1,464	96.0%	6.8	65.0	48.3%	64.0	46.8%	64.9	2,059	99.0%	
α-isovaline	9	4.04%	6.3	7.47%	6.8	1.55%	7.4	0.2	0.01%	0.03	21.8	16.5%	21	15.4%	21.4	0.1	0.00%	0.0
α-aminoisobutyric acid (α-AIB)	4.6	2.07%	5.6	6.64%	5.2	1.19%	5.1	1	0.07%	0.19	11.4	8.65%	10.4	7.64%	10.9	0.1	0.00%	0.0
γ-amino-n-butyric acid + D,L-β-AIB	3.9	1.75%	1.4	1.66%	6	1.37%	3.8	25.2	1.65%	6.69	2.4	1.82%	2	1.47%	2.2	4.9	0.24%	2.2
β-alanine	3.4	1.53%	0.9	1.07%	10	2.28%	4.8	26	1.71%	5.45	6	4.55%	16	11.8%	11	8	0.38%	0.7
δ-5-apa	2.6	1.17%	1	1.19%	1.8	0.41%	1.8	0.01	0.00%	0.01	1.8	1.37%	2.2	1.62%	2.0	0	0.00%	0.0
γ-D,L-4-apa	2.1	0.94%	0.8	0.95%	0.7	0.16%	1.2	0.01	0.00%	0.01	2.9	2.20%	0.9	0.66%	1.9	0	0.00%	0.0
γ-D,L-4-a-2-mba	2.1	0.94%	1	1.19%	1.1	0.25%	1.4	0.01	0.00%	0.01	2.1	1.59%	1.56	1.15%	1.8	0	0.00%	0.0
D,L-α-amino-n-butyric acid	1.8	0.81%	1.4	1.66%	2.9	0.66%	2.0	4	0.26%	1.97	2	1.52%	2.4	1.76%	2.2	0.7	0.03%	0.3
β-3-a-3-mba	1.3	0.58%	0.47	0.56%	1	0.23%	0.9	0.01	0.00%	0.01	4.76	3.61%	5.2	3.82%	5.0	0	0.00%	0.0
α-norvaline (L-2-apa)	1.01	0.45%	1	1.19%	0.31	0.07%	0.8	0.25	0.02%	0.32	0.15	0.11%	0.5	0.37%	0.3	0	0.00%	0.0
β-amino-n-butyric acid	0.59	0.26%	0.38	0.45%	0.64	0.15%	0.5	1.08	0.07%	2.01	3.4	2.58%	2.4	1.76%	2.9	6	0.29%	2.1
β-3-a-2,2-dmpa	0.47	0.21%	0.18	0.21%	0.17	0.04%	0.3	1	0.07%	3.66	1.9	1.44%	1.73	1.27%	1.8	0	0.00%	0.0
ε-amino-n-caproic acid (EACA)	0.4	0.18%	0.7	0.83%	1.8	0.41%	1.0	1.4	0.09%	1.45	2.2	1.67%	2.2	1.62%	2.2	0	0.00%	0.0
γ-D,L-4-a-3-mba	0.31	0.14%	0.06	0.07%	0.04	0.01%	0.1	0.01	0.00%	0.07	0.42	0.32%	0.07	0.05%	0.2	0	0.00%	0.0
β-D,L-3-apa	0.27	0.12%	0.6	0.71%	0.9	0.21%	0.6	0.5	0.03%	0.85	2.7	2.05%	2.5	1.84%	2.6	0	0.00%	0.0
β-D,L-3-a-2-epa	0.1	0.04%	0.1	0.12%	0.1	0.02%	0.1	0.1	0.01%	1.00	0.3	0.23%	0.3	0.22%	0.3	0	0.00%	0.0
β-D,L- and allo-3-a-2-mba	0.04	0.02%	0.8	0.95%	1.4	0.32%	0.7	0.01	0.00%	0.01	0.29	0.22%	0.3	0.22%	0.3	0	0.00%	0.0
Non-Proteinogenic:	34.0	15.3%	22.7	26.9%	41.0	9.3%	32.5	60.8	4.0%		70.0	50.5%	73.0	52.6%	69.1	19.8	0.95%	
Total:	223	100%	84.3	100%	438	100%	248	1,523	100%		132	100%	136	100%	134	2,079	100%	

contamination from soil but not from collection, storage, and/or handling of the samples.

As a rule, much or most AA identified in meteorites were not present as such but created through hydrolysis of carboxylic acid amides, hydroxy acid amides, lactams, carboxylactams, N-acetylamino acids, substituted hydantoins, and other chemicals from the meteorites.[1]

The laboratory processes of grinding the samples to a powder followed by high-temperature extraction with very acidic water would not have occurred naturally, but presumably hydrolysis may have occurred given enough time.

The data in table 1 often shows considerable variation for the same AA across the samples. Therefore, we

Table 3. Comparison of % L-enantiomer for amino acids obtained from Aguas Zarcas meteorite fragments (average value) and the nearby soil. Data were calculated from entries in table 1.

	UA 2741, 0.08 g			UA 2741, 0.5 g			UA 2746, 0.52 g				UA soil			Mur. 0.08			Mur. 1 g				Mur. soil		
Proteinogenic AA	L	D	% L	L	D	% L	L	D	% L	Aver. L	L	D	% L	L	D	% L	L	D	% L	Aver. L	L	D	% L
alanine	18.4	3.7	83.3%	3.5	1.6	68.6%	38	17	69.1%	73.7%	213	74.3	74.1%	3	2.2	57.7%	8.2	8.3	49.7%	53.7%	356	47	88.3%
glutamic acid	19.7	2.2	90.0%	3.7	0.59	86.2%	36	10.3	77.8%	84.7%	119	28	81.0%	6.3	1.03	85.9%	7.6	2.7	73.8%	79.9%	269	19	93.4%
valine	20.1	0.92	95.6%	1.2	0.35	77.4%	27	3.6	88.2%	87.1%	204	10	95.3%	2.8	0.55	83.6%	0.93	0.62	60.0%	71.8%	97	4	96.0%
serine	18	3.4	84.1%	1.5	0.3	83.3%	6.6	1.9	77.6%	81.7%	91.3	16.9	84.4%	3.5	0.13	96.4%	0.6	0.4	60.0%	78.2%	199	15	93.0%
threonine	14.8	0.01	99.9%	28	0.2	99.3%	56	0.7	98.8%	99.3%	107	4.2	96.2%	2.21	0.02	99.1%	0.32	0.17	65.3%	82.2%	0	0	–
aspartic	10.1	2.4	80.8%	0.5	0.16	75.8%	27	15.1	64.1%	73.6%	120	50	70.6%	3	0.59	83.6%	1.7	0.95	64.2%	73.9%	314	72	81.3%
Non-proteinogenic AA																							
α-isovaline	5	4	55.6%	3.5	2.8	55.6%	3.9	2.9	57.4%	56.2%	0.1	0.1	50.0%	11.8	10	54.1%	11.5	9.5	54.8%	54.4%	0	0.1	–
α-norvaline (L-2-apa)	0.56	0.45	55.4%	0.5	0.5	50.0%	0.16	0.15	51.6%	52.4%	0.17	0.08	68.0%	0.05	0.1	33.3%	0.25	0.25	50.0%	41.7%	0	0	–
β-amino-n-butyric acid	0.26	0.33	44.1%	0.19	0.19	50.0%	0.3	0.34	46.9%	47.0%	0.6	0.48	55.6%	1.6	1.8	47.1%	1.2	1.2	50.0%	48.5%	0	6	–

combined the L- and D-enantiomer concentrations to facilitate a comparison of relative concentrations, leading to the data shown in table 2.

The data in table 2 suggested to us a correlation between [proteinogenic AA] from soil and the fragments. We focused on the Aguas Zarcas data, since all the analyses had been performed by the same team and under very similar conditions. $[\mathrm{AA}]_{\mathrm{soil}}$ vs average $[\mathrm{AA}]_{\mathrm{meteorite}}$ for all cases where $[\mathrm{AA}]_{\mathrm{soil}} > [\mathrm{AA}]_{\mathrm{meteorite}}$ was plotted as shown in figure 1. A convincing correlation was found ($R^2 = 0.81$). Noteworthy from the regression equation is that the Y-intercept ≈ 0; i.e., when AAs were absent in the soil,

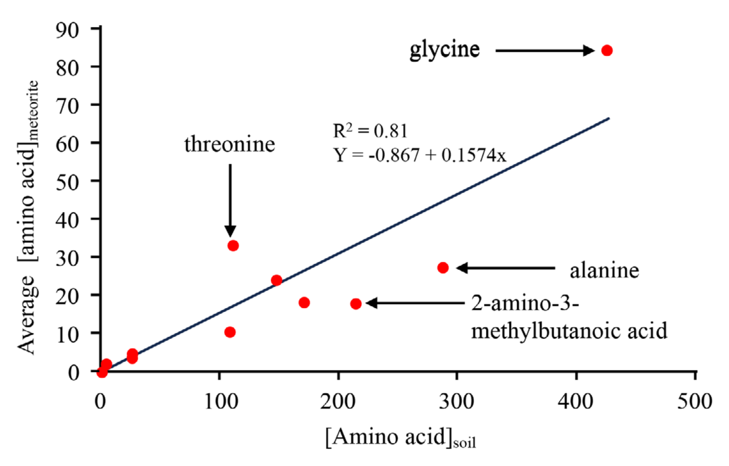

Figure 1. Concentration of AA (in nmol/g sample) in soil vs the average of three fragments from the Aguas Zarcas meteorite. Data from table 2.

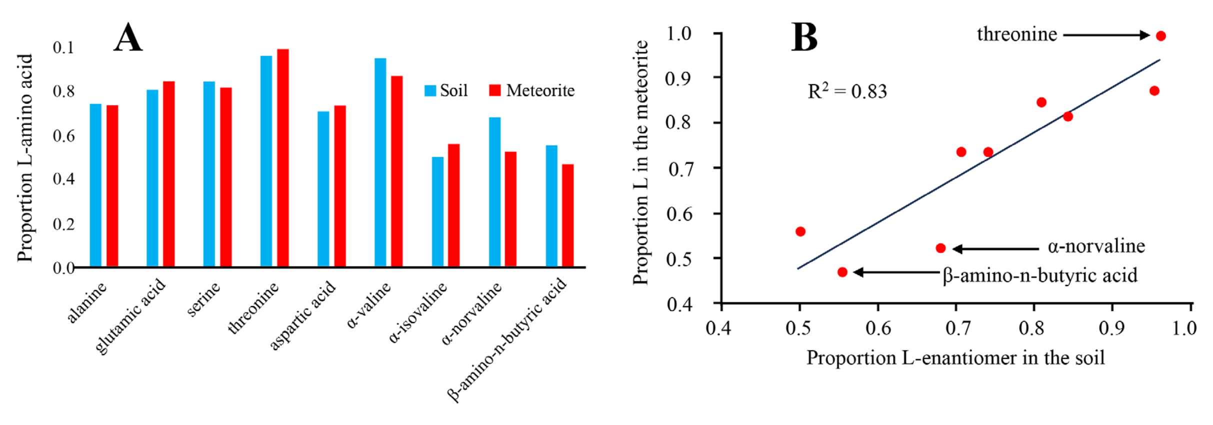

Figure 2. Comparison of proportion L-amino acid in Aguas Zarcas meteorite fragments (average value) vs from nearby soil. Data from table 3.

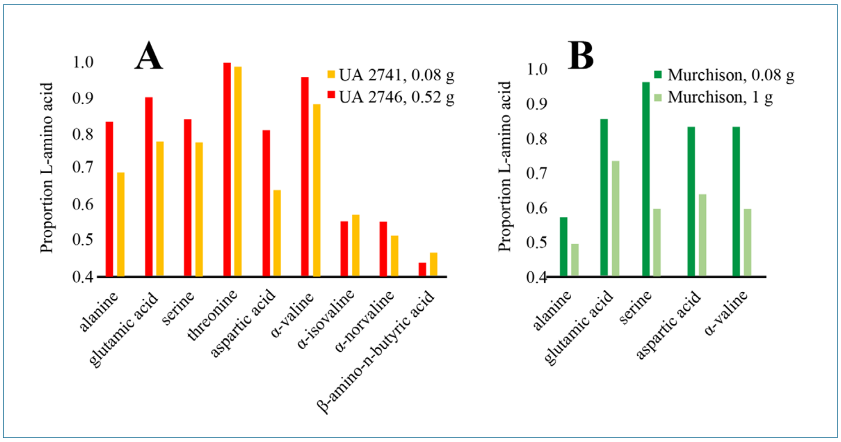

Figure 3. Comparison of A: % L-amino acids from two fragments from the Aguas Zarcas meteorite and B: both aliquots from the Murchison meteorite. Data taken from table 3.

almost none would have been found in the meteorite sample! *This suggested that very little AA would have been indigenous to the meteorite.*

Glycine, threonine, alanine and 2-amino-3-methylbutanoic acid were fairly distant from the correlation line but also had more than a 10-fold discrepancy in [AA] across the three samples.

The correlation might improve considerably if the average of several soil samples could be used, all *adjacent to the meteorite fragment analyzed*.

According to the data in table 2, the soil sample from the Murchison site contained about 33% more proteinogenic AA than the soil from the Aquas Zarcas site, whereas, on average, the Aquas Zargaes meteorite fragments contained >3 times more proteinogenic AA. Also noteworthy is that the two Murchison aliquots contained about the same total concentration of proteinogenic AA (62 vs 62.9 nmol/g), whereas for the Aguas Zarcas, they ranged from 60–367 nmol/g (columns 2, 4, and 6).

Major contamination could explain these observations: Aquas Zarcas in Costa Rica is a very humid region (unlike Murchison, Australia); much more AA could have dissolved and transferred to the meteorite fragments; for example, from morning dew. This would also explain why 4 of the 6 proteinogenic AA from the two Murchison aliquots had only 1.4–8.8 nmol/g on average, compared to 10.6–24.2 for the same AA for the three Aquas Zarcas fragments.

The concentrations of non-proteinogenic AA are very low in the meteorite and soil samples; usually ≤1 nmol/g in soil samples, as shown in table 1. β-alanine was the non-proteinogenic AA found in highest concentration in both soil samples (β-alanine is produced naturally by many organisms). Were the three UA meteorite samples contaminated? Perhaps, and to different degrees, since the concentrations measured varied from 0.9 to 10 nmol/g.

One way to test the plausibility that most of the AA was contamination from soil would be to compare % L-enantiomer from the fragments and soil. The data is shown in table 3 and plotted in figure 2.

A convincing correlation is apparent in figure 2-A and 2-B ($R^2 = 0.83$). Absent contamination, there is no apparent reason why excess L-AA manufactured biosynthetically would correlate so well with L-AA produced abiotically in space. Considerable contamination is the most parsimonious explanation. For example, the L-enantiomer for β-amino-n-butyric acid had a low mean value of 47% but a high mean value of >99.3% for threonine in the meteorite samples. The values measured in the soil sample (55.6% and 96.2%, respectively) matched these within experimental error.

In figure 3, the proportions of L-amino acids were compared for different fragments and aliquots. Systematic trends can be observed, where the L-enantiomer was almost always more abundant in the same sample. This could be explained by different amounts of contamination and also emphasizes a concern that the proportion of L-enantiomers could differ significantly between even nearby soil samples.

Analysis of $^{13}C/^{12}C$ isotope ratios

The proportion of ^{13}C and ^{12}C isotopes tends to be very different for terrestrial vs extra-terrestrial organic material, expressed as $\delta^{13}C$ values:

where

$\delta^{13}C$ is the reported value (e.g., –5‰ or –20‰; ‰ means parts per thousand),

R_{sample} is the $^{13}C/^{12}C$ ratio in the sample,

$R_{standard}$ is the $^{13}C/^{12}C$ ratio in the standard reference material, usually traceable to Vienna Pee Dee Belemnite (VPDB) for carbon isotopes.[2]

Typically, terrestrial organic carbon has a range of about –6‰ to –40‰ (Bowen 1988).[3]

Table 2 shows that about 6 times more proteinogenic AA was measured in UA 2746 than in the UA 2741 0.5 gm aliquot. Significantly, according to table 3 in reference 1, the $\delta^{13}C$ values of the proteinogenic AA examined in UA 2746 and nearby soil matched significantly, implying that most was due to contamination. However, the same proteinogenic AA from UA 2741 (which contained far less AA than in UA 2746) typically had high $\delta^{13}C$ values outside the range usually found on the earth, but their *L-enantiomers had lower* $\delta^{13}C$ values. Recalling that the concentration of L-enantiomers for these AA had been much higher than the D-enantiomers (table 2), and that very high L proportions had been found (table 3), all these facts strongly imply that much less (but still a significant amount of) contamination had occurred for the UA 2746 sample.

Take home messages

Glavin *et al.* also concluded that a considerable amount of contamination had occurred, especially for the Aguas Zarcas fragments, but did not provide an estimate of how much. In fact, plant material could clearly be seen attached to one of the fragments analyzed.

Very little terrestrial contamination from any sources would be necessary to account for a major fraction of the AA measured in meteorite samples. Using the data in table 2 and assuming a molecular weight of ≈ 100 for the proteinogenic AA shows that, on average, the Aguas Zarcas fragments contained only ≈ 20 ppm AA, and the Murchison fragments ≈ 6 ppm, by weight.

Soil samples include soluble racemizing peptide segments from dead organisms in addition to potentially very different living local biota. Proper quantification of contamination would require multiple soil samples to be collected as close as possible to each meteorite fragment. The average absolute and relative proportions of AA from the soils, their isotope ratios, and relative solubilities would need to be determined.

Although the Aguas Zarcas samples had been collected within days of landing and before rainfall, the data suggests that perhaps ≈ ⅒ of the moles of biological chemicals found (primarily proteinogenic AA) were extra-terrestrial. Alternatively, nonproteinogenic AA, like α-AIB and isovaline, were probably entirely extra-terrestrial. Since virtually all the literature reports AA from old meteorite landings, correcting for considerable amounts of contamination would:

- Eliminate all or most claims of extra-terrestrial excess of L-enantiomers.
- Decrease, significantly, the amount of proteinogenic AA delivered by meteorites.
- Raise, significantly, *the proportion of non-proteinogenic AA* delivered. Furthermore, hundreds of non-proteinogenic AA detected in Murchison samples have not been characterized yet[1] and would also have interfered with forming biological-like peptides.

References

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