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Insoluble macromolecular organic matter in the Winchcombe meteorite

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Abstract—The Winchcombe meteorite fell on February 28, 2021 in Gloucestershire, United Kingdom. As the most accurately recorded carbonaceous chondrite fall, the Winchcombe meteorite represents an opportunity to link a tangible sample of known chemical constitution to a specific region of the solar system whose chemistry can only be otherwise predicted or observed remotely. Winchcombe is a CM carbonaceous chondrite, a group known for their rich and varied abiotic organic chemistry. The rapid collection of Winchcombe provides an opportunity to study a relatively terrestrial contaminant-limited meteoritic organic assemblage. The majority of the organic matter in CM chondrites is macromolecular in nature and we have performed nondestructive and destructive analyses of Winchcombe by Raman spectroscopy, online pyrolysis–gas chromatography–mass spectrometry (pyrolysis–GC–MS), and stepped combustion. The Winchcombe pyrolysis products were consistent with a CM chondrite, namely aromatic and polycyclic aromatic hydrocarbons, sulfur-containing units including thiophenes, oxygen-containing units such as phenols and furans, and nitrogen-containing units such as pyridine; many substituted/alkylated forms of these units were also present. The presence of phenols in the online pyrolysis products indicated only limited influence from aqueous alteration, which can deplete the phenol precursors in the macromolecule when aqueous alteration is extensive. Raman spectroscopy and stepped combustion also generated responses consistent with a CM chondrite. The pyrolysis–GC–MS data are likely to reflect the more labile and thermally sensitive portions of the macromolecular materials while the Raman and stepped combustion data will also reflect the more refractory and nonpyrolyzable component; hence, we accessed the complete macromolecular fraction of the recently fallen Winchcombe meteorite and revealed a chemical constitution that is similar to other meteorites of the CM group.

INTRODUCTION

Meteorites represent witnesses to some of the earliest steps in planet formation. As fragments of asteroids, their chemical constitution is a record of primary and secondary processes in the parts of the solar system where

these bodies formed. Recently, our access to early solar system chemical evolution was enhanced by the fall of the Winchcombe meteorite on February 28, 2021 in Gloucestershire, United Kingdom (King et al., 2022). The Winchcombe fireball was recorded by multiple methods and delivered the meteorite with the best-known

provenance for its type. The recorded orbit of the Winchcombe meteorite was similar to those of previous CM carbonaceous chondrites and laboratory chemical, mineralogical, and petrographic analyses later confirmed its CM nature (King et al., 2022). One of the most remarkable characteristics of the CM chondrites, along with other low petrographic type carbonaceous chondrites, is the presence of percentage levels of organic matter (Sephton, 2014). The organic matter in CM chondrites is perhaps the richest and most varied of the carbonaceous chondrites owing to their relatively lesser amounts of aqueous and thermal processing relative to their lower and higher petrographic type counterparts (Sephton, Verchovsky, et al., 2004).

The organic matter in carbonaceous chondrites can be subdivided, based on operational characteristics, into free organic matter that is solvent soluble; labile organic matter that is a macromolecular component and easily degraded by heat and water; and refractory organic matter that is macromolecular and relatively resistant to aqueous and thermal processing (Sephton et al., 2003; Sephton, Verchovsky, et al., 2004). The macromolecular fractions are, by far, the most abundant components and the quantity and limited mobility of macromolecular materials make them the most resistant fractions to terrestrial contamination.

The macromolecular fractions are dominated by aromatic structures and their various functional groups. Yet, the insoluble nature of the macromolecular materials requires specific chemical methods to obtain information about their constitution. Nondestructive techniques include nuclear magnetic resonance spectroscopy (Cody et al., 2002; Gardinier et al., 2000), infrared spectroscopy (Hayatsu et al., 1977), X-ray absorption near edge structure spectroscopy (Orthous-Daunay et al., 2010), and Raman spectroscopy (e.g., Bonal et al., 2006; Busemann et al., 2007; Chan, Franchi, et al., 2019; Chan, Nakato, et al., 2019; Potiszil et al., 2021; Starkey et al., 2013). Destructive techniques include stepped combustion (Grady et al., 2002; Sephton et al., 2003) and online and offline pyrolysis, in the presence or absence of water or hydrogen (Sephton, 2012). Destructive techniques thermally dissociate or combust the macromolecular materials into pieces that are analytically amenable and diagnostic of the source or makeup of the parent material.

In this paper, we report analyses of the macromolecular fractions in the Winchcombe meteorite using nondestructive (Raman spectroscopy) and destructive (stepped combustion and online pyrolysis) techniques. The obtained information provides insights into the constitution of the macromolecular organic units in this meteorite and allows interpretations of similarities and differences with previously analyzed CM chondrites.

EXPERIMENTAL PROCEDURES

Sample Preparation

Just under 1 g (0.9754 g) of the Winchcombe meteorite (BM.2022,M2-14) was obtained from the Natural History Museum (NHM), London, for a combined solvent-soluble and solvent-insoluble organic analysis. The sample was originally collected after it fell on a residential driveway in Winchcombe, Gloucestershire, United Kingdom. Raman spectroscopy was initially conducted on an exposed surface from the interior of the allocated Winchcombe stone, and a ~10 mg portion was then subsampled from the powdered meteorite for thermal extraction/pyrolysis–gas chromatography–mass spectrometry (pyrolysis–GC–MS). Soluble organic matter (SOM) was extracted using hot water from the remaining powdered sample, and the SOM content is reported in a separate study (Chan et al., 2023). Chips from two separate pieces of Winchcombe (BM 2022,M1-85 and BM 2022, M1-86) were used for stepped combustion.

Raman Spectroscopy

Raman spectroscopic analysis was used to analyze the raw (uncoated, unpolished) exposed surface of the Winchcombe specimen using a Jobin-Yvon Horiba LabRam HR (800 mm) Raman microprobe at The Open University (OU). The excitation source was a 514.53 nm (green) laser. Thirty spectra in total were acquired for Winchcombe from three separate areas (5–15 spectra per area) in the spectral region 800–2200 cm^{-1} , which includes the first (~1000–1800 cm^{-1}) Raman bands of carbon. The analytical areas were selected to avoid chondrules (i.e., data were collected from the sample matrix), and only the interior of the meteorites was analyzed. Raman spectra were also taken from the fusion crust of the Winchcombe meteorite, which did not show Raman D or G bands, as the organic material was decomposed by the atmospheric entry flash heating, and therefore, these spectra were not used for calculating the Raman D and G band parameters in this study.

The slit width and the confocal pinhole aperture were set at 150 and 300 μm , respectively, and a 600 grooves mm^{-1} grating was used to disperse the Raman signal, leading to a spectral resolution of approximately 3 cm^{-1} . The laser beam was focused through a microscope equipped with a 100 \times objective (numerical aperture = 0.75). At this magnification and for the laser used, the spot size of the Raman probe was ~1 μm , and the laser power at the sample surface was ~100–150 μW . The exposure time for each spectrum was 20 s and three accumulations were obtained for each analytical spot to

identify and discard spurious signals, such as those from cosmic rays, leading to a total acquisition time of up to 180 s. Peak position was calibrated daily against a silicon wafer prior to sample analyses and no significant shift was observed. Laser power was also checked daily prior to analyses to ensure that the laser power was consistent among all samples.

The sample surface was re-examined by the optical microscope to check for any damage. We were able to confirm that no sign of physical damage was observed. Spectral peak identification and methods used in the present study were the same as outlined in the literature (Chan, Franchi, et al., 2019; Chan, Nakato, et al., 2019). The peak position (ω) and full width half maximum (FWHM, Γ) of each Raman band were determined by simultaneous peak fitting to the two-peak Lorentzian and Breit–Wigner–Fano (BWF) model (Ferrari & Robertson, 2000) and linear baseline correction. Details of the Raman peak-fitting procedures and rationales are given in the literature (Chan et al., 2017; Chan, Franchi, et al., 2019; Chan, Nakato, et al., 2019). Raman band parameters for each sample were reported as the average of all selected spectra and the uncertainties are the 1σ standard error of the mean of all used spectra. Only fitted data with $R^2 > 0.9$ are shown in this study.

Pyrolysis–GC–MS

A freshly crushed aliquot of meteorite (7.45 mg) was loaded into a quartz pyrolysis tube and held in place with quartz wool. Pyrolysis–GC–MS was performed using a 5200 Pyroprobe (CDS Analytical) coupled via a 1500 Interface (280 °C) to a 6890–5973 GC–MS (Agilent Technologies). Following heating to 300 °C at a rate of 20 °C ms^{-1} , the sample was held at this temperature for 15 s in a flow of helium and left in the interface for 5 min. The GC injector was held at 270 °C and operated at a 10:1 split 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 500 amu. After analysis at 300 °C, the sample was subsequently pyrolyzed at 650 °C, and apart from a higher heating temperature, all other conditions were the same as above. An external standard of pyrene was analyzed to enable semiquantitation of products released. Another aliquot was analyzed at 350 °C and subsequently at 650 °C.

Stepped Combustion

Two pieces of Winchcombe were taken directly from the fall site to the OU for oxygen isotope analysis. They were subsequently registered as specimens 1a-85 (BM.2022,M1-85) of 8.8 g and 1a-86 (BM.2022,M1-86) of 6.9 g. The pieces were stored in glass jars that had been baked in air at ~ 500 °C; the headspace was purged with dry nitrogen prior to sealing. Chips were broken from each of the whole rock samples of Winchcombe (5.0502 mg from 1a-85 and 5.0981 mg from 1a-86) for analysis at the Open University on the fully automated Finesse system (e.g., Grady et al., 2002; Sephton et al., 2003).

Finesse consists of two magnetic sector mass spectrometers and a quadrupole mass spectrometer all of which are operated in static vacuum mode. The mass spectrometers are connected to a common extraction system enabling simultaneous analysis by stepped combustion of the abundance and isotopic compositions of He, Ne, Ar, Xe, N, and C in a single sample.

Each sample was weighed and wrapped in a Pt foil envelope before introduction into the extraction furnace where they were first heated at ~ 100 °C for at least 0.5 h under vacuum to remove loosely adsorbed atmospheric species. Oxygen for the combustion (5–10 mbar) was generated by heating Cu(II)O to 850 °C in the presence of a Pt catalyst; at the end of a combustion step (generally 0.5 h), surplus oxygen was resorbed by Cu(I)O at 450 °C and the combustion products cryogenically separated on a series of cold fingers using liquid nitrogen.

The Winchcombe samples were analyzed using a high-resolution temperature program of 25° steps from 100 to 1400 °C; here, we report C and N data from 300 to -550 °C temperature steps, the temperature range over which most of the macromolecular material combusts and which is most analogous to the material examined by Raman spectroscopy and pyrolysis–GC–MS. The system blank was determined prior to sample analysis by stepped combustion of an empty Pt foil capsule over the same temperature range as the sample. The contribution from the system blank at temperatures below 600 °C was negligible for C and N. Calculations of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were achieved by measuring samples alternately with materials calibrated to NBS standards. Values are expressed relative to PDB for C and air for N.

RESULTS

Raman Spectroscopy

Figures 1 and 2 display the Raman responses of the Winchcombe meteorite alongside other carbonaceous

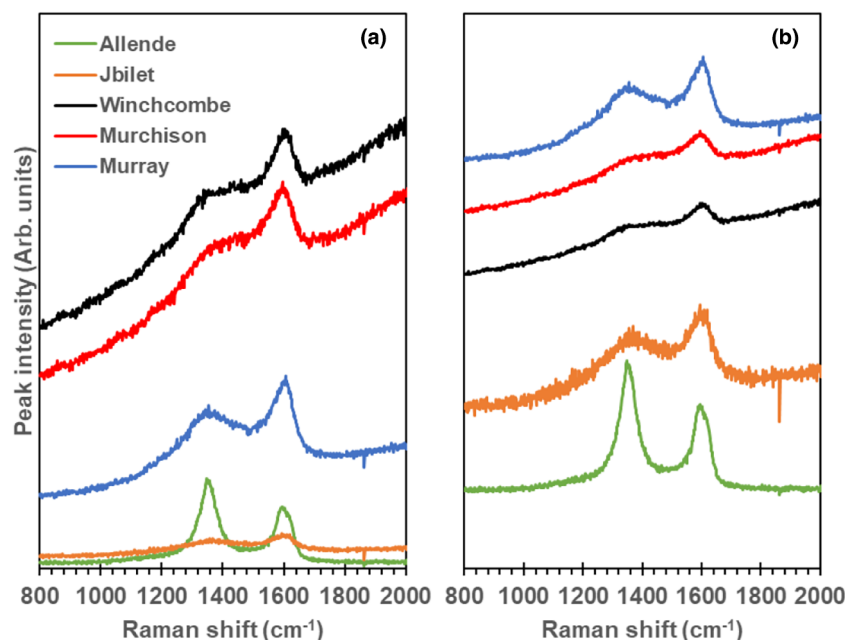


FIGURE 1. (a) Selected raw Raman spectra of the Winchcombe meteorite and several other carbonaceous chondrite samples. (b) The same Raman spectra that have been normalized with respect to the maximum intensity within the spectral range 1300–1600 cm^{-1} . The spectra have been offset vertically to enhance readability.

chondrites. Carbonaceous materials feature Raman bands in the first- and second-order regions. The most typical peaks are the first-order defect (D) band at ~ 1350 to 1380 cm^{-1} and the graphite (G) band at ~ 1580 to 1590 cm^{-1} (Tuinstra & Koenig, 1970). The Winchcombe meteorite fragment has high Raman signal intensity. As shown in Figure 1a, the raw Raman spectra of the Winchcombe meteorite are accompanied by an intense fluorescence signal leading to a steep background slope in the first-order D and G bands spectral region between 1300 and 1600 cm^{-1} .

The peak parameters of the D and G bands, such as the peak center locations (usually referred to as peak position, ω), peak widths in terms of FWHM (Γ), and the peak intensity ratios between the D and G bands (I_D/I_G), can be systematically correlated with various properties of organic matter (Figure 2). The combination of peak parameters describes the overall size distribution of the crystalline domains and the metamorphic history of the carbonaceous host (e.g., Bonal et al., 2007; Busemann et al., 2007; Chan, Franchi, et al., 2019; Chan, Nakato, et al., 2019), with for example, increased metamorphism when ω_G is high and Γ_G low. Unlike comets, where the equivalent data from a single comet span a large region (e.g., Sandford et al., 2006), data from individual meteorites tend to fall into discrete domains in the relevant parameter spaces. This is found to be the case here (Figures 1 and 2), with similarities observed to the Murray meteorite (see Discussion for details).

Pyrolysis–GC–MS

Figure 3 shows the total ion current (TIC) chromatogram for the thermal extract and pyrolysis products from the Winchcombe meteorite. The peaks represent organic and other compounds that are listed in Table 1. The TIC for the Winchcombe thermal extract (Figure 3a) displays a range of solvent soluble or free compounds including aromatic hydrocarbons, polycyclic aromatic hydrocarbons and their substituted and alkylated forms, alongside aromatic compounds with oxygen- and sulfur-containing functional groups. The TIC may also contain weakly bound organic compounds that have been liberated by the $350 \text{ }^\circ\text{C}$ thermal extraction temperature. There is a significant unresolved complex mixture (UCM) that underlies the more discrete peaks. The UCM is caused by the coelution of a range of compounds with similar chromatographic behavior. The mass spectra of the UCM reveal ions of $m/z = 55, 57, 69, 83, 97$, etc. The coeluting compounds are difficult to identify owing to overlapping mass spectrometry signals. However, we note that previous authors (Cronin & Pizzarello, 1990) described similar ($m/z = 55, 69, 83, 97$, etc.) responses for the UCM of a hexane fraction obtained by silica gel chromatography from a solvent extract of the Murchison CM2 chondrite. They attributed the mass spectrometry responses to a structurally diverse suite of branched and alkyl-substituted cycloalkanes. There are only limited contributions from long-chain

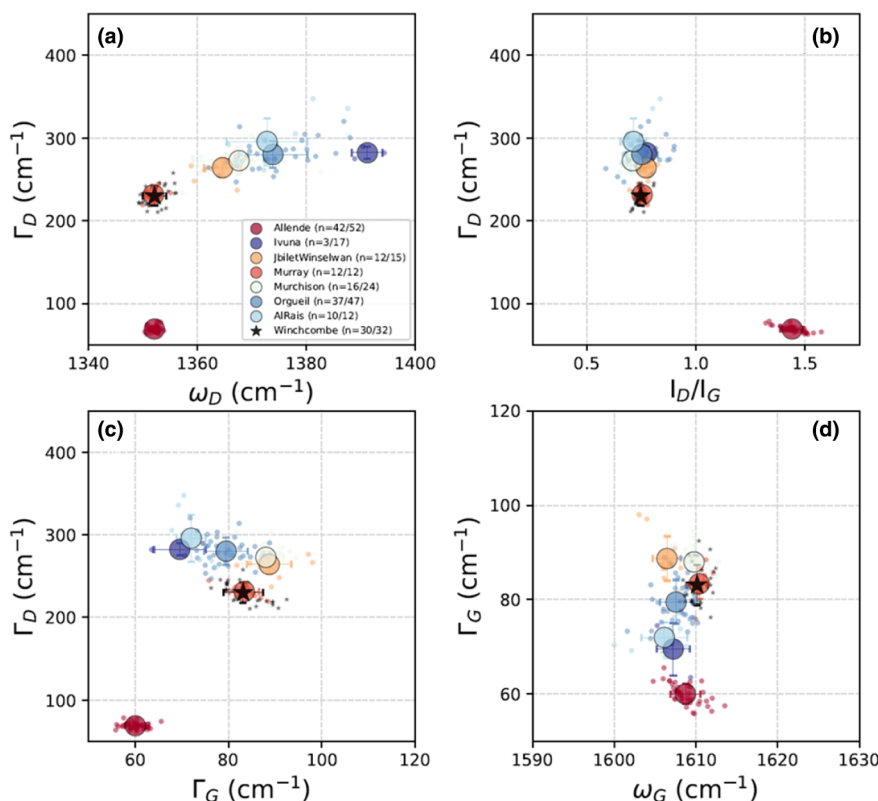


FIGURE 2. Comparison of the Raman band parameters of the organic matter in the Winchcombe meteorite to that in other carbonaceous chondrites. The subplots show (a) the full-width half-maximum (FWHM, Γ) against peak center location (ω) of the D band, (b) the FWHM of the D band against the peak intensity ratios between the D and G bands, (c) the FWHM of the D band against FWHM of the G band, and (d) the FWHM against peak center location of the G band. The mean values are presented as large symbols, and the individual points are shown as small symbols to demonstrate the spread of the data. Uncertainties are 1σ standard deviation of the mean.

aliphatic hydrocarbons. The TIC for the Winchcombe pyrolysis products (Figure 3b) shows a number of discrete peaks with the major components representing aromatic and polycyclic aromatic hydrocarbons and their substituted and alkylated forms, alongside aromatic compounds with oxygen- and sulfur-containing functional groups.

The aromatic and polycyclic aromatic hydrocarbons present in a TIC can be highlighted by means of an extracted ion chromatogram (EIC). The EIC for the aromatic and polycyclic aromatic hydrocarbons in the thermal extract and pyrolysis products of Winchcombe is presented in Figure 4. By comparison with an external standard (pyrene) that has similar ionization behavior to the compounds of interest, semiquantitation data can be generated (Table 2).

Stepped Combustion

Results for both Winchcombe stones were similar and are given in Table 3 and shown in Figure 5 (Note:

Results for the complete combustion experiments are given in King et al., 2022). Between 300 and 500 °C, around 1.3 wt% carbon and 300 ppm nitrogen combust, with variable $\delta^{13}\text{C}$ of ~ -21 to -6% and $\delta^{15}\text{N} \sim -14$ to $+33\%$. As indicated by the shapes of the carbon and nitrogen yield histograms, the variations in isotopic composition and C/N ratio, at least three distinct components are present. The most obvious component, apparent in maxima for the abundances of both carbon and nitrogen, combusts between 375 and 450 °C. The corresponding minima in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ are almost certainly indicators of the presence of meteoritic nanodiamonds, masking the organic compounds that oxidize across the same temperature range. Below 375 °C and above 450 °C, lesser quantities of carbon and nitrogen are released, with heavier but variable isotopic compositions. The C/N ratio at low temperatures is the same for the two pieces of Winchcombe, around 80–90, as it is above 450 °C at 30–40. None of these C/N values correspond to any of the specific N-bearing molecules identified by pyrolysis–GC–MS, which have C/N of 5–7

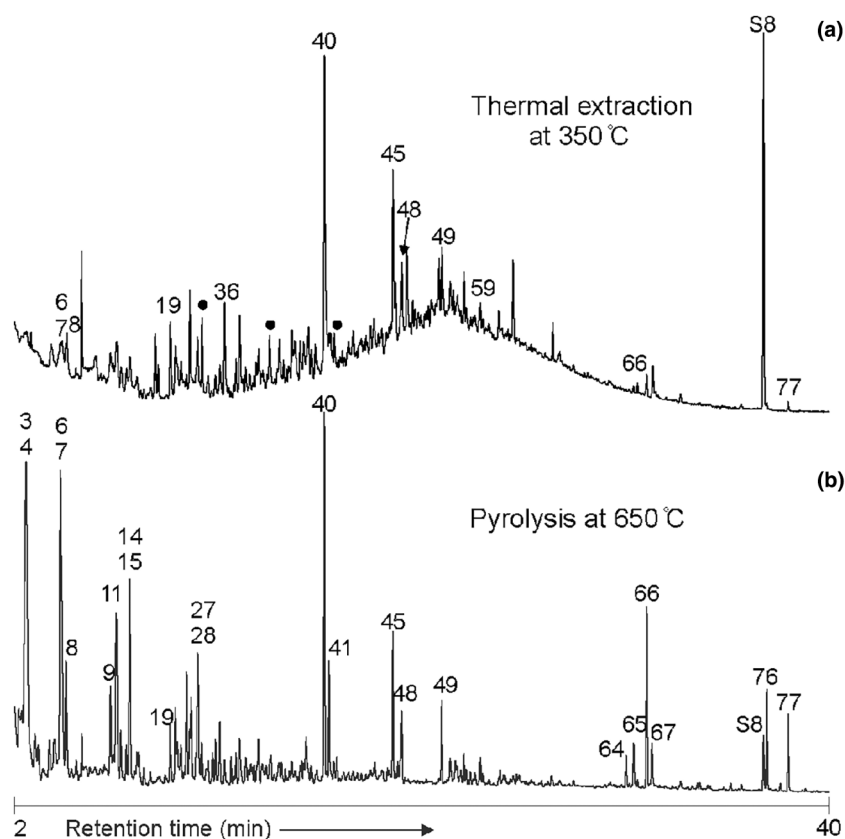


FIGURE 3. Total ion current chromatograms for the Winchcombe meteorite subjected to (a) online thermal extraction at 350 °C and (b) online pyrolysis at 650 °C. For peak assignments, see Table 1; S8 = octasulfur.

(Table 3). It seems that combustion is gradually oxidizing the underlying macromolecule, but interference from the nanodiamonds precludes a more precise identification of specific species.

DISCUSSION

Comparison to Other Meteorites

The Raman data for the Winchcombe meteorite are comparable to the primitive (unheated) CM chondrites (Figures 1 and 2), and deviate from that of the other primitive carbonaceous chondrites like CI1 Orgueil, CR2 Al Rais, and metamorphosed chondrites like CV3 Allende (Figure 2). The Rubin scale (Rubin et al., 2007) differentiates the degree of alteration, with CM3.0 being unaltered, and CM2.0 completely altered.

Among the range of CM chondrites (CM2.4/2.5 Murray, CM2.5 Murchison, CM2.3-2.7 Jbilet Winselwan; petrologic subtype based on King et al., 2019; Rubin et al., 2007), the organic matter in Winchcombe is closely matched to that of the CM2.4/2.5 Murray, which was previously shown to have undergone low to moderate degrees of parent body aqueous alteration (Lee &

Ellen, 2008; Tomeoka & Buseck, 1985). The high Raman intensity accompanied by the high fluorescence background of Winchcombe may indicate the presence of heteroatoms (e.g., N, O, and S) of conjugated C bonds and aliphatic components (Busemann et al., 2007; Munoz Caro et al., 2006), suggesting organic primitiveness, although the high Raman intensity can also be influenced by arbitrary factors such as the focus of the laser in the laboratory. The Raman C parameters of Winchcombe are clustered with low 1σ values compared to other unheated carbonaceous chondrites, which show a restricted range of D and G band parameters. For example, the average ω_D values of Murchison, Jbilet Winselwan, Al Rais, and Orgueil were 1367.6–1373.9 cm^{-1} , with 1σ values of 3.4–8.4 cm^{-1} , and the average ω_D value of Winchcombe was $1352.1 \pm 2.1 \text{ cm}^{-1}$. The clustering of spectral data observed in Winchcombe is comparable to that observed for Murray $1352.0 \pm 1.3 \text{ cm}^{-1}$. While such an observation indicates the reproducibility of the measurements, clustering of spectra parameters is typically observed for the organic matter in thermally processed meteorites, which reflects a reduced organic matter heterogeneity due to the irreversible annealing effect that homogenized the organic matter (Chan, Nakato, et al., 2019).

TABLE 1. Identifications of products released upon pyrolysis (650 °C) of the Winchcombe meteorite.

#	Compound	Rt	RI	MW
1	1-Hexene	2.2	595	84
2	Hexane	2.3	600	86
3	Benzene	2.9	659	78
4	Thiophene	2.9	664	84
5	Pyridine	4.2	746	79
6	Toluene	4.5	762	92
7	2-Methylthiophene	4.6	766	98
8	3-Methylthiophene	4.8	775	98
9	Ethylbenzene	6.8	858	106
10	Thiophene, 2-ethyl-	6.9	862	112
11	1,3- and 1,5-Dimethylbenzene	7.0	867	106
12	Thiophene, 3-ethyl-	7.3	875	112
13	Thiophene, 2-ethenyl-	7.7	888	110
14	Styrene	7.7	890	104
15	1,4-Dimethylbenzene	7.7	891	106
16	Thiophene, 3-ethenyl-	8.1	902	110
17	Isopropylbenzene	8.7	922	120
18	Benzene, 2-propenyl-	9.3	944	118
19	Propylbenzene	9.6	952	120
20	Benzene, 1-ethyl-3-methyl-	9.8	959	120
21	Benzene, 1-ethyl-4-methyl-	9.9	962	120
22	Benzene, 1,3,5-trimethyl-	10.1	968	120
23	Benzene, 1-ethyl-2-methyl-	10.3	976	120
24	Phenol	10.4	976	94
25	α -Methylstyrene	10.5	980	118
26	Benzonitrile	10.6	983	103
27	*Benzene, 1-ethenyl-3-methyl-	10.8	990	118
28	Benzene, 1,2,4-trimethyl-	10.8	992	120
29	*2-Thiophenecarbonitrile	10.8	992	109
30	*Benzene, 1-ethenyl-2-methyl-	10.9	994	118
31	Benzofuran	10.9	994	118
32	*Benzene, 1-ethenyl-4-methyl-	11.0	998	118
33	*3-Thiophenecarbonitrile	11.6	1015	109
34	Benzene, 1,2,3-trimethyl-	11.7	1019	120
35	Benzene, 1-propenyl-	11.9	1026	118
36	Indane	12.1	1033	118
37	Indene	12.4	1042	116
38	Phenol, 2-methyl-	12.6	1050	108
39	Phenol, 3-/4-methyl-	13.3	1072	108
40	Naphthalene	16.7	1184	128
41	Benzo[b]thiophene	16.9	1191	134
42	*Benzo[c]thiophene	17.6	1215	134
43	7-Methylbenzo[b]thiophene	19.6	1287	148
44	2-Methylbenzo[b]thiophene	19.9	1295	148
45	2-Methylnaphthalene	19.9	1295	142
46	5-/6-Methylbenzo[b]thiophene	20.1	1304	148
47	3-/4-Methylbenzo[b]thiophene	20.2	1308	148
48	1-Methylnaphthalene	20.3	1311	142
49	Biphenyl	22.1	1380	154
50	2/1- Ethylnaphthalene	22.5	1394	156
51	2,6-Dimethylnaphthalene	22.8	1405	156
52	2,7-Dimethylnaphthalene	22.9	1407	156
53	1,3-/1,7-Dimethylnaphthalene	23.1	1419	156
54	1,6-Dimethylnaphthalene	23.3	1423	156

TABLE 1. *Continued.* Identifications of products released upon pyrolysis (650 °C) of the Winchcombe meteorite.

#	Compound	Rt	RI	MW
55	Acenaphthene	23.5	1430	154
56	2-Methylbiphenyl	23.5	1431	168
57	1,4-/2,3-Dimethylnaphthalene	23.7	1439	156
58	1,5-Dimethylnaphthalene	23.7	1441	156
59	Acenaphthylene	23.9	1449	152
60	1,2-Dimethylnaphthalene	24.0	1453	156
61	3-Methylbiphenyl	24.8	1485	168
62	4-Methylbiphenyl	25.1	1495	168
63	Dibenzofuran	25.6	1516	168
64	9H-Fluoren-9-one	30.6	1737	180
65	Dibenzothiophene	31.0	1753	184
66	Phenanthrene	31.6	1781	178
67	Anthracene	31.8	1792	178
68	4-Methyldibenzothiophene	33.1	1856	198
69	2-/3-Methyldibenzothiophene	33.5	1873	198
70	1-Methyldibenzothiophene	33.9	1894	198
71	3-Methylphenanthrene	34.0	1895	192
72	2-Methylphenanthrene	34.1	1900	192
73	2-Methylantracene	34.3	1909	192
74	9-Methylphenanthrene	34.4	1913	192
75	1-Methylphenanthrene	34.5	1918	192
76	Fluoranthene	37.2	2060	202
77	Pyrene	38.1	2113	202

Identifications are based on retention time with retention locking, retention order relative to n-alkanes (retention indices), and mass spectra. Assignments and abbreviations include * = there is some uncertainty over the exact isomer for the identified compound; Rt = retention time; RI = Retention Index; "MW" = molecular weight.

Using the cosmothermometer developed by Busemann et al. (2007) (Equation 1), and with a Γ_D value of 229.95 cm^{-1} , the peak metamorphic temperature (PMT) of Winchcombe is estimated to be $\sim 239.4 \text{ }^\circ\text{C}$, which is consistent with the range of PMTs ($<220\text{--}240 \text{ }^\circ\text{C}$) estimated for most CMs (Huss et al., 2006). Therefore, the clustering of spectra parameters observed for Winchcombe is not accounted for by metamorphose/annealing, but should instead be influenced by other mechanisms, such as preferential removal of organic components (e.g., removal of labile organic matter from the macromolecular material) during the hydrothermal process (Sephton et al., 2003). Nevertheless, Winchcombe organic matter exhibits a moderate range in Γ_D , which may reflect some compositional heterogeneity.

$$\begin{aligned} \text{Peak metamorphic temperature (}^\circ\text{C)} \\ = 931 - 5.10 \times \Gamma_D + 0.0091 \times \Gamma_D^2 \end{aligned} \quad (1)$$

The online pyrolysis products of the Winchcombe meteorite (Figures 3 and 4, Tables 1 and 2) are consistent with previous analyses of CM carbonaceous chondrites

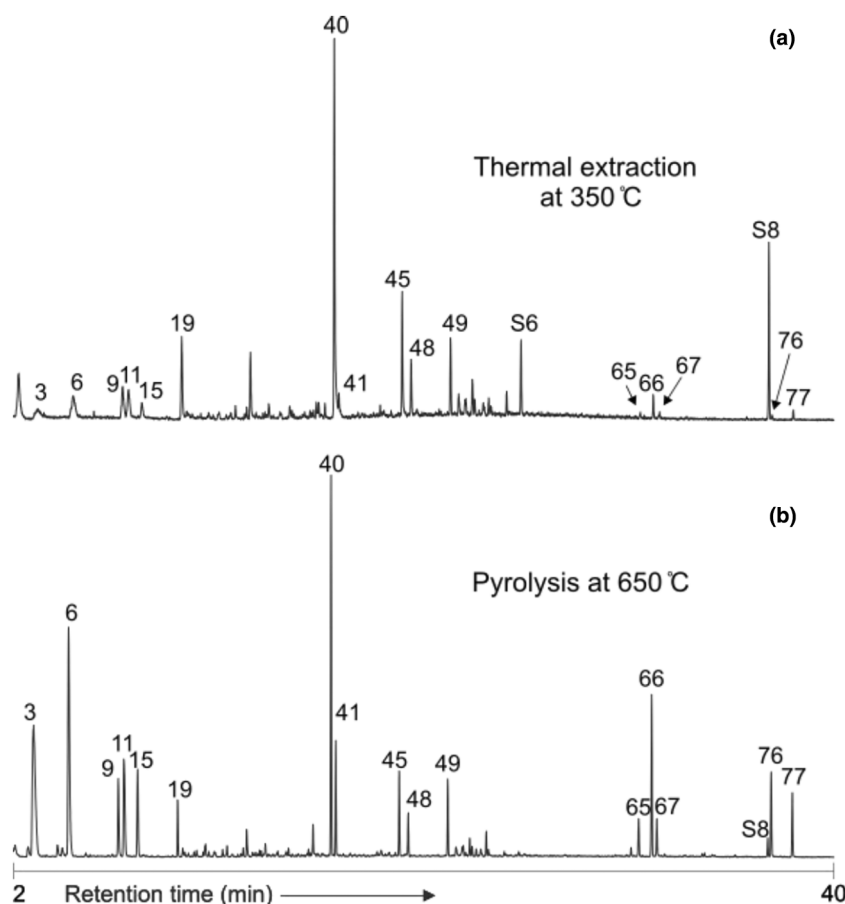


FIGURE 4. Partially reconstructed (summed) mass chromatogram (m/z 78 + 91 + 128 + 142 + 152 + 154 + 156 + 178 + 184 + 192 + 198 + 202) displaying selected aromatic, substituted and alkylated aromatic, and polycyclic aromatic hydrocarbons in the (a) thermal extract and (b) pyrolysate of the Winchcombe meteorite. For peak assignments, see Table 1; S8 = octasulfur.

which generate aromatic, heteroatomic, and hydroaromatic ring systems with various functional groups attached (Sephton [2014] and references therein). The products are consistent with theories of CM macromolecular material structure, which involve condensed aromatic, heteroatomic, and hydroaromatic ring systems with various functional groups attached (Sephton [2014] and references therein). Stepped combustion data from the Winchcombe meteorite (Figures 5 and 6, Table 3) are also similar to those from other CM chondrites (Grady et al., 2002; Sephton et al., 2003).

Thermal Extract

The thermal extract at 300 °C, and to a large extent that at 350 °C, represent those compounds that can be released from the meteorite by the application of heat at a level which does not involve breaking of chemical bonds. The thermal extract for Winchcombe (Figures 3 and 4,

Table 2) should, therefore, be generally comparable to the free compounds that are isolated by solvent extraction steps. The thermal extract does have many of the same compounds and at similar orders of magnitude as observed in the solvent extract (Chan et al., 2023). One feature of the thermal extract is the presence of an UCM with responses dominated by mass over charge (m/z) values of 55 suggesting the presence of cyclic alkanes (Figure 3). The presence of cyclic alkanes in a CM chondrite is in agreement with previous investigations of free organic matter in the CM Murchison (Cronin & Pizzarello, 1990), where their indigeneity was indicated by carbon isotope measurements (Krishnamurthy et al., 1992).

Terrestrial Contamination

The rapid collection of Winchcombe provides an opportunity to study a relatively terrestrial contaminant-limited meteoritic organic assemblage. Moreover, the

TABLE 2. Semiquantitation of selected products released upon heating and pyrolysis (300 °C followed by 650 °C and 350 °C followed by 650 °C) of Winchcombe meteorite.

	$\mu\text{g g}^{-1}$ 300 °C	$\mu\text{g g}^{-1}$ 650 °C	$\mu\text{g g}^{-1}$ 350 °C	$\mu\text{g g}^{-1}$ 650 °C
Benzene	0.175	8.769	0.288	7.526
Toluene	0.564	12.291	0.724	10.969
Ethylbenzene	0.345	1.965	0.496	1.896
1,3- and 1,5-Dimethylbenzene	0.460	4.230	0.573	3.930
1,2-Dimethylbenzene	0.171	1.952	0.177	1.782
Naphthalene	2.235	6.224	2.202	5.282
1-Methylnaphthalene	0.939	2.466	1.205	1.020
2-Methylnaphthalene	0.468	1.238	0.554	0.529
Benzothiophene	0.089	2.012	0.100	1.634
Biphenyl	0.233	0.970	0.310	0.828
Dibenzothiophene	0.013	0.738	0.025	0.587
Phenanthrene	0.050	2.528	0.104	2.149
Anthracene	0.006	0.658	0.011	0.521
Fluoranthene	0.014	1.640	0.022	1.297
Pyrene	0.010	1.248	0.051	1.005

Values are expressed as $\mu\text{g g}^{-1}$ meteorite.

online thermal extraction procedure is reasonably reagent-free and an elegant procedure, so the sample is relatively unaffected by laboratory analytical artifacts. Yet, a previous carbonaceous chondrite fall (Allende CV3) that was collected rapidly presented small amounts of contamination on the exterior but not interior of the meteorite, demonstrating that terrestrial contamination can be quickly acquired (Han et al., 1969).

The thermal extract of the Winchcombe meteorite (Figures 3 and 4, Table 2) does contain indications of free terrestrial contaminants although at very low levels. Contaminants that can be detected in the sample analyzed include a phthalate ester and 2,2,4,4,6,8,8-heptamethylnonane both probably sourced from plastics. Also present are *n*-alkanes ($\text{C}_{10}\text{--}\text{C}_{18}$) and the isoprenoidal

hydrocarbons pristane and phytane, which are just above the limit of detection; these are likely to be from petroleum partial combustion products in the atmosphere. Other likely terrestrial contaminants, that is, those organic compounds established as common meteoritic contaminants (Sephton et al., 2001; Watson et al., 2003) or with structures characteristic of synthetic materials such as plastics, include butylated hydroxytoluene, phthalate esters, and Irganox 1076 (e.g., Grosjean & Logan, 2007) which are used as additives along with hundreds of other compounds. Contamination can occur either by direct contact for nonvolatiles or by adsorption/absorption of semivolatiles from the atmosphere. Semivolatiles are typically in the diesel range of hydrocarbons ($\text{C}_{10\text{--}20}$) and include terpenoids that are produced by plants and are used in fragrances and cleaning products (e.g., Watson et al., 2003). There are a number of studies that have looked at common contaminants in the organic analysis of geological and meteorite samples that cover this subject in much greater detail (e.g., Brocks et al., 2008; George et al., 2010; Greenwood et al., 2009; Herd et al., 2016; Illing et al., 2014; Tunney et al., 2022).

Soluble–Insoluble Relationships

Concordance of chemical entities in solvent/thermal extracts and the pyrolysis products of macromolecular materials in carbonaceous chondrites has led to suggestions that they were linked by a degradation process (Simmonds et al., 1969; Studier et al., 1965). Hydrous pyrolysis of the macromolecular material in combination with compound-specific isotope analysis for the aromatic hydrocarbons in both fractions established a clear genetic link for the free and macromolecular units (Sephton et al., 1998). A similar degradation process has been proposed to explain the presence of free mono- and dicarboxylic acids (Oba & Naraoka, 2006; Yabuta et al., 2007) although not all free

TABLE 3. Stepped combustion data for the Winchcombe carbonaceous chondrite.

Temp (°C)	Winchcombe BM 2022, M1-85 (5.0502 mg)							Winchcombe BM 2022, M1-86 (5.0981 mg)						
	[C] (ppm)	$\delta^{13}\text{C}$ (‰)	$\pm \sigma$ (‰)	[N] (‰)	$\delta^{15}\text{N}$ (‰)	$\pm \sigma$ (‰)	C/N (at)	[C] (ppm)	$\delta^{13}\text{C}$ (‰)	$\pm \sigma$ (‰)	[N] (‰)	$\delta^{15}\text{N}$ (‰)	$\pm \sigma$ (‰)	C/N (at)
325	1324.3	−6.4	0.1	18.6	27.1	0.2	83	1505.8	−7.5	0.6	19.3	32.9	0.2	91
350	1456.4	−16.6	0.7	20.7	16.2	0.2	82	1543.2	−7.0	0.7	21.8	16.2	0.2	82
375	1593.3	−10.6	0.6	29.0	−2.6	0.2	64	1658.1	−10.9	0.2	32.6	0.2	0.2	59
400	1874.9	−19.0	0.5	43.0	−14.1	0.2	51	1728.8	−5.8	0.2	54.4	−8.8	0.2	37
425	2043.1	−21.1	0.5	54.6	−8.8	0.2	44	1836.1	−14.3	0.1	71.5	−5.9	0.2	30
450	1862.3	−12.2	0.2	50.8	20.3	0.2	43	2123.1	−15.4	0.4	63.9	16.2	0.2	39
475	1268.3	−12.8	0.7	33.6	31.1	0.2	44	1670.8	−11.6	0.7	47.1	31.9	0.2	41
500	637.0	−9.6	0.7	23.5	27.4	0.2	32	1050.7	−9.0	0.3	27.1	29.9	0.2	45
Total	12,059.6	−14.4	0.1	273.8	8.7	0.3		13116.6	−10.5	0.1	337.7	10.2	0.3	

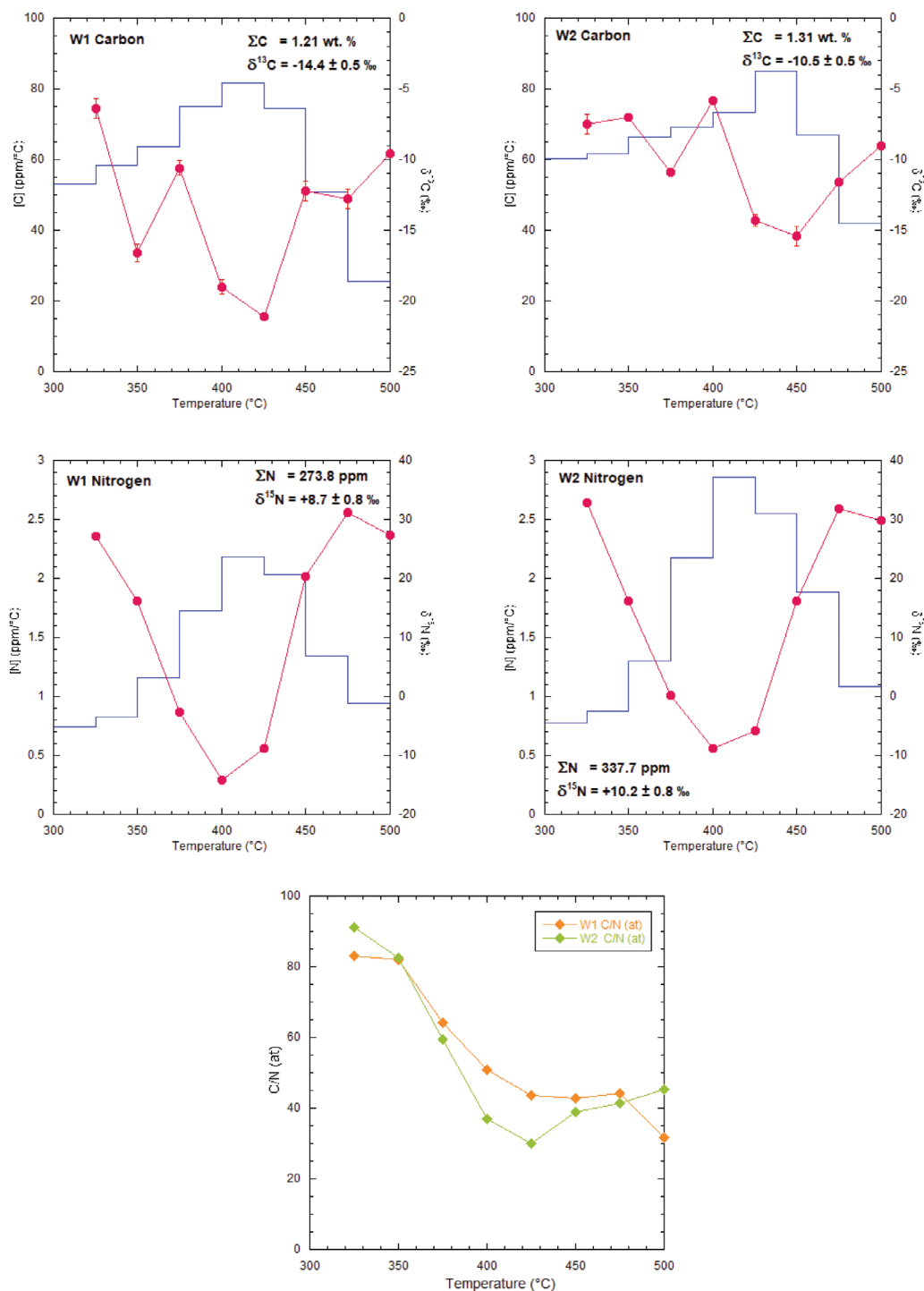


FIGURE 5. Stepped combustion data including element concentration (ppm) with temperature ($^{\circ}\text{C}$), C/N ratios, and stable isotopic composition ($\delta^{13}\text{C}_{\text{‰}}$ and $\delta^{15}\text{N}_{\text{‰}}$) for two Winchcombe meteorite stones. Error bars are less than the size of the symbol unless shown otherwise.

compound classes can be explained in this way (Remusat et al., 2005). The similarity of the thermal extract and pyrolysate for the Winchcombe organic matter (Figures 3 and 4, Tables 1 and 2) would support the concept of free compounds originating by degradation of higher

molecular weight macromolecular material, probably during parent body aqueous alteration (Sephton et al., 1998).

Table 2 reveals that for organic compounds that are present in both the thermal extract and pyrolysis

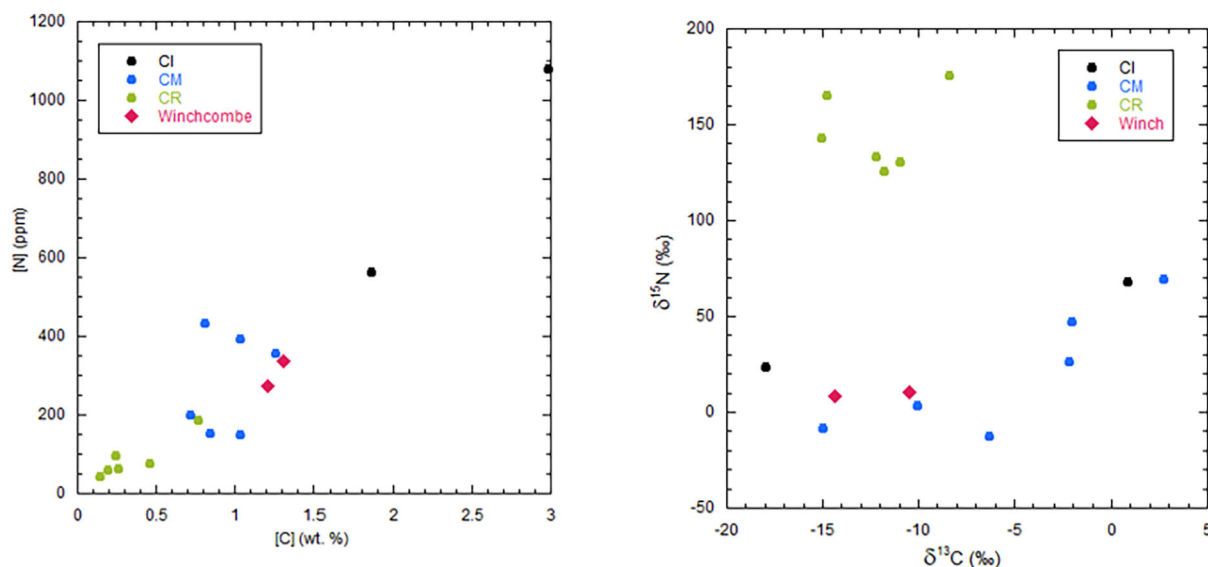


FIGURE 6. A comparison of nitrogen and carbon concentrations and isotopic compositions of the Winchcombe meteorite and other carbonaceous chondrites. Note that the two Winchcombe stones sit within the range of other CM carbonaceous chondrites. All data acquired by stepped combustion at the Open University, United Kingdom.

products, greater abundances occur in the pyrolysis products reflecting the relatively greater size of the macromolecular fraction. Considering the genetic link between at least some free and macromolecular aromatic units (Sephton et al., 1998), it follows that the relative abundance of free versus macromolecular units can be used as a proxy of degradation levels. This concept is supported by the differences between amounts in thermal extracts at 300 and 350 °C (Table 2) with the former representing straightforward thermal extraction and the latter representing a potentially greater amount of material liberated by increased thermal energy alongside thermally dissociated esterbound material and any compounds liberated by ester-related occlusion sites.

Aqueous Alteration History

There is some existing knowledge for the effects of pre-terrestrial and terrestrial aqueous alteration on meteoritic organic matter (Sephton, Bland, et al., 2004). An online pyrolysis–GC–MS comparison of the organic matter in non-Antarctic and Antarctic CM chondrites alongside Mossbauer-derived iron oxidation levels revealed that organic matter in the least altered meteorites produced pyrolysis products containing more phenols and a greater level of substitution/alkylation (Sephton, Bland, et al., 2004). The phenols in the pyrolysis products are thought to be the products of ether bond cleavage, with more extensive aqueous alteration causing a relative depletion in the phenol precursors in the macromolecular fraction (Sephton et al., 2000). The

presence of phenols and methylphenols in the pyrolysate of the Winchcombe meteorite (Figure 3, Table 1) suggests that its macromolecular organic matter has experienced only limited levels of aqueous alteration that are similar to other non-Antarctic CM chondrites.

CONCLUSIONS

We analyzed the recently fallen Winchcombe meteorite by Raman spectroscopy, stepped combustion and pyrolysis–GC–MS. The analytical techniques employed cover both the more labile and thermally sensitive portions of the macromolecular material and the more refractory and non-pyrolyzable components. The combined organic responses were similar to those observed in other CM chondrites in the group. The classification of Winchcombe as a CM meteorite was based on general elemental abundances (King et al., 2022). Detailed scanning electron microscope energy dispersive x-ray analysis of Winchcombe samples (Suttle et al., 2023) has shown that several lithologies are present, with the most common ranging from CM2.0 (most processed) to CM2.5 (least processed). This is consistent with the results found here by the Raman analysis of the carbon bands, which produced results similar to those from the Murray meteorite (type CM2.4/2.5), and with the stepped combustion and pyrolysis–GC–MS data. With its status as the meteorite with the best-known provenance for its group, the chemical constitution of the Winchcombe meteorite thus acts as a chemical probe of a specific location in our solar system, namely the main asteroid belt (2.5–2.8 AU).

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