Check for updates

The Meteoritical Society

Meteoritics & Planetary Science 59, Nr 5, 1101–1130 (2024)
doi: 10.1111/maps.13936

The amino acid and polycyclic aromatic hydrocarbon compositions of the promptly recovered CM2 Winchcombe carbonaceous chondrite

Queenie H. S. CHAN [1,2,3]*, Jonathan S. WATSON [4], Mark A. SEPHTON [4], Áine C. O'BRIEN [3,5,6], and Lydia J. HALLIS [5]

[1]Royal Holloway University of London, Surrey TW20 0EX, UK
[2]The Open University, Walton Hall, Milton Keynes MK7 6AA, UK
[3]UK Fireball Network (UKFN), UK
[4]Department of Earth Science and Engineering, Imperial College London, London SW7 2BX, UK
[5]School of Geographical and Earth Sciences, University of Glasgow, Glasgow G12 8QQ, UK
[6]UK Fireball Alliance (UKFAll), UK
*Corresponding author. E-mail: queenie.chan@rhul.ac.uk

(Received 30 June 2022; revision accepted 26 September 2022)

Abstract–The rapid recovery of the Winchcombe meteorite offers a valuable opportunity to study the soluble organic matter (SOM) profile in pristine carbonaceous astromaterials. Our interests in the biologically relevant molecules, amino acids—monomers of protein, and the most prevalent meteoritic organics—polycyclic aromatic hydrocarbons (PAHs) are addressed by analyzing the solvent extracts of a Winchcombe meteorite stone using gas chromatography mass spectrometry. The Winchcombe sample contains an amino acid abundance of ~1132 parts-per-billion that is about 10 times lower than other CM2 meteorites. The detection of terrestrially rare amino acids, including α-aminoisobutyric acid (AIB); isovaline; β-alanine; α-, β-, and γ-amino-n-butyric acids; and 5-aminopentanoic acid, and the racemic enantiomeric ratios (D/L = 1) observed for alanine and isovaline indicate that these amino acids are indigenous to the meteorite and not terrestrial contaminants. The presence of predominantly α-AIB and isovaline is consistent with their formation via the Strecker-cyanohydrin synthetic pathway. The L-enantiomeric excesses in isovaline previously observed for aqueously altered meteorites were viewed as an indicator of parent body aqueous processing; thus, the racemic ratio of isovaline observed for Winchcombe, alongside the overall high free:total amino acid ratio, and the low amino acid concentration suggest that the analyzed stone is derived from a lithology that has experienced brief episode(s) of aqueous alteration. Winchcombe also contains 2- to 6-ring alkylated and nonalkylated PAHs. The low total PAHs abundance (6177 ppb) and high nonalkylated:alkylated ratio are distinct from that observed for heavily aqueously altered CMs. The weak petrographic properties of Winchcombe, as well as the discrepancies observed for the Winchcombe SOM content—a low total amino acid abundance comparable to heavily altered CMs, and yet the high free:total amino acid and nonalkylated:alkylated PAH ratios are on par with the less altered CMs—suggest that Winchcombe could represent a class of weak, poorly lithified meteorite not been previously studied.

INTRODUCTION

Asteroids are remnants of planetary formation and one way to study these extraterrestrial materials is to analyze meteorites collected on the surface of the Earth. Meteorites are classified into different meteoritic classes based on their petrologic, chemical, and isotopic compositions; one of these classes, the carbonaceous chondrites (CCs; ~4% of all recovered meteorites), has warranted attention worldwide due to their high carbon

© 2023 The Authors. *Meteoritics & Planetary Science* published by Wiley Periodicals LLC on behalf of The Meteoritical Society.
This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

content (up to ~3.5 wt% of carbon; Alexander et al., 2017) and the hosting of diverse suites of biologically vital molecules, including a range of soluble organic molecules (SOM) such as amino acids, amines, nucleobases, polyols, and carboxylic acids (Aponte et al., 2015; Callahan et al., 2011; Cooper & Rios, 2016; Glavin et al., 2012; Krishnamurthy et al., 1992). The compositional variations of these molecules reflect their plausible synthetic origins (interstellar, early solar nebula, asteroid/comets, etc.), as well as parent body aqueous and metamorphic processes which subsequently modify these intrinsic signatures. However, the study of SOM in meteorites is met with a key challenge—the SOM content that is expected to reflect the intrinsic compositional variations is often obscured by varying extents of terrestrial contamination obtained during the terrestrial residence of essentially all meteorites. This challenge has brought our attention to just tens of CCs that share a common background—their retrievals were associated with observed and/or recorded fireball events, and thus, additional information regarding their trajectory and pre-atmospheric orbit was available. The most recent CC falls since 2000 include Tagish Lake (fell in 2000), Maribo (2009), Sutter's Mill (2012), Mukundpura (2017), Aguas Zarcas (2019), Flensburg (2019), Tarda (2020), and most recently, the Winchcombe meteorite (2021; Table 1).

The Winchcombe fireball occurred at 21:54:16 (UT) on February 28, 2021 and lasted a little over 8 s. As the meteorite fell on a clear night, its entry was optimal for eyewitnesses and instrumental records. In addition to over 1000 eyewitnesses, numerous footages of the fireball were captured on doorbell and dashboard cameras, the fireball event was also recorded by meteor camera networks such as the UK Fireball Alliance (UKFAll) networks (McMullan et al., 2023). The rapid collection of the Winchcombe meteorite preserved traces of its pre-atmospheric information that would otherwise be altered through contact with the terrestrial environment. The meteoroid was determined to have a pre-atmospheric mass of only 13 ± 3 kg based on fireball observations (entry mass was estimated to be 30 ± 10 kg based on analysis of cosmogenic nuclides), making it the smallest CC recorded on cameras (King et al., 2022). Despite the small initial mass of the Winchcombe meteoroid and the fragile nature of CCs, the low entry speed (13.5 km s^{-1}) and the shallow entry angle (~40°) led to a slow atmospheric deceleration. The meteoroid finally fragmented to four individual pieces and a modest final recovered mass of ~0.6 kg.

Based on the mineralogy, petrography, and bulk oxygen isotopic compositions, Winchcombe was classified as a CM ("Mighei-like") meteorite (King et al., 2022). Most lithologies are intermediately to highly aqueously altered (CM2.4–2.0), although one CM containing unaltered chondrules and metal has also been identified (CM2.6). Since the initial analyses of the CM2 Murchison meteorite in the 1970s (Kvenvolden et al., 1970), SOM analyses have been carried out on several CM falls focusing on a range of compounds selected based on their relevance to biology. However, not all CM falls were investigated using compound targeted analysis, as such an approach requires a substantial mass of samples for the effective detection of the containing SOM species, while some meteorite falls such as Maribo were recovered below such limits (only ~30 g of specimens recovered). The condition of the meteorite fall site also played a role; for example, Maribo was intensely rained on before collection, which hampered the SOM inventory (Haack et al., 2012), whereas Tarda was collected from a barren hot desert in Morocco and thus not as extensively influenced by terrestrial water as Maribo (Tunney et al., 2022).

Examples of most recent SOM analyses of CM falls can be drawn from the meteorites Mukundpura (2017, India; Pizzarello & Yarnes, 2018; Rudraswami et al., 2019) and Aguas Zarcas (2019, Costa Rica; Aponte et al., 2020; Glavin et al., 2021; Pizzarello et al., 2020). Mukundpura, collected from sandy soil in an agricultural field, was kept in an N_2 purged environment in a storage facility since 2 days after the observed fall. It has an amino acid content similar to Murchison, with a total free amino acid abundance of 145.5 nmol g^{-1} (which translates to ~14,550 parts-per-billion [ppb], with a molar mass of ~100 g mol^{-1}; Pizzarello & Yarnes, 2018). However, despite its prompt recovery, the L-enantiomeric excesses (*ee*) observed for alanine and lactic acid and the low $\delta^{13}C$ values of the amino acids (−2.5 to 10.6‰) in Mukundpura indicate that this meteorite has been terrestrially altered. Aguas Zarcas also has an amino acid abundance (from none detected to 43,800 ppb) similar to Murchison (Aponte et al., 2020; Glavin et al., 2021; Pizzarello et al., 2020). Although most amino acids in Aguas Zarcas exhibit low *D*/*L* ratios (alanine = 0.46; aspartic acid = 0.32, glutamic acid = 0.16), the $\delta^{13}C$ values of terrestrially rare amino acids—α-aminoisobutyric acid and D- and L-isovaline—fell outside the typical terrestrial range, indicating that Aguas Zarcas contains a fraction of amino acids that are extraterrestrial in origin. In contrast, a different Aguas Zarcas sample was found to be depleted in amino acids, and typical terrestrial contaminants (such as the L-enantiomers of alanine, serine, aspartic acid, and threonine) were also absent in this sample (Pizzarello et al., 2020). The potential absence of terrestrial contaminants was viewed as an indicator of the pristine nature of Aguas Zarcas. The disparities observed in these studies underscore the concerns for sample heterogeneity

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 1. Examples of carbonaceous chondrite falls and their corresponding recovered masses.

Meteorite	Type	Fall site	Date of observed fall	Date of first specimen recovery	Total recovered mass (kg)
Tagish Lake	C2-ung	British Columbia, Canada	January 18, 2000	January 25, 2000	10
Maribo	CM2	Region Sjaelland, Denmark	January 17, 2009	March 4, 2009	0.03*
Sutter's Mill	C	California, USA	April 22, 2012	April 24, 2012	1
Mukundpura	CM2	Rajasthan, India	June 6, 2017	June 8, 2017	2
Aguas Zarcas	CM2	Alajuela, Costa Rica	April 23, 2019	April 24, 2019	27
Flensburg	C1-ung	Schleswig-Holstein, Germany	September 12, 2019	September 13, 2019	0.03
Tarda	C2-ung	Morocco	August 25, 2020	August 26, 2020	4
Winchcombe	CM2	Winchcombe, UK	February 28, 2021	March 1, 2021	0.6

*The entire mass of the Maribo meteorite was collected after rain.

when comparing the SOM contents (and other traits) of different meteorites, or different stones of the same meteorite.

The Winchcombe meteorite has an average bulk carbon abundance of 2.0 ± 0.1 wt% and nitrogen abundance of 433.8 ± 20.3 ppm (~0.04 wt%; King et al., 2022). These values are lower than those observed in CM falls (C = ~2.2 wt% and N = ~0.1 wt%; Alexander et al., 2013). Although the carbon in CMs is not confined to organic matter, as it can also be derived from other inorganic phases such as carbonate, diamond, graphite, and silicon carbide (Chan & Zolensky, 2022), the low abundances of both carbon and nitrogen in Winchcombe potentially indicate that the meteorite has a low organic abundance, and this can be a challenge to SOM analysis. The bulk hydrogen, carbon, and nitrogen isotopic compositions ($\delta D = -142 \pm 4‰$; $\delta^{13}C = -1.7 \pm 1.1‰$; $\delta^{15}N = +16.7 \pm 0.9‰$) of the Winchcombe meteorite are comparable to most CMs (King et al., 2022; Sephton et al., 2023), and the $\delta^{15}N$ value is more consistent with the moderately aqueously altered CMs with >0.75 volume fractions of phyllosilicates (Alexander et al., 2013). If Winchcombe was more extensively altered, the free and labile organic matter would have been progressively removed during parent body aqueous alteration to leave behind an isotopically lighter ($\delta^{15}N \leq -25‰$) refractory fraction (Sephton et al., 2004). Hence, the Winchcombe meteorite provides a valuable opportunity to investigate how pristine organic materials chemically evolved during onset of parent body aqueous alteration. In this study, we have carried out, for the first time, amino acid and polycyclic aromatic hydrocarbon (PAH) analyses for the Winchcombe meteorite. Our interest in the biologically relevant molecules, amino acids—monomers of protein, is addressed by hot water extraction of a Winchcombe meteorite specimen analyzed by gas chromatography-mass spectrometry (GC-MS). We have also measured the concentration of PAHs in the soluble aromatic fraction of Winchcombe by GC-MS. We compare the amino acid and PAH abundances and structural variation to other CM chondrites, to understand the effects of parent body hydrothermal alteration on the SOM inventory in the early solar system.

EXPERIMENTAL PROCEDURES

Winchcombe Samples and Controls

The Winchcombe meteorite stones BM.2022,M2-14 (mass = 0.9754 g, hereafter simply referred to as "Winchcombe" in this study) were provided by the Natural History Museum (NHM), London (Fig. 1). Winchcombe is among the first collected samples of the Winchcombe meteorite fall retrieved from the Wilcock family's driveway on March 2, 2021 using rubber gloves. The sample was initially stored in a polyethylene sample bag and was subsequently transferred to sterile glass vial 3 days later at the NHM. A soil sample (the "fall site soil") collected in proximity of the meteorite samples was analyzed to assess terrestrial contamination from the local environment. The fall site soil sample (mass = 1.0967 g) from the Wilcocks' house was collected on March 5, 2021. There was no precipitation between the fireball on February 28, 2021 and sample collection. A powdered sample of serpentinized peridotite from Coverack, United Kingdom (henceforth described as "Procedural blank"), provided by Mark Sephton, was analyzed as the procedural blank of GC-MS analysis. The procedural blank was heated to 500 °C in air for 24 h prior to the amino acid extraction procedures. Stock solutions (10^{-3} M to 10^{-1} M) of individual amino acids were made by dissolution of standard crystals in ultrapure water. An amino acid standard mixture was made by combining individual standard solutions. The amino acid standards mixture, procedural blank, and fall site soil were subjected to the same experimental procedures as the meteorite sample.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License



Fig. 1. Images showing the analyzed Winchcombe meteorite sample, the fusion crust (marked by the black arrow; the fusion crust was manually removed by sterile tool from the Winchcombe meteorite sample prior to sample crushing), and the fall site soil stored in sterile glass vials. Scale bars are 1 cm. (Color figure can be viewed at wileyonlinelibrary.com)

Materials and Chemicals

All tools, glassware, and ceramics were sterilized by baking at 500 °C in air for 24 h. Millipore ultrapure water (18.2 MΩ cm, ≤3 ppb total organic carbon) was used for all laboratory work performed in this study. The amino acid 3-amino-3-methyl butanoic acid and 3-amino-2,2-dimethylpropanoic acid were provided by Astrobiology Analytical Laboratory at Goddard Space Flight Center, NASA. All other amino acid standard crystals/powder were purchased from Acros Organics, Sigma-Aldrich, and Fluka. Hydrochloric acid (HCl; 37%), ammonium hydroxide (NH_4OH; 28–30 wt%), isopropanol (IPA; 99.5%), and trifluoroacetic anhydride (TFAA; ≥99.0%) were purchased from Sigma-Aldrich. Acetyl chloride (99+%) and pyrene (98%) were from Acros Organics. Prepacked columns, analytical grade 50 W-X8, and hydrogen form (100–200 mesh) were acquired from Bio-Rad. Sodium hydroxide (NaOH) pellets and dichloromethane (DCM; 99.8+%) were bought from Fisher Scientific.

Sample Extraction and Desalting Procedures

The Winchcombe meteorite stone has a small visible portion of fusion crust (Fig. 1). The fusion crust was manually removed by sterile tool, and the remaining sample was powdered in a ceramic mortar and pestle inside a Bassaire laminar flow hood under HEPA-filtered positive pressure (equivalent to ISO Class 4–5). The sample was homogenized and split into five equal portions of approximately 150 mg each, which were transferred to individual test tubes (20 × 150 mm) for hot water extraction. One milliliter of Millipore ultrapure water was added to each sample. The test tubes were then flame sealed and heated to 100 °C for 24 h in a heating block. After cooling to room temperature, the test tubes were rinsed with ultrapure water, cracked open, and centrifuged for 5 min. Eighty percent of the water supernatant was transferred to small test tubes (12 × 75 mm) individually, dried under vacuum, flame sealed in larger test tube (20 × 150 mm) containing 1 mL of 6 N HCl, and then subjected to acid vapor hydrolysis for 3 h at 150 °C to determine the total (free + bound) amino acid content. Fifteen percent of the water supernatant (the nonhydrolyzed fraction) was transferred to small test tubes, and kept at ~4 °C until prior to the desalting procedure. After the hydrolysis procedure, the test tubes were rinsed with ultrapure water, and then cracked open. The small test tubes were removed and dried under vacuum.

Cation exchange was performed on prepacked columns. The columns were prepared according to the following procedures. After removing the caps and snapping off the seals on the Luer tips, the columns were filled to the top with water (~10 mL) plus one bed volume (~2 mL). Once the volume of water was just above the resin bed, three bed volume (~6 mL) of 2 M NaOH was added to desorb any contaminating amino acids. The columns were then washed by filling to the top with water twice (20 mL) until the eluting solution has a neutral pH to remove residual NaOH. Three bed volume (~6 mL) of 1.5 M HCl was added to re-acidify the columns. The columns were again washed with two bed volume of water (20 mL) to remove excess HCl until neutral pH.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

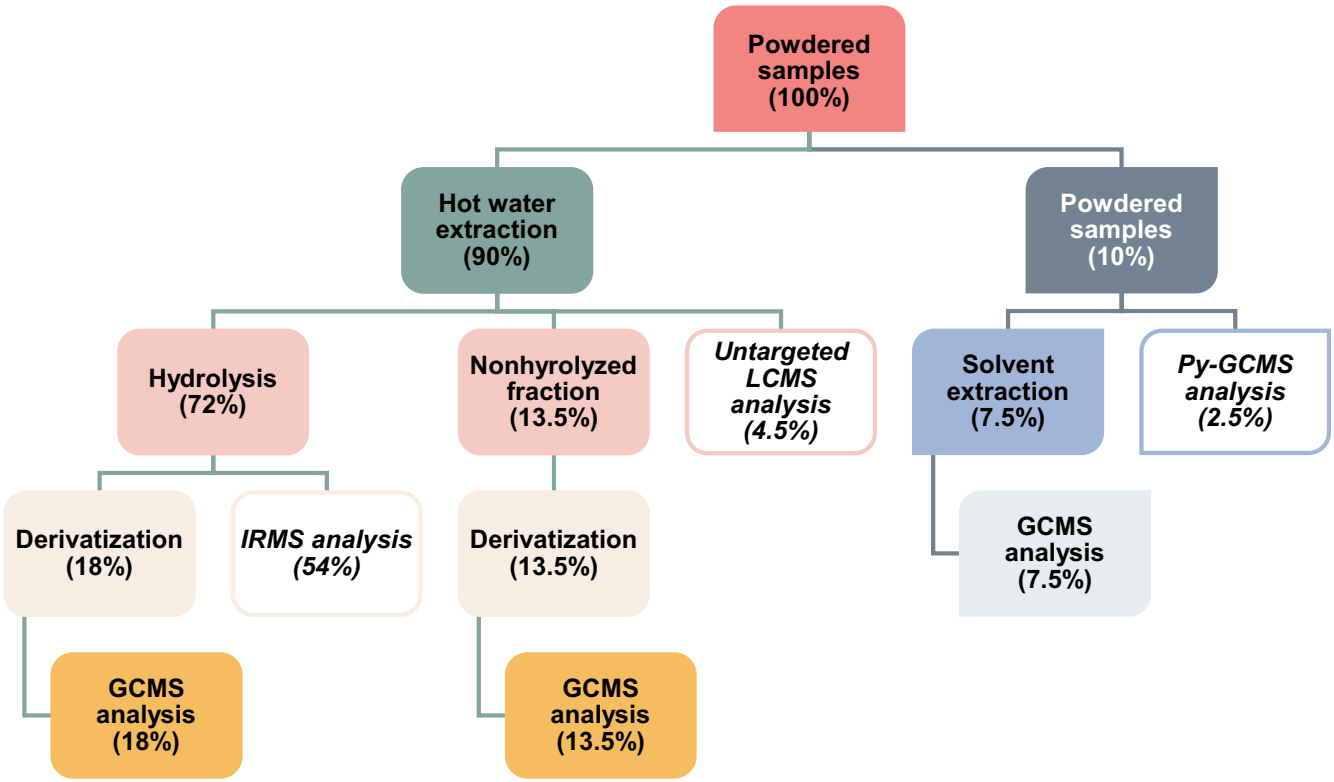


Fig. 2. Analytical scheme and sample distribution of the Winchcombe meteorite. The value (%) shown in brackets indicates the portion of the mass of the allocated Winchcombe meteorite sample being used in each of the listed procedures. Fill cells indicate procedures completed in this study. Open cells indicate the portions of samples preserved for planned future analyses. LCMS, liquid chromatography–mass spectrometry; Py-GCMS, pyrolysis gas chromatography mass spectrometry; IRMS, isotope ratio mass spectrometry. (Color figure can be viewed at wileyonlinelibrary.com)

Both hydrolyzed and nonhydrolyzed samples were then bought up in 3 × 1 mL of ultrapure water and desalted on the cation exchange resin. Different fractions of the same sample were recombined by desalting in the same column. Purified amino acids were eluted by adding 2 × 3.5 mL fractions of 2 M NH_4OH, and the eluates were collected in small test tubes, which were then evaporated to dryness by vacuum centrifugation. All sample analytical residues from above-mentioned analytical steps not analyzed in this study were preserved frozen for organic analyses by different techniques (e.g., position-specific isotopic analyses) in the future (Fig. 2).

TFAA-IPA Derivatization and GC-MS Analysis

Prior to GC-MS analysis, amino acids were derivatized by esterification with IPA and acylation with TFAA. The samples were resuspended in 2 × 50 μL of ultrapure water in inserts within GC vials. One hundred μL of acetyl chloride:IPA mixture (30:70 v/v) was added to each of the samples. The vials were tightly capped and the samples were heated in a heating block set at 110 °C for 1 h. The samples were then cooled in an ice bath and dried under a gentle stream of dry N_2. After the samples were brought to room temperature, 100 μL of DCM and 50 μL of TFAA were added to the dried sample. The vials were capped tightly again and heated to 100 °C for 10 min. The samples were then cooled to room temperature and the excess reagent was removed under a slow stream of N_2. Prior to injection, the derivatized samples were dissolved in 30 μL of DCM and 5 μL of pyrene in DCM (200 μg mL^{-1}) as an internal standard. The derivatized samples were then immediately analyzed by GC-MS.

Amino acids in the hot water extracts were analyzed by an Agilent Technologies 7890A series GC coupled to an Agilent Technologies 5975C mass selective detector (MSD). The separations of the D,L-amino acid enantiomers were achieved using a CP-Chirasil-L Val GC Column (25 m × 0.25 mm ID × 0.12 μm; Agilent Technologies). For D,L-isovaline enantiomers separation, a 6890N series GC coupled to a 5973 MSD (both Agilent Technologies) and a CP-Chirasil-Dex CB GC Column (25 m × 0.25 mm ID × 0.25 μm; Agilent Technologies) were used.

Helium was used as carrier gas and the column flow rate was set at 1.1 mL min^{-1} and injection (1 μL) was in

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 2. Amino acid peak identification in the GC-MS chromatograms, their retention times, and the molecular trace ions used for quantification and identification.

Peak#	Trace Ion (*m*/*z*)	Retention time (min)	Amino acids	Abbreviation
1	154	2.43	α-aminoisobutyric acid	α-AIB
2	168	2.70	D-isovaline (or D-2-amino-2-methylbutanoic acid)[a]	D-Iva
3	168	2.70	L-isovaline (or L-2-amino-2-methylbutanoic acid)[a]	L-Iva
4	140	3.02	D-alanine	D-Ala
5	140	3.56	L-alanine	L-Ala
6	154	3.84	D-α-amino-*n*-butyric acid	D-α-ABA
7	168	4.04	D-valine (or D-2-amino-2-methylbutanoic acid)	D-Val
8	153	4.35	D-threonine	D-Thr
9	154	4.47	L-α-amino-*n*-butyric acid	L-α-ABA
10	168	4.53	L-valine (or L-2-amino-2-methylbutanoic acid)	L-Val
11	126	4.73	Glycine	Gly
12	153	4.93	L-threonine	L-Thr
13	182	5.21	D-β-aminoisobutyric acid	D-β-AIB
14	168	5.21	D-norvaline (or D-2-aminopentanoic acid)	D-Nva
15	182	5.31	L-β-aminoisobutyric acid	L-β-AIB
16	182	5.38	D-isoleucine	D-Ile
17	140	5.39	D-β-amino-*n*-butyric acid[b]	D-β-ABA
18	168	5.42	β-alanine	β-Ala
19	140	5.53	L-β-amino-*n*-butyric acid[b]	L-β-ABA
20	182	5.70	L-alloisoleucine	L-alloIle
21	182	5.97	L-isoleucine	L-Ile
22	168	6.10	L-norvaline (or L-2-aminopentanoic acid)	L-Nva
23	140	6.31	D-leucine	D-Leu
24	139	6.39	D-serine	D-Ser
25	182	6.73	D-norleucine	D-Nle
26	184	6.94	R-3-aminopentanoic acid	R-3-APA
27	139	6.98	L-serine	L-Ser
28	184	7.07	S-3-aminopentanoic acid	S-3-APA
29	140	7.43	L-leucine	L-Leu
30	182	7.70	L-norleucine	L-Nle
31	140	8.15	D-4-amino-pentanoic acid[b]	D-4-APA
32	140	8.47	L-4-amino-pentanoic acid[b]	L-4-APA
33	196	8.56	D-2-aminoheptanoic acid[b]	D-2-AHA
34	182	8.94	γ-amino-*n*-butyric acid	γ-ABA
35	196	9.51	L-2-aminoheptanoic acid[b]	L-2-AHA
36	184	10.36	D-aspartic acid	D-Asp
37	184	10.64	L-aspartic acid	L-Asp
38	196	11.31	5-aminopentanoic acid (or 5-aminovaleric acid)	5-APA
39	210	13.50	ε-amino-*n*-caproic acid	EACA
40	198	13.62	D-glutamic acid	D-Glu
41	198	14.27	L-glutamic acid	L-Glu

[a]Isovaline enantiomers could not be separated using a CP-Chirasil-L-Val column. Instead, D- and L-isovaline enantiomers were separated using the CP-Chirasil-Dex CB column.

[b]Optically pure standard not available for enantiomeric identification. The order of elution of the D- and L-enantiomers was tentatively identified, as the D-enantiomer elutes first followed by the L-enantiomer when using the Chirasil-L-Val column.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

split mode (10:1) at 220 °C. The source and quadrupole temperatures were maintained at 230 and 150 °C, respectively; the MSD transfer line was heated to 180 °C. Standard autotunes with perfluorotributylamine (PFTBA) and air/water checks were made on a daily basis. The oven program was set at an initial temperature of 90 °C and held for 2 min, then increased by 5 °C min^{-1} to 200 °C and held for 6 min. GC-MS methods and oven program were the same for both instruments used. Total ion current chromatograms were acquired and analyzed with Agilent Technologies MSD ChemStation (6890-5973) or MassHunter (7890-5975) software. Amino acids present in the meteorite samples were identified by comparison of the retention time and mass fragmentation pattern with a known amino acid standard mixture (Table 2), and quantification was made by chromatographic data collected in the selected ion monitoring (SIM) mode. Identification was added by retention time locking of GC method and creation of a custom library from standards which include retention time and retention indices for the amino acids.

Extraction of PAHs

The powdered Winchcombe sample (58.3 mg) was placed in a test tube and internal standard of naphthalene-d8 added along with 2 mL solvent mixture of dichloromethane (DCM):methanol (93:7; v/v). The mixture was then sonicated for 3 min and centrifuged and the supernatant was removed; the extraction process was repeated three additional times and supernatants combined. After extraction, activated copper turnings were used to remove elemental sulfur, and then, the combined supernatants were concentrated under a stream of dry nitrogen gas. The extract was concentrated to ~50 μL prior to analysis by GC-MS. A procedural blank of serpentinite (105 mg) was extracted in parallel in the same way as the Winchcombe sample. A sample of the "fall site soil" (99.5 mg) was extracted in the same way as the meteorite sample except polar non-hydrocarbon compounds were removed by eluting down a short alumina column with DCM:hexane (1:1; v/v) prior to analysis by GC-MS.

GC-MS Analysis of PAHs

Analysis was conducted on a Agilent Technologies 7890-5975 GC-MS. The sample 1 μL was injected splitless with the GC injector held at 270 °C and with a helium column flow rate of 1.1 mL min^{-1}. Separation was performed on a DB-5MS ultra inert column (J&W; 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness). The GC oven temperature was held for 2 min at 40 °C and subsequently ramped to 310 °C at a rate of 5 °C min^{-1} and held at this temperature for 9 min. Mass spectra were acquired in electron impact mode (70 eV) with a scan range from 50 to 550 atomic mass unit (amu) and additionally in SIM mode.

RESULTS AND DISCUSSION

A Low Total Amino Acid Abundance

We have identified and quantified trifluoroacetyl (TFA) derivatives of two- to six-carbon (C_2–C_6) amino acids in the Winchcombe meteorite hot water extracts using GC-MS. The amino acid abundances of the derivatized (N-TFA, O-isopropyl) nonhydrolyzed and 6N HCl-hydrolyzed hot water extracts of the Winchcombe meteorite, fall site soil, and procedural blank are presented in Table 3 and Figs. 3 and 4. The amino acid abundances in Table 3 are presented in ppb calculated from the average of three separate measurements. Representative chromatograms from GC-MS analyses of the derivatized 6N HCl-hydrolyzed hot water extracts of the Winchcombe meteorite, the fall site soil, the procedural blank, and the mixed amino acid standard are shown in Fig. 3. Each peak in the chromatograms was identified by comparison of its retention time and exact molecular mass with amino acid standards (Table 2). We have separated the amino acids with carbon numbers up to C_6 and their enantiomers with no known interference or co-elution with other amino acid isomers. The individual D- and L-enantiomers of β-amino-*n*-butyric acid, 3-aminopentanoic acid, and 2-aminoheptanoic acid were clearly separated (Figs. 3 and 4), but they could not be enantiomerically identified due to the lack of optically pure standards. Nevertheless, the order of elution of their D- and L-enantiomers was determined by the elution sequence that the D-enantiomer elutes first followed by the L-enantiomer when using the Chirasil-L-Val column. For isovaline, the separation of the D- and L-isovaline enantiomers in the same derivatized 6N HCl-hydrolyzed hot water extracts of the Winchcombe meteorite and the mixed amino acid standard was achieved on a different column and the corresponding 4–8 min regions of the chromatograms are shown in Fig. 5. Multiple injections of the amino acid standard, meteorite, fall site soil, and procedural blank extracts required that the samples be analyzed on 2 consecutive days, which resulted in slight retention time differences in the GC chromatograms. Nevertheless, the sample extracts were compared to standards run on the same day, and thus, the slight retention time differences between replicates did not influence the accurate identification and quantification of the amino acids.

The total (free + bound peptide-like) amino acid abundance in the 6N HCl-hydrolyzed hot water extract

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 3. Summary of the abundances in parts-per-billion (ppb) of the C_2–C_6 amino acids in the 6 N HCl-hydrolyzed (total) hot water extracts of the Winchcombe meteorite and several CM carbonaceous chondrites as comparison.[a]

C#	Amine position	Amino acids	CM2 Winchcombe (Subtype CM2.0–2.6)		Fall site soil		CM1 MET 01070 (Subtype CM2.0)	CM2 Murchison (Subtype CM2.5)	CM2 Murray (Subtype CM2.5)	CM2 Asuka 12236 (Subtype CM3.0/2.9)
			Free	Total	Free	Total	Total	Total	Total	Total
2	α	Gly	131.7 ± 17.8	163.0 ± 17.2	13,875.0 ± 180.5	54,676.5 ± 401.9	105.0 ± 15.0	2606.0 ± 717.0	2110.0 ± 44.0	12,011.2 ± 375.4
3	α	D-Ala	47.2 ± 2.2	57.0 ± 6.9	1594.6 ± 36.7	4956.6 ± 30.6	18.0 ± 2.0	592.0 ± 99.0	617.0 ± 79.0	2494.6 ± 178.2
3	α	L-Ala	46.4 ± 2.2	50.2 ± 5.1	34,905.6 ± 606.8	54,871.9 ± 457.8	21.0 ± 3.0	718.0 ± 160.0	647.0 ± 58.0	2672.8 ± 178.2
3	β	β-Ala	n.f.	28.3 ± 3.4	1388.5 ± 11.7	2868.5 ± 11.7	187.0 ± 34.0	1081.0 ± 243.0	1063.0 ± 268.0	1871.0 ± 89.1
3	α	D-Ser	n.f.	n.f.	1694.8 ± 66.6	20,629.0 ± 654.7	<1	n.r.	n.r.	115.6 ± 21.0
3	α	L-Ser	n.f.	n.f.	19,627.0 ± 1266.4	68,247.1 ± 5404.0	<2	n.r.	n.r.	525.5 ± 21.0
4	α	α-AIB	467.1 ± 16.7	331.1 ± 33.6	n.f.	n.f.	37.0 ± 10.0	5124.0 ± 2487.0	1968.0 ± 350.0	1845.9 ± 41.2
4	α	D-α-ABA	11.6 ± 1.4[b]	12.6 ± 1.8[b]	n.f.	n.f.	23.0 ± 4.0[c]	622.0 ± 128.0[c]	463.0 ± 68.0[c]	1649.9 ± 206.2[c]
4	α	L-α-ABA	14.3 ± 1.2[b]	16.7 ± 2.5[b]	n.f.	n.f.	[c]	[c]	[c]	[c]
4	α	D-Thr	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
4	α	L-Thr	n.f.	n.f.	20,292.9 ± 272.8	40,837.1 ± 284.3	n.r.	n.r.	n.r.	n.f.
4	β	D-β-AIB	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	147.0 ± 88.0[c]	n.f.
4	β	L-β-AIB	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	[c]	n.f.
4	β	D-β-ABA	5.3 ± 3.4	8.0 ± 2.2	n.f.	n.f.	26.0 ± 4.0	349.0 ± 59.0	424.0 ± 18.0	464.0 ± 10.3
4	β	L-β-ABA	6.8 ± 3.2	12.8 ± 1.4	n.f.	n.f.	25.0 ± 2.0	320.0 ± 41.0	[c]	453.7 ± 10.3
4	γ	γ-ABA	n.f.	14.0 ± 2.3	1603.3 ± 24.8	2139.3 ± 21.2	46.0 ± 13.0	979.0 ± 97.0	717.0 ± 192.0	1247.8 ± 61.9
4	α	D-Asp	6.7 ± 1.7	6.8 ± 0.7	1252.5 ± 14.5	10,238.1 ± 32.7	<1	189.0 ± 14.0	51.0 ± 31.0	319.4 ± 13.3
4	α	L-Asp	12.7 ± 4.2	13.2 ± 1.6	18,742.3 ± 205.6	82,678.2 ± 472.4	<2	281.0 ± 23.0	65.0 ± 16.0	652.2 ± 26.6
5	α	D-Iva	196.7 ± 8.6[d]	138.3 ± 14.7[d]	n.f.	n.f.	<0.4	1263.0 ± 125.0	2834.0 ± 780.0[c]	492.0 ± 35.1
5	α	L-Iva	194.4 ± 8.5[d]	130.7 ± 13.9[d]	n.f.	n.f.	<0.5	2058.0 ± 220.0	[c]	468.6 ± 23.4
5	α	D-Val	9.2 ± 1.5	11.1 ± 1.5	n.f.	369.8 ± 0.2	<0.3	160.0 ± 5.0	n.r.	656.0 ± 105.4
5	α	L-Val	16.6 ± 2.6	14.9 ± 1.5	28,575.1 ± 476.5	30,954.7 ± 152.6	<10	330	n.r.	796.6 ± 46.9
5	α	D-Nva	3.0 ± 0.3	3.4 ± 0.6	n.f.	n.f.	<0.2	59.0 ± 4.0	n.r.	316.3 ± 23.4
5	α	L-Nva	2.7 ± 0.2	3.8 ± 0.8	n.f.	n.f.	<0.2	59.0 ± 3.0	n.r.	292.9 ± 11.7
5	β	R-3-APA	n.f.	n.f.	n.f.	n.f.	5.9 ± 0.6[e]	158.0 ± 19.0 [e]	n.r.	210.9 ± 23.4[e]
5	β	S-3-APA	n.f.	n.f.	n.f.	n.f.	[e]	[e]	n.r.	[e]
5	γ	D-4-APA	n.f.	n.f.	n.f.	n.f.	21.0 ± 2.0 [e]	444.0 ± 47.0 [e]	n.r.	171.0 ± 5.9[e]
5	γ	L-4-APA	n.f.	n.f.	n.f.	n.f.	[e]	[e]	n.r.	[e]
5	δ	5-APA	n.f.	20.3 ± 1.7	413.3 ± 10.7	846.7 ± 14.7	63.0 ± 12.0	341.0 ± 59.0	n.r.	316.3 ± 35.1
5	α	D-Glu	18.5 ± 0.0	17.8 ± 3.0	1121.4 ± 20.9	5730.8 ± 33.7	<2	503.0 ± 82.0	135.0 ± 50.0	456.1 ± 29.4
5	α	L-Glu	42.4 ± 0.0	38.9 ± 4.1	26,336.1 ± 228.5	84,811.7 ± 705.4	<2	819.0 ± 113.0	261.0 ± 15.0	1235.9 ± 73.6
6	α	D-Ile	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
6	α	L-alloIle	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.r.
6	α	L-Ile	n.f.	n.f.	16,638.6 ± 255.7	15,752.2 ± 43.1	n.r.	n.r.	n.r.	n.f.
6	α	D-Leu	5.0 ± 0.8	4.1 ± 0.1	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
6	α	D-Nle	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.r.
6	α	L-Leu	9.7 ± 1.5	6.5 ± 1.0	38,344.8 ± 536.9	26,978.6 ± 71.4	n.r.	n.r.	n.r.	n.f.
6	α	L-Nle	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.r.
6	ε	EACA	n.f.	28.6 ± 6.6	n.f.	n.f.	2014.0 ± 86.0	n.r.	n.r.	262.3 ± 5.2

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 3. *Continued*. Summary of the abundances in parts-per-billion (ppb) of the C_2–C_6 amino acids in the 6 N HCl-hydrolyzed (total) hot water extracts of the Winchcombe meteorite and several CM carbonaceous chondrites as comparison.[a]

C#	Amine position	Amino acids	CM2 Winchcombe (Subtype CM2.0–2.6) Free	CM2 Winchcombe (Subtype CM2.0–2.6) Total	Fall site soil Free	Fall site soil Total	CM1 MET 01070 (Subtype CM2.0) Total	CM2 Murchison (Subtype CM2.5) Total	CM2 Murray (Subtype CM2.5) Total	CM2 Asuka 12236 (Subtype CM3.0/2.9) Total
7	α	D-2-AHA	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.r.
7	α	L-2-AHA	n.f.	n.f.	n.f.	n.f.	n.r.	n.r.	n.r.	n.r.
Total $C_{2\text{-}4}$ amino acids			749.8 ± 25.5	713.8 ± 39.2	11,4976.5 ± 1458.8	342,142.2 ± 5505.4	494.0 ± 41.2	12,861.0 ± 2612.5	8272.0 ± 506.6	26,323.6 ± 512.2
Total C_5 amino acids			483.4 ± 12.5	379.3 ± 21.0	56,446.0 ± 529.0	122,713.6 ± 722.7	105.5 ± 12.2	6194.0 ± 299.4	3230.0 ± 781.7	5412.6 ± 154.5
Total C_6 amino acids			14.6 ± 1.7	39.2 ± 6.7	54,983.4 ± 594.7	42,730.7 ± 83.4	2014.0 ± 86.0	n.r.	n.r.	262.3 ± 5.2
Total amino acids[f]			1247.9 ± 28.4	1132.3 ± 45.0	226,405.9 ± 1661.8	507,586.6 ± 5553.3	2613.5 ± 96.1	19,055.0 ± 2629.6	11,502.0 ± 931.5	31,998.5 ± 535.1

n.f. denotes compound not present in sample above detection limits; n.r. denotes compound not reported.

[a]The associated errors are based on the standard deviation of the average value between three separate measurements (N) with a standard error, rounded to one decimal place. $\delta x = \sigma x \times N^{-1/2}$. Amino acids were identified by the representative mass fragmentation patterns and comparison to the retention time of the amino acid standards. The abundances of each of the amino acids were acquired by peak area integration of the corresponding ion fragment. The amino acid data for MET 01070 and Murchison were taken from Glavin et al. (2011). The amino acid data for the Murray meteorite were from Ehrenfreund, Glavin, et al. (2001), and the data for the Asuka 12236 meteorite were from Glavin et al. (2020). No amino acid was found in the procedural blank above the detection limit.

[b]Optically pure standard not available for enantiomeric identification. The order of elution of the D- and L-enantiomers was tentatively identified, as the D-enantiomer elutes first followed by the L-enantiomer when using the Chirasil-L-Val column.

[c]Enantiomers could not be separated under the chromatographic conditions.

[d]Isovaline enantiomers could not be separated using a CP-Chirasil-L-Val column. Instead, D- and L-isovaline enantiomers were separated using the CP-Chirasil-Dex CB.

[e]Enantiomers were separated but could not be identified due to the lack of optically pure standards.

[f]The errors of the total amino acid abundances are obtained by standard propagation calculations.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

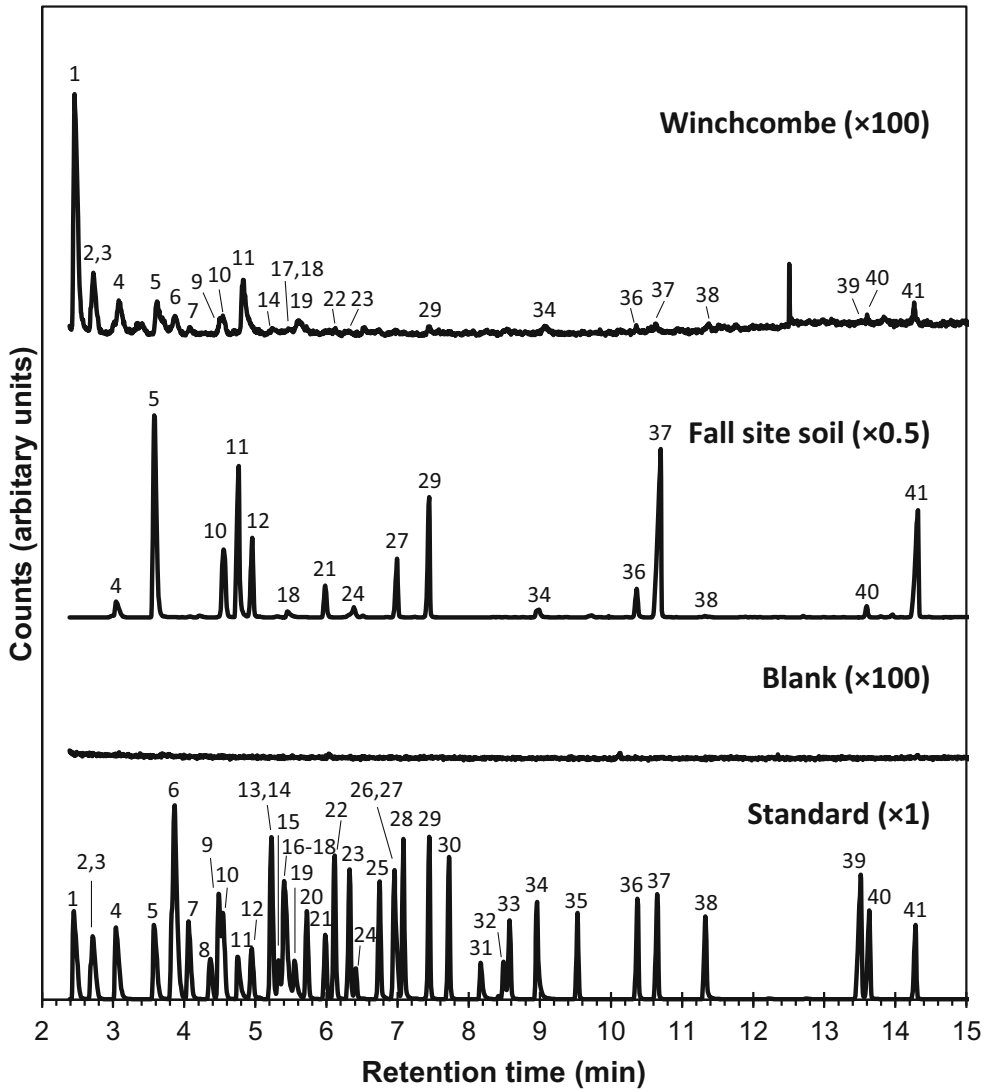


Fig. 3. The 2–15 min regions of the GC-MS total ion current (TIC) chromatograms collected in the selected ion monitoring (SIM) mode of the derivatized (N-TFA, O-isopropyl) 6N HCl-hydrolyzed hot water extracts of the Winchcombe meteorite, the fall site soil, the procedural blank, and the mixed amino acid standard. Analyte identifications are indicated as peak numbers corresponding to Table 2. The external standard pyrene (*m*/*z* 202; eluted at ~22 min) was added to each of the samples for amino acid quantification. The peak of pyrene did not co-elute with any amino acid and is not shown in the chromatograms. The data used for this figure can be found in the Supporting information.

of Winchcombe is 1132 ± 49 ppb, which is about 10 times lower than most CM falls, such as Murchison (14,600 ppb; Glavin et al., 2006), Mighei (5839 ppb; Botta et al., 2002), Mukundpura (14,550 ppb; Pizzarello & Yarnes, 2018), and Aguas Zarcas (up to 43,800 ppb; Glavin et al., 2021). The amino acid abundances for CM falls are highly variable, ranging from none detected in a stone of Aguas Zarcas (Pizzarello et al., 2020) to 43,800 ppb in a different fragment of the same meteorite (Glavin et al., 2021), and this can be accounted for by the brecciated nature of these samples. Given that the Winchcombe meteorite is lithologically highly variable with the presence of lithologies from CM2.0 to CM2.6 (Suttle et al., 2023), the amino acid contents of these lithologies can potentially span a wide range. During the initial examination of the Winchcombe meteorite, individual stones were separately allocated for the investigations of their mineral and organic contents. Furthermore, the allocated ~1 g of Winchcombe sample was insufficient to perform both mineral and organic analyses. Therefore, the mineralogy of the Winchcombe stone allocated for this study was not explored in this study.

From previous studies of amino acids in CCs, a general trend of decreasing total amino acid

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

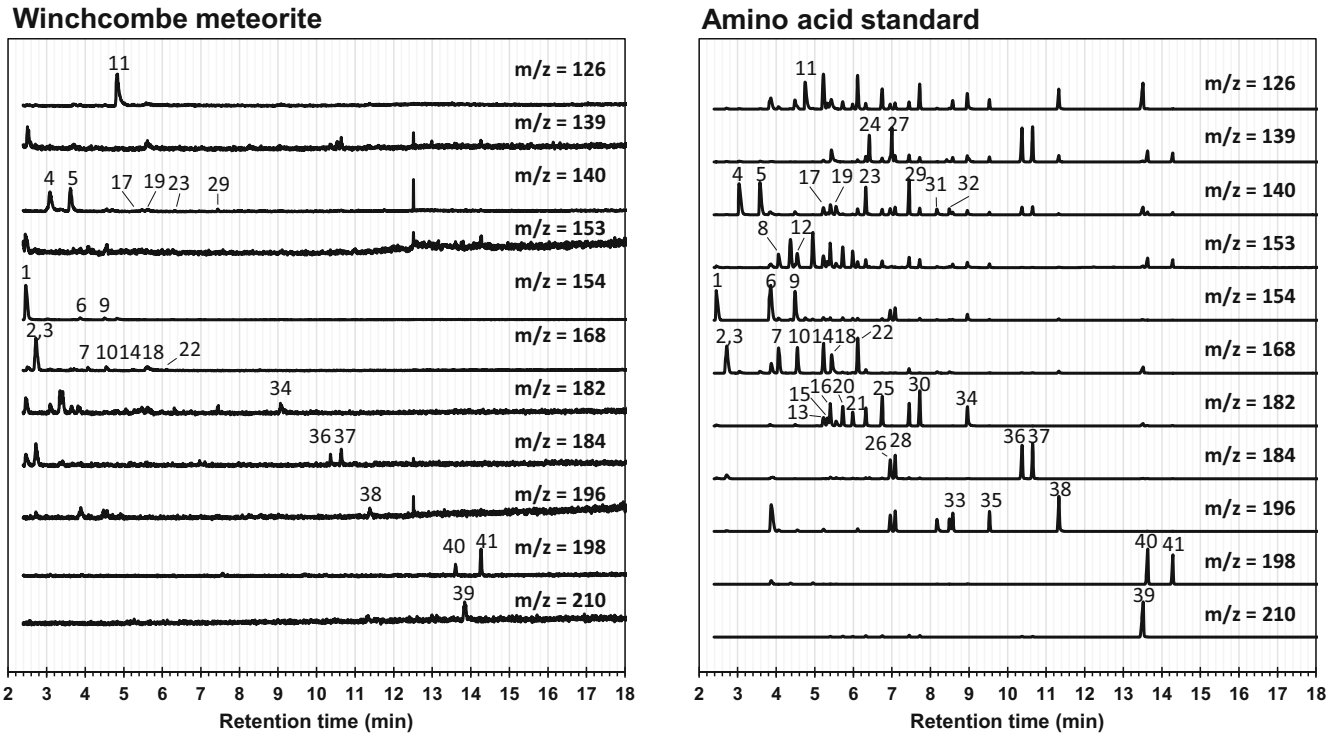


Fig. 4. The 2–15 min regions of the GC-MS chromatograms. Single-ion GC-MS traces (*m/z* 126, 139, 140, 153, 154, 168, 182, 184, 196, 198, and 210) of the derivatized (N-TFA, O-isopropyl) 6N HCl-hydrolyzed hot water extracts of the Winchcombe meteorite and the mixed amino acid standard. Analyte identifications are indicated as peak numbers corresponding to Table 2. The peaks were identified by comparing the retention time and mass fragmentation pattern to those in the amino acid standard run on the same day. D- and L-isovaline enantiomers could not be separated under the chromatographic conditions (Peaks #2 and #3), but their separation was achieved on a different column (CP-Chirasil-Dex CB GC Column; Fig. 5). Similar chromatograms for the nonhydrolyzed fractions were also obtained and can be found in the Supporting information.

abundances with increasing aqueous alteration has been observed (Glavin et al., 2020), as a result of a higher rate of thermal decarboxylation and/or hydrolysis of bound amino acid precursors (Bada et al., 1991; McCollom, 2013; Pietrucci et al., 2018). For example, aspartic acid decomposes by reversible deamination producing fumaric acid and ammonia. The half-life of this reaction is estimated to be 10^5 years at 25 °C and neutral pH (Bada et al., 1991). At high temperatures at 240 °C and neutral pH, alanine thermally decomposes and forms ethylamine as product (Shock & Schulte, 1990). Using computational modeling, Pietrucci et al. (2018) showed that aqueous processing can lead to the decomposition of the α-amino acids (glycine and isovaline) through deamination and decarboxylation. The highest amino acid abundances are observed in the least altered chondrites (e.g., ~36,000 ppb in CM3.0/2.9 Asuka [A-] 12236), and the lowest total amino acid abundances are observed in the most altered petrologic type 1 chondrites (e.g., 660 ppb in Scott Glacier [SCO] 06043; 710 ppb in Meteorite Hills [MET] 01070); these meteorites were given the subtype of 2.0 according to the classification by Rubin et al. (2007) and Glavin et al. (2011, 2020). The high abundance of amino acids in A-12236 suggests that this meteorite has been less affected by aqueous alteration than any previously studied CMs, supporting its petrologic type assignment of 3.0/2.9 built on the meteorite's texture, chemical/isotopic compositions, and the abundance of unmodified presolar silicate grains (Kimura et al., 2020; Nittler et al., 2021). Therefore, based on just the low total amino acid abundance of the Winchcombe meteorite alone, it is on par with meteorites showing a higher degree of aqueous alteration and is distinguished from other CM2s such as Aguas Zarcas and Murchison that have experienced an intermediate degree of aqueous alteration on their respective parent bodies.

The total amino acid abundance in CCs is determined by the efficiency of two competing processes —amino acid decomposition via thermal/hydrothermal decomposition and oxidation as described above, and amino acid syntheses such as the Strecker-cyanohydrin synthesis, Michael addition, and/or other synthetic routes (Cooper & Cronin, 1995; Koga & Naraoka, 2017;

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

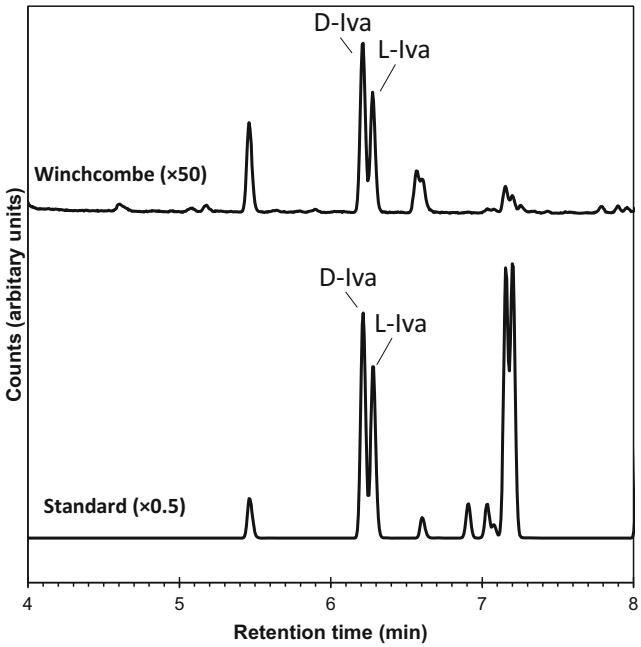


Fig. 5. The 4–8 min regions of the GC-MS total ion current (TIC) chromatograms collected in the selected ion monitoring (SIM) mode, focusing on the resolution of D- and L-isovaline, of the derivatized (N-TFA, O-isopropyl) 6N HCl-hydrolyzed hot water extracts of the Winchcombe meteorite and the mixed amino acid standard.

Miller, 1957; Peltzer et al., 1984). Therefore, in contrast to their decomposition during hydrothermal alteration as previously discussed, the low amino acid concentration in Winchcombe can potentially be explained by brief episode(s) of aqueous alteration events on the Winchcombe parent body, therefore yielding only a small fraction of amino acids, and a lower extent of aqueous process-associated amino acid decomposition. The amino acid decomposition rate via aqueous process is between 10^{-11} and 10^{-13} s^{-1} at 100 °C, which is equivalent to half-lives between one and several tens of thousands of years (Pietrucci et al., 2018). Therefore, even though liquid water could have been present inside the parent body for several millions of years (Doyle et al., 2015; Fujiya et al., 2012), the alteration event may have only been episodic that retained some of the amino acids previously synthesized. Variation in the types of carbonates (e.g., calcite, dolomite, aragonite, breunnerite) and their isotopic compositions ($\delta^{13}C$ values ranging from +37 to +60‰, $\delta^{18}O$ values from +25 to 32‰, and $\delta^{17}O$ values from +10 to 16‰) have been observed for CM chondrites that support the view that aqueous alteration episodes could have taken place as discrete events on the parent body (Chan et al., 2017; Tyra et al., 2007, 2012). Investigation of the organo-carbonate associations in CM chondrites also showed that the carbonates might not have formed under equilibrium conditions from a single fluid—the early formed carbonates are organic matter-barren indicating that they were formed from highly oxidized fluids that led to the oxidation of the organic matter; the later formed carbonates were found to contain organic material suggesting that they were formed from a more evolved aqueous fluid (Chan et al., 2017). Thus, rather than a continuous heating regime caused by the radioactive decay of short-lived radionuclides, small amounts of liquid water could have been produced episodically by short-term processes like impact, which resulted in short duration, episodic aqueous alteration throughout the history of the asteroid parent body (Brearley, 2006; Lange et al., 1985). While deformed aragonite crystals observed in Winchcombe suggest a history of impact, multiple generations of carbonates in Winchcombe suggest that the Winchcombe parent body has experienced episodic aqueous alteration that involved three discrete, and potentially short-term, alteration events (Lee et al., 2022).

While the extent of low-temperature parent body aqueous processes (<25 °C as estimated for CM2 chondrites; Zolensky et al., 1989, 1993) can influence the total amino acid abundances in meteorites, thermal processes can result in the thermal decomposition of amino acids in CM2 chondrites that have experienced higher metamorphic temperatures, such as Sutter's Mill (150–400 °C; Jenniskens et al., 2012), thermal metamorphosed CCs (e.g., CV, CO, ordinary chondrites, and ureilites; 200–600 °C; Huss et al., 2006), and other range of CCs that had been thermally metamorphosed subsequent to aqueous alteration (TMCCs; or termed the "CYs") such as Yamato (Y-) 86029 and Y-980115 (up to 600 °C; Harries & Langenhorst, 2011; King et al., 2019; Nakamura, 2005; Tonui et al., 2002, 2003, 2014). At these elevated temperatures, amino acids are either thermally destroyed via solid-phase thermal decomposition (Rodante et al., 1992) or a range of amino acids structurally different from that typically formed by low-temperature aqueous process could be synthesized, such as through Fischer–Tropsch-type (FTT) reactions (Anders et al., 1973). However, the Winchcombe meteorite does not display any evidence of high-temperature alteration such as phyllosilicate dehydration (Suttle et al., 2023). The presence of tochilinite in Winchcombe also supports a low-temperature condition of the aqueous event, as tochilinite precipitates under reducing, alkaline (pH > 11.5) fluids and at low temperatures (<160 °C; Vacher et al., 2019). Therefore, the mineralogy of Winchcombe indicates that it has not experienced post-hydration thermal metamorphism, and thus, the low amino acid abundance is not due to their destruction through high-temperature thermal

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

decomposition, but more likely a result of their synthesis during a series of brief, episodic aqueous alteration events.

Assessing the Free to Total Amino Acid Ratios

The majority of the amino acids in the Winchcombe meteorite are present in the free form, with a free:total amino acid ratio of ~1:1. Amino acids from terrestrial sources are typically bound as proteins and therefore have much lower free:total amino acid ratios (Botta et al., 2007; Burton, Grunsfeld, et al., 2014; Glavin et al., 2006). Therefore, the higher free:total amino acid ratio (~1:1) indicates the presence of indigenous amino acids in the Winchcombe stone, whereas the free amino acid content is contributed mostly by the free, non-proteinogenic α-AIB in the sample. The feature of having α-methyl amino acids presenting as "free" amino acids is expected as they are less prone than α-H amino acids to form derivatives (Cronin & Pizzarello, 1983). The free:total ratio of glycine (~80% free) is also among the higher end of the value obtained for glycine in other CCs, although not as high as observed in the CM3.0/2.9 A-12236 (~97% free; Glavin et al., 2020). The overall free:total ratio observed for the Winchcombe meteorite is higher than the typical range from ~30% to 70% measured in other CI, CM, and CR chondrites, such as CM2 Murchison (~30% free), CM2.7 Paris (~45% free), and CM3.0/2.9 A-12236 (~83% free amino acids; Glavin et al., 2006, 2011, 2020; Martins et al., 2015; Pizzarello et al., 2008). With these observations, the free:total amino acid ratio has been suggested to link to the extent of aqueous alteration CC chondrites have experienced, with higher free:total amino acid ratios (relatively higher abundance of free amino acids compared to the total amino acid abundance) observed for meteorites exhibiting a lower degree of aqueous alteration. This correlation, initially observed for Antarctic CR2 chondrites, was not obvious in the less aqueously altered CR3 chondrite Queen Alexandra Range (QUE) 99177 when compared to the CR2 Elephant Moraine (EET) 92042 analyzed in the same study (Glavin et al., 2011), and thus, the authors determined that there was a need for further amino acid analyses from additional carbonaceous chondrites that experienced minimal aqueous alteration to validate such tentative correlation. In the case for the Winchcombe meteorite, its amino acid content is not entirely comparable to any particular meteorite from the range of CM chondrites—while the low total amino acid abundance is comparable to that of heavily altered CMs, the high free:total amino acid ratio is on par with that observed in CMs that show very low degrees of aqueous alteration. Such discrepancies, echoing the wide range of degrees in aqueous alteration indicated by its mineralogy (CM2.0 to CM2.6 clasts held together by a weak cataclastic matrix), suggest that Winchcombe could represent a class of weak, poorly lithified meteorite not previously studied.

Amino acids can be released from their bound form upon acid hydrolysis in CCs from two sources: (1) L-amino acids derived from terrestrial protein and/or (2) extraterrestrial amino acids derived from derivatives and/or acid labile precursors (e.g., dipeptides [the smallest peptides], diketopiperazines [cyclic dimers of amino acids], hydantoins; Bada et al., 1991; Kalník et al., 2021; Shimoyama & Ogasawara, 2002). On the contrary, extensive parent body aqueous alteration involving multiple cycles of wet–dry processes would have formed a larger quantity of peptides, through the condensation of amino acid monomers to form dimers, resulting in a lower free:total amino acid ratio as observed in the more aqueously altered CCs (Glavin et al., 2011). Condensation of amino acids can take place in aqueous solution at low temperatures (i.e., ~25 °C, which is also a possible temperature estimated for the aqueous environment on CM parent bodies; Zolensky et al., 1993), through the process of glycine + glycine = glycylglycine + H_2O or glycine + glycine = 2,5-diketopiperazine + $2H_2O$ (Shimoyama & Ogasawara, 2002). As seen from these processes, the oligomerization of amino acids requires an effective medium, such as clay minerals, to efficiently remove the water produced from the reaction. The bulk of the fine-grained material in Winchcombe is composed of serpentine and tochilinite, similar to the majority of serpentine group mineral observed for CM chondrites matrix (Zolensky et al., 2018), suggesting such water was consumed via serpentinization which hydrated olivine during the parent body aqueous alteration event. The surface of these phyllosilicates has also been shown to be capable of producing amino acids as well as adsorbing peptides (Fuchida et al., 2014; Vinogradoff et al., 2020; Wang & Lee, 1993). Therefore, the presence of larger quantities of extraterrestrial amino acids in the bound form in CCs would indicate that these free organic monomers have evolved to bound peptide-like amino acids through asteroidal processes. The presence of Fe-rich phyllosilicate can hamper the formation of amino acids. As the Winchcombe meteorite is composed predominantly of Fe- and Mg-bearing serpentines, the phyllosilicates can limited the production of α-amino acids and *n*-ω-amino acids via the pathways of formose (condensation of formaldehyde) and Maillard-type reactions (amine–sugar reactions; Vinogradoff et al., 2020), and account for the overall low amino acid abundance in particular for the high molecular-weight species. Nevertheless, some amino acids, in particular the α-amino acids, could still be synthesized via other

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

pathways such as the Strecker cyanohydrin synthesis, which requires a hydrogen cyanide or nitrile source of precursor molecules. It is not surprising that if given a full extent of aqueous event occurring on Winchcombe's parent body, abundant and structurally diverse amino acids could be effectively synthesized and potentially oligomerized into peptides. The composition of mostly free amino acids including the terrestrially rare ones in Winchcombe suggests that such asteroidal chemical evolution is not at its full possible extent, and is consistent with a short duration of low-temperature aqueous activity inside the parent body.

Distribution of Indigenous Amino Acids

Although Winchcombe was collected on the soil-free driveway of the Wilcock house, a soil sample was collected from the garden (adjacent to the driveway) and analyzed to provide an account for the potential terrestrial contaminations from the local environment—if the amino acids in the meteorite were derived from the local area, the meteorite and soil samples would share a common amino acid distribution. The amino acid abundance and distribution of the hydrolyzed and nonhydrolyzed hot water extracts of the Winchcombe meteorite are distinct from that of the hot water extracts of the fall site soil.

The total amino acid abundance of the soil (507,588 ppb) is significantly higher than that of the Winchcombe meteorite (1132 ppb). The most abundant amino acids found in the soil are the proteinogenic amino acids glycine, alanine, aspartic and glutamic acids, and valine, ranging from 54,677 to 90,542 ppb, making a striking contrast to the low levels of both proteinogenic and non-proteinogenic amino acids detected in the Winchcombe meteorite (4–331 ppb). Furthermore, the procedural blank is essentially free of targeted amino acids above the detection limit of the GC-MS (10 pg of amino acid; Fig. 3). However, the low amino acid abundances in the procedural blank and the meteorite sample do not rule out the possibility of amino acid contamination from the terrestrial environment of the fall site, during collection, handling, and curation of the Winchcombe sample prior to the introduction of the witnessing procedural blank. Therefore, in order to understand the indigenous amino acid content of Winchcombe, it is essential to determine the abundances of terrestrially rare amino acids in the Winchcombe meteorite, and contrast their relative abundances to that observed for the fall site soil. The contrasting amino acid contents between the Winchcombe meteorite, fall site soil, and the procedural blank indicate that the level of terrestrial amino acid contamination accrued from the fall site and sample processing in the laboratory is low in this study (Figs. 3 and 6).

The Winchcombe meteorite contains a range of C_2–C_6 α-, β-, γ-, δ-, and ε-amino acids (Table 3). The most abundant amino acid identified in the Winchcombe meteorite is the terrestrially rare α-aminoisobutyric acid (AIB; 331 ppb), which is followed by the proteinogenic amino acid glycine (163 ppb), and then another non-proteinogenic amino acid isovaline (269 ppb). Trace to low levels (4–57 ppb) of alanine; aspartic and glutamic acids; β-alanine; α-, β-, and γ-amino-*n*-butyric acids (ABA); C_5 amino acids valine; norvaline; 5-aminovaleric acid (5-ava, or 5-aminopentanoic acid, 5-apa); and C_6 amino acids leucine and ε-amino-*n*-caproic acid (or ε-amino-hexanoic acid; EACA) were identified. The C_6 amino acid EACA (20 ppb) from the Winchcombe meteorite extract is present only in the bound form. EACA has previously been attributed to contamination from the hydrolysis of the polymer (peptide) Nylon-6 H-$[NH(CH_2)_5CO]_n$-OH derived from storage bags used in sample collection and curation (Glavin et al., 2006). However, the Winchcombe stones have only been stored in polyethylene $(C_2H_4)_n$ sample bags; therefore, the origin of EACA in this study is not obvious, potentially traces of Nylon-6 from nylon storage bags used for the containment of other samples in the curation facility. We have also explored the plausibility of whether EACA is indigenous to the Winchcombe meteorite. EACA, a *n*-ω-amino acid, was suggested to have an extraterrestrial origin in thermally altered meteorites as it was found to be present in high abundance and occur predominantly in the free form in these meteorites (Burton et al., 2012). However, as EACA was found only in the bound form in the Winchcombe meteorite, it is difficult to establish an extraterrestrial origin for EACA without other supporting evidence such as compound-specific isotopic composition.

An example of the presence of amino acids indigenous to the Winchcombe meteorite sample is given by the detection of terrestrially rare amino acids in the meteorite extracts, including AIB, ABA, and isovaline. The elevated abundances of some of these compounds, such as α-AIB (331 ± 36 ppb) and isovaline (391 ± 17 ppb), which are also the two most abundant amino acids in Winchcombe and are both not present in the soil and procedural blank above the analytical detection limit (Fig. 3; Peak#1 = α-AIB; Peak#2,3 = isovaline), provide a strong indication that these amino acids are extraterrestrial in origin. However, other C_5 non-proteinogenic amino acids previously identified in CM2s like the Aguas Zarcas and Murchison meteorites (Glavin et al., 2021), such as the R,S-3-aminopentanoic acid (3-apa), D,L-4-aminopentanoic acid (4-apa), 5-aminopentanoic acid (5-apa), 3-amino-3-methylbutanoic acid (3-a-3-mba), and 3-amino-2,2-dimethylpropanoic acid (3-a-2,2-dmpa), were not

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

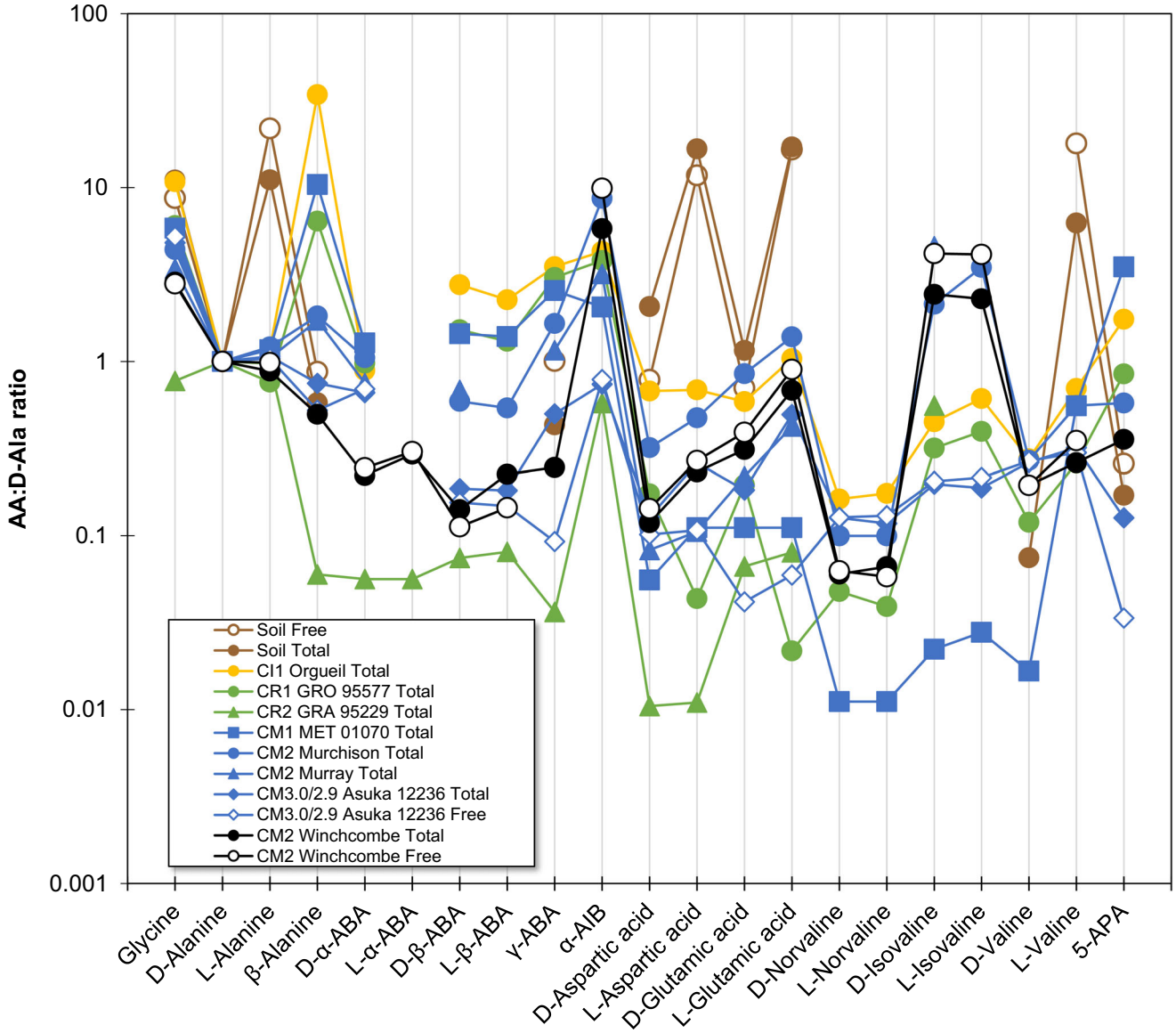


Fig. 6. The relative abundances (relative to D-alanine = 1) of amino acids in the 6 N HCl-hydrolyzed, hot water extracts of selected carbonaceous chondrites. The amino acid abundances for the Winchcombe meteorite and the fall site soil sample were taken from the data in Table 3. The amino acid data for Orgueil, MET 01070, Grosvenor Mountains 95577, and Murchison were taken from Glavin et al. (2011). The amino acid data for the Murray meteorite were from Ehrenfreund, Glavin, et al. (2001), the data for the Graves Nunataks 95229 meteorite were from Martins, Alexander, et al. (2007), and the data for the Asuka 12236 meteorite were from Glavin et al. (2020). (Color figure can be viewed at wileyonlinelibrary.com)

identified in the nonhydrolyzed Winchcombe meteorite extract, and only 5-apa was detected at low level (~20 ppb) in the hydrolyzed extract. The elevated levels of the non-proteinogenic amino acids α-AIB and isovaline have also been reported for CM chondrites such as the Murchison meteorite (Cronin & Pizzarello, 1983; Glavin et al., 2021). Although either the L- or D-enantiomer of isovaline has been observed in some microbial peptides (Bada, 1997), and it has been shown that microfungi can produce AIB and isovaline (both racemic and an L_{ee} of 15.5% have been observed for fungi-associated isovaline) in standard conditions on agar plates (Brückner et al., 2009), these were reported to be of trace amounts, and their abundances relative to proteinogenic amino acids like glycine were not reported in their study. Therefore, their association with fungal peptide does not directly rule out the possibility that they are indigenous in the meteorite samples, in particular when both α-AIB and isovaline are present at a notable dominance over other common terrestrial proteinogenic

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

amino acids. A contamination source contributing large amounts of non-proteinogenic amino acids to only the Winchcombe meteorite but not the soil or procedural blank samples is highly improbable, but such possibility cannot be entirely ruled out without the support from isotopic data. Future compound-specific stable isotopic analyses (CSIA) of amino acids would help constrain the origin of these protein amino acids. CSIA measurements of the amino acids in the Winchcombe meteorite were not possible for this study due to their extremely low abundances and limited meteorite sample available for analysis. With a detection limit of 1 nmol for carbon CSIA using the gas chromatography-isotope ratio mass spectrometry (GC-IRMS) at Imperial College London, future analysis of amino acids by CSIA requiring at least 10 g of samples may help constrain the origin of the non-racemic ($D/L \neq 1$) amino acids in the Winchcombe meteorite.

Enantiomeric Ratios of Amino Acids

Terrestrial biology uses only the L-enantiomers of chiral amino acids except in rare scenarios. On the contrary, abiotic, extraterrestrial amino acid synthetic pathways such as the Strecker-cyanohydrin synthesis result in racemic mixtures of amino acids ($D/L \sim 1$; Peltzer et al., 1984; Wolman et al., 1972). Therefore, the indigenous nature of the detected amino acids in Winchcombe can be established by the racemic mixtures of their D- and L-enantiomers. Interpretation of the enantiomeric ratios of amino acids and using these values as a metric to evaluate the pristine nature of these molecules have focused mainly on the α-methyl amino acids (i.e., amino acids with the structure of R–C[CH_3][NH_2]–COOH, such as α-AIB and isovaline). It is because unlike α-methyl amino acids, the α-hydrogen amino acids (i.e., amino acids with the structure of R–CH[NH_2]–COOH, such as glycine, alanine, aspartic acid, and glutamic acid) are common in terrestrial biology, and thus, their interpretations are not as straightforward and may also be influenced by terrestrial contamination. Furthermore, α-methyl amino acids are known to resist racemization and have helix-inducing and stabilizing effects (Pizzarello et al., 2003; Pollock et al., 1975); therefore, these amino acids can retain their initial enantiomeric excesses despite exposure to aqueous processes on the parent body, and thus have become the focus of the discussions of molecular asymmetry in meteorites and the roles of amino acids in prebiotic chemistry.

High D/L ratios have been obtained for the proteinogenic amino acid alanine (1.13 ± 0.16) and non-proteinogenic amino acids norvaline and isovaline (0.91 and 1.06, respectively), and moderate D/L ratios (0.63–0.75) for α-ABA, β-ABA, valine, and leucine, indicating that a large fraction of these amino acids is indigenous to the Winchcombe meteorite. Proteinogenic α-H-amino acids that are commonly derived from terrestrial contamination, such as serine and threonine, are found predominantly as the L-enantiomers (D/L ratio was as low as 0.09 for serine, down to almost enantiopure for threonine) in the soil collected from the meteorite fall site, and these two amino acids are absent in the Winchcombe meteorite.

The D/L enantiomeric ratios calculated for the amino acids in the Winchcombe meteorite and the corresponding L_{ee} values ($\%L_{ee} = [L - D]/[L + D] \times 100$) are presented in Table 4. Large L_{ee} of the terrestrially rare α-methyl amino acid isovaline of over 18% has previously been reported for the aqueously altered CCs such as CM1 SCO 06043, CM2 Murchison and Agua Zarcas, and CI1 Orgueil (Botta et al., 2002; Glavin et al., 2011, 2021; Glavin & Dworkin, 2009; Martins, Hofmann, Gnos, et al., 2007). The high L_{ee} value of over 18% cannot be accounted for solely by their preferential destruction in ice through photolysis by circularly polarized radiation generated from nearby massive O- or B-type stars, as this mechanism has a lower theoretical *ee* boundary of ~2.5% (Modica et al., 2014; Takano et al., 2007); therefore, it has been proposed that the small initial L_{ee} was subsequently amplified by processes like asymmetric autocatalysis (Soai et al., 1995, 1999) and crystallization/racemization of enantiomeric conglomerate crystals (Viedma et al., 2008). L_{ee} of isovaline has only been observed in the intermediate to heavily aqueous altered CCs and not in the pristine, least altered ones such as CM3.0/2.9 A-12236 (−2.4%) and CM2.7 Paris (0.2%; Glavin et al., 2020; Martins et al., 2015). In the Winchcombe meteorite, the D/L enantiomeric ratios of isovaline for both the free ($D/L = 1.01 \pm 0.06$; $L_{ee} = -0.6\%$) and total ($D/L = 1.06 \pm 0.15$; $L_{ee} = -2.8\%$) amino acid extracts are racemic, and thus, L_{ee} has not been observed for this meteorite. This observation supports the abiotic origin for isovaline, however, it contradicts the general observation that L_{ee} of isovaline is associated with more aqueously altered meteorites (petrologic type <2.6, whereas Winchcombe is a CM 2.0–2.6; Suttle et al., 2023). Nevertheless, the magnitude of isovaline L_{ee} varies significantly from 0% to 15.2% within different Murchison stones, and these isovaline L_{ee} values were found to be positively correlated to the amount of the hydrous silicate serpentine and the anhydrous silicate forsterite (Pizzarello et al., 2003). Hence, the racemic ratio observed for isovaline in the Winchcombe stone in this study could indicate that this stone is derived from a less aqueously altered lithology of the heterogeneous Winchcombe meteorite.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 4. D/L amino acid enantiomeric ratios and the L-enantiomeric excess (*ee*) values (%) in the 6N HCl-hydrolyzed (total) hot water extracts of the Winchcombe meteorite and several CM carbonaceous chondrites as comparison.[a]

Amino acids	CM2 Winchcombe (subtype CM2.0–2.6)	Fall site soil	CM1 MET 01070 (subtype CM2.0)	CM2 Murchison (subtype CM2.5)	CM2 Murray (subtype CM2.5)	CM2 Asuka 12236 (subtype CM3.0/2.9)
Iva	1.06 ± 0.15 (−2.8%)	n.f.	0.80 (11.1%)	0.61 ± 0.15 (17.2%)	n.r.	1.05 ± 0.09 (−2.4%)
Ala	1.13 ± 0.16 (−6.3%)	0.09 ± 0.01 (83.4%)	0.86 ± 0.18 (7.7%)	0.82 ± 0.28 (9.6%)	0.95 ± 0.16 (2.4%)	0.93 ± 0.10 (3.4%)
α-ABA	0.75 ± 0.20 (14%)	n.f.	n.r.	n.r.	n.r.	n.r.
Val	0.74 ± 0.17 (14.7%)	0.01 ± 0.00 (97.6%)	0.03 (94.2%)	0.48 ± 0.03 (34.7%)	n.r.	0.82 ± 0.17 (9.7%)
Nva	0.91 ± 0.28 (5%)	n.f.	1.00 (0%)	1.00 ± 0.08 (0%)	n.r.	1.08 ± 0.08 (−3.8%)
β-ABA	0.63 ± 0.29 (23%)	n.f.	1.04 ± 0.17 (−2%)	1.09 ± 0.21 (−4.3%)	n.r.	1.02 ± 0.03 (−1.1%)
Leu	0.63 ± 0.16 (22.7%)	n.f.	n.r.	n.r.	n.r.	n.f.
Asp	0.51 ± 0.16 (32.4%)	0.12 ± 0.01 (78%)	0.50 (33.3%)	0.67 ± 0.11 (19.6%)	0.78 ± 0.66 (12.1%)	0.49 ± 0.06 (34.2%)
Glu	0.46 ± 0.20 (32.4%)	0.07 ± 0.01 (78%)	1.00 (33.3%)	0.61 ± 0.21 (19.6%)	0.52 ± 0.37 (12.1%)	0.37 ± 0.09 (34.2%)

n.f. denotes compound not present in sample above detection limits; n.r. denotes compound not reported.
[a]The D/L ratios were obtained from the amino acid concentrations as listed in Table 3. The errors (uncertainties) are obtained by standard propagation calculations using the absolute errors shown in Table 3. The L-enantiomeric excess are presented as $L_{ee}(\%) = (L - D)/(L+D) \times 100$. Negative % values indicate D-excesses.

Lower D/L enantiomeric ratios were observed for other α-H-amino acids including aspartic and glutamic acids in the Winchcombe meteorite (D/L = 0.51 and 0.46, corresponding to large L_{ee} values of 32.4% and 37.2%, respectively; Table 4). Although a strong case for the extraterrestrial origin of the L_{ee} observed in the α-H-amino acids aspartic and glutamic acids cannot be made in the absence of isotopic data, similar large L_{ee} values have also been reported for aspartic and glutamic acids in CCs, and a racemic ratio was observed for alanine, another proteinogenic amino acid, simultaneously in the very same meteorites (Ehrenfreund, Glavin, et al., 2001; Glavin et al., 2010, 2020, 2021; Pizzarello & Cooper, 2001). The L_{ee} observations in some of these studies were supported by extraterrestrial carbon isotopic values that emphasized that such L_{ee} is not derived from terrestrial contamination but is potentially contributed by extraterrestrial processes. For example, the $\delta^{13}C$ values of aspartic and glutamic acid with L_{ee} in Murchison range from −6‰ to +32‰ (Glavin et al., 2012; Pizzarello et al., 2004; Pizzarello & Cooper, 2001), which fall outside of the typical low $\delta^{13}C$ values in terrestrial biology from −60.9‰ to −0.3‰ (Scott et al., 2006). In the Tagish Lake meteorite, the $\delta^{13}C$ values for D- and L-aspartic acid are +24‰ and +29‰ (Glavin et al., 2012), respectively, and thus, the L_{ee} cannot be explained by terrestrial L-aspartic acid contamination. Nevertheless, the moderate $\delta^{13}C$ values of L-aspartic acid and L-glutamic acid (−6‰ and +7‰, respectively) in Murchison could indicate a fraction of terrestrial L-aspartic acid and L-glutamic acid contamination of the meteorite, as mixing terrestrial L-aspartic acids (with a carbon isotope range from −54‰ to −4‰ measured for aspartic acids in a diverse set of terrestrial microorganisms; Scott et al., 2006) with isotopically heavy extraterrestrial aspartic acids of $\delta^{13}C \approx +25‰$ can lead to the observed moderate $\delta^{13}C$ value (Pizzarello et al., 2004). Therefore, the extraterrestrial origin of L_{ee} can be supported by an unequivocally high $\delta^{13}C$ value.

The L_{ee} observed for aspartic and glutamic acids has been attributed to the capability of these amino acids in forming single solid-state metastable conglomerate crystals under "near equilibrium" aqueous condition, through "Ostwald ripening," and eventually reaching enantiopurity with a slight initial *ee* (Viedma, 2005; Viedma et al., 2008). In the conventional crystallization process of chiral compounds, an equal number of D- and L-crystals would be formed in a saturated aqueous solution. During crystallization, two processes occur simultaneously: the continual dissolution and the reaccretion of molecules upon existing crystals. As the solution is not supersaturated, these two rates are balanced at equilibrium, and no new crystals nucleate. However, by adding glass beads to the system (attrition) accompanied by rapid stirring of the solution (Viedma et al., 2008), it increased the solubility. With the molecules dissolved from the solid phase, it caused a slight supersaturation in the solution, and the dissolved molecules also had a preference of adding to larger crystals in the solid phase, that is, Ostwald ripening. The

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

capability of aspartic acid in forming single solid-phase chiral conglomerate crystals is based on its efficiency in two processes: (1) dissolution/recrystallization mass transfer processes and (2) racemization (convert from one enantiomer to the other until the mixture approaches a racemic ratio) in the solution phase further reducing the abundance of the minor enantiomer in solution, and thus without the mechanical energy input, Viedma et al. (2008) demonstrated that aspartic acid may also achieve chirality enhancements. The reactive hindrance of the alkyl substituent accounts for the formation of α-methyl amino acid derivatives and the resistance to racemization of these amino acids lacking an α-hydrogen during aqueous processes, and thus, compared to α-H amino acids, α-methyl amino acids like isovaline are less prone to forming larger structures (Pollock et al., 1975). Similarly, and in contrast to aspartic and glutamic acids, alanine and the majority of the chiral α-H-amino acids preferentially form racemic crystals (Klussmann et al., 2006), on grounds of the lower efficiency of alanine racemization compared to aspartic acid—at aqueous conditions of 25 °C and pH 7.6, alanine has a racemization half-life of 12,000 years, which is more than three times of aspartic acid (3500 years; Bada, 1985). Given that the large L_{ee} in aspartic and glutamic acids and racemic alanine were previously shown to be indigenous to those analyzed aqueously altered meteorites, it is possible that the similar observations made for Winchcombe are also extraterrestrial. Future CSIA analysis of these amino acids can help firmly establish their origin. Although different in context, the same Ostwalt's rule has been used to explain that, while both two or more polymorphs of a compound (e.g., aragonite and calcite) are present in supersaturated solutions on the parent body of Murchison and Murray, the least stable polymorph crystallizes first (in the case of $CaCO_3$, aragonite), followed by polymorphs of greater stability (calcite; Lee et al., 2013; Threlfall, 2003). For Winchcombe, deformed aragonite, which is the least stable carbonate polymorph, crystallized before undeformed calcite, and this sequence is consistent with the Ostwalt's rule (Lee et al., 2022). Therefore, the observed carbonate formation sequence and the deformation of only aragonite in Winchcombe suggest that the parent body aqueous alteration occurred as discrete episodic events.

The large L_{ee} observed for aspartic and glutamic acids accompanied by racemic alanine in the Winchcombe meteorite can potentially support the notion that aqueously processed CCs could have contributed a portion of nonracemic α-H amino acids leading to the origin of homochirality possibly predating the onset of life on Earth. This mechanism, alongside other symmetry-breaking processes such as enantioselective photolysis (Barron, 2000; Meierhenrich et al., 2005; Meinert et al., 2012), adsorption of chiral molecules onto chiral inorganic surfaces (Eckhardt et al., 1993; Hazen et al., 2001; Hazen & Sholl, 2003; Lahav & Leiserowitz, 1999), that can initiate a small *ee*, favors further reactions among the molecules of the adsorbed enantiomer or the remaining enantiomer in solution and subsequently amplify the *ee*.

Amino acids would be expected to retain their initial enantiomeric ratios if they were formed in a cool (~0 to 25 °C) solution that exists for a short duration (10^3 years; Cohen & Coker, 2000). However, as discussed above, on grounds of the low total amino acid abundance and the high free:total amino acid ratio, it is likely that the analyzed Winchcombe stone belongs to the less aqueously altered lithology. Therefore, although the crystallization of metastable conglomerate crystals could be a mechanism that produced the large L_{ee} observed for aspartic and glutamic acids and racemic alanine in some of the aqueous altered CMs, it is not clear if the same mechanism accounts for the L_{ee} observed in CMs that show limited degree of parent body aqueous alteration, such as CM3.0/2.9 A-12236, CM2.7 Paris, as well as in the Winchcombe meteorite analyzed in this study. In other words, it is not certain if the amplification of *ee* can be achieved effectively without the need for an extensive aqueous process. In addition, the racemization half-life of amino acids depends on the particular amino acid, temperature, pH, ionic strength, metal ion chelation, etc. (Bada, 1985). The temperature and pH conditions of the aqueous alteration on CM parent bodies have been estimated to be at temperatures of 1 to approximately 25 °C, with a solution pH of 7 increasing to pH 12 as aqueous alteration advances (Zolensky et al., 1989). Therefore, the racemization rates at lower temperatures and neutral pH are about two to three times and ~ 10 times slower than in 6N HCl and 2 M NaOH, respectively, and thus further understanding of the aqueous condition on Winchcombe's parent body is necessary to establish the linkage to the observed L_{ee}. Yet, a caveat in linking the degree of meteoritic L_{ee} to parent body aqueous alteration is that there could have been multiple aqueous episodes of varying extents; therefore, it is necessary to differentiate these events and if their extents and durations are correlated to the observed L_{ee}.

On the grounds of the heterogeneous nature of CC parent bodies, we also explore the possibility of the redistribution of amino acid L_{ee} to the least altered zones through the circulation of hydrothermal fluid from areas experiencing higher degrees of aqueous alteration. Asteroid parent bodies were initially heated from the decay of the short-lived radionuclides ^{26}Al in an "onion-shell" fashion, with the most strongly heated material

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

located deeply in the interior and gradually decreasing in bands outward. In deeper zones where aqueous alteration was more extensive, amino acids would have quickly lost their initial *ee* signature through racemization (Cohen & Coker, 2000), or they would have been decomposed by thermal alteration if the hydration process completely consumed the water and the dried substrate continued to heat up (Rodante et al., 1992). The "onion-shell" model could account for the presence of CM-like material in zones that never get hotter than 25 °C but still experience hydration. These zones can maintain such low temperatures as the water involved in the exothermic hydration reaction was either completely consumed by the reaction or was frozen out at the asteroid's surface. As these zones are not isolated from each other, amino acids with L_{ee} synthesized via aqueous processes in zones relatively closer to the heat source with higher degree of aqueous alteration could subsequently be remobilized through hydrothermal fluids to the adjacent, less altered bands. Examples of aqueous fluid circulation and the redistribution of dissolved organics can be drawn from an organic-rich vein preserved within a primitive xenolithic CI-like clast hosted in the H4–5 Carancas meteorite (Chan et al., 2018), a CI-like clast in the H3–6 Zag meteorite (Kebukawa et al., 2020), and bright carbonate veins on asteroid (101955) Bennu (Kaplan et al., 2020). Therefore, CC parent bodies are essentially large, chemically open hydrothermal systems where extensive water flow could take place and potentially redistribute amino acids exhibiting L_{ee}. Nevertheless, we have not located any similar vein feature in the Winchcombe meteorite; therefore, this hypothesis remains speculative and will require further evidence to validate.

Alkylated and Nonalkylated PAHs Compositions Indicating Low Degree of Aqueous Alteration

Targeted GC-MS analysis reveals a number of expected PAHs in the Winchcombe extract that were not observed in the procedural blank (Fig. 7). The abundances of the detected PAHs in Winchcombe, fall site soil, and the serpentinite blank are shown in Table 5. The hydrocarbon composition of Winchcombe ranged from naphthalene (2 rings; $C_{10}H_8$) to benzo(ghi)perylene (6 rings; $C_{22}H_{12}$) including alkylated and nonalkylated PAHs, and a total PAH abundance of 6177 ppb (~6 ppm). Concentrations for the few reported CM2 samples are varied with the Winchcombe sample between the endmembers and closer to the least altered CM2s (Kalpana et al., 2021; Martins et al., 2015; Naraoka et al., 1988; Pering & Ponnamperuma, 1971).

The most abundant PAHs in the Winchcombe meteorite are pyrene ($C_{16}H_{10}$; 1553 ppb), fluoranthene ($C_{16}H_{10}$; 1405 ppb), naphthalene ($C_{10}H_8$; 608 ppb), and phenanthrene ($C_{14}H_{10}$; 582 ppb; Table 5). The distribution of PAHs is comparable to those previously reported for the Murchison meteorite, which shares the same four most abundant PAHs (Basile et al., 1984; Krishnamurthy et al., 1992). The PAH composition in Winchcombe is distinct from that observed for CIs, which was found to contain mainly the 3-ring PAHs phenanthrene/anthracene, but no detectable levels of the 2- and 4-ring PAHs naphthalene and pyrene/fluoranthene (Wing & Bada, 1991). However, extracts from other CM2s do seem to have a slightly different distribution of PAHs with fluoranthene and pyrene being less prominent in results presented by Shimoyama et al. (1989) and Naraoka et al. (2000). Although the number of meteorites analyzed for PAHs by solvent extraction and GC-MS is limited, these data are consistent with Winchcombe being a CM2.

The PAHs identified in the soil indicate a high-temperature source (Yunker et al., 2002) and the distribution is consistent with asphalt tar being the source (e.g., Kumpiene et al., 2021), which is a reasonable conclusion from this location and is likely to be from the driveway/road. The PAH distributions, presented as PAH to phenanthrene ratios (phenanthrene was chosen because it was one of the PAHs detected in all samples), of the Winchcombe meteorite and soil samples and their comparison to other CM carbonaceous chondrites are shown in Fig. 8. The PAH abundances of the 2- to 3-ring PAHs relative to phenanthrene of the Winchcombe meteorite sample are comparable to that observed for the Murchison meteorite, which suggests that some of the aromatic hydrocarbons in the meteorite (e.g., naphthalenes, dibenzothiophene, anthracene, methylphenanthrene) may be indigenous to the Winchcombe meteorite. The relative (to phenanthrene) abundances of fluoranthene and pyrene observed in the Winchcombe meteorite are comparable to that in Mukundpura and Paris, and the abundances are intermediate between that observed for the Murchison meteorite and the Winchcombe meteorite's fall site soil. For the 5-ring PAHs such as benzo[e]pyrene and benzo[a]pyrene, their relative abundances in the Winchcombe meteorite are significantly lower than that observed in fall site soil and are similar to the levels observed for the Paris meteorite. These observations indicate that some of the observed PAHs could be indigenous to the meteorite. Analysis of another sample of the Winchcombe meteorite that was collected from a different location may provide more of an insight if not contaminated with PAH; compound-specific isotope analysis ($\delta^{13}C$) may also provide further insights.

While varied positional homologs are observed among the alkylated PAHs in Winchcombe (e.g., methylnaphthalene, dimethylnaphthalene, abundances

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

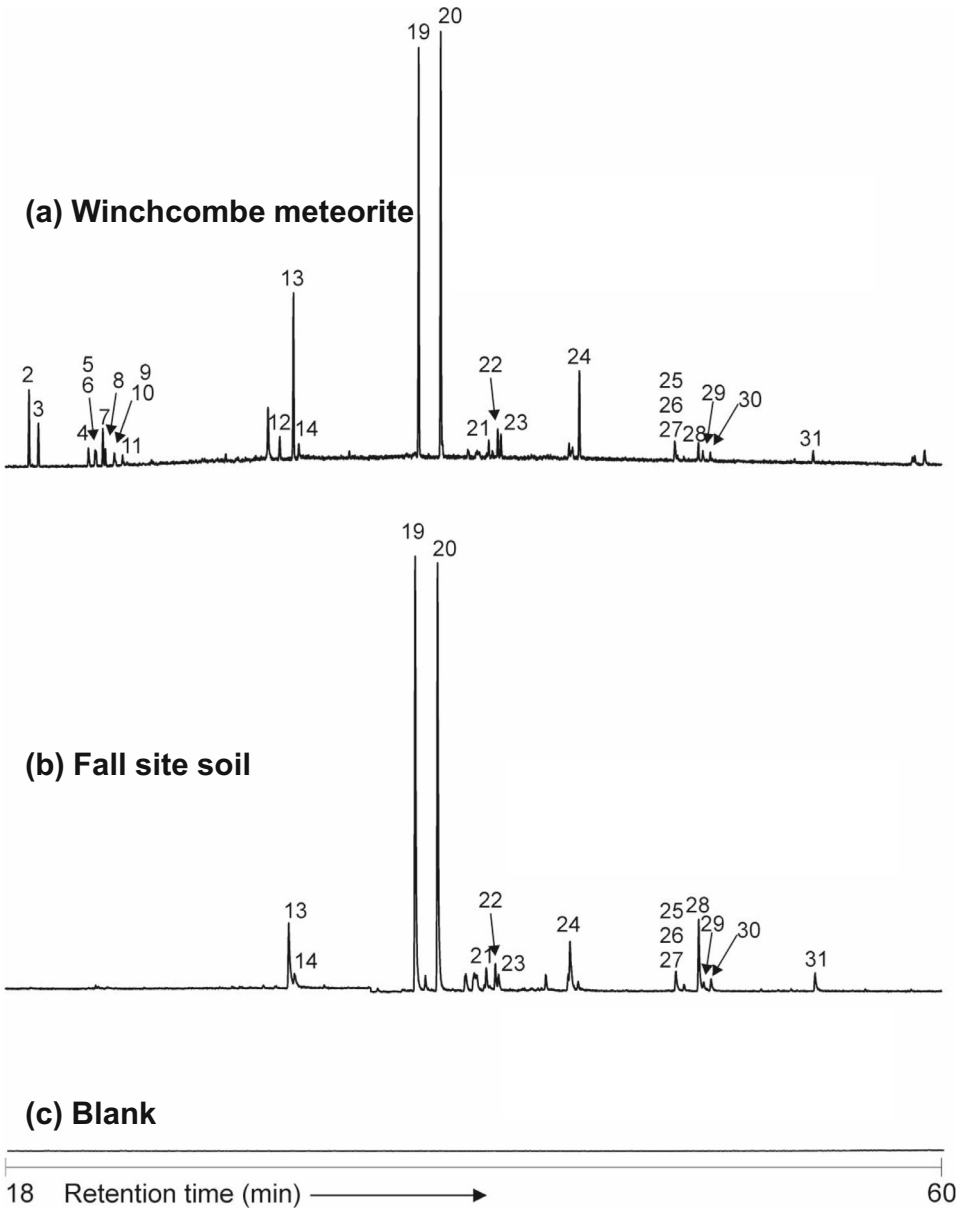


Fig. 7. GC-MS partially reconstructed (summed) mass chromatogram (m/z 142 + 156 + 178 + 184 + 202 + 216 + 228 + 252 + 276) displaying the distribution of selected PAHs in (a) Winchcombe meteorite, (b) fall site soil, and (c) the procedural blank. The chromatograms of the meteorite and soil are normalized against the largest peak and the procedural blank is at the same scale as the meteorite. See Table 5 for numbers referring to PAHs. Although sulfur was removed by copper turnings, there was still some present in the chromatogram giving m/z 128 and m/z 192 fragments, and therefore, these fragments are not used to reconstruct the chromatogram to improve figure clarity (these do not interfere with the quantitation of naphthalene and methylphenanthrenes).

ranging 14–257 ppb), the parent nonalkylated PAHs (e.g., naphthalene, 608 ppb) are always the most abundant. If the observed PAHs were derived from terrestrial contamination, they would appear to have a common signature of extensive alkylation (Clemett et al., 1998; Gingrich et al., 2001). Therefore, although CSIA measurement for the PAHs in the Winchcombe meteorite was not possible due to the limited meteorite sample available for analysis, the level of alkylation of the PAHs observed for Winchcombe is on par with other meteorites in which contamination was not suspected (Elsila et al., 2005; Naraoka et al., 1988). Therefore, considering that (1) the PAH contents between Winchcombe and other CM2s are comparable, (2) the procedural blank is essentially contaminant free, and (3) the predominance of parent nonalkylated PAHs over the

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 5. Identified and quantified PAHs (in ppb) within the Winchcombe meteorite measured by GC-MS and comparison to the PAH content of CM2 Murchison meteorite.

	Compound	Trace Ion (m/z)	CM2.0–2.6 Winchcombe	Fall site soil	CM2.0 Serpentinite (procedural blank)	Mukundpura[a]	CM2.5 Murchison (sample I)[b]	CM2.5 Murchison (sample II)[b]	CM2.7/2.8 Paris[c]
1	Naphthalene	128	608	n.f.	n.f.	n.r.	1120	6400	n.f.
2	2-Methylnaphthalene	142	257	n.f.	n.f.	n.r.	320	1600	n.f.
3	1-Methylnaphthalene	142	153	n.f.	n.f.	n.r.	320	1000	n.f.
4	2/1-Ethylnaphthalene	156	61	n.f.	n.f.	n.r.	n.r.	n.r.	n.r.
5	2,6-Dimethylnaphthalene	156	47	n.f.	n.f.	n.r.	640	1200	n.f.
6	2,7-Dimethylnaphthalene	156	44	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
7	1,3−/1,7-Dimethylnaphthalene	156	122	n.f.	n.f.	n.r.	5	500	n.f.
8	1,6-Dimethylnaphthalene	156	52	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
9	1,4−/2,3-Dimethylnaphthalene	156	48	n.f.	n.f.	n.r.	3	300	n.f.
10	1,5-Dimethylnaphthalene	156	14	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
11	1,2-Dimethylnaphthalene	156	28	n.f.	n.f.	n.r.	n.r.	n.r.	n.f.
12	Dibenzothiophene	184	90	n.f.	n.f.	4800	n.r.	n.r.	n.f.
13	Phenanthrene	178	582	861	6	60,300	2560	4800	1662
14	Anthracene	178	49	139	n.f.	8900	50	100	164
15	3-Methylphenanthrene	192	42	145	n.f.	n.r.	110	200	n.f.
16	2-Methylphenanthrene	192	49	238	n.f.	n.r.			n.f.
17	9-Methylphenanthrene	192	40	189	n.f.	n.r.			n.f.
18	1-Methylphenanthrene	192	20	187	n.f.	n.r.	110	200	n.f.
19	Fluoranthene	202	1405	4588	n.f.	144,000	3700	4900	3455
20	Pyrene	202	1553	4494	n.f.	153,000	3300	4900	3089
21	2-Methylpyrene	216	52	242	n.f.	n.r.	n.r.	n.r.	n.r.
22	4-Methylpyrene	216	104	276	n.f.	n.r.	n.r.	n.r.	n.r.
23	1-Methylpyrene	216	85	161	n.f.	n.r.	n.r.	n.r.	n.r.
24	Chrysene	228	338	744	n.f.	5100	n.r.	n.r.	n.r.
25	Benzo[b]fluoranthene	252	98	234	n.f.	n.r.	n.r.	n.r.	n.r.
26	Benzo[k]fluoranthene	252	22	43	n.f.	n.r.	n.r.	n.r.	n.r.
27	Benzo[j]fluoranthene	252	11	61	n.f.	n.r.	n.r.	n.r.	n.r.
28	Benzo[e]pyrene	252	77	844	n.f.	n.r.	n.r.	n.r.	52
29	Benzo[a]pyrene	252	42	1010	n.f.	n.r.	n.r.	n.r.	90
30	Perylene	252	32	138	n.f.	n.r.	n.r.	n.r.	n.r.
31	Benzo[ghi]perylene	276	52	256	n.f.	n.r.	n.r.	n.r.	n.r.
	Total		6177	14,850	6	376,100	12,238	26,100	8512

n.f. denotes compound not present in sample above detection limits; n.r. denotes compound not reported.
[a]Data from Kalpana et al. (2021).
[b]Data from Pering and Ponnamperuma (1971).
[c]Data from Martins et al. (2015).

alkylated ones, our findings indicate that a limited terrestrial PAH contamination of the Winchcombe meteorite occurred during sample processing and extraction.

The concentrations of the total PAHs reported in the solvent extracts of the CM2.0 Mukundpura were 505 ppm, CM2.5 Murchison was 13–28 ppm, and the CM2.7 Paris meteorite was 9 ppm (these values are slightly higher than that shown in Table 5 because not all PAHs reported in these studies are shown in the table, e.g., 2.4 ppm of fluorene in Mukundpura; Kalpana et al., 2021; Martins et al., 2015; Pering & Ponnamperuma, 1971). These values exhibit a trend that higher total PAH abundances were observed for meteorites that are more extensively aqueously altered. Although Winchcombe's PAH abundance (~6 ppm) is more than two times of that observed for CM2.6–2.9 Y-791198 (a meteorite that is among the most weakly altered CM chondrite currently known; Brearley, 2004; Lentfort et al., 2021), it is only <2% of the PAH abundance observed for the heavily altered CM2.0 Mukundpura (Elsila et al., 2005; Kalpana et al., 2021). By comparing the naphthalene alkylation distributions for nine CM2s, Elsila et al. (2005) observed a correlation between the extent of aqueous alteration and naphthalene alkylation pattern, where the most aqueously altered

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

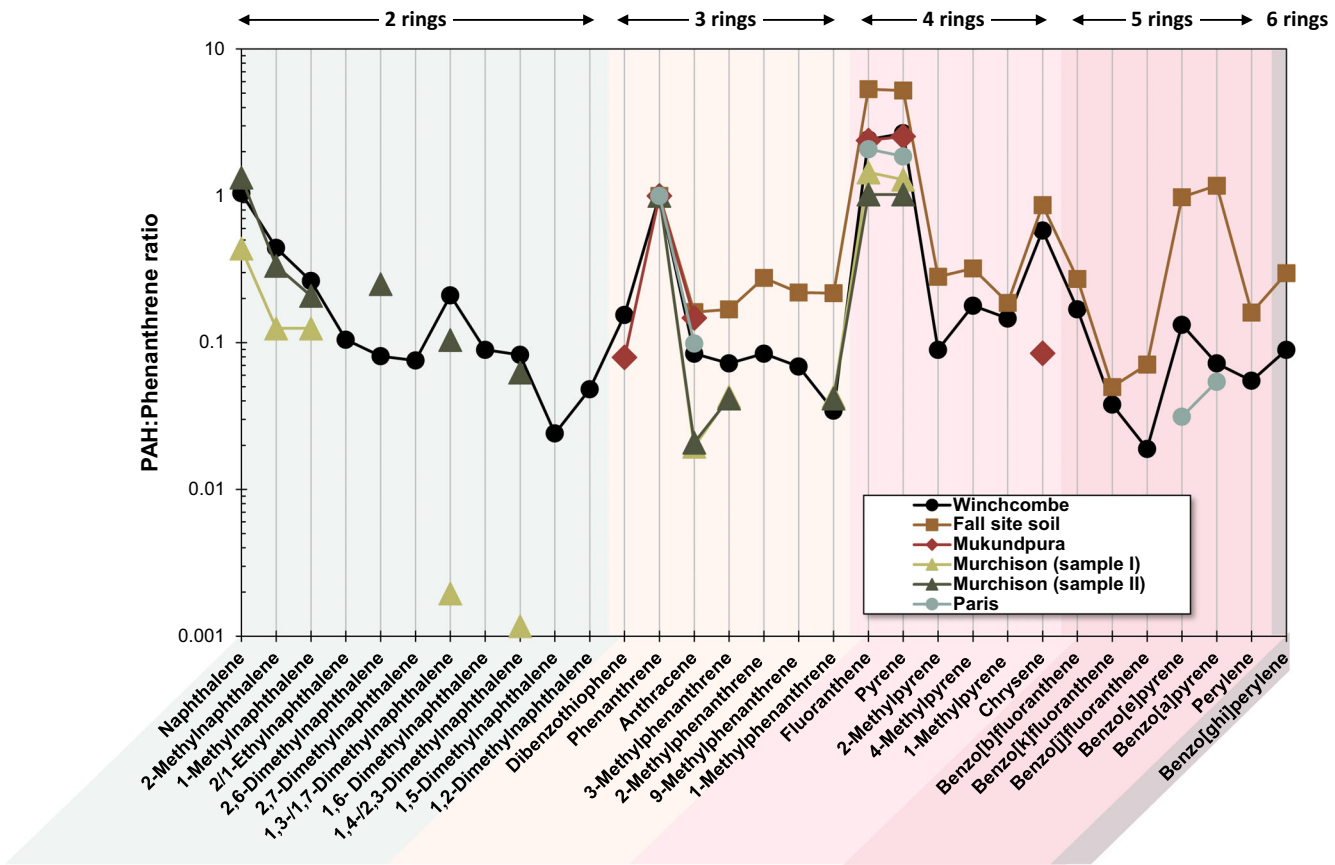


Fig. 8. The relative abundances (relative to phenanthrene = 1) of PAHs in the Winchcombe meteorite, fall site soil, and other CM carbonaceous chondrites including CM2.0 Mukundpura, CM2.5 Murchison, and CM2.7/2.8 Paris. The PAH abundances were taken from the data presented in Table 5. (Color figure can be viewed at wileyonlinelibrary.com)

CM2 meteorites have the highest amount of naphthalene alkylation. The authors attributed the observed correlation to the differences in solubility and volatility between nonalkylated and alkylated PAHs. In the heavily aqueously altered Nogoya meteorite, for example, the PAH content shows the highest level of alkylation, with an abundance of C_3-naphthalene more than twice the nonalkylated naphthalene. The nonalkylated, C_1-, and C_2- (i.e., mono- and dialkylated) naphthalene abundances of Winchcombe are 608 ppb, 410 ppb, and 355 ppb, respectively, with a ratio of naphthalene:C_1-naphthalene:C_2-naphthalene = 1:0.67:0.58. This ratio is similar to that of the less aqueously altered CMs like Murchison and Murray among the nine compared CM2s, and in contrast to the more extensively altered CM2s like Nogoya, Cold Bokkeveld, and Mukundpura (Elsila et al., 2005; Kalpana et al., 2021). It has been proposed that aqueous processing involving PAHs and/or other condensed organic compounds could have produced assemblages of SOM including amino acids (Shock & Schulte, 1990). Therefore, the low PAH abundance in Winchcombe compared to other CMs may account for the limited availability of organic precursors required for the synthesis of amino acids, leading to the low total amino acid abundance we have observed for the Winchcombe meteorite. Nevertheless, the contributions and roles of other organic precursors of amino acids, such as amines, dicarboxylic acids, and lactams, shall also be explored in future studies of the Winchcombe meteorite.

Parent Body and Pre-atmospheric Alteration History

The majority of amino acids in Winchcombe are present as α-amino acids in which the amino group NH_2 is on the carbon closest to the carboxylic group COOH. For example, amino acids are present predominantly as α-alanine (107 ppb) in contrast to the smaller amount of its β-configuration (β-alanine = 28 ppb); for the AIB isomers, they are present predominantly as α-AIB (331 ppb) and no β-AIB was observed; and for the ABA isomers, a gradual decrease in amino acid concentration was observed, from α-ABA (29 ppb), to β-ABA (21 ppb) and γ-ABA (14 ppb; Table 3). These observations are consistent with a formation pathway associated with

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

low-temperature (25–150 °C) aqueous activity via the Strecker-cyanohydrin synthesis on the parent body, similar to that observed for most other CM and CR chondrites, and in contrast to a dominantly small, straight-chain amine terminal (*n*-ω-amino) amino acid composition in the thermally altered meteorites like the CV3, CO3, and several unusual Antarctica carbonaceous chondrites such as the Yamato (Y) and Belgica (B) group meteorites (collectively referred to as the "CYs"; Burton, Glavin, et al., 2014; Chan et al., 2016). These *n*-ω-amino acids could have been synthesized through high-temperature (150–700 °C) FTT and Haber Bosch (HB) mineral surface-catalyzed reactions of H_2, CO, and NH_3 gases on iron or nickel surfaces in the parent body (Hayatsu et al., 1971; Yoshino et al., 1971).

Aqueous processing can lead to the decomposition of the α-amino acids through deamination and decarboxylation, resulting in an increase in relative abundance of β-amino acids compared to α-amino acids in meteorites with increasing levels of aqueous processing, and the production of primary amines or α-β-unsaturated monocarboxylic acid (Bada et al., 1991; Pietrucci et al., 2018). Therefore, the variation of amino acid distributions across different meteorites can be assessed by comparing their relative amino acid abundances. Figure 6 shows the comparison of the distribution of individual amino acids relative to D-alanine of Winchcombe, fall site soil, and other CCs. In this study, we compare the amino acid distribution relative to the D-alanine instead of glycine as reported in previous studies (e.g., Chan et al., 2012; Glavin et al., 2006), as glycine is a common proteinogenic amino acid and the unknown amount of terrestrial contribution of glycine may influence the proper interpretation of these values. We choose the D-enantiomer of α-alanine as it is commonly detected across different meteorite samples, and yet it is less commonly associated with terrestrial contamination than the L-enantiomer of alanine, thus allowing the differentiation between amino acids that were likely to be contributed from terrestrial contamination and those that were not.

With enrichments in α-AIB, isovaline, and glycine relative to D-alanine, Winchcombe has an amino acid content similar to that of the mildly aqueously altered CM2 chondrites such as Murchison and Murray, and is clearly distinct from that of CM1, CM3.0/2.9, and other CI and CR chondrites. For example, the relative abundance of α-AIB in the extensively altered CM1 (classified as CM2.0 according to Rubin et al., 2007) MET 01070 is >100 times lower than that observed for the CM2 Murchison (Glavin et al., 2011). The amino acid contents of the mildly altered CM2 chondrites are typically more enriched in α-amino, α-hydroxy, and α-imino acids than β-, γ-, and δ-amino acids. The relative abundances of α-methyl amino acids, such as α-AIB and isovaline, are higher in CM2 Winchcombe and CM2 Murchison, as opposed to their relative low levels observed in CI1 Orgueil, CM1 MET 01070, and CR1 Grosvenor Mountains (GRO) 95577. The relative β-alanine, β-ABA, and γ-ABA to D-alanine ratios are also higher in the heavily altered meteorites like CI1 Orgueil, CM1 MET 01070, and CR1 GRO 95577 as compared to that in the mildly altered meteorites including Winchcombe, CM2 Murchison, CM3.0/2.9 A-12236, and CR2 Graves Nunataks 95229 (Ehrenfreund, Glavin, et al., 2001; Glavin et al., 2011, 2020). In addition, similar to Murchison and A-12236, relative to D-alanine Winchcombe is dominated by C_5 α-amino acids (valine, isovaline, and norvaline) over the C_5 β-, γ-, and ε-amino acids (3-APA, 4-APA, and 5-APA). α-amino acids are thought to be the products of simple organic precursors (synthesized in protosolar nebula, molecular cloud, and interstellar medium; Bernstein et al., 2002; Herbst & Van Dishoeck, 2009) produced through Strecker-cyanohydrin reaction pathway during low-temperature parent body aqueous alteration (Peltzer et al., 1984). The result suggests that Winchcombe has only been mildly aqueously altered, which synthesized predominantly α-amino acids but at low concentrations.

A strong correlation has also been observed between the relative abundance of β-alanine to glycine and the degree of aqueous alteration in CI, CM, and CR carbonaceous chondrites (Glavin et al., 2006, 2011, 2020; Martins, Alexander, et al., 2007; Martins, Hofmann, et al., 2007; Martins et al., 2015). The β-alanine/D-alanine ratio shown in Fig. 6 also appears to be correlated with aqueous alteration in a similar way as β-alanine/glycine discussed in the literature. In this study, we have observed a very low abundance of β-alanine (relative to D-alanine) in the Winchcombe meteorite (β-ala/D-α-ala = 0.50), which is in contrast to the higher ratios observed for the moderately altered CM2 Murchison (~1.83) and in the heavily altered CM1 MET 01070 (10.39), up to a ratio of as high as 34.15 observed for the most aqueously altered CI1 Orgueil. Rather, the low β-ala/D-α-ala ratio observed for Winchcombe is more comparable to the weakly altered A-12236 (β-ala/D-α-ala = 0.52). Therefore, the low relative abundance of β-alanine in Winchcombe provides another line of evidence that although the amino acid distribution is consistent with that synthesized via the Strecker-cyanohydrin reaction, the associated aqueous event could have been episodic.

One of the challenges in comprehending the organic inventory of the parent bodies of CC chondrites is that their intrinsic organic compositions driven by radiolysis processes are further altered, destroyed, and/or transformed into complex organics resulting from various

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

solar system processes, ranging from post-accretion parent body "secondary" alteration to alteration of the surfaces of airless bodies exposed to the space weathering processes (including irradiation by solar ion populations, galactic cosmic rays, electrons, UV and X-rays, and bombardment by micrometeorites; Brunetto et al., 2014, 2015), solar radiation heating during perihelion passages (Delbo et al., 2015), and atmospheric entry heating (Chan et al., 2020; Love & Brownlee, 1991). Working backward from the landing of the meteorite on the Earth's surface, the most "recent" alteration events were probably via the interaction with the terrestrial environment, and flash heating during atmospheric entry. The addition of extraneous terrestrial components can be monitored by scrutinizing the range of biologically relevant organic components. The pyrolytic temperatures experienced by meteorites of size ranging from 10^{-3} to 10 m extend to only ~1 mm depth, which form the dark meteorite fusion crust, and yet, organic compounds from the interior of a meteorite are efficiently protected from the heating (Basiuk & Douda, 1999), or sublimed into the Earth's atmosphere by vaporization off the surface, and recondensed on ice crystals in the cold upper atmosphere (Glavin & Bada, 2001). Therefore, the next most "recent" alteration mechanism traces backward to the space environment to which the meteoroid has been exposed in the near-Earth space. Thanks to the optimal optical records of the Winchcombe fireball, the calculation of the Winchcombe meteoroid's pre-atmospheric orbit has provided information related to its recent dynamical past. CM chondrites typically have cosmic ray exposure (CRE) ages (CRE ages measure the length of time a body spends between its final breakup by impact, which places its interior within a few meters of the radiation environment, and delivery to the Earth) that are <2 million years (Myr; Krietsch et al., 2021). When the interior of the parent body is exposed to cosmic ray radiation, free amino acids and their precursors are prone to photodestruction (Ehrenfreund, Bernstein, et al., 2001; Pilling et al., 2008), while bound amino acids and the cyclic precursor are more radiostable (Kobayashi et al., 2021). Furthermore, the Winchcombe meteoroid was determined to have entered near-Earth space (perihelion distance <1.3 astronomical unit [AU]) at about ~80,000 years (~0.08 Myr) ago, and remained at >0.7 AU throughout its history (King et al., 2022). At these distances, where the Winchcombe meteoroid had close approaches to the Sun with maximum temperatures potentially exceeding ~175 °C, the surface of the meteoroid can be further altered by solar irradiation with a penetration depth of typically a few centimeters (Delbo et al., 2015). Although the chance that the surviving Winchcombe meteorite fragment was derived from the top few centimeters of the original impactor with a pre-atmospheric diameter of ~30 cm is very low, mineralogical features of dehydration observed in thermally metamorphosed aqueously altered CYs and the preferential loss of low-retentive cosmogenic noble gases in some ordinary chondrites suggest that surficial alteration processes, such as solar radiation, or heating process during exposure to cosmic rays, could account for the alteration characteristics observed on these meteorites (Eugster et al., 1993; Nakamura et al., 2017). Further analyses of the Winchcombe meteorites would help to constrain the alteration history and allow us to better understand how these mechanisms have influenced its organic inventory.

CONCLUSIONS

The Winchcombe meteorite is the most recent, promptly recovered CM2 fall of which the fireball event has been widely observed and recorded permitting detailed numerical modeling of the fireball trajectory. It has provided us with pristine astromaterials to be studied for the intrinsic organic record of a carbon-rich asteroidal body. The slow atmospheric deceleration of the Winchcombe meteoroid owing to its low entry speed and the shallow entry angle has allowed the fragile material to survive atmospheric entry and reach the Earth's surface. Although the small total recovered mass of ~0.6 kg has impeded compound-specific isotopic analysis, which typically requires a substantial mass of CC samples for the detection of targeted molecules above the instrumental detection limit, amino acid analysis of the Winchcombe meteorite hot water extracts has identified a range of proteinogenic and non-proteinogenic amino acids with distributions clearly distinct from the fall site soil indicating their indigeneity. Some of these amino acids, including alanine, isovaline, and norvaline, have enantiomeric ratios of 0.91–1.13 supporting an extraterrestrial origin. The most abundant extraterrestrial, non-proteinogenic amino acids observed in Winchcombe are α-aminoisobutyric acid and isovaline that are also commonly observed in CM2. However, the amino acid abundance of Winchcombe is low, which is unexpected for a CM2 meteorite that demonstrates moderate to intense aqueous alteration. The high free:total amino acid ratio and the racemic ratio observed for isovaline are also inconsistent with an extensive aqueous history. Analyzing the PAH content of the solvent extract of the Winchcombe meteorite reveals a composition of 2- to 6-ring alkylated and nonalkylated PAHs. The low total PAH abundance (6177 ppb) and high nonalkylated:alkylated ratio is well aligned with that observed for the less aqueously altered CMs. Mineralogical and petrographic observations suggest that Winchcombe presents a wide range of degrees in aqueous

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

alteration spanning from intensely altered CM2.0 to moderately altered CM2.6 clasts held together by a weak cataclastic matrix, suggesting that Winchcombe could represent a class of weak, poorly lithified meteorite not been previously studied. While the soluble organic content of the Winchcombe meteorite indicates that some of the organic compounds like the α-amino acids could have been synthesized via low-temperature Strecker-cyanohydrin pathway prevailing on the CM parent bodies, the amino acid content is not strictly comparable to other CM2 meteorites, suggesting that the weakly lithified Winchcombe meteorite represents an unusual sample that would not typically survive atmospheric entry. The intriguing heterogeneity of the Winchcombe meteorite warrants continued analysis of more stones deriving from different lithologies to help us better understand if Winchcombe is truly distinct from other CM2 falls and finds in the terrestrial collection.

Acknowledgments—This publication is part of the Winchcombe science team consortium, organized by the UK Fireball Alliance and conducted by the UK Cosmochemistry Network. This study was supported by urgency funding from the UK's Science and Technology Facilities Council (STFC) as part of the project "Curation and Preliminary Examination of the Winchcombe Carbonaceous Chondrite Fall" (ST/V000799/1). The authors of this paper would like to thank the UK Fireball Alliance, its constituent networks (UK Fireball Network, SCAMP, UKMON, AllSky7, NEMETODE, GMN), international collaborators (FRIPON, Global Fireball Observatory, Desert Fireball Network, University of Western Ontario, and University of Helsinki), and the meteor observation camera owners who participate in the UK Fireball Alliance network for their aid in observing the fireball and helping to predict its fall position. We would also like to thank the scientists and volunteers who participated in the UK Fireball Alliance-led search and recovery of the Winchcombe meteorite, and the local community, who generously reported and donated meteorite finds and enabled the team to search the strewn field. Natural History Museum staff are acknowledged for their curatorial support. We would also like to thank the Astrobiology Analytical Laboratory at Goddard Space Flight Center for providing the laboratory synthesized C_5 amino acid standards including the 3-amino-3-methyl butanoic acid, 3-amino-2,2-dimethylpropanoic acid, and 4-amino-pentanoic acid. This paper has benefited greatly from thorough and constructive comments of the anonymous reviewers. The authors of this paper would also like to thank Clement Regnault, Douglas Morrison, Gavin Blackburn, Eleanor McKay, Phil Whitfield, and Martin Lee in the earlier discussion of the organic analysis of the Winchcombe meteorite, and Ashley King for reviewing the initial manuscript of this paper. Q.H.S.C. greatly appreciates for the extended time provided for the investigation of the Winchcombe meteorite beyond her maternity leave.

Data Availability Statement—The data that support the findings of this study are available in the Royal Holloway University of London's Figshare data repository (royalholloway.figshare.com) and in the supplementary material of this article.

Editorial Handling—Dr. Daniel Patrick Glavin

REFERENCES

Alexander, C. M. O'D., Cody, G. D., De Gregorio, B. T., Nittler, L. R., and Stroud, R. M. 2017. The Nature, Origin and Modification of Insoluble Organic Matter in Chondrites, the Major Source of Earth's C and N. *Geochemistry* 77: 227–56.

Alexander, C. M. O'D., Howard, K. T., Bowden, R., and Fogel, M. L. 2013. The Classification of CM and CR Chondrites Using Bulk H, C and N Abundances and Isotopic Compositions. *Geochimica et Cosmochimica Acta* 123: 244–60.

Anders, E., Hayatsu, R., and Studier, M. H. 1973. Organic Compounds in Meteorites they May Have Formed in the Solar Nebula, by Catalytic Reactions of Carbon Monoxide, Hydrogen, and Ammonia. *Science* 182: 781–90.

Aponte, J. C., Dworkin, J. P., and Elsila, J. E. 2015. Indigenous Aliphatic Amines in the Aqueously Altered Orgueil Meteorite. *Meteoritics & Planetary Science* 50: 1733–49.

Aponte, J. C., McLain, H. L., Simkus, D. N., Elsila, J. E., Glavin, D. P., Parker, E. T., Dworkin, J. P., Hill, D. H., Connolly, H. C., Jr., and Lauretta, D. S. 2020. Extraterrestrial Organic Compounds and Cyanide in the CM2 Carbonaceous Chondrites Aguas Zarcas and Murchison. *Meteoritics & Planetary Science* 55: 1509–24.

Bada, J. L. 1985. Racemization of Amino Acids. In *Chemistry and Biochemistry of the Amino Acids*, edited by G. C. Barrett. London: Chapman and Hall.

Bada, J. L. 1997. Extraterrestrial Handedness? *Science* 275: 942–3.

Bada, J. L., Eglinton, G., and Curry, G. B. 1991. Amino Acid Cosmogeochemistry. *Philosophical Transactions of the Royal Society of London. Series B: Biological Sciences* 333: 349–58.

Barron, L. D. 2000. Chirality, Magnetism and Light. *Nature* 405: 895–6.

Basile, B. P., Middleditch, B. S., and Oró, J. 1984. Polycyclic Aromatic Hydrocarbons in the Murchison Meteorite. *Organic Geochemistry* 5: 211–6.

Basiuk, V. A., and Douda, J. 1999. Pyrolysis of Simple Amino Acids and Nucleobases: Survivability Limits and Implications for Extraterrestrial Delivery. *Planetary and Space Science* 47: 577–84.

Bernstein, M. P., Dworkin, J. P., Sandford, S. A., Cooper, G., and Allamandola, L. J. 2002. Racemic Amino Acids from

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

the Ultraviolet Photolysis of Interstellar Ice Analogues. *Nature* 416: 401–3.
Botta, O., Glavin, D. P., Kminek, G., and Bada, J. L. 2002. Relative Amino Acid Concentrations as a Signature for Parent Body Processes of Carbonaceous Chondrites. *Origins of Life and Evolution of the Biosphere* 32: 143–63.
Botta, O., Martins, Z., and Ehrenfreund, P. 2007. Amino Acids in Antarctic CM1 Meteorites and their Relationship to Other Carbonaceous Chondrites. *Meteoritics & Planetary Science* 42: 81–92.
Brearley, A. J. 2004. In Situ Location and Characterization of Carbon-Bearing Phases in Carbonaceous Chondrites: Insights from Yamato 791198, a Weakly-Altered CM2 Chondrite (Abstract #1896). 35th Lunar and Planetary Science Conference. CD-ROM.
Brearley, A. J. 2006. *The Action of Water*, 584–624. Tucson, Arizona: The University of Arizona Press.
Brückner, H., Becker, D., Gams, W., and Degenkolb, T. 2009. Aib and Iva in the Biosphere: Neither Rare nor Necessarily Extraterrestrial. *Chemistry & Biodiversity* 6: 38–56.
Brunetto, R., Lantz, C., Ledu, D., Baklouti, D., Barucci, M. A., Beck, P., Delauche, L., et al. 2014. Ion Irradiation of Allende Meteorite Probed by Visible, IR, and Raman Spectroscopies. *Icarus* 237: 278–92.
Brunetto, R., Loeffler, M. J., Nesvorný, D., Sasaki, S., and Strazzulla, G. 2015. Asteroid Surface Alteration by Space Weathering Processes. In *Asteroids IV*, edited by P. Michel, F. E. DeMeo, and W. F. Bottke, 597–616. Tucson, Arizona: University of Arizona Press.
Burton, A. S., Elsila, J. E., Callahan, M. P., Martin, M. G., Glavin, D. P., Johnson, N. M., and Dworkin, J. P. 2012. A Propensity for n-ω-Amino Acids in Thermally Altered Antarctic Meteorites. *Meteoritics & Planetary Science* 47: 374–86.
Burton, A. S., Glavin, D. P., Elsila, J. E., Dworkin, J. P., Jenniskens, P., and Yin, Q. Z. 2014. The Amino Acid Composition of the Sutter's Mill CM2 Carbonaceous Chondrite. *Meteoritics & Planetary Science* 49: 2074–86.
Burton, A. S., Grunsfeld, S., Elsila, J. E., Glavin, D. P., and Dworkin, J. P. 2014. The Effects of Parent-Body Hydrothermal Heating on Amino Acid Abundances in CI-Like Chondrites. *Polar Science* 8: 255–63.
Callahan, M. P., Smith, K. E., Cleaves, H. J., Ruzicka, J., Stern, J. C., Glavin, D. P., House, C. H., and Dworkin, J. P. 2011. Carbonaceous Meteorites Contain a Wide Range of Extraterrestrial Nucleobases. *Proceedings of the National Academy of Sciences* 108: 13995–8.
Chan, H. S., Martins, Z., and Sephton, M. A. 2012. Amino Acid Analyses of Type 3 Chondrites Colony, Ornans, Chainpur, and Bishunpur. *Meteoritics & Planetary Science* 47: 1502–16.
Chan, Q. H. S., Chikaraishi, Y., Takano, Y., Ogawa, N. O., and Ohkouchi, N. 2016. Amino Acid Compositions in Heated Carbonaceous Chondrites and their Compound-Specific Nitrogen Isotopic Ratios. *Earth, Planets and Space* 68: 7.
Chan, Q. H. S., Franchi, I. A., Zhao, X., Stephant, A., Wright, I. P., and Alexander, C. M. O'D. 2020. Organics Preserved in Anhydrous Interplanetary Dust Particles: Pristine or Not? *Meteoritics & Planetary Science* 55: 1320–48.
Chan, Q. H. S., and Zolensky, M. 2022. Water and Organics in Meteorites. In *New Frontiers in Astrobiology*, edited by R. Thombre, and P. Vaishampayan. Amsterdam: Elsevier Inc. https://www.sciencedirect.com/science/article/pii/B9780128241622000087
Chan, Q. H. S., Zolensky, M. E., Bodnar, R. J., Farley, C., and Cheung, J. C. H. 2017. Investigation of Organo-Carbonate Associations in Carbonaceous Chondrites by Raman Spectroscopy. *Geochimica et Cosmochimica Acta* 201: 392–409.
Chan, Q. H. S., Zolensky, M. E., Kebukawa, Y., Franchi, I., Wright, I., Zhao, I., Rahman, Z., and Utas, J. 2018. Primitive Oxygen-, Nitrogen-, and Organic-Rich Vein Preserved in a Xenolith Hosted in the Metamorphosed Carancas meteorite (Abstract #1191). 49th Lunar and Planetary Science Conference. CD-ROM.
Clemett S., Dulay M. T., Seb Gillette J., Chillier X., Mahajan T., and Zare R. 1998. Evidence for the Extraterrestrial Origin of Polycyclic Aromatic Hydrocarbons in the Martian Meteorite ALH84001. *Faraday Discussions* 109: 417–36.
Cohen, B. A., and Coker, R. F. 2000. Modeling of Liquid Water on CM Meteorite Parent Bodies and Implications for Amino Acid Racemization. *Icarus* 145: 369–81.
Cooper, G., and Rios, A. C. 2016. Enantiomer Excesses of Rare and Common Sugar Derivatives in Carbonaceous Meteorites. *Proceedings of the National Academy of Sciences* 113: E3322–31.
Cooper, G. W., and Cronin, J. R. 1995. Linear and Cyclic Aliphatic Carboxamides of the Murchison Meteorite: Hydrolyzable Derivatives of Amino Acids and Other Carboxylic Acids. *Geochimica et Cosmochimica Acta* 59: 1003–15.
Cronin, J. R., and Pizzarello, S. 1983. Amino Acids in Meteorites. *Advances in Space Research* 3: 5–18.
Delbo, M., Mueller, M., Emery, J. P., Rozitis, B., and Capria, M. T. 2015. Asteroid Thermophysical Modeling. In *Asteroids IV*, 107–28. Tucson, Arizona: University of Arizona Press.
Doyle, P. M., Jogo, K., Nagashima, K., Krot, A. N., Wakita, S., Ciesla, F. J., and Hutcheon, I. D. 2015. Early Aqueous Activity on the Ordinary and Carbonaceous Chondrite Parent Bodies Recorded by Fayalite. *Nature Communications* 6: 1–10.
Eckhardt, C. J., Peachey, N. M., Swanson, D. R., Takacs, J. M., Khan, M. A., Gong, X., Kim, J. H., Wang, J., and Uphaus, R. A. 1993. Separation of Chiral Phases in Monolayer Crystals of Racemic Amphiphiles. *Nature* 362: 614–6.
Ehrenfreund, P., Bernstein, M. P., Dworkin, J. P., Sandford, S. A., and Allamandola, L. J. 2001. The Photostability of Amino Acids in Space. *The Astrophysical Journal* 550: L95–9.
Ehrenfreund, P., Glavin, D. P., Botta, O., Cooper, G., and Bada, J. L. 2001. Extraterrestrial Amino Acids in Orgueil and Ivuna: Tracing the Parent Body of CI Type Carbonaceous Chondrites. *Proceedings of the National Academy of Sciences* 98: 2138–41.
Elsila, J. E., de, Leon, N. P., Buseck, P. R., and Zare, R. N. 2005. Alkylation of Polycyclic Aromatic Hydrocarbons in Carbonaceous Chondrites. *Geochimica et Cosmochimica Acta* 69: 1349–57.
Eugster, O., Michel, T., Niedermann, S., Wang, D., and Yi, W. 1993. The Record of Cosmogenic, Radiogenic, Fissiogenic, and Trapped Noble Gases in Recently Recovered Chinese and Other Chondrites. *Geochimica et Cosmochimica Acta* 57: 1115–42.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Fuchida, S., Masuda, H., and Shinoda, K. 2014. Peptide Formation Mechanism on Montmorillonite under Thermal Conditions. *Origins of Life and Evolution of Biospheres* 44: 13–28.

Fujiya, W., Sugiura, N., Hotta, H., Ichimura, K., and Sano, Y. 2012. Evidence for the Late Formation of Hydrous Asteroids from Young Meteoritic Carbonates. *Nature Communications* 3: 627.

Gingrich, S. E., Diamond, M. L., Stern, G. A., and McCarry, B. E. 2001. Atmospherically Derived Organic Surface Films along an Urban-Rural Gradient. *Environmental Science & Technology* 35: 4031–7.

Glavin, D. P., Aubrey, A. D., Callahan, M. P., Dworkin, J. P., Elsila, J. E., Parker, E. T., Bada, J. L., Jenniskens, P., and Shaddad, M. H. 2010. Extraterrestrial Amino Acids in the Almahata Sitta Meteorite. *Meteoritics & Planetary Science* 45: 1695–709.

Glavin, D. P., and Bada, J. L. 2001. Survival of Amino Acids in Micrometeorites during Atmospheric Entry. *Astrobiology* 1: 259–69.

Glavin, D. P., Callahan, M. P., Dworkin, J. P., and Elsila, J. E. 2011. The Effects of Parent Body Processes on Amino Acids in Carbonaceous Chondrites. *Meteoritics & Planetary Science* 45: 1948–72.

Glavin, D. P., and Dworkin, J. P. 2009. Enrichment of the Amino Acid L-Isovaline by Aqueous Alteration on CI and CM Meteorite Parent Bodies. *Proceedings of the National Academy of Sciences* 106: 5487–92.

Glavin, D. P., Dworkin, J. P., Aubrey, A., Botta, O., Doty, J. H., III, Martins, Z., and Bada, J. L. 2006. Amino Acid Analyses of Antarctic CM2 Meteorites Using Liquid Chromatography–Time of Flight–Mass Spectrometry. *Meteoritics & Planetary Science* 41: 889–902.

Glavin, D. P., Elsila, J. E., Burton, A. S., Callahan, M. P., Dworkin, J. P., Hilts, R. W., and Herd, C. D. K. 2012. Unusual Nonterrestrial l-Proteinogenic Amino Acid Excesses in the Tagish Lake Meteorite. *Meteoritics & Planetary Science* 47: 1347–64.

Glavin, D. P., Elsila, J. E., McLain, H. L., Aponte, J. C., Parker, E. T., Dworkin, J. P., Hill, D. H., Connolly, H. C., Jr., and Lauretta, D. S. 2021. Extraterrestrial Amino Acids and L-Enantiomeric Excesses in the CM2 Carbonaceous Chondrites Aguas Zarcas and Murchison. *Meteoritics & Planetary Science* 56: 148–73.

Glavin, D. P., McLain, H. L., Dworkin, J. P., Parker, E. T., Elsila, J. E., Aponte, J. C., Simkus, D. N., et al. 2020. Abundant Extraterrestrial Amino Acids in the Primitive CM Carbonaceous Chondrite Asuka 12236. *Meteoritics & Planetary Science* 55: 1979–2006.

Haack, H., Grau, T., Bischoff, A., Horstmann, M., Wasson, J., Sørensen, A., Laubenstein, M., et al. 2012. Maribo—A New CM Fall from Denmark. *Meteoritics & Planetary Science* 47: 30–50.

Harries, D., and Langenhorst, F. 2011. Sulfides in CM and CM/CI-Like Chondrites and their Record of Thermal Metamorphism: A FIB-TEM Study. *Meteoritics & Planetary Science Supplement* 74: 5166.

Hayatsu, R., Studier, M. H., and Anders, E. 1971. Origin of Organic Matter in Early Solar System—IV. Amino Acids: Confirmation of Catalytic Synthesis by Mass Spectrometry. *Geochimica et Cosmochimica Acta* 35: 939–51.

Hazen, R. M., Filley, T. R., and Goodfriend, G. A. 2001. Selective Adsorption of L- and D-Amino Acids on Calcite: Implications for Biochemical Homochirality. *Proceedings of the National Academy of Sciences* 98: 5487–90.

Hazen, R. M., and Sholl, D. S. 2003. Chiral Selection on Inorganic Crystalline Surfaces. *Nature Materials* 2: 367–74.

Herbst, E., and Van Dishoeck, E. F. 2009. Complex Organic Interstellar Molecules. *Annual Review of Astronomy and Astrophysics* 47: 427–80.

Huss, G. R., Rubin, A. E., and Grossman, J. N. 2006. Thermal Metamorphism in Chondrites. In *Meteorites and the Early Solar System II*, edited by D. S. Lauretta, and H. J. McSween, Jr., 567–86. Tucson, Arizona: The University of Arizona Press.

Jenniskens, P., Fries, M. D., Yin, Q.-Z., Zolensky, M., Krot, A. N., Sandford, S. A., Sears, D., et al. 2012. Radar-Enabled Recovery of the Sutter's Mill Meteorite, a Carbonaceous Chondrite Regolith Breccia. *Science* 338: 1583–7.

Kalník, M., Gabko, P., Bella, M., and Koóš, M. 2021. The Bucherer–Bergs Multicomponent Synthesis of Hydantoins—Excellence in Simplicity. *Molecules* 26: 1–33.

Kalpana, M. S., Babu, E. V. S. S. K., Mani, D., Tripathi, R. P., and Bhandari, N. 2021. Polycyclic Aromatic Hydrocarbons in the Mukundpura (CM2) Chondrite. *Planetary and Space Science* 198: 105177.

Kaplan, H. H., Lauretta, D. S., Simon, A. A., Hamilton, V. E., DellaGiustina, D. N., Golish, D. R., Reuter, D. C., et al. 2020. Bright Carbonate Veins on Asteroid (101955) Bennu: Implications for Aqueous Alteration History. *Science* 370: eabc3557.

Kebukawa, Y., Zolensky, M. E., Ito, M., Ogawa, N. O., Takano, Y., Ohkouchi, N., Nakato, A., et al. 2020. Primordial Organic Matter in the Xenolithic Clast in the Zag H Chondrite: Possible Relation to D/P Asteroids. *Geochimica et Cosmochimica Acta* 271: 61–77.

Kimura, M., Imae, N., Komatsu, M., Barrat, J. A., Greenwood, R. C., Yamaguchi, A., and Noguchi, T. 2020. The most Primitive CM Chondrites, Asuka 12085, 12169, and 12236, of Subtypes 3.0–2.8: Their Characteristic Features and Classification. *Polar Science* 26: 100565.

King, A., Daly, L., Rowe, J., Joy, K., Greenwood, R., Devillepoix, H., Suttle, M., et al. 2022. The Winchcombe Meteorite, a Unique and Pristine Witness from the Outer Solar System. *Science Advances* 8: eabq3925.

King, A. J., Bates, H. C., Krietsch, D., Busemann, H., Clay, P. L., Schofield, P. F., and Russell, S. S. 2019. The Yamato-Type (CY) Carbonaceous Chondrite Group: Analogues for the Surface of Asteroid Ryugu? *Geochemistry* 79: 125531.

Klussmann, M., Iwamura, H., Mathew, S. P., Wells, D. H., Pandya, U., Armstrong, A., and Blackmond, D. G. 2006. Thermodynamic Control of Asymmetric Amplification in Amino Acid Catalysis. *Nature* 441: 621–3.

Kobayashi, K., Mita, H., Kebukawa, Y., Nakagawa, K., Kaneko, T., Obayashi, Y., Sato, T., et al. 2021. Space Exposure of Amino Acids and their Precursors during the Tanpopo Mission. *Astrobiology* 21: 1479–93.

Koga, T., and Naraoka, H. 2017. A New Family of Extraterrestrial Amino Acids in the Murchison Meteorite. *Scientific Reports* 7: 636.

Krietsch, D., Busemann, H., Riebe, M. E. I., King, A. J., Alexander, C. M. O'D., and Maden, C. 2021. Noble Gases in CM Carbonaceous Chondrites: Effect of Parent Body Aqueous and Thermal Alteration and Cosmic Ray Exposure Ages. *Geochimica et Cosmochimica Acta* 310: 240–80.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Krishnamurthy, R., Epstein, S., Cronin, J. R., Pizzarello, S., and Yuen, G. U. 1992. Isotopic and Molecular Analyses of Hydrocarbons and Monocarboxylic Acids of the Murchison Meteorite. *Geochimica et Cosmochimica Acta* 56: 4045–58.

Kumpiene, J., Larsson, M. O., Carabante, I., and Arp, H. P. H. 2021. Roads with Underlying Tar Asphalt—Spreading, Bioavailability and Toxicity of their Polycyclic Aromatic Hydrocarbons. *Environmental Pollution* 289: 117828.

Kvenvolden, K. A., Lawless, J. G., Pering, K., Peterson, E., Flores, J., and Ponnamperuma, C. 1970. Evidence for Extraterrestrial Amino-Acids and Hydrocarbons in the Murchison Meteorite. *Nature* 228: 923–6.

Lahav, M., and Leiserowitz, L. 1999. Spontaneous Resolution: From Three-Dimensional Crystals to Two-Dimensional Magic Nanoclusters. *Angewandte Chemie International Edition* 38: 2533–6.

Lange, M. A., Lambert, P., and Ahrens, T. J. 1985. Shock Effects on Hydrous Minerals and Implications for Carbonaceous Meteorites. *Geochimica et Cosmochimica Acta* 49: 1715–26.

Lee, M. R., Daly, L., Trimby, P. W., and Piazolo, S. 2022. Sequences of Carbonate Mineralization in the CM Carbonaceous Chondrites Revealed by the Winchcombe Meteorite. In 85th Annual Meeting of the Meteoritical Society, Glasgow, UK, 6431.

Lee, M. R., Sofe, M. R., Lindgren, P., Starkey, N. A., and Franchi, I. A. 2013. The Oxygen Isotope Evolution of Parent Body Aqueous Solutions as Recorded by Multiple Carbonate Generations in the Lonewolf Nunataks 94101 CM2 Carbonaceous Chondrite. *Geochimica et Cosmochimica Acta* 121: 452–66.

Lentfort, S., Bischoff, A., Ebert, S., and Patzek, M. 2021. Classification of CM Chondrite Breccias—Implications for the Evaluation of Samples from the OSIRIS-REx and Hayabusa 2 Missions. *Meteoritics & Planetary Science* 56: 127–47.

Love, S. G., and Brownlee, D. E. 1991. Heating and Thermal Transformation of Micrometeoroids Entering the Earth's Atmosphere. *Icarus* 89: 26–43.

Martins, Z., Alexander, C. M. O'D., Orzechowska, G. E., Fogel, M. L., and Ehrenfreund, P. 2007. Indigenous Amino Acids in Primitive CR Meteorites. *Meteoritics & Planetary Science* 42: 2125–36.

Martins, Z., Hofmann, B. A., Gnos, E., Greenwood, R. C., Verchovsky, A., Franchi, I. A., Jull, A. J. T., et al. 2007. Amino Acid Composition, Petrology, Geochemistry, 14C Terrestrial Age and Oxygen Isotopes of the Shişr 033 CR Chondrite. *Meteoritics & Planetary Science* 42: 1581–95.

Martins, Z., Modica, P., Zanda, B., and d'Hendecourt, L. L. S. 2015. The Amino Acid and Hydrocarbon Contents of the Paris Meteorite: Insights into the most Primitive CM Chondrite. *Meteoritics & Planetary Science* 50: 926–43.

McCollom, T. M. 2013. The Influence of Minerals on Decomposition of the n-Alkyl-α-Amino Acid Norvaline under Hydrothermal Conditions. *Geochimica et Cosmochimica Acta* 104: 330–57.

McMullan, S., Vida, D., Devillepoix, H., Rowe, J., Daly, L., King, A., Cupák, M., et al. 2023. The Winchcombe Fireball—That Lucky Survivor. *Meteoritics & Planetary Science*.

Meierhenrich, U. J., Muñoz, C. G. M., Schutte, W. A., Thiemann, W. H. P., Barbier, B., and Brack, A. 2005. Precursors of Biological Cofactors from Ultraviolet Irradiation of Circumstellar/Interstellar Ice Analogues. *Chemistry—A European Journal* 11: 4895–900.

Meinert, C., Bredehöft, J. H., Filippi, J.-J., Baraud, Y., Nahon, L., Wien, F., Jones, N. C., Hoffmann, S. V., and Meierhenrich, U. J. 2012. Anisotropy Spectra of Amino Acids. *Angewandte Chemie International Edition* 51: 4484–7.

Miller, S. L. 1957. The Mechanism of Synthesis of Amino Acids by Electric Discharges. *Biochimica et Biophysica Acta* 23: 480–9.

Modica, P., Meinert, C., de Marcellus, P., Nahon, L., Meierhenrich, U. J., and d'Hendecourt, L. L. S. 2014. Enantiomeric Excesses Induced in Amino Acids by Ultraviolet Circularly Polarized Light Irradiation of Extraterrestrial ice Analogs: A Possible Source of Asymmetry for Prebiotic Chemistry. *The Astrophysical Journal* 788: 79.

Nakamura, T. 2005. Post-Hydration Thermal Metamorphism of Carbonaceous Chondrites. *Journal of Mineralogical and Petrological Sciences* 100: 260–72.

Nakamura, T., Golabek, G., Ohtsuka, K., and Matsuoka, M. 2017. Solar-Radiation Heating as a Possible Heat Source for Dehydration of Hydrous Carbonaceous Chondrites. In 80th Annual Meeting of the Meteoritical Society, 6233.

Naraoka, H., Shimoyama, A., and Harada, K. 2000. Isotopic Evidence from an Antarctic Carbonaceous Chondrite for Two Reaction Pathways of Extraterrestrial PAH Formation. *Earth and Planetary Science Letters* 184: 1–7.

Naraoka, H., Shimoyama, A., Komiya, M., Yamamoto, H., and Harada, K. 1988. Hydrocarbons in the Yamato-791198 Carbonaceous Chondrite from Antarctica. *Chemistry Letters* 17: 831–4.

Nittler, L. R., Alexander, C. M. O'D., Patzer, A., and Verdier-Paoletti, M. J. 2021. Presolar Stardust in Highly Pristine CM Chondrites Asuka 12169 and Asuka 12236. *Meteoritics & Planetary Science* 56: 260–76.

Peltzer, E. T., Bada, J. L., Schlesinger, G., and Miller, S. L. 1984. The Chemical Conditions on the Parent Body of the Murchison Meteorite: Some Conclusions Based on Amino, Hydroxy and Dicarboxylic Acids. *Advances in Space Research* 4: 69–74.

Pering, K. L., and Ponnamperuma, C. 1971. Aromatic Hydrocarbons in the Murchison Meteorite. *Science* 173: 237–9.

Pietrucci, F., Aponte, J. C., Starr, R., Pérez-Villa, A., Elsila, J. E., Dworkin, J. P., and Saitta, A. M. 2018. Hydrothermal Decomposition of Amino Acids and Origins of Prebiotic Meteoritic Organic Compounds. *ACS Earth and Space Chemistry* 2: 588–98.

Pilling, S., Andrade, D. P. P., de Castilho, R. B., Cavasso-Filho, R. L., Lago, A. F., Coutinho, L. H., de Souza, G. G. B., Boechat-Roberty, H. M., and de Brito, A. N. 2008. Survival of Gas Phase Amino Acids and Nucleobases in Space Radiation Conditions. *Proceedings of the International Astronomical Union* 4: 371–6.

Pizzarello, S., and Cooper, G. W. 2001. Molecular and Chiral Analyses of some Protein Amino Acid Derivatives in the Murchison and Murray Meteorites. *Meteoritics & Planetary Science* 36: 897–909.

Pizzarello, S., Huang, Y., and Alexandre, M. R. 2008. Molecular Asymmetry in Extraterrestrial Chemistry: Insights from a Pristine Meteorite. *Proceedings of the National Academy of Sciences* 105: 3700–4.

Pizzarello, S., Huang, Y., and Fuller, M. 2004. The Carbon Isotopic Distribution of Murchison Amino Acids. *Geochimica et Cosmochimica Acta* 68: 4963–9.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Pizzarello, S., and Yarnes, C. T. 2018. The Soluble Organic Compounds of the Mukundpura Meteorite: A New CM Chondrite Fall. *Planetary and Space Science* 164: 127–31.

Pizzarello, S., Yarnes, C. T., and Cooper, G. 2020. The Aguas Zarcas (CM2) Meteorite: New Insights into Early Solar System Organic Chemistry. *Meteoritics & Planetary Science* 55: 1525–38.

Pizzarello, S., Zolensky, M., and Turk, K. A. 2003. Nonracemic Isovaline in the Murchison Meteorite: Chiral Distribution and Mineral Association. *Geochimica et Cosmochimica Acta* 67: 1589–95.

Pollock, G., Cheng, C. N., Cronin, S. E., and Kvenvolden, K. 1975. Stereoisomers of Isovaline in the Murchison Meteorite. *Geochimica et Cosmochimica Acta* 39: 1571–3.

Rodante, F., Marrosu, G., and Catalani, G. 1992. Thermal Analysis of some α-Amino Acids with Similar Structures. *Thermochimica Acta* 194: 197–213.

Rubin, A. E., Trigo-Rodríguez, J. M., Huber, H., and Wasson, J. T. 2007. Progressive Aqueous Alteration of CM Carbonaceous Chondrites. *Geochimica et Cosmochimica Acta* 71: 2361–82.

Rudraswami, N. G., Naik, A. K., Tripathi, R. P., Bhandari, N., Karapurkar, S. G., Prasad, M. S., Babu, E. V. S. S. K., and Vijaya Sarathi, U. V. R. 2019. Chemical, Isotopic and Amino Acid Composition of Mukundpura CM2.0 (CM1) Chondrite: Evidence of Parent Body Aqueous Alteration. *Geoscience Frontiers* 10: 495–504.

Scott, J. H., O'Brien, D. M., Emerson, D., Sun, H., McDonald, G. D., Salgado, A., and Fogel, M. L. 2006. An Examination of the Carbon Isotope Effects Associated with Amino Acid Biosynthesis. *Astrobiology* 6: 867–80.

Sephton, M. A., Chan, Q. H. S., Watson, J. S., Burchell, M. J., Spathis, V., Grady, M. M., Verchovsky, A. B., Abernethy, F. A. J., and Franchi, I. A. 2023. Insoluble Macromolecular Organic Matter in the Winchcombe Meteorite. *Meteoritics & Planetary Science*.

Sephton, M. A., Verchovsky, A. B., and Wright, I. P. 2004. Carbon and Nitrogen Isotope Ratios in Meteoritic Organic Matter: Indicators of Alteration Processes on the Parent Asteroid. *International Journal of Astrobiology* 3: 221–7.

Shimoyama, A., Naraoka, H., Komiya, M., and Harada, K. 1989. Analyses of Carboxylic Acids and Hydrocarbons in Antarctic Carbonaceous Chondrites, Yamato-74662 and Yamato-793321. *Geochemical Journal* 23: 181–93.

Shimoyama, A., and Ogasawara, R. 2002. Dipeptides and Diketopiperazines in the Yamato-791198 and Murchison Carbonaceous Chondrites. *Origins of Life and Evolution of the Biosphere* 32: 165–79.

Shock, E. L., and Schulte, M. D. 1990. Amino-Acid Synthesis in Carbonaceous Meteorites by Aqueous Alteration of Polycyclic Aromatic Hydrocarbons. *Nature* 343: 728–31.

Soai, K., Osanai, S., Kadowaki, K., Yonekubo, S., Shibata, T., and Sato, I. 1999. D- and L-Quartz-Promoted Highly Enantioselective Synthesis of a Chiral Organic Compound. *Journal of the American Chemical Society* 121: 11235–6.

Soai, K., Shibata, T., Morioka, H., and Choji, K. 1995. Asymmetric Autocatalysis and Amplification of Enantiomeric Excess of a Chiral Molecule. *Nature* 378: 767–8.

Suttle, M. D., Daly, L., Jones, R. H., Jenkins, L., Van Ginneken, M., Mitchell, J. T., Bridges, J. C., et al. 2023. The Winchcombe Meteorite—A Regolith Breccia from a Rubble-Pile CM Chondrite Asteroid. *Meteoritics & Planetary Science*.

Takano, Y., Takahashi, J.-I., Kaneko, T., Marumo, K., and Kobayashi, K. 2007. Asymmetric Synthesis of Amino Acid Precursors in Interstellar Complex Organics by Circularly Polarized Light. *Earth and Planetary Science Letters* 254: 106–14.

Threlfall, T. 2003. Structural and Thermodynamic Explanations of Ostwald's Rule. *Organic Process Research & Development* 7: 1017–27.

Tonui, E., Zolensky, M., Hiroi, T., Nakamura, T., Lipschutz, M. E., Wang, M.-S., and Okudaira, K. 2014. Petrographic, Chemical and Spectroscopic Evidence for Thermal Metamorphism in Carbonaceous Chondrites I: CI and CM Chondrites. *Geochimica et Cosmochimica Acta* 126: 284–306.

Tonui, E. K., Zolensky, M. E., Hiroi, T., Wang, M. S., and Lipschutz, M. E. 2002. Petrographic, Chemical and Spectroscopic Data on Thermally Metamorphosed Carbonaceous Chondrites (Abstract #1288). 33rd Lunar and Planetary Science Conference. CD-ROM.

Tonui, E. K., Zolensky, M. E., Lipschutz, M. E., Wang, M.-S., and Nakamura, T. 2003. Yamato 86029: Aqueously Altered and Thermally Metamorphosed CI-Like Chondrite with Unusual Textures. *Meteoritics & Planetary Science* 38: 269–92.

Tunney, L. D., Hill, P. J. A., Herd, C. D. K., and Hilts, R. W. 2022. Organic Compounds in the Tarda C2 Ungrouped Carbonaceous Chondrite: Evaluating the Sources of Contamination in a Desert Fall. *Meteoritics & Planetary Science* 57: 850–65.

Tyra, M. A., Farquhar, J., Guan, Y., and Leshin, L. A. 2012. An Oxygen Isotope Dichotomy in CM2 Chondritic Carbonates—A SIMS Approach. *Geochimica et Cosmochimica Acta* 77: 383–95.

Tyra, M. A., Farquhar, J., Wing, B. A., Benedix, G. K., Jull, A. J. T., Jackson, T., and Thiemens, M. H. 2007. Terrestrial Alteration of Carbonate in a Suite of Antarctic CM Chondrites: Evidence from Oxygen and Carbon Isotopes. *Geochimica et Cosmochimica Acta* 71: 782–95.

Vacher, L. G., Truche, L., Faure, F., Tissandier, L., Mosser-Ruck, R., and Marrocchi, Y. 2019. Deciphering the Conditions of Tochilinite and Cronstedtite Formation in CM Chondrites from Low Temperature Hydrothermal Experiments. *Meteoritics & Planetary Science* 54: 1870–89.

Viedma, C. 2005. Chiral Symmetry Breaking during Crystallization: Complete Chiral Purity Induced by Nonlinear Autocatalysis and Recycling. *Physical Review Letters* 94: 065504.

Viedma, C., Ortiz, J. E., Torres, T. D., Izumi, T., and Blackmond, D. G. 2008. Evolution of Solid Phase Homochirality for a Proteinogenic Amino Acid. *Journal of the American Chemical Society* 130: 15274–5.

Vinogradoff, V., Remusat, L., McLain, H. L., Aponte, J. C., Bernard, S., Danger, G., Dworkin, J. P., Elsila, J. E., and Jaber, M. 2020. Impact of Phyllosilicates on Amino Acid Formation under Asteroidal Conditions. *ACS Earth and Space Chemistry* 4: 1398–407.

Wang, X.-C., and Lee, C. 1993. Adsorption and Desorption of Aliphatic Amines, Amino Acids and Acetate by Clay Minerals and Marine Sediments. *Marine Chemistry* 44: 1–23.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Wing, M., and Bada, J. 1991. The Origin of the Polycyclic Aromatic Hydrocarbons in Meteorites. *Origins of Life and Evolution of the Biosphere* 21: 375–83.

Wolman, Y., Haverland, W. J., and Miller, S. L. 1972. Nonprotein Amino Acids from Spark Discharges and their Comparison with the Murchison Meteorite Amino Acids. *Proceedings of the National Academy of Sciences* 69: 809–11.

Yoshino, D., Hayatsu, K., and Anders, E. 1971. Origin of Organic Matter in Early Solar System—III. Amino Acids: Catalytic Synthesis. *Geochimica et Cosmochimica Acta* 35: 927–38.

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and Sylvestre, S. 2002. PAHs in the Fraser River Basin: A Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition. *Organic Geochemistry* 33: 489–515.

Zolensky, M., Barrett, R., and Browning, L. 1993. Mineralogy and Composition of Matrix and Chondrule Rims in Carbonaceous Chondrites. *Geochimica et Cosmochimica Acta* 57: 3123–48.

Zolensky, M. E., Abreu, N. M., Velbel, M. A., Rubin, A., Chaumard, N., Noguchi, T., and Michikami, T. 2018. Chapter 2—Physical, Chemical, and Petrological Characteristics of Chondritic Materials and their Relationships to Small Solar System Bodies. In *Primitive Meteorites and Asteroids*, edited by N. Abreu, 59–204. Amsterdam: Elsevier Inc. https://www.sciencedirect.com/science/article/pii/B9780128133255000021

Zolensky, M. E., Bourcier, W. L., and Gooding, J. L. 1989. Aqueous Alteration on the Hydrous Asteroids: Results of EQ3/6 Computer Simulations. *Icarus* 78: 411–25.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Appendix S1. Supplementary Materials.

Table S1. Amino acid abundances, amino acid to D-alanine ratios, D/L enantiomeric ratios, and L-enantiomeric excesses of the Winchcombe meteorite and several other carbonaceous chondrites as comparison.

Figure S1. The 2–30 min regions of the GC-MS total ion current (TIC) chromatograms collected in the selected ion monitoring (SIM) mode of the derivatized (N-TFA, O-isopropyl) amino acid standards.

Figure S2. The 2–15 min focused regions of the GC-MS total ion current (TIC) chromatograms collected in the selected ion monitoring (SIM) mode of the derivatized (N-TFA, O-isopropyl) amino acid standards. In particular, this figure shows clearly the separation of individual amino acids in the 4–6 min region.

Figure S3. The mass fragmentation patterns of amino acid standards that were used to identify peaks in the derivatized amino acid extracts of the Winchcombe meteorite.

Data S1. Raw (unprocessed) data of the chromatographs run on the CP-Chirasil-L Val column, the retention times, peak heights, and peak areas used for amino acid abundance quantification in this study.

Data S2. Raw (unprocessed) data of the chromatographs run on the CP- Chirasil-Dex CB column, the retention times, peak heights, and peak areas used for the quantification of isovaline in this study.

19455100, 2024, 5, Downloaded from https://onlinelibrary.wiley.com/doi/10.1111/maps.13936 by Test, Wiley Online Library on [30/05/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License