

THE AMINO ACID COMPOSITION OF THE WINCHCOMBE METEORITE. Q. H. S. Chan^{*1,2,3}, J. S. Watson⁴ and Mark A. Sephton⁴, ¹Royal Holloway University of London, Egham TW20 0EX, Surrey, UK (queenie.chan@rhul.ac.uk), ²The Open University, Walton Hall, Milton Keynes MK7 6AA, UK, ³UK Fireball Network, UK, ⁴Department of Earth Science and Engineering, Imperial College London, London SW7 2BX, UK

Introduction: The Winchcombe fireball occurred at 21:54:16 (UT) on the 28 February 2021 and lasted a little over eight seconds. The rapid recovery of the Winchcombe meteorite offers a valuable opportunity to study the soluble organic matter (SOM) profile in pristine carbonaceous astromaterials. Based on the mineralogy, petrography and bulk oxygen isotopic compositions, Winchcombe was classified as a CM (“Mighei-like”) meteorite [1]. SOM analyses have been carried out on CM falls focusing on a range of compounds selected based on their relevance to biology. Examples of most recent SOM analyses of CM falls can be drawn from the meteorites Mukundpura (2017, India), Aguas Zarcas (2019, Costa Rica) [e.g., 2, 3].

The Winchcombe meteorite provides a valuable opportunity to investigate how pristine organic materials chemically evolved during onset of parent body aqueous alteration. 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).

Methods: The Winchcombe meteorite stones BM.2022,M2-14 (mass = 0.9754) was provided by the Natural History Museum (NHM), London. A soil sample (the “fall site soil”) collected in proximity of the meteorite samples was analyzed to assess terrestrial contamination from the local environment. A powdered sample of serpentinized peridotite from Coverack, UK was analyzed as the procedural blank.

The Winchcombe meteorite sample was powdered. The samples were subjected to hot-water extraction (ultrapure water; 100 °C, 24 h), acid vapor hydrolysis (6 N HCl, 150 °C, 3 h) to determine the total (free + bound) amino acid content, desalted by cation exchange. Purified amino acids were eluted by 2M NH₄OH, and the eluates were evaporated to dryness. Amino acids were derivatized by esterification with isopropanol and acylation with trifluoroacetic anhydride.

The derivatized samples 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. 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 were used. The oven programs for both GC-MS

were set at an initial temperature of 90 °C and held for 2 minutes, then increased by 5 °C/min to 200 °C and held for 6 min.

Results and discussion:

Low total amino acid abundance. The total amino acid abundance in the HCl-hydrolyzed hot water extract of Winchcombe is 1132 ± 49 ppb, which is about ten times lower than most CM falls, e.g., Murchison (14,600 ppb), Mighei (5,839 ppb), Mukundpura (14,550 ppb), and Aguas Zarcas (up to 43,800 ppb) [e.g., 2, 3]. The Winchcombe meteorite contains various C₂–C₆ α -, β -, γ -, δ - and ϵ -amino acids (**Figure 1**). The most abundant amino acids identified in the Winchcombe meteorite are α -aminoisobutyric acid (AIB) (331 ppb), glycine (163 ppb), and isovaline (269 ppb).

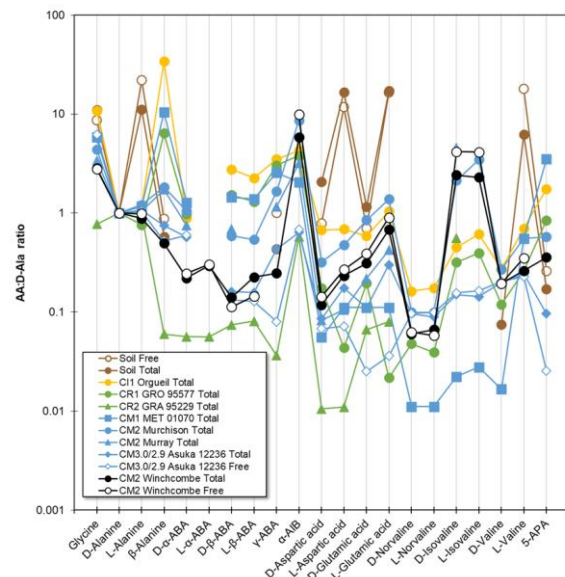


Figure 1. The relative abundances (relative to D-alanine = 1) of amino acids in the 6 N HCl-hydrolyzed, hot water extracts of Winchcombe compared to select carbonaceous chondrites

A general trend of decreasing total amino acid abundances with increasing aqueous alteration has been observed in previous studies [e.g., 4], as a result of a higher rate of thermal decarboxylation and/or hydrolysis of bound amino acid precursors. However, multiple generations of carbonates in Winchcombe suggest that the Winchcombe parent body has experienced episodic aqueous alteration that involved

three discrete, short-term, alteration events [5]. Hence, the low amino acid concentration in Winchcombe can potentially be explained by brief episode(s) of aqueous alteration event on the parent body, yielding only a small fraction of amino acids.

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 observed for meteorites exhibiting a lower degree of aqueous alteration [6]. The majority of the amino acids in the Winchcombe meteorite are present in the free form, with a free:total amino acid ratio of $\sim 1:1$. The high free:total amino acid ratio is on par with that observed in CMs that show very low degrees of aqueous alteration (**Figure 1**).

Enantiomeric ratios of amino acids. The indigenous nature of the detected amino acids in Winchcombe can be established by the racemic mixtures of their D- and L-enantiomers. 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) (**Figure 2**), 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.

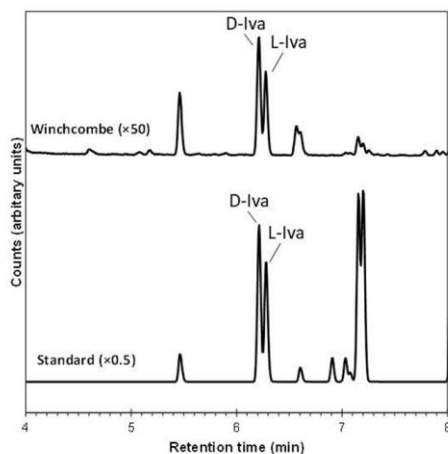


Figure 2. GC-MS total ion current chromatograms of Winchcombe and amino acid standard mixture focusing on the resolution of D- and L-isovaline.

Parent body alteration history. 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 is clearly distinct from that of CM1, CM3.0/2.9 and other CI and CR chondrites (**Figure 1**).

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 [e.g., 4, 6]. 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 contrast to the higher ratios observed for the moderately altered CM2 Murchison (~ 1.83) and in the heavily altered CM1 MET 01070 (10.39). 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.

Conclusions: The Winchcombe meteorite is the most recent, promptly recovered CM2, and has provided us with pristine astromaterials to be studied for the intrinsic organic record of a carbon-rich asteroidal body. 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. The amino acid content is not strictly comparable to other CM2 meteorites, suggesting that the weakly lithified Winchcombe meteorite represent an unusual sample that would not typically survive atmospheric entry.

Acknowledgements: This study was supported by urgency funding from the UK's Science and Technology Facilities Council. Natural History Museum is acknowledged for their curatorial support and the provision of the meteorite sample. This publication is part of the Winchcombe science team consortium, organized by the UK Fireball Alliance and conducted by the UK Cosmochemistry Network.

References: [1] King, A.J., et al. *Science Advances*, 2022. 8(46): p. eabq3925. [2] Pizzarello, S. and C.T. Yarnes. *Planetary and Space Science*, 2018. 164: p. 127-131. [3] Glavin, D.P., et al. *Meteoritics & Planetary Science*, 2021. 56(1): p. 148-173. [4] Glavin, D.P., et al. *Meteoritics & Planetary Science*, 2020. 55(9): p. 1979-2006. [5] Lee, M.R., et al., *MetSoc* 2022. [6] Glavin, D.P., et al. *Meteoritics & Planetary Science*, 2011. 45: p. 1948-1972.