

Supplementary Information.

Supplementary Note 1:

Calculation of irradiation dose:

The irradiation dose is calculated by the equation 1 as given in [1]:

$$D = \frac{I \cdot t \cdot m}{e \cdot N_A \cdot \rho \cdot A \cdot d_{eff}} (E_0 - f_{trans} \cdot E_{trans} - f_{bs} \cdot E_{bs}) \quad (1)$$

where D is the irradiation dose in eV molecule⁻¹, with the current I in Amperes, the irradiation time t in seconds, the molecular mass of the molecule m in amu, the electron charge e in Coulomb, the Avogadro's constant N_A , the density of the ice ρ in gm cm⁻³, the irradiated area A in cm², and the initial electron energy E_0 in eV. The average penetration depth d_{eff} in cm, the fractions f_{trans} and f_{bs} , and the energies E_{trans} and E_{bs} of transmitted and backscattered electrons, respectively, were derived with the software Monte Carlo simulation of electron trajectory in solids (CASINO, v2.4.8.1)[2]. Since the f_{trans} and E_{trans} are extremely small in comparison to the other terms, they were not included in the energy calculation.

Supplementary Note 2:

Identification convention:

Due to the high complexity of energetically processed ice that can form during the irradiation, a combination of exact mass match, chromatographic separation and tandem mass spectrometry in combination with a standard was needed. Identification confidence follows the convention set in a previous article [3] and the analysis is described below:

Analysis procedure

To assess reproducibility, four independent samples were analyzed for exact mass and retention time match, whereas tandem mass spectrometry was performed on two independent samples. The amino acids, dipeptides and cyclic dipeptides searched for in this study is given in Supplementary Table 1. The analytical procedure is as follows:

- Exact mass match:

Exact masses were determined using "Free Style 1.8 SP2 QF1" software. The measured accurate masses agreed with the theoretical exact masses, with a mass accuracy within ± 3 ppm. Molecular formulas were assigned based on these accurate mass matches.

- Chromatographic separation and retention time match:

The corresponding ¹²C standards were analysed using the same chromatographic method as the samples. All compounds reported in this study exhibited retention times within ± 0.18 min of their corresponding standards, with most agreeing within ± 0.10 min (mean deviation = +0.01 min). Proline, cyclic glycylalanine, and valylalanine eluted at slightly greater retention times than their standards, whereas most other compounds exhibited small negative retention time shifts. For most m/z values,

multiple chromatographic peaks were observed in the sample extracts, consistent with the high molecular complexity of the residues and the presence of structural isomers.

The observed retention time shifts are comparable to those reported in previous co-elution studies of samples and authentic standards [4]. In the present work, the most likely source of the small deviations in retention time is matrix effects associated with the complex composition of the organic residues, which contain numerous co-eluting compounds, in contrast to the individually analysed pure standards. [5].

- Tandem mass spectrometry (MS²) match:

MS² spectra of the ¹²C-standards were first acquired at different collision energies to determine conditions that produced diagnostic fragment ions consistent with those reported in the literature [6, 7] and the NIST database. This optimization also enabled the identification of the correct retention time for the target compound when multiple peaks were present in the standard. Subsequently, MS² spectra of the samples were acquired at the selected collision energy and corresponding retention time immediately following UHPLC separation.

The MS² spectra of the samples contained all diagnostic fragments observed for the corresponding ¹²C-standard, supporting the unambiguous presence of the respective ¹³C-products shown in Figure 2 and Supplementary Figures 1-7. In cases where the retention time had larger deviation in comparison to standards or the fragmentation profiles did not appear similar to the ¹²C-standard, the detection was considered high confidence (those marked with an asterisk in Figure 3 and Supplementary Figures 8-10). The mismatch may be due to the signals originating from structurally similar isomers. Amino acids and dipeptides for which only the retention time matched the standard without the confirmation from MS², are reported as tentative matches (those marked with a double asterisk in Figure 3 and Supplementary Figures 11-19).

Due to the complexity of the sample matrix and the MS² isolation window (± 0.2 u), co-eluting compounds frequently interfered with fragmentation [8]. To verify fragment assignments in MS² spectra, their extracted ion chromatograms (EICs) were further examined. We show here one example for all threonine fragment ions with sufficient signal intensity, allowing fragments originating from threonine to be distinguished from interfering ions (Supplementary Figure 2 and 3). However, owing to the complexity of the mixture, this approach could not be applied systematically to all detected compounds. More comprehensive confirmation would require improved chromatographic separation.

Validation of product assignments and exclusion of contaminants

- Isotope labeling:

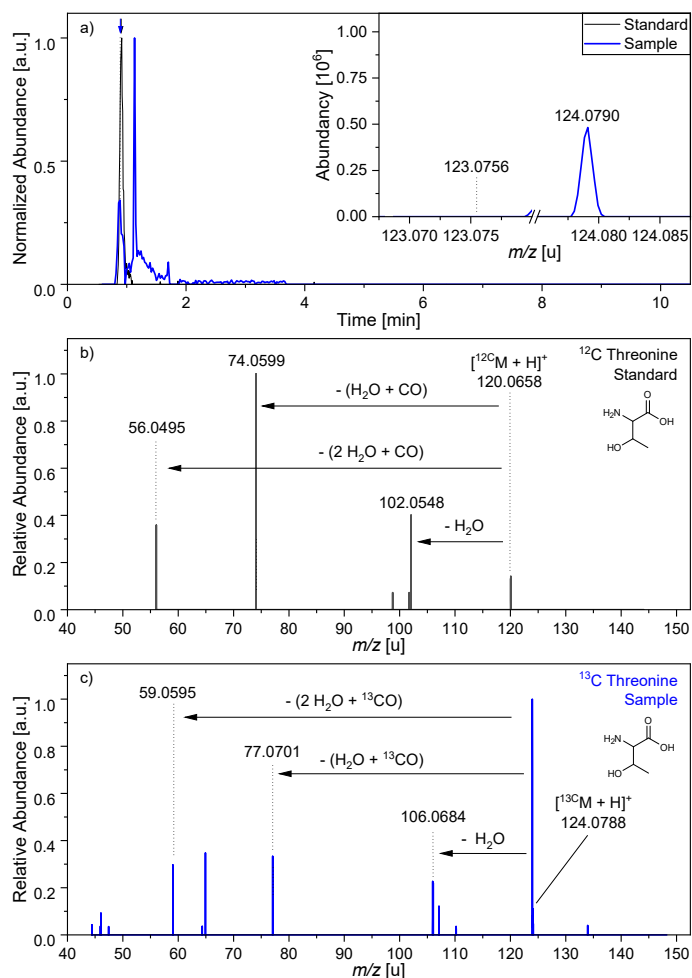
¹³C labelled ethanolamine was used as the precursor, enabling isotopic tracing of the resulting products. No partially ¹²C-labelled products were detected at abundances that would suggest significant biological contamination.

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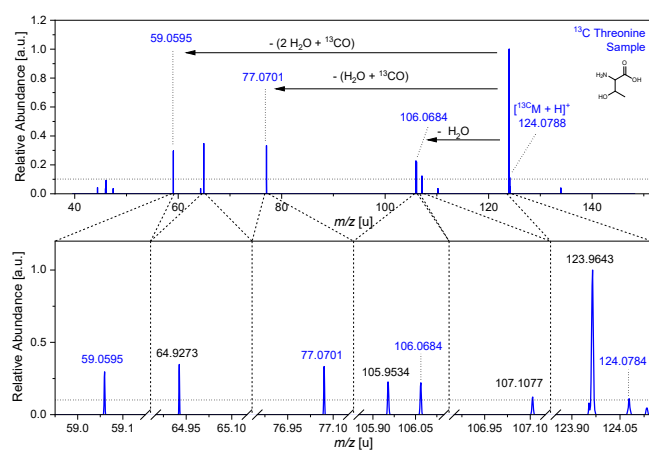
To further rule out any contamination, ¹³C-isotope-labeled ethanolamine was processed under identical conditions but without the irradiation step. Under these conditions, none of the investigated compounds were detected.

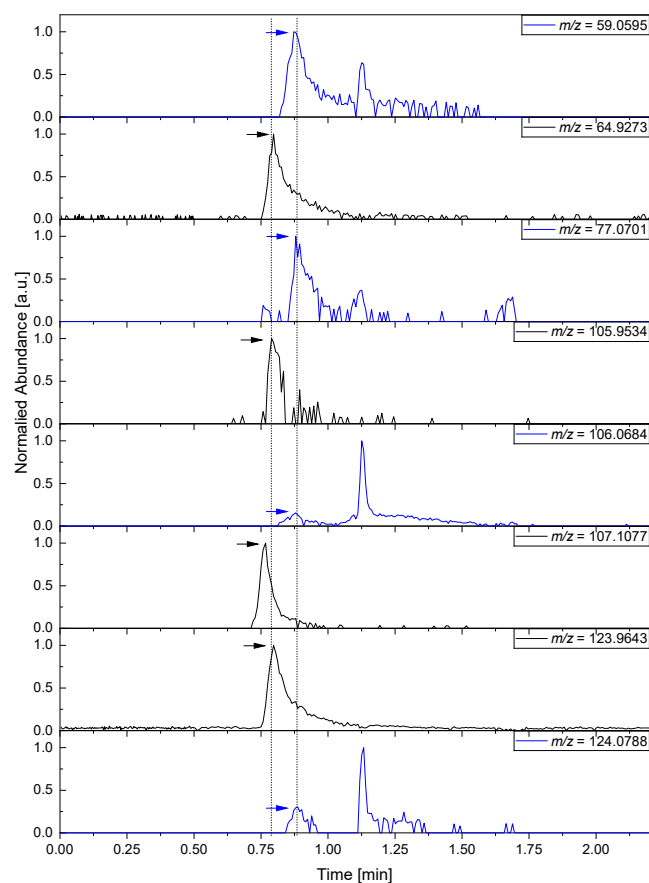
Table 1 Scope of experiment. List of commercially available amino acids, dipeptides and cyclic dipeptides which have been searched in this study.

Compound	Formula	^{12}C -Standard [$M + H$] $^{+}$	^{13}C -Sample [$M + H$] $^{+}$
Amino acids			
Glycine (Gly)	$\text{C}_2\text{H}_5\text{NO}_2$	76.0393	78.0460
Alanine (Ala)	$\text{C}_3\text{H}_7\text{NO}_2$	90.0550	93.0650
Serine (Ser)	$\text{C}_3\text{H}_7\text{NO}_3$	106.0499	109.0599
Proline (Pro)	$\text{C}_5\text{H}_9\text{NO}_2$	116.0706	121.0874
Valine (Val)	$\text{C}_5\text{H}_{11}\text{NO}_2$	118.0863	123.1030
Threonine (Thr)	$\text{C}_4\text{H}_9\text{NO}_3$	120.0655	124.0789
Iso/leucine (Ile/ Leu)	$\text{C}_6\text{H}_{13}\text{NO}_2$	132.1019	138.1220
Asparagine (Asn)	$\text{C}_4\text{H}_8\text{N}_2\text{O}_3$	133.0608	137.0742
Aspartic Acid (Asp)	$\text{C}_4\text{H}_7\text{NO}_4$	134.0448	138.0582
Glutamine (Gln)	$\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$	147.0764	152.0932
Lysine (Lys)	$\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2$	147.1128	153.1329
Glutamic Acid (Glu)	$\text{C}_5\text{H}_9\text{NO}_4$	148.0604	153.0772
Histidine (His)	$\text{C}_6\text{H}_9\text{N}_3\text{O}_2$	156.0768	162.0969
Phenylalanine (Phe)	$\text{C}_9\text{H}_{11}\text{NO}_2$	166.0863	175.1164
Arginine (Arg)	$\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$	175.1190	181.1391
Tyrosine (Tyr)	$\text{C}_9\text{H}_{11}\text{NO}_3$	182.0812	191.1114
Tryptophan (Trp)	$\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2$	205.0972	216.1341
Dipeptides			
Gly-Ala	$\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$	147.0764	152.0932
Ala-Gly	$\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$	147.0764	152.0932
Ala-Ala	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3$	161.0921	167.1122
Pro-Gly	$\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3$	173.0921	180.1156
Gly-Val	$\text{C}_7\text{H}_{14}\text{N}_2\text{O}_3$	175.1077	182.1312
Ala-Pro	$\text{C}_8\text{H}_{14}\text{N}_2\text{O}_3$	187.1077	195.1346
Pro-Ala	$\text{C}_8\text{H}_{14}\text{N}_2\text{O}_3$	187.1077	195.1346
Gly-Ile	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$	189.1234	197.1502
Gly-Leu	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$	189.1234	197.1502
Ile-Gly,	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$	189.1234	197.1502
Leu-Gly	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$	189.1234	197.1502
Ala-Val	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$	189.1234	197.1502
Val-Ala	$\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$	189.1234	197.1502
Pro-Gln	$\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_4$	244.1292	254.1627
Leu-His	$\text{C}_{12}\text{H}_{20}\text{N}_4\text{O}_3$	269.1608	281.2011
Cyclic dipeptides			
$^{\text{C}}$ Gly-Gly (Piperazine-2,5-dione)	$\text{C}_4\text{H}_6\text{N}_2\text{O}_2$	115.0502	119.0636
$^{\text{C}}$ Gly-Ala (3-Methylpiperazine-2,5-dione)	$\text{C}_5\text{H}_8\text{N}_2\text{O}_2$	129.0659	134.0826

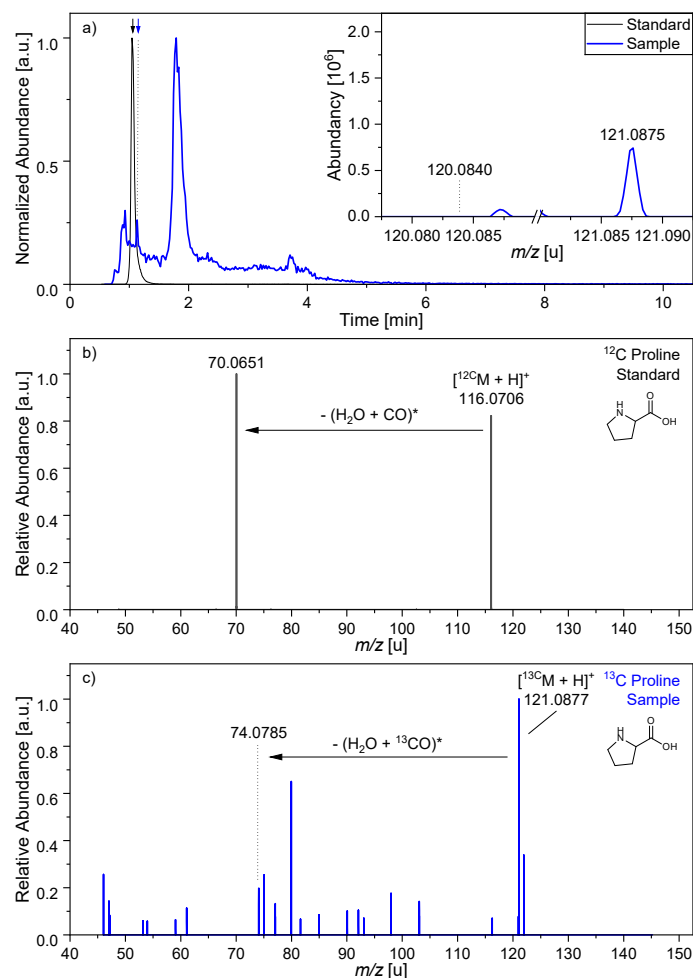


Supplementary Information Fig. 1 Identification of ^{13}C -labeled threonine ($^{13}\text{C}_4\text{H}_9\text{NO}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -threonine standard ($RT = 0.91 \text{ min}$) and the ^{13}C -threonine sample ($RT = 0.89 \text{ min}$). The arrows indicate the retention times at which MS² spectra were acquired. The inset highlights the presence of the ^{13}C -threonine ion ($[^{13}\text{C}_4\text{H}_9\text{NO}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 124.0789$) in the analyte and the absence of a significant corresponding partially ^{12}C -threonine ion ($[^{13}\text{C}_3^{12}\text{C}_1\text{H}_9\text{NO}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 123.0756$) at 0.89 min . b) MS² spectrum of ^{12}C -threonine standard with a collision energy (CE) of 40 a.u. at 0.91 min . c) MS² spectrum at 0.90 min , confirming the presence of ^{13}C -threonine through its characteristic fragmentation pattern at 40 a.u.

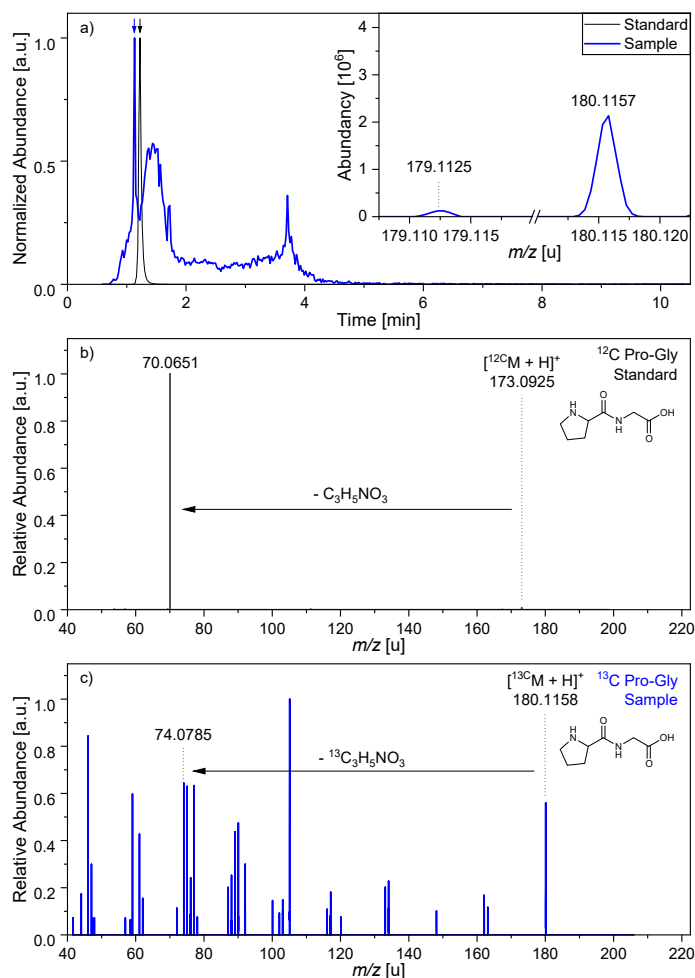




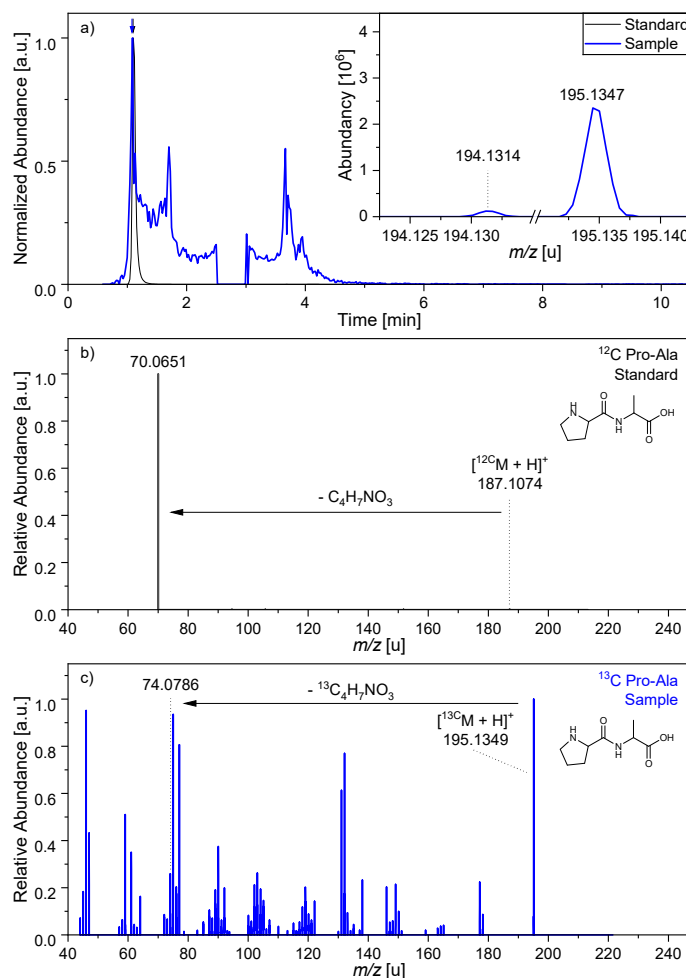
Supplementary Information Fig. 3 EICs of all fragments with relative intensities above 10% from **Supplementary Figure 2**. The threonine related signals elute at approximately 0.89 min (blue) and are clearly separated from other signals eluting around a retention time of 0.80 min (black).



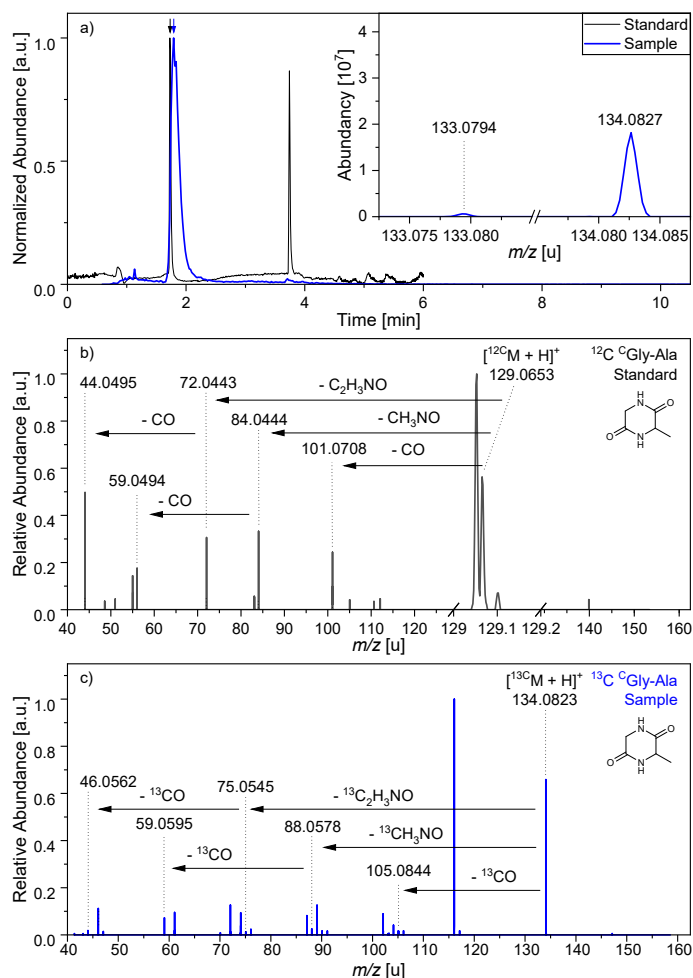
Supplementary Information Fig. 4 Identification of ^{13}C -labeled proline ($^{13}\text{C}_5\text{H}_9\text{NO}_2$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -proline standard ($RT = 1.04$ min) and the ^{13}C -proline sample ($RT = 1.13$ min). The arrows indicate the retention times at which MS^2 spectra were acquired. The inset highlights the presence of the ^{13}C -proline ion ($^{13}\text{C}_5\text{H}_9\text{NO}_2 + \text{H}^+$; $m/z_{calc.} = 121.0874$) in the analyte and the absence of a significant corresponding partially ^{12}C -proline ion ($^{13}\text{C}_4^{12}\text{CH}_9\text{NO}_2 + \text{H}^+$; $m/z_{calc.} = 120.0840$) at 1.13 min. b) MS^2 spectrum of ^{12}C -proline standard with a collision energy (CE) of 40 a.u. at 1.06 min. c) MS^2 spectrum at 1.07 min, confirming the presence of ^{13}C -proline through its characteristic fragmentation pattern at 40 a.u.



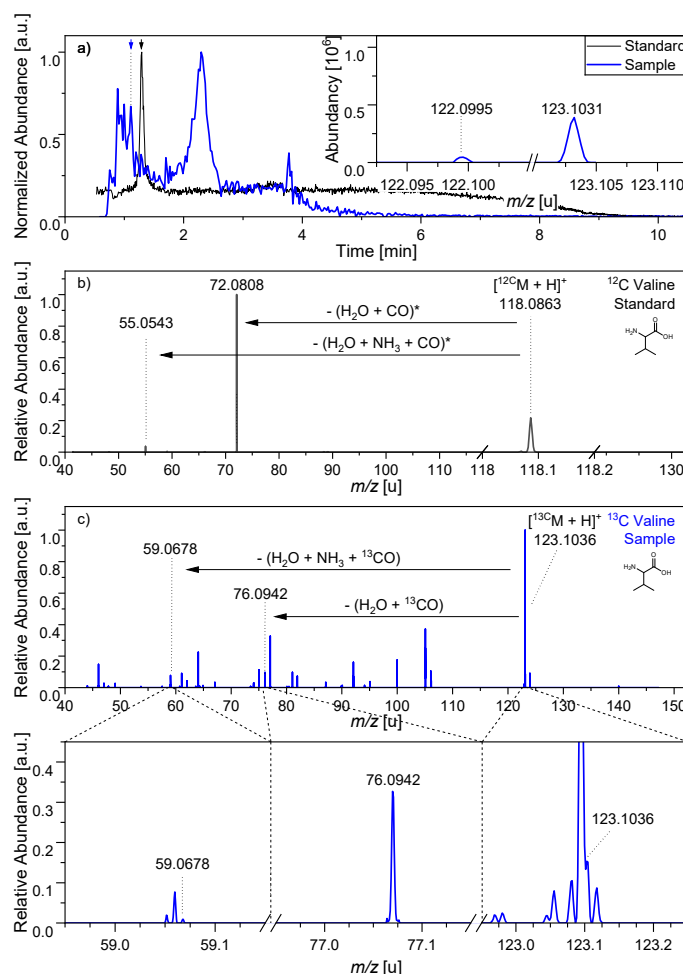
Supplementary Information Fig. 5 Identification of ^{13}C -labeled Pro-Gly ($^{13}\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -Pro-Gly standard ($RT = 1.22 \text{ min}$) and the ^{13}C -Pro-Gly sample ($RT = 1.13 \text{ min}$). The arrows indicate the retention times at which MS^2 spectra were acquired. The inset highlights the presence of the ^{13}C -Pro-Gly ion ($[^{13}\text{C}_7\text{H}_{12}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 180.1156$) in the analyte and the absence of a significant corresponding partially ^{12}C -Pro-Gly ion ($[^{13}\text{C}_6^{12}\text{C}\text{H}_{12}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 179.1122$) at 1.13 min. b) MS^2 spectrum of ^{12}C -Pro-Gly standard with a collision energy (CE) of 60 a.u. at 1.23 min. c) MS^2 spectrum at 1.14 min, confirming the presence of ^{13}C -Pro-Gly through its characteristic fragmentation pattern at 60 a.u.



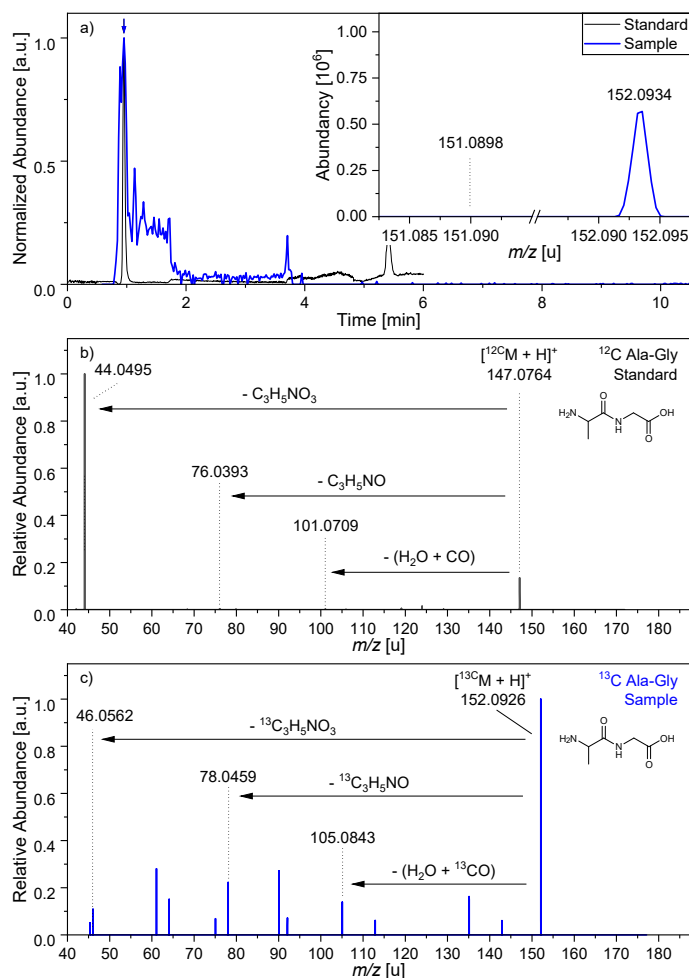
Supplementary Information Fig. 6 Identification of ^{13}C -labeled Pro-Ala ($^{13}\text{C}_8\text{H}_{14}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -Pro-Ala standard ($RT = 1.09 \text{ min}$) and the ^{13}C -Pro-Ala sample ($RT = 1.10 \text{ min}$). The arrows indicate the retention times at which MS^2 spectra were acquired. The inset highlights the presence of the ^{13}C -Pro-Ala ion ($[^{13}\text{C}_8\text{H}_{14}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 195.1346$) in the analyte and the absence of a significant corresponding partially ^{12}C -Pro-Ala ion ($[^{13}\text{C}_7^{12}\text{C}_1\text{H}_{14}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 194.1312$) at 1.10 min . b) MS^2 spectrum of ^{12}C -Pro-Ala standard with a collision energy (CE) of 60 a.u. at 1.11 min . c) MS^2 spectrum at 1.11 min , confirming the presence of ^{13}C -Pro-Ala through its characteristic fragmentation pattern at 60 a.u.



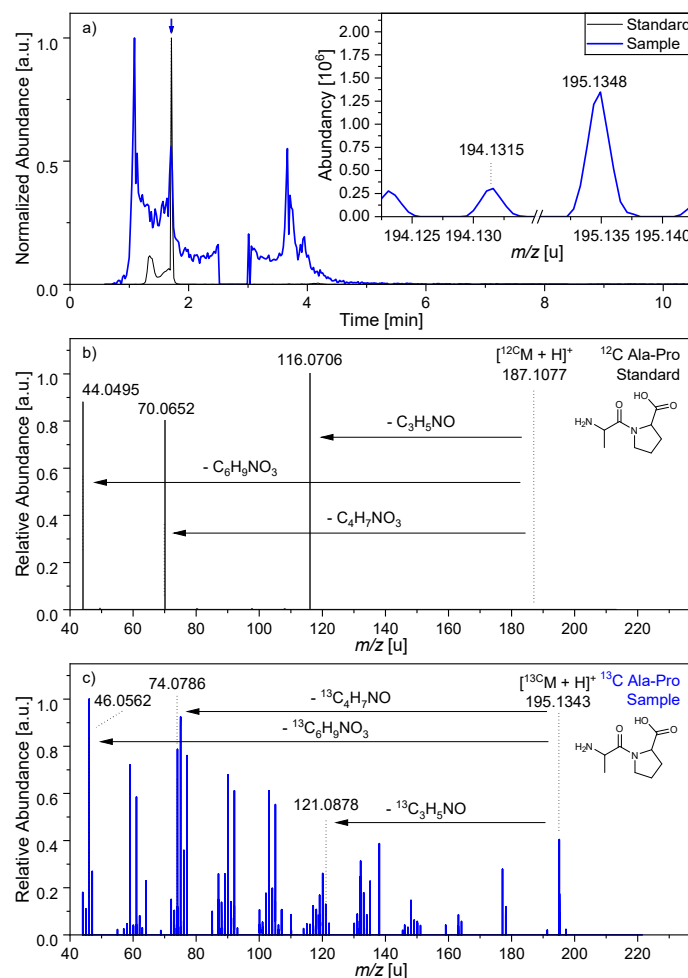
Supplementary Information Fig. 7 Identification of ^{13}C -labeled $^{\text{C}}$ Gly-Ala ($^{13}\text{C}_5\text{H}_8\text{N}_2\text{O}_2$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C - $^{\text{C}}$ Gly-Ala standard ($RT = 1.73 \text{ min}$) and the ^{13}C - $^{\text{C}}$ Gly-Ala sample ($RT = 1.79 \text{ min}$). The arrows indicate the retention times at which MS^2 spectra were acquired. The inset highlights the presence of the ^{13}C - $^{\text{C}}$ Gly-Ala ion ($[^{13}\text{C}_5\text{H}_8\text{N}_2\text{O}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 134.0826$) in the analyte and the absence of a significant corresponding partially ^{12}C - $^{\text{C}}$ Gly-Ala ion ($[^{13}\text{C}_4^{12}\text{C}\text{H}_8\text{N}_2\text{O}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 133.0793$) at 1.79 min . b) MS^2 spectrum of ^{12}C - $^{\text{C}}$ Gly-Ala standard with a collision energy (CE) of 45 a.u. at 1.73 min . c) MS^2 spectrum at 1.72 min , confirming the presence of ^{13}C - $^{\text{C}}$ Gly-Ala through its characteristic fragmentation pattern at 45 a.u.



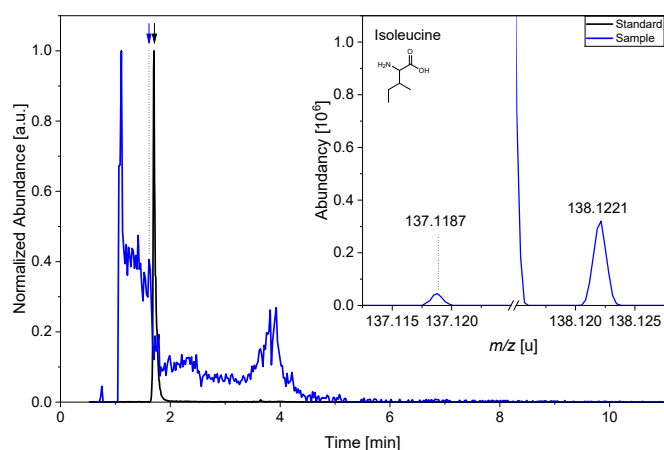
Supplementary Information Fig. 8 High confidence in the identification of ^{13}C -labeled valine ($^{13}\text{C}_5\text{H}_{11}\text{NO}_2$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -valine standard ($RT = 1.29 \text{ min}$) and the ^{13}C -valine sample ($RT = 1.11 \text{ min}$). The arrows indicate the retention times at which MS² spectra were acquired. The inset highlights the presence of the ^{13}C -valine ion ($[\text{}^{13}\text{C}_5\text{H}_{11}\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 123.1030$) in the analyte and the absence of a significant corresponding partially ^{12}C -valine ion ($[\text{}^{13}\text{C}_4^{12}\text{C}\text{H}_{11}\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 122.0997$) at 1.11 min. b) MS² spectrum of ^{12}C -valine standard with a collision energy (CE) of 40 a.u. at 1.23 min. c) MS² spectrum at 1.07 min, confirming the presence of ^{13}C -valine through its characteristic fragmentation pattern at 40 a.u.



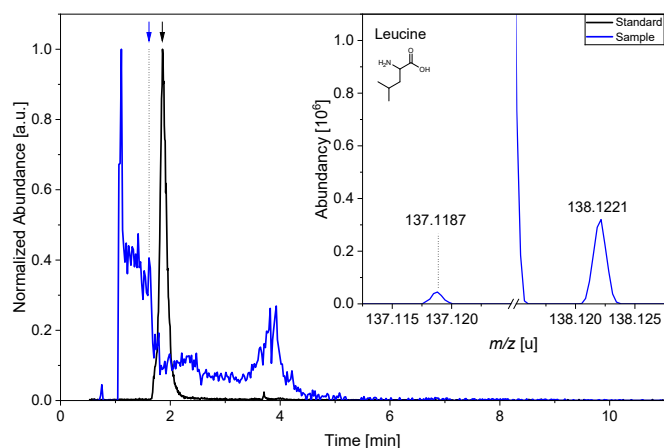
Supplementary Information Fig. 9 High confidence in the identification of ^{13}C -labeled Ala-Gly ($^{13}\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -Ala-Gly standard ($RT = 0.94 \text{ min}$) and the ^{13}C -Ala-Gly sample ($RT = 0.95 \text{ min}$). The arrows indicate the retention times at which MS^2 spectra were acquired. The inset highlights the presence of the ^{13}C -Ala-Gly ion ($[^{13}\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 152.0932$) in the analyte and the absence of a significant corresponding partially ^{12}C -Ala-Gly ion ($[^{13}\text{C}_4^{12}\text{C}\text{H}_{10}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 151.0898$) at 0.95 min . b) MS^2 spectrum of ^{12}C -Ala-Gly standard with a collision energy (CE) of 30 a.u. at 0.96 min . c) MS^2 spectrum at 0.96 min , confirming the presence of ^{13}C -Ala-Gly through its characteristic fragmentation pattern at 30 a.u.



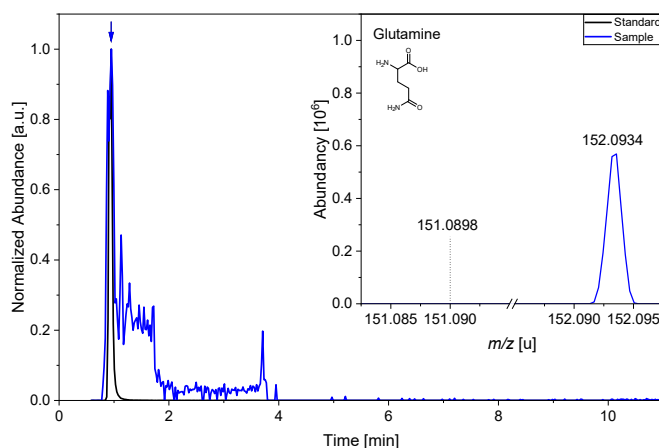
Supplementary Information Fig. 10 High confidence in the identification of ^{13}C -labeled Ala-Pro ($^{13}\text{C}_8\text{H}_{14}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. a) Normalized extracted ion chromatogram of ^{12}C -Ala-Pro standard ($RT = 1.71 \text{ min}$) and the ^{13}C -Ala-Pro sample ($RT = 1.70 \text{ min}$). The arrows indicate the retention times at which MS² spectra were acquired. The inset highlights the presence of the ^{13}C -Ala-Pro ion ($[^{13}\text{C}_8\text{H}_{14}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 195.1346$) in the analyte and the absence of a significant corresponding partially ^{12}C -Ala-Pro ion ($[^{13}\text{C}_7^{12}\text{C}\text{H}_{14}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 194.1312$) at 1.70 min . b) MS² spectrum of ^{12}C -Ala-Pro standard with a collision energy (CE) of 60 a.u. at 1.72 min . c) MS² spectrum at 1.69 min , confirming the presence of ^{13}C -Ala-Pro through its characteristic fragmentation pattern at 60 a.u.



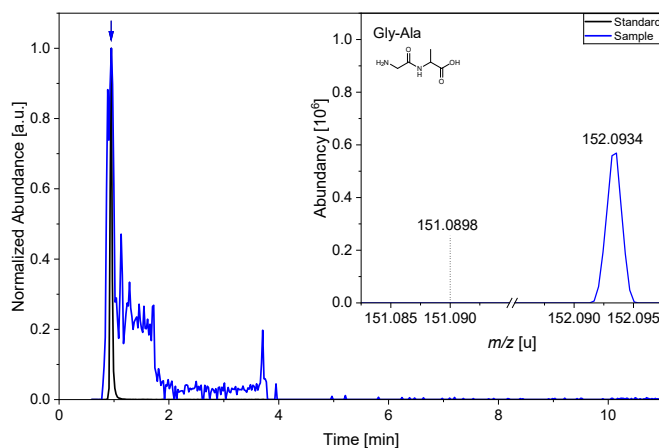
Supplementary Information Fig. 11 Tentative identification of ^{13}C -labeled isoleucine ($^{13}\text{C}_6\text{H}_{13}\text{NO}_2$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -isoleucine standard ($RT = 1.70 \text{ min}$) and the ^{13}C -isoleucine sample ($RT = 1.61 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -isoleucine ion ($[^{13}\text{C}_6\text{H}_{13}\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 138.1220$) in the analyte and the absence of a significant corresponding partially ^{12}C -isoleucine ion ($[^{13}\text{C}_5^{12}\text{CH}_{13}\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 137.1187$) at 1.61 min .



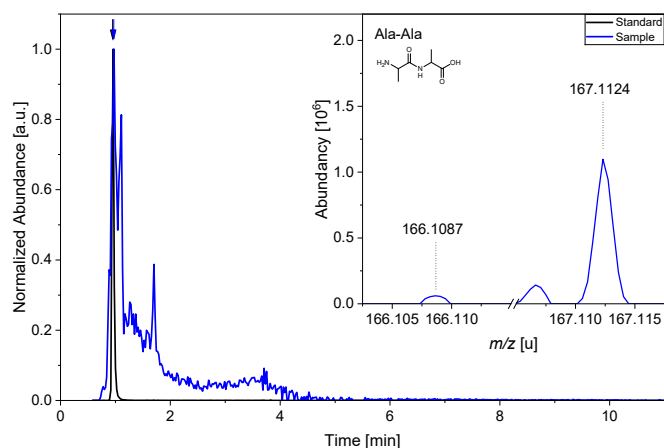
Supplementary Information Fig. 12 For a tentative identification of ^{13}C -labeled leucine ($^{13}\text{C}_6\text{H}_{13}\text{NO}_2$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -leucine standard ($RT = 1.86 \text{ min}$) and the ^{13}C -leucine sample ($RT = 1.61 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -leucine ion ($[^{13}\text{C}_6\text{H}_{13}\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 138.1220$) in the analyte and the absence of a significant corresponding partially ^{12}C -leucine ion ($[^{13}\text{C}_5^{12}\text{CH}_{13}\text{NO}_2 + \text{H}]^+$; $m/z_{\text{calc.}} = 137.1187$) at 1.61 min . When comparing leucine and isoleucine, isoleucine is the more likely candidate because leucine exhibits a significantly greater retention time shift.



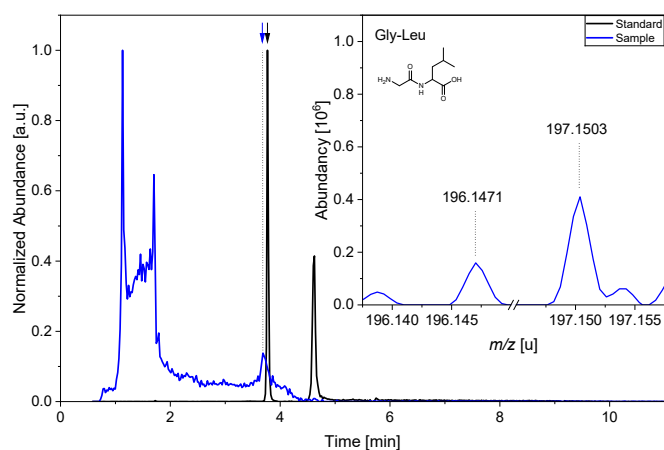
Supplementary Information Fig. 13 Tentative identification of ^{13}C -labeled glutamine ($^{13}\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -glutamine standard ($RT = 0.95 \text{ min}$) and the ^{13}C -glutamine sample ($RT = 0.95 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -glutamine ion ($[^{13}\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 152.0932$) in the analyte and the absence of a significant corresponding partially ^{12}C -glutamine ion ($[^{13}\text{C}_4^{12}\text{CH}_{10}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 151.0898$) at 0.95 min .



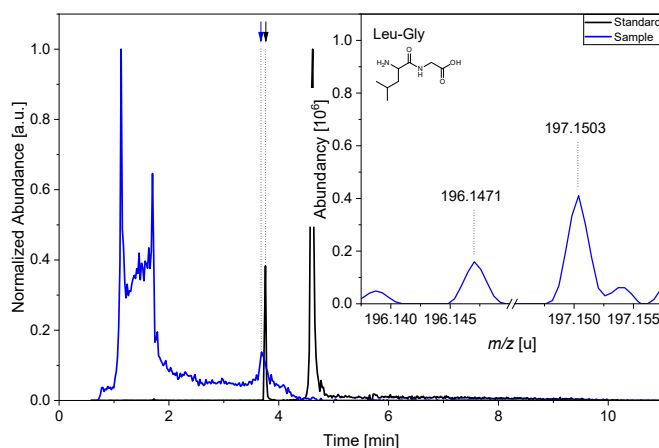
Supplementary Information Fig. 14 Tentative identification of ^{13}C -labeled Gly-Ala ($^{13}\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -Gly-Ala standard ($RT = 0.95 \text{ min}$) and the ^{13}C -Gly-Ala sample ($RT = 0.95 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -Gly-Ala ion ($[^{13}\text{C}_5\text{H}_{10}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 152.0932$) in the analyte and the absence of a significant corresponding partially ^{12}C -Gly-Ala ion ($[^{13}\text{C}_4^{12}\text{CH}_{10}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 151.0898$) at 0.95 min .



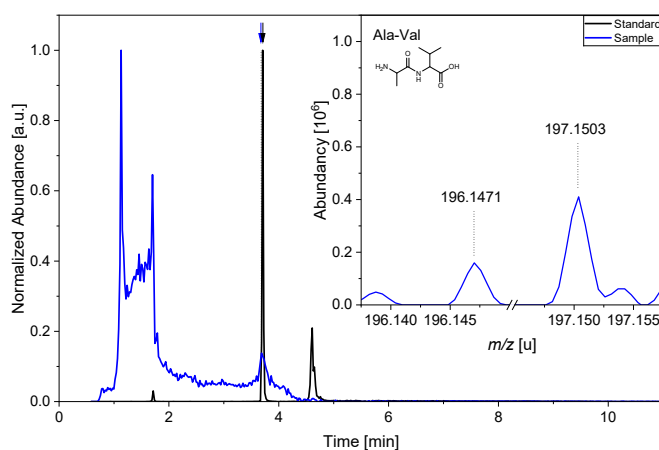
Supplementary Information Fig. 15 Tentative identification of ^{13}C -labeled Ala-Ala ($^{13}\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -Ala-Ala standard ($RT = 0.96 \text{ min}$) and the ^{13}C -Ala-Ala sample ($RT = 0.97 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -Ala-Ala ion ($[^{13}\text{C}_6\text{H}_{12}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 167.1122$) in the analyte and the absence of a significant corresponding partially ^{12}C -Ala-Ala ion ($[^{13}\text{C}_5^{12}\text{CH}_{12}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 166.1088$) at 0.97 min .



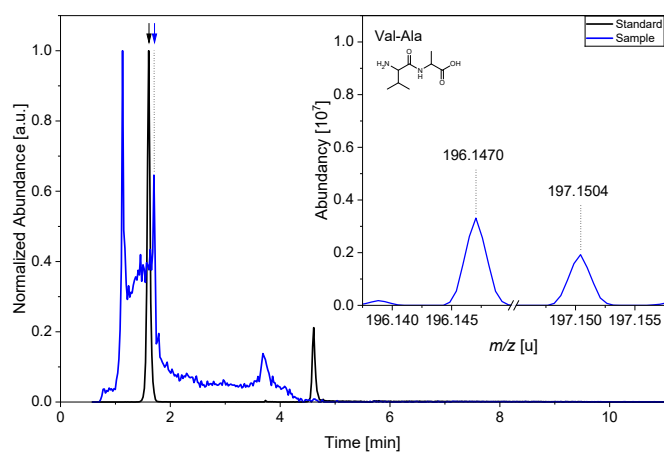
Supplementary Information Fig. 16 Tentative identification of ^{13}C -labeled Gly-Leu ($^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -Gly-Leu standard ($RT = 3.77 \text{ min}$) and the ^{13}C -Gly-Leu sample ($RT = 3.69 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -Gly-Leu ion ($[^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 197.1502$) in the analyte and the absence of a significant corresponding partially ^{12}C -Gly-Leu ion ($[^{13}\text{C}_7^{12}\text{CH}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 196.1469$) at 3.69 min .



Supplementary Information Fig. 17 Tentative identification of ^{13}C -labeled Leu-Gly ($^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -Leu-Gly standard ($RT = 3.76 \text{ min}$) and the ^{13}C -Leu-Gly sample ($RT = 3.69 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -Leu-Gly ion ($[^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 197.1502$) in the analyte and the absence of a significant corresponding partially ^{12}C -Leu-Gly ion ($[^{13}\text{C}_7^{12}\text{CH}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 196.1469$) at 3.69 min .



Supplementary Information Fig. 18 Tentative identification of ^{13}C -labeled Ala-Val ($^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -Ala-Val standard ($RT = 3.71 \text{ min}$) and the ^{13}C -Ala-Val sample ($RT = 3.69 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -Ala-Val ion ($[^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 197.1502$) in the analyte and the absence of a significant corresponding partially ^{12}C -Ala-Val ion ($[^{13}\text{C}_7^{12}\text{CH}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 196.1469$) at 3.69 min .



Supplementary Information Fig. 19 Tentative identification of ^{13}C -labeled Val-Ala ($^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3$) in the organic residues. Black trace indicates the commercially bought standard. Blue trace indicates the analyte from the sample. Normalized extracted ion chromatogram of ^{12}C -Val-Ala standard ($RT = 3.61 \text{ min}$) and the ^{13}C -Val-Ala sample ($RT = 3.69 \text{ min}$) are shown. The arrows indicate the presence of the $^{12/13}\text{C}$ compound. The inset highlights the presence of the ^{13}C -Val-Ala ion ($[^{13}\text{C}_8\text{H}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 197.1502$) in the analyte and the absence of a significant corresponding partially ^{12}C -Val-Ala ion ($[^{13}\text{C}_7^{12}\text{C}\text{H}_{16}\text{N}_2\text{O}_3 + \text{H}]^+$; $m/z_{\text{calc.}} = 196.1469$) at 3.69 min .

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