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Amino acid analysis in micrograms of meteorite sample by nanoliquid chromatography–high-resolution mass spectrometry

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ABSTRACT

Amino acids and their enantiomers in a 360 microgram sample of Murchison meteorite were unambiguously identified and quantified using chemical derivatization and nanoliquid chromatography coupled to nanoelectrospray ionization high resolution orbitrap mass spectrometry techniques. The distribution and abundance of amino acids were similar to past studies of Murchison meteorite but the samples used here were three orders of magnitude lower. The analytical method was also highly sensitive, and some amino acid reference standards were successfully detected at a level of ~200 attomoles (on column). These results may open up the possibility for investigating other less studied, sample-limited extraterrestrial samples (*e.g.*, micrometeorites, interplanetary dust particles, and cometary particles) for biologically-relevant organic molecules

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1. Introduction

Most meteorites are fragments of asteroids; therefore, laboratory analyses of meteorites can provide a window into the extraterrestrial organic chemistry that took place during the formation of the solar system. Carbonaceous chondrites, a rare class of chondritic meteorites, have been found to be the most complex in terms of organic composition. Among the organics in carbonaceous chondrites, a diverse suite of over 100 amino acids have been detected [1,2]. Amino acids, the monomers of peptides and proteins, are essential in modern life and were most likely critical for nascent biochemistry. Additionally, nitrogen heterocycles [3–5], sugar-related organic compounds [6], and (potential) metabolic precursors [7,8] have also been identified in carbonaceous chondrites. The detection of numerous biologically-relevant organic compounds in carbonaceous chondrites has led to the assertion that these meteorites delivered important organics for the origin of life on the early Earth (and elsewhere). However, this belief has been criticized by many researchers based on estimates of carbonaceous meteorite flux (being relatively low compared to other extraterrestrial material) [9] coupled to the observations of low abundances of meteoritic organic compounds—typically in the parts-per-billion (ppb) to parts-per-million (ppm) concentration range [10].

Micrometeorites ($<10^{-4}$ g) and interplanetary dust particles (IDPs) ($<10^{-6}$ g) represent the present day dominant source of extraterrestrial material delivered to Earth [11,12], and these sources were more likely to have provided a steady-state flux and more significant quantities of prebiotic reagents to the early Earth compared to carbonaceous chondrites [9]. Unfortunately, there have been limited studies examining their organic composition [13–20], especially with regard to biologically-relevant molecules that may have been important for the origin of life [21,22], due to the miniscule size of these samples. Thus, it would be highly desirable to have analytical instrumentation and methods that could address these issues. Here, we demonstrate the chiral separation, identification, and quantitation of amino acids in an extraction of 360 micrograms of the well-characterized Murchison meteorite, which serves as an analog for future micrometeorite/IDP studies. This was achieved by using a nanoliquid chromatograph (nano-LC) coupled to a linear ion trap–orbitrap hybrid mass spectrometer *via* a nanoelectrospray ionization (nano-ESI) source. These instruments represent the current state-of-the-art for laboratory analytical science but have been underutilized in the analysis of organics in extraterrestrial materials.

In this study, the nano-LC primarily serves two purposes. The first is to perform efficient separation of chiral amino acids. To achieve this, we employ a precolumn chiral derivatization of primary amines using *o*-phthaldialdehyde/*N*-acetyl-L-cysteine

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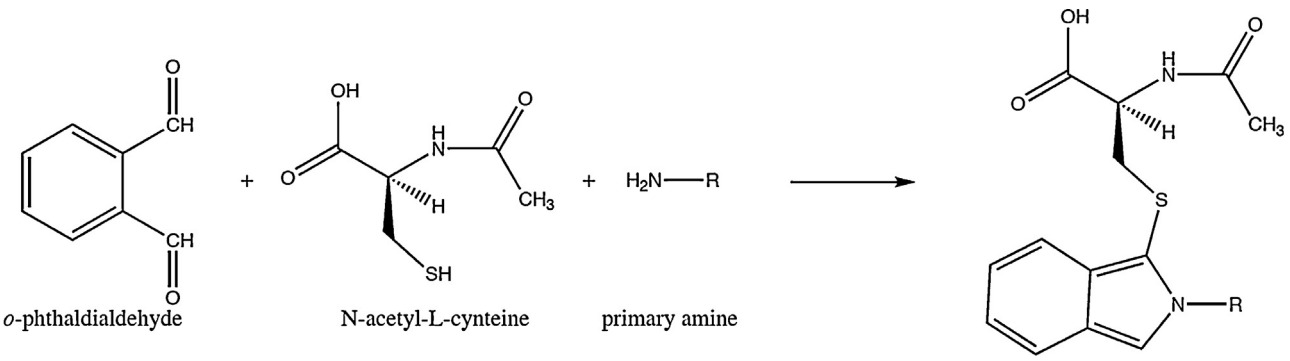

Figure 1. The chemical derivatization scheme to produce OPA/NAC amino acid derivatives.

(OPA/NAC) so that the resulting diastereomer products (Figure 1) can be separated using a nonchiral chromatography column [23]. The second purpose is to deliver the necessary low flow rates required for the efficient operation of a nano-ESI source.

Since its introduction, nano-ESI has enabled extremely high sensitivity mass spectrometry (in part) due to the reduced droplet size compared to conventional electrospray ionization [24–27]. This high sensitivity along with the excellent mass accuracy (<2 ppm), high mass resolution (>30,000 m/Δm), and MS/MS data afforded by the linear ion trap–orbitrap mass spectrometer significantly aids in the accurate identification and quantitation of targeted and unknown molecules in complex samples such as meteorites.

Our analytical method was first optimized using selected amino acid standards before being applied to an acid-hydrolyzed, hot water extract of a powdered sample of the Murchison meteorite.

2. Experiments

2.1. Chemicals and reagents

All of the chemicals used in this study were purchased from Sigma-Aldrich, Fisher Scientific, and Acros Organics. To prepare amino acid stock solutions (~10^{-3} M), individual compounds were dissolved in ultrapure water (18.2 MΩ·cm, < 3 ppb total organic carbon provided by a Millipore Milli-Q Integral 10 system). These solutions were then combined to enable their measurement in a single chromatographic separation. Serial dilutions (10^{-6} M to 10^{-10} M) were prepared for generation of the calibration curves. Ultrapure water was used exclusively for this study.

The OPA/NAC reagent used for amino acid derivatization was prepared by mixing 300 μL 0.01 M OPA (in methanol) with 15 μL 1 M NAC and 685 μL 0.1 M sodium borate buffer (pH 9) [28]. Solutions of sodium borate were prepared from solid sodium tetraborate decahydrate (Sigma Ultra 99.5–100% purity) that was heated in air at 500 °C for 3 h to remove any organic contaminants prior to dissolution in water. A 0.1 M hydrazine (NH_2NH_2) solution was prepared by double vacuum distillation of anhydrous hydrazine (98% purity) and subsequent dilution in water. The 6 M HCl solution for the acid hydrolysis procedure was also prepared by double vacuum distillation and subsequent dilution in water. For the LC–MS analyses, ammonium formate buffer was prepared by NH_4OH titration of a 10 mM formic acid solution to pH 8.3 and then methanol was added to a final concentration of 5% (v/v). Methanol was Optima® grade from Fisher Scientific.

2.2. Sample handling and extraction procedures

Several interior pieces of the Murchison meteorite (USNM 5453) were provided by the Smithsonian National Museum of Natural History. No fusion crust was observed on these meteorite samples. Sample-handling tools, ceramics, and glassware were all rinsed with ultrapure water, wrapped in aluminum foil, and heated in air at 500 °C for 24 h to remove any organic contaminants. The Murchison meteorite was crushed into a fine powder using a clean mortar and pestle in a Class 100 laminar flow hood (Labconco) under high-efficiency particulate air filtered positive pressure.

We weighed 360 micrograms (arbitrary mass, but in the range of an individual micrometeorite) of Murchison meteorite into a tared glass ampoule using a Mettler Toledo XP56 microbalance. We added 1 mL water to the glass ampoule before it was flame-sealed and placed in an oven set at 100 °C for 24 h. After extraction, the ampoule was cooled, centrifuged for 5 min (Labconco CentriVap) to separate the solid particulate from water supernatant, and then opened. The water supernatant was transferred into a separate glass tube, dried under vacuum and subjected to acid hydrolysis under 6 M HCl vapor at 150 °C for 3 h to liberate any "bound" amino acids. The acid-hydrolyzed extract (representing the total amino acid content) was dried under vacuum (LabConco Centrivap) and redissolved in 1 mL of water. The extract was then desalted by cation exchange column (AG 50W-X8, 100–200 mesh, hydrogen form, BIO-RAD) using water followed by 2 M NH_4OH. The NH_4OH eluate was dried under vacuum and redissolved in 100 μL water. This meteorite extract was stored in a -20 °C freezer until precolumn derivatization and LC–MS analysis.

2.3. Chemical derivatization

For OPA/NAC amino acid derivatization, 10 μL meteorite extract (or amino acid standard solution) was mixed with 10 μL 0.1 M sodium borate buffer (pH 9) and derivatized with 5 μL OPA/NAC in an HPLC vial. The derivatization reaction was then quenched after 15 min at room temperature with 75 μL 0.1 M hydrazine.

2.4. Nano-LC-high resolution MS analysis

OPA/NAC amino acid derivatives were analyzed using a Waters nano-ACQUITY Ultra Performance LC (UPLC) coupled to a Thermo Scientific LTQ Orbitrap XL hybrid mass spectrometer. Amino acid separation was achieved with a Waters nano-Acquity UPLC column (150 μm × 100 mm, 1.7 μm BEH130 C18) maintained at 30 °C. The mobile phase consisted of (A) 10 mM ammonium formate buffer with 5% methanol, pH 8.3 and (B) methanol. The composition of the mobile phase changed by adding increasing proportions of (B) as follows: 0–2 min 5% B, 2–10 min 5–10% B, 10–50 min 10–50% B, 50–51 min 50–5% B, 51–70 min 5% B. A flow rate of 1.5 μL/min was used. Samples were injected into a 2 μL loop. During initial method development for the chromatographic separation of amino acids, we coupled the nano-LC to a laser induced fluorescence (LIF) detector (Picometrics ZetaLIF, excitation wavelength 355 nm, total emission collection) because the OPA/NAC amino acid

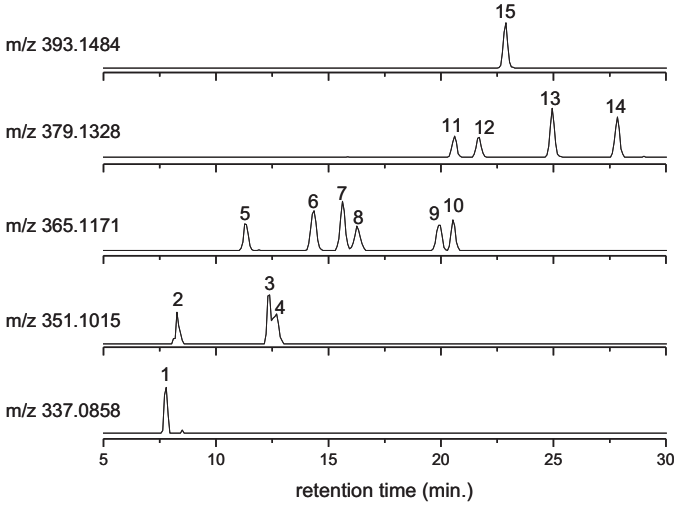

Figure 2. Extracted ion chromatograms (5 ppm mass window) of OPA/NAC derivatives of amino acid standards using a 10^{-9} M solution (2 μL injection volume). The amino acids are: glycine (1), β-alanine (2), D-alanine (3), L-alanine (4), γ-amino-*n*-butyric acid (5), D-β-amino-*n*-butyric acid (6), L-β-amino-*n*-butyric acid (7), α-aminoisobutyric acid (8), D-α-amino-*n*-butyric acid (9), L-α-amino-*n*-butyric acid (10), D-isovaline (11), L-isovaline (12), L-valine (13), D-valine (14), and ε-amino-*n*-caproic acid (15).

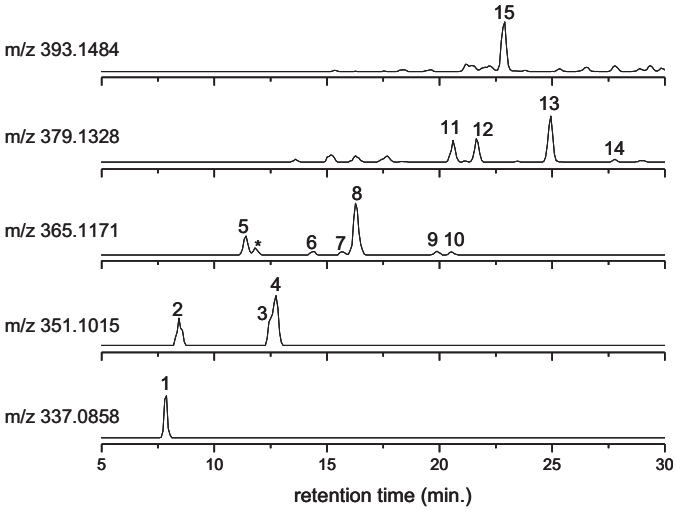

Figure 3. Extracted ion chromatograms (5 ppm mass window) of OPA/NAC derivatives of amino acids from a 360 microgram sample of Murchison meteorite. The amino acids are: glycine (1), β-alanine (2), D-alanine (3), L-alanine (4), γ-amino-*n*-butyric acid (5), D-β-amino-*n*-butyric acid (6), L-β-amino-*n*-butyric acid (7), α-aminoisobutyric acid (8), D-α-amino-*n*-butyric acid (9), L-α-amino-*n*-butyric acid (10), D-isovaline (11), L-isovaline (12), L-valine (13), D-valine (14), and ε-amino-*n*-caproic acid (15). The * represents D,L-β-aminoisobutyric acid, which was not in our reference standard; however, we assign this peak based on previous analyses of the Murchison meteorite [2].

derivatives are highly fluorescent. Once we had adequate separation, we removed the LIF detector for the tandem mass spectrometer so that we minimized the number of connections between instruments to minimize peak broadening.

A Thermo Scientific nano-ESI source was equipped with a metal coated 30 μm emitter tip (coating P200P, New Objective) and a voltage of 1.3 kV was applied directly to the emitter tip to produce a stable spray. The ion transfer capillary voltage and ion transfer capillary temperature were 7 V and 250 °C, respectively. The tube lens was set at 70 V. No gases were used for desolvation. Full scan spectra were acquired over a mass range of *m/z* 200 to 600. To maintain a sufficient number of data points across chromatographic peaks, a mass resolution setting of 30,000 (at full-width-half-maximum for *m/z* 400) was used. Automated gain control (AGC) was set to 5×10^5 ions with a maximum injection time of 1 s. External calibration for positive ion mode in the range of *m/z* 120 to 2000 was performed using a mixture of caffeine, MRFA (L-methionyl-arginyl-phenylalanyl-alanine acetate hydrate) peptide, and Ultramark 1621 in an acetonitrile-methanol-water solution containing 1% acetic acid. A polysiloxane compound (*m/z* 371.10124, $[(C_2H_6SiO)_5 + H]^+$) found in ambient air was used as an internal lock mass, which resulted in a typical mass accuracy of 0.3 ppm.

Amino acids in the Murchison meteorite extract were identified by (1) correlating sample compounds with known standards at the experimentally determined chromatographic retention times and (2) comparing accurate mass measurements with theoretical exact masses of the OPA/NAC amino acid derivatives. Elemental compositions were calculated from the $[M + H]^+$ protonated molecule with introduced limits of carbon (0–30), hydrogen (0–60), nitrogen (0–10), oxygen (0–15), and sulfur (0–1) and a mass tolerance of 1 ppm. With these elemental limits, sub-ppm mass accuracy is required for the unambiguous assignment of molecular formulae

Table 1
Summary of mass measurement data for OPA/NAC derivatives of amino acids extracted from a 360 microgram sample of Murchison meteorite. An internal lock mass was used so that the mass accuracy was routinely sub-ppm, which led to an unambiguous assignment of molecular formula. Molecular formulae correspond to protonated molecules. The relative mass error, in ppm, is calculated as $10^6 \times (mass_{experimental} - mass_{theoretical})/mass_{theoretical}$). The relative concentrations of amino acids are listed in parts-per-billion (ppb). The * represents D,L-β-aminoisobutyric acid, which was not in our reference standard; however, we assign this peak based on previous analyses of the Murchison meteorite [2].

Peak #	Compound (as OPA/NAC derivative)	Measured Mass $[M + H]^+$	Theoretical Mass $[M + H]^+$	Molecular Formula	Mass Error (ppm)	Mass Resolution	Relative Concentration (ppb)
1	glycine	337.08529	337.08527	$C_{15}H_{17}N_2O_5S$	0.06346	38435	1795
2	β-alanine	351.10102	351.10092	$C_{16}H_{19}N_2O_5S$	0.30026	39011	674
3	D-alanine	351.10098	351.10092	$C_{16}H_{19}N_2O_5S$	0.16520	38684	369
4	L-alanine	351.10097	351.10092	$C_{16}H_{19}N_2O_5S$	0.15167	38788	789
5	γ-aminobutyric acid	365.11661	365.11657	$C_{17}H_{21}N_2O_5S$	0.12405	37369	362
*	D,L-β-aminoisobutyric acid	365.11671	365.11657	$C_{17}H_{21}N_2O_5S$	0.38663	37678	n/a
6	D- β- aminobutyric acid	365.11671	365.11657	$C_{17}H_{21}N_2O_5S$	0.39716	36748	42
7	L- β- aminobutyric acid	365.11668	365.11657	$C_{17}H_{21}N_2O_5S$	0.31100	38050	38
8	α- aminoisobutyric acid	365.11670	365.11657	$C_{17}H_{21}N_2O_5S$	0.35110	36780	1037
9	D- α- aminobutyric acid	365.11667	365.11657	$C_{17}H_{21}N_2O_5S$	0.26733	36875	67
10	L- α- aminobutyric acid	365.11672	365.11657	$C_{17}H_{21}N_2O_5S$	0.40890	38083	60
11	D-isovaline	379.13228	379.13222	$C_{18}H_{23}N_2O_5S$	0.14840	37094	625
12	L-isovaline	379.13227	379.13222	$C_{18}H_{23}N_2O_5S$	0.12378	36970	699
13	L-valine	379.13225	379.13222	$C_{18}H_{23}N_2O_5S$	0.07009	36899	648
14	D-valine	379.13236	379.13222	$C_{18}H_{23}N_2O_5S$	0.35894	38693	39
15	ε-aminocaproic acid	393.14790	393.14787	$C_{19}H_{25}N_2O_5S$	0.06607	34781	1099

corresponding to OPA/NAC derivatized amino acids; however, this requirement is relaxed (to ~3 ppm mass accuracy) if limits explicitly include the OPA/NAC label. Peak areas were obtained by either manual integration or the ICIS peak algorithm in the Xcalibur software package.

3. Results and Discussion

High-resolution/accurate-mass (HR/AM) extracted ion chromatograms of a standard mixture of amino acids using nano-LC coupled to linear ion trap–orbitrap mass spectrometry is shown in Figure 2. Our method was tested for the detection of 15 amino acids (including five chiral amino acid pairs) in 30 min. These amino acids are: glycine (1), β-alanine (2), D-alanine (3), L-alanine (4), γ-amino-*n*-butyric acid (5), D-β-amino-*n*-butyric acid (6), L-β-amino-*n*-butyric acid (7), α-aminoisobutyric acid (AIB) (8), D-α-amino-*n*-butyric acid (9), L-α-amino-*n*-butyric acid (10), D-isovaline (11), L-isovaline (12), L-valine (13), D-valine (14), and ε-amino-*n*-caproic acid (15). The amino acids AIB and D, L-isovaline have been previously viewed as particularly important target molecules since they are rare on Earth and their presence is a good indicator that there are some amino acids that are indigenous to the meteorite [29]. The linearity of calibration curves was verified over three orders of magnitude by using amino acid standard solutions with a concentration range from 10^{-6} to 10^{-9} M (see Supplementary Content). For some of the nonproteinogenic amino acids, we could detect 10^{-10} M solutions, which represent ~200 attomoles on column (taking into account the dilution from the derivatization reaction). Product ion spectra (or accurate masses of characteristic fragments) were used as additional confirmation of derivatized amino acids (see Supplementary Content).

Figure 3 and Table 1 show HR/AM extracted ion chromatograms and the mass measurement summary, respectively, of OPA/NAC amino acid derivatives measured in a hot water, acid-hydrolyzed extract of the Murchison meteorite. All 15 selected amino acids were detected in the Murchison meteorite despite extracting only 360 micrograms, and these results were consistent with previous analyses of Murchison using much larger samples (~200 milligrams or greater) and using other analytical techniques [2]. The most abundant amino acids were glycine (1.8 ppm), ε-amino-*n*-caproic acid (1.1 ppm), and α-aminoisobutyric acid (1.0 ppm). D- and L-β-amino-*n*-butyric acid and D- and L-α-amino-*n*-butyric acid were nearly racemic, which is suggestive of an extraterrestrial origin. The chromatographic resolution of D- and L-alanine was lower compared to other amino acids; therefore, it is difficult to quantitate these two amino acids. Despite this overlap, L-alanine is clearly in excess, which indicates that there may be some terrestrial L-alanine contamination of this Murchison meteorite sample. The very low D/L ratio (0.06) of valine also supports the notion that there is some terrestrial contamination in this particular Murchison meteorite sample. Finally, it is worth mentioning that L-isovaline, an α-methyl amino acid that is difficult to racemize, was measured at 5.6% enantiomeric excess. Although this experiment should be repeated for more accurate quantitation, the small L-enantiomeric excess falls within the range of previous results. Observations of L-enantiomeric excesses in meteoritic amino acids have spawned the hypothesis that amplification of cosmochemically L-biased amino acids [2,30–34] was the origin of homochirality in proteins. Thus, future investigations of micrometeorites and IDPs may bring additional insight into the ubiquity of chiral asymmetry in extraterrestrial materials.

As listed in Table 1, accurate mass measurements allowed for unambiguous assignment of molecular formulae (especially when using the chemical specificity provided by the addition of the primary amine reactive OPA/NAC derivatization group). The mass error on the orbitrap analyzer was consistently less than 0.5 ppm and the mass resolution was always greater than 34,000, which was significantly better than our previous analyses using a time-of-flight mass spectrometer (typical mass error >30 ppm and resolution ~5000 [35]). This high mass accuracy and high resolution also extends to any ion in the full scan spectrum. Thus, it becomes possible for queries to be raised about the data (postacquisitionally) with any theoretical mass and perform nontargeted screening with high specificity. Comparable analysis, for example, by multiple reaction monitoring using a triple quadrupole mass spectrometer would require independent optimization for each compound (assuming the standard is available or could be synthesized), which would take considerable time and cost to develop.

4. Conclusion

We have demonstrated that very small (microgram) meteorite samples can be extracted and analyzed for amino acids by nano-LC coupled to high resolution orbitrap mass spectrometry. The combination of chromatographic retention time and accurate mass measurements (<1 ppm error) allowed for the unambiguous identification of amino acids. Meteorite samples are finite and therefore precious commodities. Previous analytical methods for analyzing amino acids in meteorites typically required orders of magnitude more sample (*e.g.*, >0.2 g). This amount can represent a prohibitively large sample depending on the meteorite to be analyzed. For example, the entire collection of 16 CM1 meteorites in the Antarctic Meteorite Collection at NASA Johnson Space Center ranges from 26 grams (Meteorite Hills 01070) to 0.01 grams (LaPaz Ice Field 031252 and MacAlpine Hills 02869). Thus, our analytical method can enable the amino acid analyses of sample-limited meteorites that otherwise would go unanalyzed for these organic compounds. More importantly, our analytical method may open up the possibility for studying the organic composition of individual micrometeorites and, potentially, interplanetary dust particles and cometary particles, which are primarily analyzed by techniques focused on inorganic composition. Expanding the range of samples that can be analyzed will undoubtedly bring new insights in the distribution and abundance of amino acids (and other organics) and how these extraterrestrial materials could have influenced prebiotic chemistry and the origin of life on early Earth.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2014.01.032.

References

[1] J.R. Cronin, S. Pizzarello, Geochimica Et Cosmochimica Acta 50 (1986) 2419.
[2] D.P. Glavin, M.P. Callahan, J.P. Dworkin, J.E. Elsila, Meteoritics & Planetary Science 45 (2010) 1948.

[3] M.P. Callahan, K.E. Smith, H.J. Cleaves, J. Ruzicka, J.C. Stern, D.P. Glavin, C.H. House, J.P. Dworkin, Proceedings of the National Academy of Sciences of the United States of America 108 (2011) 13995.
[4] P.G. Stoks, A.W. Schwartz, Nature 282 (1979) 709.
[5] P.G. Stoks, A.W. Schwartz, Geochimica Et Cosmochimica Acta 46 (1982) 309.
[6] G. Cooper, N. Kimmich, W. Belisle, J. Sarinana, K. Brabham, L. Garrel, Nature 414 (2001) 879.
[7] G. Cooper, C. Reed, D. Nguyen, M. Carter, Y. Wang, Proceedings of the National Academy of Sciences of the United States of America 108 (2011) 14015.
[8] S. Pizzarello, Y.S. Huang, L. Becker, R.J. Poreda, R.A. Nieman, G. Cooper, M. Williams, Science 293 (2001) 2236.
[9] M. Pasek, D. Lauretta, Origins of Life and Evolution of Biospheres 38 (2008) 5.
[10] M.A. Sephton, Natural Product Reports 19 (2002) 292.
[11] S.G. Love, D.E. Brownlee, Science 262 (1993) 550.
[12] S. Taylor, J.H. Lever, R.P. Harvey, Nature 392 (1998) 899.
[13] S.J. Clemett, X.D.F. Chillier, S. Gillette, R.N. Zare, M. Maurette, C. Engrand, G. Kurat, Origins of Life and Evolution of Biospheres 28 (1998) 425.
[14] S.J. Clemett, C.R. Maechling, R.N. Zare, P.D. Swan, R.M. Walker, Science 262 (1993) 721.
[15] S.J. Clemett, S.A. Sandford, K. Nakamura-Messenger, F. Horz, D.S. McKay, Meteoritics & Planetary Science 45 (2010) 701.
[16] G.J. Flynn, L.P. Keller, M. Feser, S. Wirick, C. Jacobsen, Geochimica Et Cosmochimica Acta 67 (2003) 4791.
[17] G. Matrajt, S. Messenger, D. Brownlee, D. Joswiak, Meteoritics & Planetary Science 47 (2012) 525.
[18] G. Matrajt, S. Pizzarello, S. Taylor, D. Brownlee, Meteoritics & Planetary Science 39 (2004) 1849.
[19] G. Matrajt, S. Taylor, G. Flynn, D. Brownlee, D. Joswiak, Meteoritics & Planetary Science 38 (2003) 1585.
[20] S.A. Sandford, J. Aleon, C.M.O. Alexander, T. Araki, S. Bajt, G.A. Baratta, J. Borg, J.P. Bradley, D.E. Brownlee, J.R. Brucato, M.J. Burchell, H. Busemann, A. Butterworth, S.J. Clemett, G. Cody, L. Colangeli, G. Cooper, L. D'Hendecourt, Z. Djouadi, J.P. Dworkin, G. Ferrini, H. Fleckenstein, G.J. Flynn, I.A. Franchi, M. Fries, M.K. Gilles, D.P. Glavin, M. Gounelle, F. Grossemy, C. Jacobsen, L.P. Keller, A.L.D. Kilcoyne, J. Leitner, G. Matrajt, A. Meibom, V. Mennella, S. Mostefaoui, L.R. Nittler, M.E. Palumbo, D.A. Papanastassiou, F. Robert, A. Rotundi, C.J. Snead, M.K. Spencer, F.J. Stadermann, A. Steele, T. Stephan, P. Tsou, T. Tyliszczak, A.J. Westphal, S. Wirick, B. Wopenka, H. Yabuta, R.N. Zare, M.E. Zolensky, Science 314 (2006) 1720.
[21] K.L.F. Brinton, C. Engrand, D.P. Glavin, J.L. Bada, M. Maurette, Origins of Life and Evolution of Biospheres 28 (1998) 413.
[22] D.P. Glavin, G., Matrajt, J.L. Bada, in M.P. Bernstein, M., Kress, R. Navarro-Gonzalez (Editors), Space Life Sciences: Steps toward Origin(S) of Life, 2004, p. 106.
[23] M.X. Zhao, J.L. Bada, Journal of Chromatography A 690 (1995) 55.
[24] P.E. Andren, M.R. Emmett, R.M. Caprioli, Journal of the American Society for Mass Spectrometry 5 (1994) 867.
[25] M.R. Emmett, R.M. Caprioli, Journal of the American Society for Mass Spectrometry 5 (1994) 605.
[26] M. Wilm, M. Mann, Analytical Chemistry 68 (1996) 1.
[27] M.S. Wilm, M. Mann, International Journal of Mass Spectrometry 136 (1994) 167.
[28] D.P. Glavin, J.P. Dworkin, A. Aubrey, O. Botta, J.H. Doty, Z. Martins, J.L. Bada, Meteoritics & Planetary Science 41 (2006) 889.
[29] K.A. Kvenvolden, J.G. Lawless, C. Ponnamperuma, Proceedings of the National Academy of Sciences of the United States of America 68 (1971) 486.
[30] R. Breslow, Z.L. Cheng, Proceedings of the National Academy of Sciences of the United States of America 106 (2009) 9144.
[31] R. Breslow, M.S. Levine, Proceedings of the National Academy of Sciences of the United States of America 103 (2006) 12979.
[32] J.R. Cronin, S. Pizzarello, Science 275 (1997) 951.
[33] D.P. Glavin, J.P. Dworkin, Proceedings of the National Academy of Sciences of the United States of America 106 (2009) 5487.
[34] S. Pizzarello, J.R. Cronin, Geochimica Et Cosmochimica Acta 64 (2000) 329.
[35] M.P. Callahan, A.S. Burton, J.E. Elsila, E.M. Baker, K.E. Smith, D.P. Glavin, J.P. Dworkin, Meteoritics & Planetary Science 48 (2013) 786.