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Differentiating Indigenous and Exogenous Soluble Organic Matter in CM Carbonaceous Chondrites

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M.Sci Astronomy & Physics Submitted in fulfilment of the requirements of the Degree of Master of Science in Geology

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Abstract

It is accepted that life, as we understand it, must be carbon-based. The study of extraterrestrial organic molecules is a venture into understanding why our planet is unique in hosting its diverse range of life, and which others may be capable of hosting life. One theory suggests that the building blocks of life were brought to Earth by meteorites from the asteroid belt. More specifically, CM carbonaceous chondrites are particularly carbon and water-rich samples which have already been found to contain prebiotic molecules such as amino acids. In the early solar nebula, secondary processes such as aqueous alteration modified the meteorite parent bodies, and as a result, also altered the organic content, water content and volatile element abundances in the meteorites that bombarded the early Earth and the inner Solar System.

The work presented in this thesis aims to firstly identify the organic molecules present in two CM chondrite samples of differing extents of aqueous alteration- a more extensively aqueously altered sample (named NWA 10853, a CM2.0) and a less aqueously altered sample (Murchison, CM2.5). This will be achieved using gas chromatography-mass spectrometry in a meteoritics organics identification protocol developed at the University of Glasgow. The meteorite NWA 10853 is presented with its first 3D-rendering through X-ray computed tomography, and its elemental composition outlined through SEM-EDS study.

Secondly, this thesis discusses meteorite contamination risks and sources of contamination in the samples used, and subjects the detected compounds to several contaminant identification checks. We present this alongside an evaluation of potential methods for improving the confidence rate with which geochemists in meteoritics can determine the source of an organic molecule as extra-terrestrial or terrestrial in origin. Lastly, the link between the extent of aqueous alteration and the abundance of organics in CM chondrites is discussed, and we begin explore to which extent aqueous alteration of parent bodies affects the variability in organic content within different meteorites.

The results and analysis undertaken in this study concludes that the long-chain organic compounds intrinsic to the sample of NWA 10853 studied are nonanoic acid, decanoic acid, dodecanoic acid, myristic acid, pentadecanoic acid and palmitelaidic acid. Those intrinsic

to the sample of Murchison studied are nonanoic acid, tetradecanol, and myristic acid. This work also recommends that NWA 10853 is reclassified from CM2.0 to a CM2.1 carbonaceous chondrite, based on results of XCT, SEM-EDS, and its organics abundances, which all suggest less extensive alteration than suggested by optical study.

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Author's Declaration

I declare that, except where explicit reference is made to the contribution of others, that this dissertation is the result of my own work and has not been submitted for any other degree at the University of Glasgow or any other institution.

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Definitions & Abbreviations

ASE: accelerated solvent extraction

BECS: Biomarkers for Environmental and Climate Science (lab at the University of Glasgow)

BSTFA: N,O-bis(trimethylsilyl)trifluoroacetamide

CAI: calcium-aluminium rich inclusion

CC: carbonaceous chondrite

DCM: dichloromethane

GEMS: Geoanalytical Electron Microscopy and Spectroscopy Centre (lab at the University

of Glasgow)

GC-MS: Gas chromatography-mass spectrometry

IDP: interplanetary dust particle

ISM: interstellar medium

LC-MS: liquid chromatography-mass spectrometry

LHB: late heavy bombardment

NC: non-carbonaceous chondrite

NWA: Northwest Africa

OSIRIS-REx: Origins, Spectral Interpretation, Resource Identification, Security-Regolith

Explorer, NASA

SCMA: straight-chain monocarboxylic acid

SEM: scanning electron microscopy

SOM: soluble organic matter

TLE: total lipid extract

UofG : University of Glasgow

VSMOW: Vienna Standard Mean Ocean Water

XCT: X-ray computed tomography

Introduction

1.1 Our Solar System

1.1.1 Formation and Cosmochemistry

Our Solar System began as a cloud of interstellar gas and dust, sometimes called a molecular cloud. There exists a critical mass, the Jeans mass (Equation 1), above which the outwards gas pressure becomes insufficient to support an equilibrium state in the dense cores of a molecular cloud, and gravitational collapse will begin. This happened to our Solar System's gas cloud, around 4.5 Ga ago, and most other stars in the universe. The gravitational collapse triggered an increase in pressure, temperature and, thus, energy. This high-pressure collapsed cloud began to spin, pushing the gas and dust into a planar disk, with an ignited protostar at its centre thanks to the increase in temperature. The feeding of disk material into the protostar is still not fully understood, and consequently, accretion disk theory is a highly researched area of stellar astrophysics. It typically takes 5 Myr for a low-mass protostar to begin hydrogen fusion in its core and become a star. The protoplanetary disk contains the spinning dust and gases leftover after protostar ignition.

$$M_J = \left(\frac{5kT}{Gm}\right)^{\frac{3}{2}} \left(\frac{3}{4\pi\rho}\right)^{\frac{1}{2}} \tag{1}$$

Equation 1: The Jeans mass equation, with parameters k for the Boltzmann constant (relates kinetic energy to thermal energy), T for temperature in degrees Kelvin, G for the gravitational constant, m for the average individual mass of the particles in the cloud, and ρ for the cloud density. If the cloud mass is greater than the Jeans mass, M_J , then collapse under self-gravity will occur.

In the disk, the dust particles continued to accrete to one another via low-temperature, radiation-driven chemistry, and those large enough began to collide with other disk objects, forming planetisimals (large "planetary embryos") which would go on to form the planets, their moons, comets and the asteroid belt that we see today. In the protoplanetary disk, soon after the ignition of our young Sun, there existed a snowline. This is a radial point out from a protostar where ice forms immediately from H_2O in its gaseous state and skips the liquid phase- this state change is known as deposition, and occurs in space at temperatures of between 150-170 K. Beyond the snowline, gas giants form more easily, due to this sudden



Figure 1: The mathematical relationship for surface density with increasing radius from a central star for Hayashi's minimum mass solar nebula. It shows the break in relationship for the surface density of solid's at the snowline, with the surface density increasing at the snowline, before continuing to decrease in the same proportionality as inside the snowline. The gases in such a nebula are the most volatile elements, existing as vapours, and are unaffected by the snowline due to their high volatility. Image credit: [1]

increase in the surface density of solids. This increases the mass that a pre-formed body (in this case, a planetary embryo, or core) can accrete from planetesimals. Additionally, cores which form beyond the snowline are larger than those that form within it, such as the Earth, and gas giant cores can also form faster due to a proportional relationship between planet formation rate and surface density.

Although analysis of presolar grains in primitive meteorites has shown that much of our Solar System incorporated extrasolar materials, much of the variation in composition of the planets and bodies of our Solar System can be explained by the location of their formation within the protoplanetary disk. For example, the isotopic differences between carbonaceous (CC) and non-carbonacous (NC) chondritic meteorites suggests that their parent bodies formed from two different reservoirs of Solar System material. The process through time is described in Figure 2. It begins with the formation of the oldest known solids in our Solar System, calcium-aluminium-rich inclusions (CAIs), which are commonly found in carbonaceous chondrites. These formed close to the young Sun, as condensates at temperatures of over 1300 K, and were then transported outwards with the Sun's outflow and growth of the planetary disk, supplied by infalling material enriched in neutron-rich isotopes [2], blasted across interstellar space from the deaths of stars across our galaxy, also known as supernovae. As time goes on, the material supplied to the planetary disk depleted in neutron-



Figure 2: Schematic diagram showing three stages of the life of the early Solar System. Stage 1 indicates the formation of CAIs close to the Sun, fed by supernova-derived nuclides. Stage 2 shows the movement of inner materials, including CAIs, to the outer Solar System, and vice versa. Stage 3 shows the separation of the two reservoirs of materials by a young Jupiter, separating carbonaceous and non-carbonaceous materials. Image credit: [2]

rich isotopes, and a mixing of these two groups of materials in the planetary disk begins. However, due to the snowline, the rapid formation of Jupiter's protoplanetary core halts the mixing, effectively trapping two reservoirs on either side of the giant protoplanet- with noncarbonaceous materials on the inner side closer to the Sun, and carbonaceous material closer to the outer regions. It is here where the CAIs transported to the outer parts of the system must have accreted to carbonaceous material, forming the carbonaceous chondrites we see today as meteorites. This supports the Grand Tack hypothesis- that the first-formed planet, Jupiter, underwent a two-way migration, first inwards towards the Sun, then outwards before the gas giant's orbital resonance was balanced out with Saturn's mass, scattering asteroids and planetisimals both inwards and outwards with them. This explains the presence of both CC and NC bodies in today's asteroid belt, as well as the presence of volatile elements and even water to the inner planets. Between our Sun becoming a stable adult star and the planets and asteroids that we see today however, many physical and geological processes occurred on the planetisimals in the planetary disk. Over time, solar ices that accreted to early bodies (and their minerals, such as olivine and pyroxene) in the outer Solar System would melt from new sources of heat energy, and the melt water interacted with these minerals, producing what we call "secondary mineral phases". Secondary (post-accretion) processes such as radiogenic decay heating and impact shock heating resulted in thermal metamorphism of these rocky parent bodies, and produces dehydrated minerals. Water flowing through or on rocky bodies is known as aqueous alteration, and produces hydrated minerals.

Many bodies in our Solar System today have differentiated cores- that is, they have a crust, a mantle, and perhaps even an iron/heavy metal core. All accepted planets of the Solar System are included in this, as well as some differentiated asteroids such as Vesta. The internal temperatures of a differentiated planetary body are always greater than zero on the Kelvin scale, and in the case of asteroids, this can typically be explained by two thermal causes. One, as aforementioned, is the thermal energy released by the decay of radioactive Aluminium-26 (the stable isotope is Al-27). Interestingly, some icy bodies in the Solar System may never reach the melting temperature of ice, due to their low initial ratios of Al-26/Al-27 [3]. This is a factor in determining which bodies will have experienced more extensive aqueous alteration- bodies with more Al-26 will have experienced more severe aqueous alteration, as there are more radioactive isotopes to release thermal energy. Alternatively, periods of thermal metamorphism can be the result of impact events- at shock pressures of over 50 GPa, rock melting can occur [4]. Short-lived impact events are thought to explain the varying lithologies in brecciated meteorites, with different extents of alteration observed in their CAIs and chondrules. Some examples of which include the Jbilet Winselwan CM2 chondrite or the Winchcombe CM2 meteorite, both of which contain many lithologies [5, 6].

The oldest dated solids in our Solar System are these CAIs, with a mean age of 4.567 Gyr, and these have given us our best estimate of the age of our Solar System [7]. Chondrule formation also began around this time. Once CAIs and chondrules had formed, these began to come together in a long period of chondrite formation, creating the chondritic materials we see today in chondritic meteorites. Processes affecting the primitive chondrites began

 \sim 100 Myr later, such as thermal metamorphism. It's important to note that accretion of larger bodies also began around this time, which is often assumed to be the main cause of thermal alteration. Aqueous alteration processes are believed to have begun slightly later in the life of the Solar System, and peaked around 3.5Myr later [8].

1.1.2 Volatiles and Organics in the Solar System

Despite having a robust theory of evolution, how the building blocks of life were initially brought to the early Earth remains undetermined by the scientific community. The building blocks of life are often spoken about as its acronym, the CHNOPS elements (carbon, hydrogen, nitrogen, oxygen, phosphorus, and sulphur). These elements are described as the "building blocks of life" because they go on to form molecules necessary for life- amino acids, nucleic acids, carbohydrates, water, to name a few. All of these molecules and compounds help to construct DNA, proteins, and energy sources for life as we understand it. It is accepted that, along with these elements, life can exist given a suitable set of preconditions. According to [9], extremophiles (microbial organisms which can survive in extreme environments, or require such environments to grow) have been found to survive within the bounds of the following physical conditions:

- Temperatures: -12 to 122 $^{\circ}C$
- Pressures: 0 to 120 MPa
- Salinity: 0 to 33 %v/w
- pH: 0 to 13

Whether these elements already existed on the planet, or were brought in bulk via exogenous delivery methods, and then whether they came together on the planet or were formed in space before delivery, are all debated points in this field. In terms of organic molecules, there are three main theories. That is, that the prebiotic organic molecules that started primitive life were formed either in the early-Earth atmosphere, around deep-sea hydrothermal vents [10, 11], or were brought to the planet by extra-terrestrial rocks and dust. This project focuses mostly on the latter theory.

The theory of the Late Heavy Bombardment (LHB), which describes an intense period of bombardment of the inner Solar System around 4 Gyr ago, is often accredited with explaining when and why life was able to begin on Earth. The LHB was so intense that scientists believe life as we know it could only have started after this period of time, as the high temperatures caused by such intense impacts would have vaporised the majority of any water that could have been on the surface of Earth (and the other inner planets). Once believed to have lasted for a significant portion of the Earth's lifetime, as of late it is generally more accepted that the LHB lasted a few hundred Myr. It is yet to be fully understood how so much spare material was available to bombard the inner planets, a billion years after the Solar System formed. This mystery will likely become more transparent with the return of humans to the Moon to retrieve more samples for geological study [12]. It is also hypothesised that such a heavy bombardment, which occurred during the Hadean eon (named after the Greek god of the underworld), although violent and generally viewed as unfavorable conditions for life, may have been vital in creating a warmer climate. Specifically, the violent impact events may be responsible for forcing the release of excess carbon dioxide from the subsurface, which then become entrapped by the atmosphere allowing the Earth to reach a temperature suitable for life [13].

Also, as aforementioned, is also now believed that some water was brought to the early Earth by planetesimals that were thrown out of orbit by the migration of Jupiter and Saturn, as it was far too hot on the early Earth to have had such a high volatile element abundance as it has today. Volatile elements include Hydrogen, Carbon, Nitrogen, Oxygen, Sulphur, and noble gases such as Helium, Neon, and Argon. Volatile elements and compounds have extremely low melting points and so most are found in gaseous form, and can include hydrogenated molecules such as ammonia and methane. Volatiles are key indicators to understanding planetary formation, as they dictate the initial conditions of planetary surfaces and atmospheres, and are found in the atmospheres of all the terrestrial planets. However, since the Earth and Mars are estimated to contain no more than 4% of CC materials each [14], this alone cannot explain the amount of water that the Earth has, nor the amount that Mars used to have. However, other sources [15] have stated that accretion of CC materials in the Earth's final stages of planetary formation, perhaps in the Moon-forming impact event, would be



Figure 3: Some early Solar System objects, shown according to their (non-scaled) radial distance from the Sun. The blue objects are carbonaceous materials, that formed separately in the outer Solar System due to Jupiter's rapid formation. The red objects are the non-carbonaceous materials that formed in the inner Solar System. The small grey objects represent clusters of planetesimal formation, which occurs at condensation fronts. The tar line and snowline and their typical temperatures are represented by the dashed line. This schematic does not account for curvature or eccentricity of the Solar System and its objects' orbits, it is a linear representation. Figure adapted from [17] with additional information from [18].

sufficient to account for the water seen on Earth. For this to be true, the impactor would need to contain at least 2 ± 1 % of CI chondrite-like material [16]. It is known that the impactor for the Moon-forming event gave the Earth 10% of its current mass, and it is suggested that such an impactor is likely to contain this necessary equivalent of CI-like material, in terms of water and volatile elements.

In the same way that volatile elements and compounds have the snowline, organic matter has the 'tar line', a radial point out from the proto-Sun where organic compounds are stable but water still exists as vapour. This is significant because it indicates the proximity to the Sun that organic matter can withstand, but still allows us to consider the organic chemistry of the early inner Solar System with its higher temperatures. Insoluble organic compounds are typically stable at higher temperatures, around 350-450 K, and so this line lies between the Sun's corona and the snowline (Figure 3). These molecules contain more refractory elements rather than volatiles.

1.2 Sources of Meteorites

Meteorites can come to Earth via a variety of events beyond our atmosphere. Impact events with meteors and Mars have ejected Martian material into space, and some of it got caught in orbit and eventually made its way to Earth, resulting in a small catalog of Martian meteorite samples. Such meteorites have shown us similarities and differences between the Earth and Martian geological, atmospheric, and hydrospheric compositions. For example, the Martian meteorite Yamato 980459 is a particularly primitive meteorite. From this meteorite, it was found that Mars may have accreted water from the same, or a similar, source as the Earth did [19]. Studying Martian geology through meteorites has its challenges, such as contamination and curation management, and so with the upcoming Mars sample return mission collaboration between NASA and ESA, the preparations for in-situ (Rosalind Franklin rover, equipped with its Mars Organic Molecule Analyzer (MOMA) instrument [20]) and ex-situ organics studies have never been more vital. See J. Douglas' MSc thesis [21] for deeper information on this.

Meteorites from the asteroid belt make up the vast majority of all meteorites that have come to Earth. Asteroids are the remnants of planetary formation, and can largely be split into either S and C-type spectral classes, reflecting their differing locations of origin in the early Solar System. C-type asteroids, or carbonaceous asteroids, make up the majority of known asteroids, with a high volatile content. The descriptor "carbonaceous" is something of a misnomer- the carbon content of the resultant meteorites of such asteroid is not overwhelming of the other minerals and elements, and most meteorites of this type contain on average around 2% pw carbon. They are named so because of their black, burnt appearancereminiscent of charcoal. They thus have a low albedo, typically reflecting 3-5% of sunlight [22]. S-type asteroids are considerably rarer, and have a high iron and magnesium-silicate content. They are brighter than C-types, and the two types have very different absorption spectra. As we know from Chapter 1.1.1, many planetesimals were thrown into new orbits after their formation due to the interplay of orbital resonances of newly-formed Jupiter and Saturn, causing many objects in the asteroid belt to collide. This is one theory behind why we often see brecciated meteorites from the asteroid belt- they are the combination of different parent bodies. The daughter asteroids produced may contain different lithologies, which



Figure 4: Estimated delivery flux of organics to the early Earth, from interplanetary dust particles (IDPs), airbursts, comet impacts and meteorites. The dashed line for airbursts is an upper bound, as the estimate does not account for organic matter destroyed by the airburst event. Taken from Chyba and Sagan, 1992 [25].

we can go on to study in such brecciated meteorites.

Interplanetary dust particles (IDPs) falling to Earth are thought to have brought a significant amount of organics to the early Earth, alongside comet and meteorite impacts. Airbursts are also responsible for dissipating organic matter, as these events occur in the atmosphere upon the impact of a sufficiently large comet or asteroid fragment. Most meteors over 2 metres in diameter will explode at high altitude, creating airbursts of energies over 1 kiloton (kinetic yield of impacts can be quantified in units of kilotons or megatons, where one kiloton is 4.184×10^{12} Joules) [23]. Comets and meteorites that do make it to Earth are calculated to contribute less exogenous organic matter than airbursts or IDPs, but their organic matter content is easier to study by bulk analytical techniques as these objects can be collected, whereas particles cannot. Figure 4 shows an estimate of how much organic matter was brought to Earth by these different mechanisms. A recent study estimated that on average, 17,600 meteorites of masses greater than 50 grams fall to Earth every year [24].

1.3 Carbonaceous Chondrites

1.3.1 History

Chondrites are meteorites that are defined by three main characteristics- CAIs, chondrules, embedded within a fine-grained matrix. This matrix will be constructed of hydrated phyllosilicate minerals if the rock has undergone aqueous processing, and the matrix may then be referred to as a fine-grained phyllosilicate matrix (FGM) [26]. Chondrites, carbonaceous or otherwise, are stoney meteorites with small, round granules, called chondrules. Up to 80% of a chondrite can be made up of chondrules [27]. Chondrules form molten or partially molten, before accreting to parent asteroids, and are ferromagnesian silicates (contain iron and magnesium). Chondrules can dissolve via interactions with water, demonstrating the need for quick recovery of meteorites as any contact with rain water or soil moisture could result in dissolving of key chemical information.

Chondrites can be split into two groups- O chondrites, for ordinary, and C chondrites, for carbonaceous. Carbonaceous chondrites, or CCs, therefore originate from C-type asteroids, such as Bennu, which has recently had samples taken from it by the NASA OSIRIS-REx mission [28]. CCs can contain other geologically-interesting features, such as refractory inclusions, sulphides, silicates, and iron-nickel (Fe-Ni) metals. All of these components are held within the rock's FGM, which results in the dark colour of this matrix within which the chondrules are buried. CCs therefore tend to be darker and more primitive than other asteroid belt rocks. In visible and near-IR wavelengths, these rocks have relatively neutral (flat) reflectance spectra, except in a few samples which have a prominent absorption feature near 3 μ m [22]. This absorption feature is characteristic of C-type asteroids, and is used in asteroid studies today to indicate the presence of water. The primitivity of CCs makes them ideal for planetary science study because primitive meteorites are largely unchanged from their formation in the early Solar System, and so they provide an insight into the chemical constituents of the Solar System as it was forming, and contain geological imprints of the elements and molecules that were brought to the inner rocky planets millions of years ago.

We study the petrology of meteorites to learn about the processes that formed their parent bodies and those which occurred on their surfaces post-formation. Mineralogy is more concerned with the chemical study of meteorites, as well as their crystal structures. The most primitive chondrites preserve minerals from the early Solar System, such as olivine, enstatite, and iron and nickel-bearing inclusions. Other minerals formed on the parent bodies during alteration processes, such as thermal metamorphism, aqueous alteration, and shock metamorphism. Chondrites are undifferentiated, meaning they came together from the initial molecular grains in the solar nebula and accreted to form parent bodies. Differentiated meteorites contain minerals associated with magma crystallisation, such as plagioclase, pyroxene, and sulphides. However, undifferentiated meteorites will contain some of these as well, specifically the silicates pyroxene and olivine. By eye, differentiated meteorites may appear more metallic, and undifferentiated meteorites more "stoney". Along with individual mineralogies, petrologies, physical measures such as density, magnetism, spectral reflectance and more, meteorites can also contain organic matter. Specifically, two types of organic matter- soluble organic matter (SOM; includes volatile molecules such as methane, and labile molecules such as amino acids) and insoluble organic matter (IOM; includes refractory inclusions) [29]. The organic matter carried in meteorites provides a fascinating look into the complex molecules that formed in space, either in our Solar System or that which was brought to our corner of space on dust particles through the ISM. The existence of organic matter in seemingly desolate space probes the question- could it have been extra-terrestrially formed organic matter that provided the ingredient for life today? Did life on Earth really, at its most fundamental levels, begin on Earth?

Overall, CCs carry the story of primary and secondary geological, chemical and physical processes that have occurred in the space environment. When studying organics in meteorites, distinguishing primordial and secondary phases is key to understanding the composition of the original (unaltered) parent body. The components of unequilibrated chondrites (rocks with unevenly-mixed geochemistries) provide information about the interstellar dust and accretional events at the time of solar formation. However, such meteorites are considerably rare, as most asteroids are altered via some secondary process or processes. Primary processes are those that affected the individual components of chondrites before the components accreted. Secondary processes, such as aqueous alteration, shock metamorphism and thermal metamorphism occur once the whole asteroid or planetesimal has accreted. Most



Figure 5: The Winchcombe meteorite, which fell to England, UK in 2021, showing its chondrules (light-coloured inclusions) embedded within a dark grey matrix. The raised brown area is part of its fusion crust, which formed as the outside of the meteorite rapidly heated during atmospheric entry. Image take from [30].

chondrites have experienced some of these secondary processes to varying extents, but this doesn't mean we cannot learn from them- we can learn about the conditions and durations of these processes in planetesimals in the planetary nebula, helping us to piece together the picture of planetary formation. For example, by studying chondrites and their olivine and plagioclase contents, it was found that in the early Solar System during the Period of Heavy Bombardment, shock pressures reached as high as 90 GPa. Radioactive dating of CAIs in chondrites was also responsible for giving us our best-estimate of the age of the Solar System.

1.3.2 Classification Systems

There are many scales and definitions used to define and categorise meteorites through time. From early discoveries, it was clear that each meteorite could be different, with different textures, colours, grain sizes, minerals, magnetism and more. In terms of chondritic meteorites, they are either undifferentiated or differentiated. This is an easy characteristic to spot, as differentiated meteorites come from differentiated parent bodies and will include some forms of hardened magma or igneous features. Carbonaceous chondrites are undifferentiated meteorites, and there exists 4 other main types or branches of undifferentiated chondrites- ordinary chondrites, enstatite chondrites, R chondrites and K chondrites (see Figure 6). Beneath these titles, there are further ways we can define and group meteorites. In the carbonceous chondrite group, there exists nine types, indicated by a letter- for example, the CI chondrites are named after the Ivuna meteorite, and the CM chondrites are named after the Migehi meteorite.

The earliest comprehensive scale for classifying carbonaceous chondrites is the Wiik scale (1956), but the Wood and Van Schmus scale (1967) is more widely recognised as it includes more groupings and definitions- the Wiik scale [31] took three groups, Type 1, 2, and 3, and categorised them by carbon and water content. All carbonaceous chondrites are grouped into Wiik's Type 1 and 2, and non-carbonaceous chondrites fall into Type 3.

However, the Wood and Van Schmus petrographic scale [32] takes more characteristics into consideration than the Wiik scale; the homogeneity of silicates; ratios of monoclinic pyroxene to orthorhombic pyroxene (which indicates extents of recrystallisation); feldspar (visible in thin section); igneous glass (which is less present in more recrystallised chondrites); metallic minerals; sulphide minerals; coarse or homogeneous textures (delineated chondrules indicate unmetamorphosed meteorites; merged chondrules indicate metamorphosed meteorites); and finally, carbon and water content. Wood and Van Schmus created six petrographic types, rather than Wilk's three, and these six vary from Type 1 (which contains the highest volatile content and is extremely fine-grained) to Type 6 (heavily recrystallised and therefore heavily thermally altered, and the most altered from its state of being when it initially formed in space) [32]. Each carbonaceous meteorite group (CI, CM, etc.) can fit in one or two of the three Wood and Van Schmus types. Therefore, meteorites can be grouped first into whether they are chondritic or not, then if they are carbonaceous or non-carbonaceous. Then, in the case of CCs, the letter grouping would be added and finally a number grade identifying the petrographic type. Figure 6 shows these groups, along with other groupings of undifferentiated chondritic meteorites. Figure 7 shows that low-temperature alteration occurred aqueously, and high-temperature alteration caused asteroids to metamorphose thermally, and these different types of post-formation alteration created different mineralogical footprints in the meteorites we can study. Figure 8 lists some of the minerals commonly associated with the different Wood and Van Schmus types.

However, with more meteorite discoveries and analyses, the Wood and Van Schmus scale was found to lack the distinction within types due to differing extents of aqueous alteration, particularly in the CM Type 2 group. The Rubin scale [33], proposed in 2007, adds on a numerical decimal sub-type to further describe the extent of aqueous alteration. Rubin et al suggested starting with the most aqueously altered (CM Type 1, or CM1 for short) and assigning a subtype of 2.0 to this. The most altered meteorite used in the creation of the scale has a subtype of 2.6. More information on this classification is detailed in Chapter 1.4. This scale has been heavily adopted in the CM2 research community, and is what will be referred to for the rest of this thesis. It should be noted that since the creation of the Rubin scale in 2007, a partially altered CM2 chondrite fell to Paris, and has been assigned a more pristine classification of 2.9 [34].

1.4 CM-type Carbonaceous Chondrites

Most CMs found on Earth so far tend to be of type 2 (CM2)- this classification indicates a little aqueous alteration between formation and stability (see Figure 7). CM2s tend to have around 20% of their volume as chondrules, and 60% of it as fine-grained, phyllosilicate-rich matrix [38]. Phyllosilicates are a class of silicates characterised by a sheet-like structure, and are hydrated minerals (i.e., includes H₂O or OH groups in their chemical composition) [39]. CMs contain around 9 wt% H₂O⁺ (indigenous water), bound in the phyllosilicate matrix [40]. The chondrules embedded within the matrix of CMs have a typical diameter of $270\pm240\mu$ m [41].

The aforementioned Rubin scale is useful for describing the variations within the CM group itself. Such meteorites are defined by "essentially no mafic silicates" - that is, very little to no olivine, pyroxene, amphibole, biotite, or other mafic minerals. They are also characterised by "chondrule pseudomorphs" composed mainly of phyllosilicate. The full list of characteristics used to create the Rubin scale is shown in Table 1. As all of the rocks studied to create this scale were CM2s, the chondrule mesostasis is always phyllosilicate, and the matrix phyllosilicates themselves are abundant.

The study of the aqueous alteration of CM chondrites can help us understand the transportation of water, volatiles and carbon around the early Solar System, and gives one in-



Figure 6: The carbonaceous chondrites are listed with their petrographic types as according to the Wood and Van Schmus scale. Also shown are the ordinary chondrites, where H indicates high iron, L for low iron, and LL for very low iron. The CR classification is from [35]. CK classification is from [36].



Figure 7: The petrographic types of some carbonaceous chondrites, in relation to the extent of aqueous alteration and thermal metamorphism experienced. It is clear in this diagram that the least altered petrographic type is type 3. Figure adapted from [37].



Figure 8: Sub-groups of meteorites, with mineralogical information on carbonaceous chondrites (green). Non-carbonaceous chondrites has been used as an umbrella term for ungrouped, enstatites, rumurati, kahangari, and ordinary chondrites. The minerals typically associated with both aqueous and thermal secondary processes are shown in the bottom row, along with the Wood and Van Schmus petrographic types that these processes produce. Physical processes are in purple, the characterised meteorite products of these processes are in yellow.

Table 1: The diagnostic criteria used to classify unbrecciated meteorites in the Rubin scale. *po, pyrrhotite; pn, pentlandite; int, intermediate sulfide; Ca, calcium; PCP, poorly-characterised phases.*

*Applies to the	alteration of	phenocyrsts	within	chondrules.	Adapted	from [33].
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Petrologic subtype	2.6	2.5	2.4	2.3	2.2	2.1	2.0
Metallic Fe-Ni abundances	1 vol %	0.03-0.30 vol %	0.03–0.30 vol %	0.03–0.30 vol %	0.03–0.30 vol %	\leq 0.02 vol %	\leq 0.02 vol %
Mafic SiO ₄ phenocrysts*	Unaltered	Unaltered	Unaltered	2-15% altered	2-15% altered	85-99% altered	Completely altered
Large PCP clumps	15-40 vol %	15-40 vol %	15-40 vol %	15-40 vol %	15-40 vol %	2-5 vol %	2-5 vol %
PCP composition (FeO:SiO ₂)	2.0-3.3	2.0-3.3	1.5 - 2.0	1.5-2.0	1.0 - 1.7	1.0-1.7	1.0-1.7
Sulfides	Mainly po + pn	Mainly po + pn	po + pn + int	po + pn + int	Mainly pn + int	Mainly pn + int	Mainly pn + int
Carbonate types	Ca	Ca	Ca	Ca	Ca	Ca & complex	Ca & complex

dication of how much was brought to the early Earth. Understanding the different parent bodies of such organic-rich meteorites may help to explain the movement of organic matter too, and which asteroids to visit in future sample return missions. This would be a profound discovery, with implications for biological development on our planet, and why life has not been so successful on the other inner planets.

Bulk composition studies have shown that it is likely that CM1s formed on a different asteroid from CM2s [42], which would make sense considering our classification systems pick up on different abundances of hydrated minerals, metals, and extents of alteration of chondrules (Table 1). However, the oxygen isotopic compositions of CM1 chondrites are similar to the least altered CM2s [43]. The current understanding is that the hydration of CM1s could have occurred for similar water to rock ratios as the hydration of the CM2s, but at higher temperatures or for a more sustained amount of time [44]. CM chondrites in the early Solar System experienced aqueous alteration and then drastic temperature changes to over 900 °C, likely due to increased impact events. This post-hydration heating affected different CMs at different points in their life cycles. For fully-formed chondrites, such drastic heating removed most of their volatile components. This explains the difference between CM subtypes- CM2s are relatively volatile-rich, CM1s are very volatile-rich. However, CM2s are more organic-rich, and CM1s are less so. Consider the effect of the tar line in the early days of Solar System formation in Chapter 1.1- organic molecules remain stable at higher temperatures than volatile elements and water does. CM material has been found embedded in other meteorites, indicating that the CM parent body was disrupted, leaving behind several daughter CM asteroids. It is such asteroids that have provided CM meteorites to Earth.

1.4.1 Isotope Plots and their Properties

Isotope plots are useful visualisations of the variety of sources of material in our Solar System. The most useful types in this project are the Oxygen three-isotope plots, which give information about the ratios of ¹⁷O and ¹⁸O, to ¹⁶O, the most stable isotope of oxygen. Alongside these in importance, we have δD plots, which give information on the ratio of deuterium to hydrogen in a material. The δ -notation indicates a ratio- for example, $\delta^{18}O$ indicates the ratio of the isotope ¹⁸O to the stable isotope, ¹⁶O. The terrestrial fractionation

line (TFL) is a straight line on a plot of δ^{17} O to δ^{18} O, with a gradient of 0.5 (since it is easier to evaporate ¹⁷O than it is to evaporate ¹⁸O because the relative mass difference from the stable isotope of ¹⁶O is 1:2, or $\frac{1}{2}$). This means that all substances on Earth, throughout the movement and transference of oxygen from one place to another via melting or crystallisation, the overall isotope composition will always change in this way. The relative change in the ratio of ¹⁷O to ¹⁶O will always change half as much as that of ¹⁸O to ¹⁶O. It holds that each planetary body has its own oxygen three-isotope fractionation line, depending on their own abundances of oxygen isotopes [45]. The TFL has had the same slope and intercept for 4.0 Ga, according to oxygen three-isotope analyses of some of the oldest Earth rocks. Additionally, the Moon lies on the same line as the Earth, indicating that both bodies formed homogenised oxygen isotope reservoirs at the same time, during or before the impact that created the Moon as we know it today- see Figure 9. Meteorite sub-types can be identified by measuring the total H/ δ D composition. One can then compare the ratio of the difference between the sample and a standard (the standard typically used is VSMOW, the Vienna Standard Mean Ocean Water, which allows the Earth's fractionation line to intercept the y-axis at 0). The δ -notation indicates the variation of an isotopic ratio as compared to the variation of an isotopic ratio of a given standard. Another example of isotopic analysis is the H/ δD ratio, which indicates the ratio of hydrogen (H) to the isotopic signature of Deuterium (D). These ratios are used in planetary science to quantify the isotope ratios of other bodies for easy comparison to those of the Earth. The Young and Russel (Y&R) line is another line that appears on some isotope plots, and has a gradient of exactly 1.00 in a plot of δ^{17} O against δ^{18} O. It follows that this should be representative of the primitive oxygen isotope reservoir in the early solar nebula. An example of the Y&R line against VSMOW is available in Figure 10.

1.5 Organic Matter in Meteorites

1.5.1 Types of Soluble Organic Matter

A key component to life as we know it are amino acids, which are hydrocarbon-based compounds vital to the structure of proteins, and thus, DNA. Prebiotic molecules have been discovered in many CM2 chondrites via GC-MS- for example, 35 new amino acids were dis-



Figure 9: An example of the Solar System oxygen three-isotope fractionation line, showing the Earth and Moon line compared to the Sun and CAIs, taken from [46].



Figure 10: Another example of a δ^{17} O to δ^{18} O plot, showing the terrestrial fractionation line, the Youngs and Russel (Y&R) line, representing a reservoir of primitive oxygen available to the early solar nebula. The diagram also shows where different carbonaceous chondrite groups lie. This plot describes where CMs lie on the TFL in comparison to other carbonaceous chondrites, in a study of CM water.

covered in the Murchison CM2 meteorite after further study [47]; over 30 monocarboxylic acids found in meteorite A-881458, recovered from Antarctica in 1988 [48]). The extractable carbon of CI and CM chondrites is made up of between 2-10% SOM [49], and of this fraction amino acids are the most abundant type of compound. The most abundant fatty acids in CM2 meteorites are straight-chain monocarboxylic acids (SCMA) by parts per million (ppm), with most CMs having SCMA abundances of between 1 and 100 ppm [50]. Additionally, Murchison is known to contain over 300 ppm of carboxylic acids [51]. In CM meteorites, the most abundant SCMA compounds will have the shortest chain lengths [50], and this trend is one way of determining extra-terrestrial origin of SCMA compounds. A good test of terrestrial origins is to look at enantiometric ratios (see Chapter 1.5.2), or carry out specific isotopic analyses to compare to the TFL.

Amino acids are a pre-requisite to life as we understand it, and their abiotic origins in both meteorites and deep-sea hydrothermal vents probe some exciting questions about the requirements for the beginnings of life on Earth- and possibly other planetary bodies with evidence of Earth-like hydrothermal systems. In terms of their formation, amino acid decomposition and synthesis processes compete against each other to ascertain the overall abundance level in carbonaceous chondrites. At 373 K, amino acids decompose via aqueous processes at a rate of $10-13 \text{ s}^{-1}$. This is equivalent to half-lives of one to several tens of thousands of years [52], however the temperatures typically associated with icy bodies in the asteroid belt tend to lie between 70 and 130 K. Therefore it is generally too cold in the belt for the decomposition is seen in studies of the Winchcombe meteorite. It contains surprisingly low amino acid abundances when compared to other less-altered CMs, and this could be explained by brief episodes of aqueous alteration on the parent body, removing a large portion of its organic content [53], rather than continuous processing.

CM2s are known to have a high soluble organic material (SOM) content, and this is expected to reflect the intrinsic composition of their parent body/bodies. However, the SOM signatures within most meteorites have already been modified by aqueous and thermal metamorphic processes on their parent bodies, and to make matters more complex, the SOM content is often further obscured by terrestrial contamination. The quick recovery of ob-
served meteorite falls is key in minimising the damage to the quality of organics research, and also in reducing changes to its mineralogy. For example, rainfall can create hydrated veins of calcite minerals through meteorites, altering its mineralogical structure. The definition of organic molecules in this framework are molecules that contain carbon, specifically a chain of carbon atoms with other elements or functional groups ¹ bonded to it.

Generally, one can use the umbrella term "aliphatic" to describe any organic hydrocarbon that doesn't have its functional group attached to a benzene ring (these include straight-chain saturated alkanes, aldehydes, alcohols, carboxylic acids, amino acids, esters, aldehydes, and many other compound types). The term "aromatic" can be used to describe the opposite case, where benzene rings are attached directly to the compound functional group, such as phenols. GC-MS studies detect aliphatic and aromatic compounds.

The Paris meteorite, a CM2.9, is the least altered CM chondrite found so far. Organics analyses have indicated that its parent body experienced weak thermal metamorphism, as it contains non-alkylated PAHs (along with considerably long-chain alkanes, compared to more altered meteorites, with carbon lengths ranging from 16-25). It contains no alkylated PAHs, whereas the more altered meteorite Murchison has been found to contain such molecules [54]. This is significant because alkylation processes require heat, leading to conclusions that the parent body of the Paris meteorite formed in the very early initial stages of Solar System formation, potentially with some interstellar components to form one of the most primitive and unaltered meteorites studied to date [55]. It is largely accepted in the planetary science community that some of the organics found in CM chondrites are likely from beyond our own star system, perhaps blasted from the supernovae of other stars in our galaxy and sent through interstellar space on microscopic dust particles, making up a (minuscule but potentially extremely important for life on Earth) component of the interstellar medium (ISM). Some groups of SOM found in famous meteorites have been summarised in Table 2.

1.5.2 Chirality and Enantiometric Ratios

In terms of amino acids, some useful terminology is that of the L- and D- amino acid transporters. Enantiomers are chiral molecules- chirality is a concept of orientation of particles

¹Functional groups are responsible for a molecule or compound's characteristic chemical reactions.

Table 2: Organic compound presence in various meteorites. Crosses represent a blank test result for the presence of that compound type, and "no data" refers to a lack of published data. Data on PAHs in Murchison are from [56], amino acid data from [57], aliphatic hydrocarbon data from [58], carboxylic acid data from [59]. Data on amino acids and hydrocarbons in Paris taken from [54], alcohols data are from [60]. Amino acid and PAH data for Winchcombe taken from [53], carboxylic acid and alcohols data from [61].

Meteorite	Paris	Murchison	Winchcombe	NWA 10853
Fall year	2001	1969	2021	purchased 2016
Rubin scale classification	CM2.9	CM2.5	CM2.1-2.6	CM2.0
Amino acids	\checkmark	\checkmark	\checkmark	no data
Alkenes	no data	\checkmark	no data	no data
Alcohols	\checkmark	\checkmark	\checkmark	no data
PAHs	\checkmark	\checkmark	\checkmark	no data
Aliphatic hydrocarbons	\checkmark	\checkmark	\checkmark	no data
Carboxylic acids	\checkmark	\checkmark	\checkmark	no data

and molecules. Chiral molecules are those whose mirror images cannot be superimposed onto each other. Enantiomers of compounds often show different chemical reactions with other enantiometric substances, and their ratios (the ratio of L to D configurations in organic molecules) can indicate whether amino acids in a sample are terrestrial or not. Figure 11 shows an example of an achiral molecule, the straight-chain alkane, heptane. Alkanes are all achiral, as their mirror image can be superimposed onto itself and the molecule will appear the same from different orientations and mirroring, due to its lack of functional group. Largely speaking, a molecule is likely to be chiral if it has a functional group anywhere but in the middle of its carbon chain- examples include alcohols (functional group -OH) and carboxylic acids (-COOH).

In nature, only L-amino acids are biologically useful. Over time, biologically dead Lamino acids will decay into D-amino acids. Pristine meteorites will have approximately racemic mixtures (50:50 split) of D to L enantiomers, such that $\frac{D}{L} \approx 1$, however in recent research there have been cases where L-excesses are detected- for example, there was an 18.5 ± 2.6% L-isovaline excess detected in Murchison [62]. Isovaline (chemical formula C₅H₁₁NO₂) is a rare amino acid that, on record, was first brought to Earth in Murchison. It is hypothesised that UV light in our nebular cloud was circularly polarised, destroying D-amino acids and giving rise to L-amino acid excesses [63]. However L-isovaline is found in excess in CMs and CIs and has caused some issues with this hypothesis. The correlation, as we understand it, between enantiomeric excess of isovaline and the degrees of aqueous alteration indicates that isovaline formed within CM and CI parent body/bodies, which means that it would not have interacted with circularly polarised UV light. Additionally, the most likely precursor of isovaline is achiral in nature, and so isovaline could not have been biased towards chirality. Although the exact formation of L-isovaline and other extra-terrestrial amino acids remains unclear today, the detection of non-terrestrial L-proteinogenic amino acid excesses in the Tagish Lake meteorite [64], in the Aguas Zarcas meteorite [65] and in Murchison, just to name a few, supports the theory of abiotic production of amino acids and L-enantiomeric enrichments.

The bias towards L-enantiomer excesses may be a fact of nature- three of the four fundamental forces of nature are achiral (gravity, electromagnetism and the strong nuclear force), and the one that is chiral is responsible for nuclear decay (the weak nuclear force). The decay products of radioactive nuclei tend to favor one orientation of molecular spin, which means that decay products are chiral in nature and once again causes destruction of Denantiomers. Therefore, in the Milky Way galaxy at least, the chirality of the photons that compose starlight and of nuclear radiation means that L-amino acids are more stable than Damino acids, and therefore make more suitable prebiotic matter. This has heavily influenced our dictation of biomarkers when looking at extraterrestrial matter- however this does have its limitations².



Figure 11: The chemical structure of heptane (named after its 7 carbon molecules in its backbone), the seventh straight-chain alkane. In the top image, the carbon atoms are the grey circles and the hydrogen atoms are the small white circles. Chemical formula: C_7H_{16} . Top image is taken from the National Centre for Biotechnology Information [67].

 $^{^{2}}$ A review of chirality as a biomarker is available here [66] for interested readers, but is not directly relevant to this work.

1.6 Aims of This Project

It is agreed that the ingredients for life on Earth were brought to the planet in its early life by exogenous modes, such as meteorites and interplanetary dust particles. To build upon our understanding of life on Earth, and thereby gain insight into the potential of that of other planets, we must study the types of organic matter within different modes of delivery. CM chondrites hold key information about the environment of the early Solar System, as they are primitive meteorites with geological features which are largely unchanged from their time of formation, 4.6 billion years ago. This makes such meteorites highly valuable in researching the conditions of their parent bodies in space and the conditions at the time of its formation in the outer Solar System. The aim of this thesis is to build upon our understanding of the amount of abiotic organic compounds found in such meteorites, and the interaction of water with these organic compounds on the meteorite parent bodies. The questions we are aiming to answer are, in what way does aqueous alteration affect organic content? And are there differences in abundance of different types of organic matter through variations of CM chondrite?

Specifically, this thesis will:

- Verify or challenge the current classification of CM2.0 (CM1) for the meteorite known as NWA 10853, using in-situ X-ray computed tomography (XCT) carried out at the University of Strathclyde, and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) in thin section to study its elemental composition;
- Use a bulk analytical gas chromatography-mass spectrometry protocol developed at the University of Glasgow [68] to identify soluble organic compounds in two samples of CM carbonaceous chondrites of varying aqueous alteration;
- Investigate potential contaminants detected in the bulk analysis and determine possible contamination sources.

The research carried out is formatted in the main chapters: 1 (Background Information), 2 (Samples), 3 (Methodology), 4 (Physical & Petrological Results and Analysis), 5 (GC-MS Results & Analysis), 6 (Discussion) and 7 (Conclusions). Descriptions of the relevant techniques used are detailed in Chapter 3, along with a summary of previous studies and their results. All concentration and uncertainty calculations of detected organics are detailed in Chapter 5. The implications of all results and future work suggestions are discussed in Chapter 6. The conclusions in Chapter 7 are the main points drawn from the results and their analysis, with some considerations and suggestions for future work.

2 Samples

Table 3: The meteorites studied in this project, alongside their published Rubin scale classifications and whether they were falls or finds, their fall site information and year of discovery, and the techniques the samples were subjected to in this study.

Meteorite Name	Rubin Type	Fall site	Techniques used
NWA 10853	CM2.0, find	Northwest African desert (2016)	XCT, SEM, GC-MS
Murchison	CM2.6, fall	Murchison, Australia (1969)	GC-MS

2.1 NWA 10853

According to the Wood and Van Schmus scale [32], Type 1 CMs are characterised by their high volatile content and lack of chondrule. A CM1 is severely aqueously altered, and the extent of alteration will have chemically changed most, if not all, of their olivine and pyroxene components- these primary minerals will be replaced by secondary phases. The most aqueously altered sample used in this project is called NWA 10853, found in the northwest African desert. With a mass of 109.3 g, it is largely covered in fusion crust. Its chondrules are completely serpentinized (indicating extensive hydrous alteration of olivine minerals to form serpentinites), and no olivine to be found, indicating high levels of aqueous alterationhence the CM1 classification. Its oxygen isotope plot is shown in Figure 13. According to the Meteoritical Bulletin 105 [69], it has low levels of terrestrial weathering, and was classed as a CM1 through petrographic study in thin section at the University of Washington, Seattle, USA. The published data indicate this classification was given due to "serpentinized chondrules" and apparent no olivine. Aside from the thin section study at UWS, this meteorite has been studied very little and has even been excluded from organics studied in the past [70], and so it is necessary to obtain raw mineralogical information. The chip will be studied via XCT and as thin section via SEM as part of this study (see Chapter 3 for more).

Interestingly, this meteorite was excluded from a study of the relationship between fluid alteration and brecciation in CMs due to its heavy oxygen isotopic composition. It is presumed that this composition is due to post-alteration thermal metamorphism [70]. This may be useful to keep in mind through the investigation, as such heating may have removed organic content. The background of the chip is not accurately known, but it is known that it was handled without use of gloves and outwith sterile conditions, at a conference in Glasgow, 2022. Since its storage at UofG began, it had been stored in a paper towel within a plastic box and then in non-combusted tin foil for 24 hours before the experimental work began- see Figure 12. It is also unlikely to have come into direct contact with vegetation, as it is a hot-desert find.



Figure 12: The tin foil storage of the chip of NWA 10853 for the 24 hours before crushing began.

2.2 Murchison

The Murchison meteorite fell to Victoria, Australia in 1969, with some of it landing on roads, and the largest whole specimen breaking through a roof and landing in a pile of hay. It is one of the most well-studied meteorites so far, thanks to its large mass and high organic matter content. In 2020, it was discovered that some of the silicon carbide grains in Murchison could be over 7 billion years old [71], exceeding the estimated age of the Solar System by more than 2 billion years, making the components of Murchison the oldest material known to man. Two samples of Murchison will be used in this study, one unheated sample and one sample that has been heated to 1200 °C for use in a previous, yet unpublished, study. It is expected that the unheated sample will act as a comparison for the quality of the GC-MS protocol, since it is so rigorously studied that it will provide a good benchmark for comparing the reliability of the results. The heated sample will show what happens to meteoritic organics when hydrated meteorites experience drastic thermal changes as a secondary process. Both the heated and unheated samples came from one original chip, which was purchased by M. Lee, University of Glasgow. The unheated sample had been used in a previous $\delta D/H$ ratio study at



Figure 13: Oxygen isotope graph with an orange cross indicating the location of NWA 10853, as compared to CI, CM, CO, CV and CK meteorites. The terrestrial fractionation line (TFL), Y&R slope 1 line, and carbonaceous chondrite anhydrous minerals (CCAM) mixing line are shown. The weighted oxygen isotope values are as follows; $\delta^{18}O = 13.54$, $\delta^{17}O = 5.29$, $\Delta^{17}O = -1.86$. Values taken from the Meteoritical Bulletin 105 [69]. Figure taken from the Meteoritical Society Bulletin: Oxygen Isotopes Plot webpage.

UofG. It has been kept in a plastic box within a plastic grip seal bag since its dehydrationsee Figure 14 for images of the storage of both unheated and heated chips.

According to [51], one should expect a range of organic molecules from Murchison. Relevant molecules have been selected and presented in Table 4. Some of the organics found in Murchison include nucleobases (one fundamental component of DNA) and over 80 amino acids, including alanine and glycine, which go on to make proteins. Murchison's amino acids exist in predominantly racemic mixtures (abiotic in origin), but it also has an approximately 15% excess in L-isovaline.

Table 4: Typical abundances of different types of organic compounds found in Murchison, adapted from [51].

Compound type	Abundance (ppm)
Alcohols	11
Aliphatic hydrocarbons	>35
Aromatic hydrocarbons	3319
Carboxylic acids	>300
Phosphoric acids	2
Amino acids	16-70
Aldehydes and ketones	27



Figure 14: *Left:* Unheated Murchison sample, which was obtained in the form of 0.17g of powder and 0.25g of a chip. The powder was kept in a glass vial. The chip was kept in tin foil; whether this had been combusted or not before storage is unknown. *Right:* Heated Murchison sample storage.



Figure 15: Oxygen three-isotope plot for Type I and Type II clasts and an anhydrous sample of Murchison. Taken from [72].

3 Methodology

3.1 Mineralogical and Petrofabric Techniques

The lack of published information on NWA 10853 is challenged in this thesis by studying it in 3D as a bulk sample through XCT, and its mineralogy defined via study in thin section in SEM-EDS.

3.1.1 X-Ray Computed Tomography

An X-ray computed tomography (XCT) scan produces a 3D volume image of a rock sample, which shows structural information. XCT can also provide valuable information on a sample's porosity, chemical composition, and petrography in 3D [73]. The sample is subjected to X-rays of a chosen wavelength for a sample size-dependent period of time (scans could take several hours or just 40 minutes), which will attenuate differently as the waves interact with the minerals within the sample- some materials will absorb more photons, others may reflect more. The 3D image is reconstructed by filter-back projection of the attenuated Xrays. There have been concerns in the past regarding whether heating from X-rays or indeed interactions with such high energies destroys any organic matter within meteorites- however it has since been shown that the amino acid abundance and enantiometric ratios contained in carbonaceous chondrites were completely unaffected for monochromatic X-ray sources of 48.6 keV and 46.6 keV [49]. The X-ray source used in this thesis can impart up to 225 kV X-rays onto the target, but is a micro-CT machine and so it is safe to assume that it falls under the scope of investigations carried out previously into effects on organic matter, and overall will impart a negligible effect. The data itself can be transferred to a computer in stacks of 2D cross-sections from three axes, which can be compiled and reconstructed into a 3D volume image, using visualisation softwares such as Avizo.

The chip of NWA 10853 was scanned using the 225 kV X-ray transmission source inside the Nikon XT H 225 LC X-ray CT scanner at the University of Strathclyde Advanced Materials Research Laboratory (with thanks to K. Dobson and M. Divers at the University of Strathclyde) in order to model it in 3D for the first time. The parameters for scanning were a beam energy of 90kV, with a current of 110μ A, 2 second exposure time, and a 13.9 μ m voxel size.

3.1.2 Scanning Electron Microscopy

A scanning electron microscope (SEM) is used to generate high-resolution images by scanning the surface of an object with an electron beam. The electrons interact with the object's atoms, producing secondary electrons, back-scattered electrons or luminescent electrons- all of which have different energies (and therefore wavelengths and colours, since $E=h\nu$, thus energy E is proportional to frequency ν) and originate from different depths within a 3-dimensional sample. The backscattered electron images gives the composition and density, and come from deeper within a thin section, and the secondary electron images gives only the surface topography. SEM ultimately shows us the spatial variations in chemical composition within a sample, down to nanometre scales. Energy dispersive X-ray spectroscopy (EDS) obtains chemical analyses of these variations. SEM-EDS is typically used on thin section samples of rocks, which this study will use to obtain the elemental composition of the sample of NWA 10853. The main goal of utilising SEM-EDS is to gain an overview of the sample texture and its mineralogy, and to carry out point spectral analysis in EDS to determine specific minerals.

This technique was carried out in the Geoanalytical Electron Mircoscopy and Spectroscopy Centre (GEMS) at UofG, using the Carl Zeiss Sigma Variable Pressure Field Emission gun Analytical SEM, equipped with an Ultim Max 170mm² energy-dispersive X-ray spectrometer, from Oxford Instruments. Secondary electron and backscattered electron images were acquired, as well as EDS false-colour images. The data processing was carried out in software *AZtec*. The set up used was a 60 μ m aperture size, 20kV accelerating voltage, in high current mode and in high vacuum conditions. The thin section was coated with 20 nm of carbon.

3.2 GC-MS: Sample Crushing

3.2.1 Cleaning and Preparation

The set up of the work area, and the cleaning protocols are detailed in Figure 16. With a lab coat, nitrile gloves and a face mask on, sterilisation of tools was undertaken under a fume hood. The agate pestle and mortar has a depth of 15mm and was bought new for this experiment. An A&D Series HR-100AZ digital analytical balance was used to measure masses of glassware and samples. The repeatability (standard deviation) of the device is 0.1mg, and the display refresh rate is 5 times per second. Any digital scale uncertainty is \pm the most insignificant unit of measurement presented, in this case this is ± 0.0001 g.

3.2.2 Crushing Methodology

Once the work area was set up, the crushing could begin. For each sample, a sterilised beaker was weighed alone. The balance was then zeroed and the whole (uncrushed) sample added to the beaker to measure the sample mass, and then zeroed again and reweighed together to measure the combined total mass. A sterile 15ml vial was also weighed at the beginning of each sample crushing. The whole sample was tipped from the beaker into the cleaned mortar-see Figure 17 to see the equipment set up and the mortar with the unheated Murchison sample in the mortar. The sample was then carefully crushed by hand with the pestle into as fine a powder as possible. The powdered sample was then tipped back into the weighing beaker and weighed on the analytical balance. Once the new masses had been recorded, the powder was poured into the sterile 15ml vial and weighed once again.

Between crushing different samples, the cleaning protocol (Fig. 16) was repeated, with the equipment being rinsed with deionised water, dried, then washed in a 50:50 mixture of acetone:methanol and dried in an oven at 60°C. A new combusted tin foil catchment bowl was also made each time. Crushing took place over two consecutive days. The same work space was used on both days.

3.2.3 Tracking Sample Loss

If following a similar procedure, some sample loss is to be expected, as some powdered grains may stick to the mortar or the inside of the glass beaker. Additionally, for very rocky and hard samples, some small fragments may ping off when crushing, hence the use of a combusted foil catchment area. To track this sample loss with meteoritic samples, it was decided that masses of individual pieces of equipment should also be taken at every opportunity, pre- and post-crushing. The initial sample masses before crushing are shown in Table 5. The masses of the Murchison samples were pre-determined as these masses were all that was available. A much larger sample (around 3cm in diameter) of NWA 10853 is kept at the



Figure 16: The cleaning and set up of the work station area and the necessary tools and equipment.

University of Glasgow; a chip was removed from this larger sample by scalpel in the BECS lab. The mass of the chip is listed in Table 5. The procedural blank used was 0.4247 grams of sand that had been furnaced for 16 hours at 450 °C. This was the first sample to be crushed in the mortar. The sand mass was chosen is order to follow the mass of the heaviest sample. The sample name "Sand" was assigned to this procedural blank.

Starting Masses of Sample Before Crushing

Sample name	Initial mass (g)
NWA 10853	0.3237
Unheated Murchison	0.4199
Murchison	0.0661
Sand	0.4247

Table 5: Initial masses of samples before crushing, as weighed in glass beakers with the lone individual beaker weights subtracted.





Figure 17: *Left:* the crushing station set up, with sterilised tweezers and combusted tin foil catchment area. *Right:* The unheated sample of Murchison in the mortar after the mortar had been rinsed in deionised water, then DCM, then dried in a 60° C oven.

3.3 GC-MS: Extracting Organics

The ASE 350 (accelerated solvent extractor) within the Biomarkers for Environmental and Climate Science (BECS) laboratories at UofG was used to extract the organics from samples. The ASE has 24 10ml cells. A 250ml collection bottle was placed in the rinse slot for rinse waste. Prior to beginning solvent extraction from the 4 samples, a BECS lab identification number was assigned to each sample. An additional blank of unpowdered combusted sand

was also used to show contamination differences between the solvent extraction and crushing processes- from here on, this new (not crushed) sand blank will be called "blank", and the crushed sand blank will be called "sand". The equipment collected was five 60ml combusted glass collection vials, tin foil, 5 collection vial caps, a metal funnel, 10 extraction cells, 5 combusted glass fibre filters, a stainless steel spatula and stainless steel tweezers. The funnel, spatula and steel tweezers were washed in DCM before use. The ASE preparation and how the samples are loaded into the cells is shown in Figure 18.

Table 6: Sample names and their corresponding BECS identification numbers. The blank, uncrushed sand sample does not require a BECS ID, and so has been labelled 'BLK' for 'blank'.

BECS ID	Sample name
BLK	Blank
4680	NWA 10853
4681	Unheated Murchison
4682	Heated Murchison
4683	Sand

The ASE was turned on and the flow of nitrogen started. The ASE was first rinsed 3 times with a 9:1 Dichloromethane (DCM):Methanol (MeOH) mixture, with the rinse volume setting fixed to 60%. Once the machine was rinsed, the samples and their corresponding labelled collection vials (with open-hole caps on) were loaded into the machine in numerical order. The running cycle operates at a furnace temperature of 120°C. Then static extraction commenced for 5 minutes, and the cells flushed with fresh solvent. This excess solvent was then purged from the system for 100 seconds, and the cells were ready to be unloaded, with the Total Lipid Extract (TLE) extracted from the samples kept in the corresponding collection vials.

Whilst the ASE cycle was running, 5 combusted glass 8ml vials were labelled and weighed using an analytical balance, which would go on to be used to store the TLE in. The masses of these vials without TLE are recorded in Table 11. Once the ASE was finished, the collection vials were removed and placed in a test tube holder. The cells were also removed, and their contents disposed of. Generally, when the TLE mass is low, this can be run on a GC-MS machine as it is, or in the case of a higher TLE mass, the TLE can be split into different fractions before being run on the GC-MS.



Figure 18: ASE preparation and sample loading steps.

3.4 GC-MS: Preparing Standards

The BECS lab uses a standard mixture of alkanes to calibrate detections against. The shortest of which is hexadecane ($C_{16}H_{34}$), and the longest is heptatriacontane ($C_{37}H_{76}$). GC-MS requires three concentrations of this standard to compare results to; $10\mu g/ml$, $5\mu g/ml$ and $2.5\mu g/ml$. The $10\mu g/ml$ is as the standard is already prepared, so $50\mu l$ of this was measured with a syringe and placed inside a clean insert within a GC vial containing a spring. The $5\mu g/ml$ is prepared by placing $30\mu l$ inside a GC vial, along with $30\mu l$ hexane. The $2.5\mu g/ml$ standard is prepared by placing $25\mu l$ inside a GC vial insert along with $75\mu l$ of hexane. The GC vial caps were tightly secured and the vials stored in the fridge. This procedure was carried out under a fume hood.

3.5 GC-MS: Evaporation Protocol

The next step after solvents are extracted is to evaporate off the excess solvents which were used to extract the organic contents.

The collection vials were uncapped and placed in the TurboVap LV evaporator for around 20 minutes at 35°C. They were then placed in a test tube holder and moved to a tin foil covered work surface under a laminar flow hood. More DCM was put into the vials that had appeared to have entirely dried up. Using sterilised glass pipettes, the contents of each collection vial were moved into their corresponding labelled 8ml vials. The now-filled 8ml vials were placed in the Techne Sample Concentrator for 10 minutes, to further remove any solvent under a flow of nitrogen. The vials were removed from the concentrator and again placed in test tube holders. They were then individually weighed using an accurate analytical balance and this mass compared to the empty vial masses to calculate the mass of the concentrated TLE.

The resulting compounds from each sample are now ready to be transferred into their GC vials, which are sterilised 2ml glass vials, each labelled according to BECS ID. Firstly, small springs were inserted into each GC vial, then a small glass insert placed inside the spring in the vial (Figure 19), using tweezers. A 500 μ l glass syringe was rinsed three times with DCM, then used to measure 200 μ l of DCM and place inside the 8ml vials with the sample. This is in order to dissolve the compounds. Dissolving in DCM allows for optimal organics



Figure 19: A schematic diagram of the GC vials with glass insert and spring. Not to scale.

detection [21]. The internal walls of the 8ml vials were washed in DCM, and then the full amount inside the vial was drawn into the syringe and placed inside the glass insert. This was repeated for each sample, taking care to ensure the correct sample was placed inside the correspondingly labelled GC vial. These 2ml vials were placed in a Techne Sample Concentrator again to dry out, at 35°C. The GC vials were removed from the concentrator. A 100 μ l glass syringe was washed three times with DCM. Then, the following volumes of DCM were added to each sample with this syringe.

Table 7: Volumes of DCM added to concentrated TLE from each sample.

BECS ID	Volume (µl)
BLK	50
4680	200
4681	200
4682	150
4683	100

More DCM was placed into 4680 and 4681 (i.e. the two most promising samples for organics detections, NWA 10853 and the unheated Murchison) due to their heavier TLE masses. Since there is more TLE, more DCM is needed to fully dissolve all the compounds and to optimise evaporation during GC-MS. The GC caps were tightly screwed on, making the samples ready for running on the GC-MS equipment.

3.6 GC-MS

3.6.1 Theory

Gas chromatography-mass spectrometry is a method for identifying complex compounds and includes noise analysis [74]. We are utilising GC-MS because this technique separates com-

plex mixtures of materials, and thus is used a lot on environmental materials [75]. However, GC-MS is prone to detecting alkanes and fatty acids over other compounds, which is not ideal considering we are not specifically investigating for one type of compound and are instead interested in the whole organic picture of the samples. Another downside of GC-MS is that it involves the sample being evaporated, and thereby destroying it, and so many researchers will favour non-destructive techniques over GC-MS, or liquid chromatography-mass spectrometry (LC-MS) which works similarly. However, it does work well for gaseous samples or samples with high abundances of volatile elements or compounds. The GC-MS takes solvents extracted from samples and vaporises them before running these vapours through a column with a carrier gas (most GC-MS machines use hydrogen gas or helium gas). The compounds will appear as peaks on a chromatogram, of varying widths and heights depending on their size and volatility. The concentration of each compound can also be calculated by integrating the peak areas on the chromatograms. Compounds are usually identified by electron-impact ionisation of the gases within the mass spectrometer part of the machine, and then comparison with a mass spectra library gives the compound name. Each compound name identified will have an associated probability, indicating the sureness of the identification.

Derivatisation is a chemical analysis technique one can perform to make the mass spectra peaks more thin, in order to improve the accuracy of identification of compounds by GC-MS and to reduce the chances of broad peaks potentially covering over other smaller detections. It is useful in the instances where the compounds detected are highly polarised- this occurs when there are compounds with functional groups, including -OH (alcohols), -COOH (carboxylic acids), -NH (amines), and -CONH (amides). In straight chain molecules, such as fatty acids, there is a highly polar region on the molecule (i.e. the end of the molecule where its functional group is attached) that reduces its overall volatility. The GC-MS is reliant on the volatility of molecules in order for it to identify molecules correctly, as their ability to be vaporised will determine how far the vapour will be carried along the chromatogram. Derivatisation replaces these polar functional groups with a reagent, R-X, where R is some low-polarity element or small molecule, and X is an active element or small compound which can bond to hydrogen under the right conditions, making it very reactive [76]. The process

of derivatisation is summarised in Equation 2, where Y-H is the analyte with its hydrogen bonded to it, and R-X is the added reagent.

$$Y - H + R - X \longrightarrow Y - R + H - X \tag{2}$$

Derivatisation makes identifying highly polar compounds such as fatty acids easier for the mass spectrometer by altering the chemical structure to make the compounds more volatile, and less labile, thus also reducing its chances of breaking apart at the temperatures required to vaporise the extracted organics in GC-MS. In the UofG BECS lab, standard procedure is to use bis(trimethylsilyl)trifluoroacetamide (BSTFA) as the derivisation agent. Derivatising different functional groups varies in effectiveness and simplicity. The most easily derivatisable functional groups are alcohols, with amines and amides being the most difficult. BSTFA is preferred for sterically-hindered compounds [77], which are compounds whose bulkiness prevents them from performing different reactions. Other facilities may utilise different agents, such N-t-Butyldimethylsilyl-N-methyltrifluoroacetamid (MTB-STFA). This agent is known to produce the most thermally stable derivatives, but produces little to no analytical signal on sterically-hindered compounds [78]. Instead, BSTFA produces volatile reaction products, which greatly aids the vaporisation of sterically-hindered compounds such as carboxylic fatty acids or amino acids into the gas phase [79]. BSTFA also works best for compounds with a lower molecular mass [78].

3.6.2 GC-MS Method

The GC vials were placed in the Agilent Technologies gas chromotographer-mass spectrometer (GC7890b-MS5977A) (hereby called "the GC-MS"), along with the standards prepared in Chapter 3.4. Organic compounds are detected and identified by the mass spectrometer by comparing the peaks on the chromatogram to two mass spectrometry libraries- one internal library on the mass spectrometer, and the National Institute of Standards and Technology (NIST) library. After retrieving the initial mass spectrometer results of the compounds, it was decided further analysis was needed in order to precisely identify some compounds.

Derivatisation was carried out in order to reduce the widths of the chromatogram peaks, to give results with more certainty and to lower the chances of wider peaks covering up smaller peaks and hiding potential detections. Derivatisation was carried out under the BECS lab protocol, written by lab leader, J. Toney. The derivatisation was carried out between the author and M.A. Salik.

First, the samples kept in GC vials from previous analysis were brought to the BECS lab, the oven pre-heated to 80°C and BSTFA and pyridine were brought out from storage in a fridge. The BSTFA is the derivatisation agent, and the pyridine is the chemical catalyst. The springs were replaced in the GC vials, and a 100 μ l syringe washed four times in DCM. 15 μ l of BSTFA was placed into each sample insert using the syringe. The syringe was rinsed three more times in DCM before 20 μ l of pyridine was placed inside the inserts. Then, to protect the samples from any released substances due to the heating of the plastic caps within the GC-MS machine, tin foil was placed between the cap and the vial opening before the caps were screwed on, creating a tin foil seal between the plastic and the opening. The samples were placed in a block and put inside the pre-heated oven for 2 hours to enable a complete reaction between the reactants and catalyst.

The derivatised samples were then removed from the oven and allowed to cool, before being dried by a stream of N_2 . The dried samples were moved under a fume hood, ready for addition of DCM. The volumes used for the derivatised samples differ from the nonderivatised samples described in Chapter 3.5 because upon inspection of the initial GC-MS results, some of the peaks were too heavily concentrated that they saturated when reaching the upper limits of the calibration range. This means that smaller volumes are required to obtain a full picture of the GC peak. Thus, the volumes of DCM added to each derivatised sample are listed below.

 Table 8: Volumes of DCM added to derivatised samples

BECS ID	Volume (µl)
BLK	50
4680	150
4681	150
4682	100
4683	100

Each run on the GC-MS equipment requires new standards to be prepared. The BECS lab

standards were again prepared as described in Chapter 3.4 are placed in the ready slots within the GC-MS machine, along with the samples above, and the run sequence started.

4 Physical & Petrological Results and Analysis

4.1 Characterising NWA 10853

This chapter outlines the initial results of the XCT and SEM-EDS studies of NWA 10853, where we identify main sites of interest, structure sizes, and general mineralogical information. It then presents the analysis of these images, largely by false-colour analysis, in which we carry out structural analyses and mineralogical interpretations which lead to the final conclusion on the characterisation of NWA 10853 from these two analyses.

4.1.1 XCT Results

Raw XCT images were retrieved using the Avizo software to reconstruct the 3D image. The three cross-sections are shown together in Appendix 8A. The white inclusions are denser regions, and darker colours indicate less dense features. Points of interest in the volume image (and the 2D cross-section images) are the dark fracture-like features- these could be physical cracks in the rock, or low-density veins within the meteorite. The grey globules vary in size from around 300 microns (0.3mm) to, at largest, 1000 microns (1mm), which is the higher end of the size scale for CM2 chondrules [41]. As this sample is presumed a CM1, however, one should be wary of this size reference. It's likely that these are not CAIs due to their large size and dark colour- CAIs would be expected to be bright white as their metal content would make them very dense in contrast to the surrounding matrix. Instead, the grey globules may be pseudomorphs, which have been known to replace chondrules in aqueously altered chondritic meteorites- the CM1 LAP 02277 had its chondrules replaced with phyllosilicates, oxides, and sulfides [33]. It is clear that to extract mineralogical information, further study via SEM-EDS is required. This will shed light on what these dark fracture-like features consist of (if anything), whether the globules truly are chondrules, and if these light inclusions are indeed metallic or not.

The XCT image directed our choice of areas for investigation within the thin section. Those being:

- identifying the minerals within the brightest (most dense) spots;
- investigating fracture-like features to determine if they are physical cracks in the rock or veins;



Figure 20: The sample of NWA 10853 held at the University of Glasgow after a small sample was removed for GC-MS, shown through the *xy* plane. This image was generated through X-ray CT scanning at the facilities shared between UofG and Strathclyde University. Thanks to the Advanced Materials Laboratory team at the University of Strathclyde.

- investigating these fractures for any trapped indicators of terrestrial weathering;
- determining if circular features are chondrules, chondrule replacement, pseudomorphs, or another feature altogether.

4.1.2 SEM-EDS Results

The SEM-EDS process resulted in two cross-section images of the whole thin section. These can now be compared with the cross-sections from the XCT to allow us to analyse the mineral composition of the globules, or the high-density areas identified from XCT. 10 sites for EDS investigation were identified across the thin section, with significant areas being those around cracks to investigate the extent of terrestrial weathering, and within round or elliptical structures to investigate possible chondrules or their replacements. For indications of terrestrial weathering, we would expect salts (sodium-bearing minerals) or calcites, particularly because it is known to have fallen to a hot sand desert. We would also expect oxygenated products. Chondrule pseudomorphic features to look for are oxides, sulphides, and phyllosilicates. One could also look for elliptical structures and strong foliation as indicators.



Figure 21: Backscattered electron image of a thin section of NWA 10853, annotated with sites for analysis.

Firstly, upon examining the backscattered electron (BSE) image (Figure 21), the brighter spots are representative of denser minerals or elemental inclusions. In NWA 10853's case, these are Fe-Ni sulphides, with some phosphides. The Fe-Ni total abundance is high in this meteorite, with low sulphate totals, but more thin sections are required to form a quantitative conclusion. From the BSE alone, we can see that the primary texture has largely been preserved- a smoother texture and lighter backscattered colours closer to white would indicate higher extents of alteration- and so it is immediately clear that the previous CM1 classification can be scrutinised.

The false-colour EDS image (Figure 22) shows that the sample is rich in olivine and phyllosilicate, with iron-sulphides and calcides scattered throughout. There are also calcium carbonates throughout this sample, and various regions appear more extensively altered than others, such as the upper right hand side, indicated by its extremely fine-grained matrix

texture and lack of remaining chondrules. Oxygen was not included in the colour map as the epoxy contains oxygen, which was creating misleading information about the fractures and empty spaces. The main phases in this sample are bright green olivine, green-yellow phyllosilicates, pink carbonates, and yellow sulphides.



Figure 22: The thin section of NWA 10853 shown in false colour via SEM-EDS. Green represents magnesium, red representing iron, pink being calcium, blue representing silicon and yellow for sulphur.

4.2 Thin Section Analysis

A total of 10 investigation sites were chosen during initial analysis of the whole specimen. The catalogue of images can be found in Appendix 8B. Firstly looking at the SEM-BSE image (Figure 21), we determine the large fracture-like features seen in the XCT images are not mineral veins, but instead cracks in the thin section itself. This can be assumed to be due to the fissile nature of the sample. The matrix of the thin section is largely composed of phyllosilicates. Despite this, most chondrule relics have alteration rims around them but appear to remain partially preserved, particularly in the centre of this thin section. This indicates that although the sample has experience aqueous alteration, this alteration has not changed all of the minerals present. Specifically, when looking at the SEM-EDS false-colour image (Figure 22) and observing the spectra of the iron oxides, they exist in this sample in the form of Fe₃O₄, the mineral magnetite. This is typically extra-terrestrial and believed to have formed due to aqueous processes on meteorite parent bodies [80]. Its presence in the sample shows that this meteorite has not been as significantly terrestrially weathered as thought from optical study. Additionally, the upper right hand side of the sample is clearly more altered than other areas of it, with a very fine-grained matrix here.

We have selected three of the 10 investigation sites in this chapter to discuss here. When looking at Site 1 (Figure 23), there is a clear fine-grained alteration rim around this circular object. The object has an approximate diameter of $450\pm50\mu$ m. The object itself contains subhedral olivine crystals, which have been partially replaced by phyllosilicates. Their angular shape, as opposed to circular or smoothed, indicates that these olivines are primary features of this chondrite. The BSE image also shows a dendritic texture between the olivine grains, which indicates the preservation of primary radial pyroxenes within this chondrule complex relic. This specific object at this site is likely a porphyritic olivine chondrule, and as some of its primary textures are still preserved, this meteorite cannot be a completely altered CM1. Further, looking to Site 2 (Figure 24), a smaller chondrule (approximately 100 μ m diameter) which again has a fine-grained rim. Amongst a highly altered matrix, we have a chondrule that has been perforated by the alteration, presumably by a feature similar to a geological triple junction. This shows that this chondrule was entirely altered by aqueous processing through these fractures. Comparing to Site 1, it has a very different elemental composition, and conversely shows that some chondrules have been fully aqueously altered. One can also examine the extent of terrestrial weathering in Site 2, by the very limited presence of sodium salts (blue) in the lower right hand side crack around the chondrule. Finally, Site 3 (Figure 25) is a medium-sized chondrule of around 400 μ m. The texture surrounding the relic olivine grains in this site is different at the bottom left of the image from the rest of the surrounding texture, which suggests a change in matrix composition and indicates encroachment of water into this chondrule, creating the phyllosilicates. There are significant and well-preserved melt inclusions within this ex-chondrule (areas where trapped lava inside olivines cooled), which are the areas of finer-grained texture within the central ex-chondrule. There are chromium features on the rims of these inclusions (approximately 5 μ m wide by 20 μ m long) on the left hand side of the chondrule. It also includes primary magnetite inclusions, and a very small number of magnesium oxides. These artefacts are again strong evidence for less extensive aqueous alteration than previously thought.

From the SEM-EDS analysis, the parent body of NWA 10853 was likely altered both on the asteroid parent body and during its terrestrial residence in Northwest Africa. From the analysis of the XCT and SEM-EDS images, the largely-altered matrix would suggest CM1, however, the partial preservation of primary chondrules does not fit with this classification. The observed elemental compositions and aqueous alteration characteristics seen in this sample best fits the diagnostic of 85-99% of mafic phenocrysts being altered; consistent with CM2.1 classification. Due to the presence of calcium carbonates, there is potential for it be classed as something even less altered - perhaps as a CM2.2. This further distinction will have to be left as future work, due to financial and temporal constraints on this Masters project.



Figure 23: A zoomed-in section of Figure 22, investigation site 1. This is the largest chondrule in this thin section of NWA 10853. The angular crystalline edges of the olivine grains are clear in bright green. A few primary iron-containing features can be seen in red at the top of the chondrule. The chondrule is surrounded by a finer-grained alteration rim.



Figure 24: SEM-EDS of site 2. Silicon is shown in dark blue, iron in red, phosphorous in purple, nickel in cyan, calcium in pink, and sulphur in yellow. The bright orange features are sulphur-iron inclusions. The dark blue in the crack at the bottom of the image is silicon from the polishing of the thin section. There is a clear alteration rim of finer-grained rock around this perforated chondrule. The image shows a triple junction alteration feature into the ex-chondrule, with veins that are less Fe-rich and slightly richer in Mg. This feature likely used to be olivine, which was annealed and altered. There are sulphides within and around this globule, and some calcium phosphate (CaPO₄) nearby in bright purple.



100 µm

Figure 25: Site 3 of investigation. This false-colour image shows phosphorus (purple), chromium (orange), nickel (cyan), calcium (pink), and oxygen (blue). Chromium inclusions are shown in bright orange. Some calcium phosphate minerals (bright purple) are visible outside the ex-chondrule. The texture within this ex-chondrule is synchronous with that of melt inclusions, indicating thermal alteration, as well as the aqueous alteration rim surrounding the ex-chondrule.

5 GC-MS Results & Analysis

This chapter lays out the analysis plan for the organic detections via GC-MS, before presenting the numerical uncertainty analysis to provide numerically-rigorous final results of concentrations. The analysed and manipulated data in this chapter goes on to underpin the discussions and final conclusions of this work.

5.1 GC-MS Results

5.1.1 GC-MS Preparation: Sample Loss and Final Masses

The initial and final sample masses for each sample are shown in Table 9. The sample loss is from pieces flying off of the sample during crushing, as well as from smaller powder-like particles sticking to the inside of the beakers, which would be impossible to remove from the beaker without using tools directly on the crushed sample. It was advised against this to reduce contamination risk.

The initial masses were calculated by taking the starting masses of the equipment used for sample storage in the crushing stages of the experiment, when empty, when containing the initial mass of sample, then subtracting the initial sample plus the beaker mass from the empty beaker mass (see Chapter 3.2 for more details).

Empty 15ml vials were weighed for each sample. Then the powdered samples were tipped into the beakers and weighed, then were transferred into the previously empty vials. The beakers were weighed again to show that not all contents of each sample were completely emptied into the mortar before crushing. The final sample masses are calculated by subtracting the empty vial mass from the vial with sample mass. The precise measurements taken of the empty equipment and the equipment with samples at each stage are detailed in Appendix 8C.

Table 9: The initial and final masses of each sample going into extraction, with their individual sample losses given as a percentage of their initial mass.

Sample name	Initial Mass (mg)	Final Mass (mg)	Sample loss (%)
NWA 10853	323.7	317.2	2.0
Unheated Murchison (UM)	419.9	294.1	30.0
Heated Murchison (HM)	66.1	53.5	19.1
Sand	424.7	311.8	26.6

The stark difference between the lack of sample loss of NWA 10853 as opposed to the


Comparative sample loss

Figure 26: The sample loss as a percentage of the initial starting mass of each sample, shown comparatively. The percentage uncertainties for each sample are calculated using the standard digital uncertainty of ± 0.0001 g. The translated uncertainties are comparatively too small to plot. The values are; Sand $\pm 0.06\%$; NWA10853 $\pm 0.07\%$, UM $\pm 0.09\%$, HM $\pm 0.34\%$; as upper bounds on the uncertainties.

other samples (Figure 26) was surprising. The low sample loss in this case was thanks to the crumbly and powder-y nature of NWA 10853, a large amount of which had already reduced to powder upon removing a chip to be sampled from the main mass. Between the other three samples, the average percentage sample loss via hand crushing is 25.202%.

5.1.2 GC-MS: Solvent Extraction

The final masses going into solvent extraction are detailed below in Table 10, with their corresponding BECS ID and the addition of a procedural blank of non-crushed combusted sand added in the solvent extraction lab. This was not weighed, and was poured directly into the vial in the lab. The mass balance in the solvent extraction lab measures only to 2 decimal places.

Table 11 shows the masses of the empty vials, and masses of the vials after ASE and concentration which contain the TLE in the vials. Subtracting the empty vial mass from the vial mass after extraction and concentration allows us to calculate the mass of TLE from each sample, which are also shown in this table. As expected, the unheated Murchison has the highest TLE mass (i.e. the most organic compounds by mass), followed by NWA 10853,

then the heated Murchison. The sand sample had the least of our main samples, but noting that the lab blank also has 0.0003g may indicate that 0.0003g of contaminating lipids were picked up during the solvent extraction and concentration processes.

BECS ID	Sample name	Sample masses after transfer (g)
BLK	Blank	n/a
4680	NWA 10853	0.32
4681	Unheated Murchison	0.29
4682	Heated Murchison	0.05
4683	Sand	0.31

Table 10: The sample masses after transfer from crushing vials to the extraction cells.

Table 11: The masses of the 8ml vials and the masses of these same vials containing the TLE obtained from the solvent extraction and concentration processes.

BECS ID	Sample name	Empty vial mass (g)	Vial mass post-ASE (g)	TLE mass (g)
BLK	Blank	7.7010	7.7013	0.0003
4680	NWA 10853	7.7267	7.7273	0.0006
4681	U.M	7.7071	7.7091	0.0020
4682	H.M	7.7351	7.7356	0.0005
4683	Sand	6.6976	6.6980	0.0004

5.1.3 GC-MS: Non-derivatised Qualitative Results

The GC-MS results as identified by mass spectrometry are given in Table 12, and are the best matches from the *NIST MS* software program (version B.07.00, service pack 2). The peaks in the procedural blank and the sand sample were compared to the BECS standards graph to identify any new contaminants. Benzenes and diphenol sulphone were found in every sample and in the extraction lab blank (BLK), but left out of this table. There are 11 identifications of interest in total between the four samples. The full list of identified compounds can be found in Appendix 8D. This run has detected 5 fatty carboxylic acids, 1 aldehyde, 1 alcohol, and 4 likely contaminants (tetramethyl decynediol, o-hydroxybiphenyl, diethylene-glycol, and octabenzone).

5.1.4 GC-MS: Derivatised Qualitative Results

After running the derivatised samples through the GC-MS, 15 organic compounds of interest were detected between the four samples- an increase of 4 identified peaks upon derivatisation as compared to without derivatisation. The detected compounds are listed in Table 13. This

Organic compound	Retention time (mins)	Blank	Sand	NWA 10853	U.M	H.M
n-decanoic acid	13.74	×	×	\checkmark	×	×
dodecanal	14.66	×	×	×	\checkmark	×
tetramethyl decynediol	14.83	×	×	\checkmark	×	×
1-dodecanol	16.33	×	×	×	\checkmark	×
o-hydroxylbiphenyl	16.82	×	×	\checkmark	×	×
dodecanoic acid	17.85	×	×	\checkmark	×	×
diethylene-glycol	19.07	×	×	×	\checkmark	×
myristic acid	22.11	×	×	\checkmark	×	×
palmitic acid	26.17	×	×	\checkmark	×	×
oleic acid	29.415	×	×	\checkmark	×	×
octabenzone	39.24	×	×	\checkmark	×	×

Table 12: A list of organics of interest detected in the non-derivatised GC-MS run.

run has detected 9 fatty carboxylic acids, 2 alcohols, and 4 likely contaminants (biphenyl, diethylene-glycol, nonylphenol, and octyloxy-biphenyl-methanone). It should be noted that all detections have a TMS addition to its chemical structure, which has been removed from the compound names for consistency. It is likely that octyloxy-biphenyl-methanone was octabenzone before derivatising the compound. There are two detections of decanoic acid (n-decanoic acid, and decanoic acid (TMS)), indicating that this compound did not fully complete the derivatisation reaction and has left a small amount of the non-derivatised form of this compound. For analysis purposes, this small amount of underivatised compound has been left in the detections table and will go on to contribute to the concentration calculation of decanoic acid (TMS), but is not listed as its own compound in Table 13. It is clear that the lab contaminants are palmitic, oleic and steric acids, as these are in every blank and most samples.

Descriptions of the listed compounds are listed in Chapter 5.2, along with a summary of whether they were detected in the non-derivatised, derivatised, or both runs of the GC-MS. The full list of detections can be found in Appendix 8D.

Organic compound	Retention time (mins)	Blank	Sand	NWA 10853	U.M	H.M
Nonanoic acid	13.83	×	×	\checkmark	\checkmark	×
Decanoic acid	15.85	×	×	\checkmark	×	×
1-Dodecanol	18.42	×	\checkmark	×		
biphenyl	18.83	×	×	\checkmark	×	×
diethylene-glycol	19.10	×	×	×		×
Dodecanoic acid	20.04	×	×	\checkmark	\checkmark	×
Tert-nonylphenol	22.04	×	×	×		×
Tetradecanol	22.58	×	×	×	\checkmark	×
Myristic acid	24.14	×	×	✓		×
Pentadecanoic acid	26.06	×	×	✓	×	×
Palmitelaidic acid	27.42	×	×	✓	×	×
Palmitic acid	27.97	\checkmark	\checkmark	✓	\checkmark	
Oleic acid	31.02	\checkmark	\checkmark	\checkmark	×	×
Stearic acid	31.497	\checkmark	\checkmark	✓		
Octyloxy-biphenyl-methanone*	38.94	×	×	✓	\times	\times

Table 13: The list of organics of interest detected by GC-MS of the derivatised samples. All are TMS-derivatives.

5.2 Qualitative Organics Analysis

Using the flow chart in Figure 27, qualitative research was carried out to determine how likely it was that a compound was intrinsic to the meteorites, whether that be extra-terrestrially, picked up as contamination from the fall site or during curation, or if it is present as a lab contaminant. Following this, the further analysis steps are to consider the signal to noise ratio (SNR) of the detections, and then to consider the derivatised results and whether the detections have occurred in both runs or not.

Figure 28 shows a list of descriptions for every compound of interest and which experiments they were detected in, with green boxes indicating a compound that was only found in the first (non-derivatised) run, blue boxes indicating compounds that were only detected in the second (derivatised) run, and red boxes indicating compounds that were detected in both runs. Following literature research on each compound, the identifications that are likely to be contaminants from curation or the environment are shown in Table 14. Specifically , diethylene glycol likely came from the lab environment as it is a key ingredient in the freezing agent used in the GC-MS lab within the facilities at UoG.



Figure 27: The analysis plan, combining qualitative and quantitative analyses to determine whether compounds detected in GC-MS are either extra-terrestrial in origin, or contamination.

Compound Name	Carbon	Description and uses
Negencie esid	number	Carls and lie fetty acid, was due ad activally in means plants
Nonanoic acid	9	Presence suggests partial reaction with TMS group.
Decanoic acid	10	Carboxylic fatty acid.
Dodecanal	10	Aldehyde, the product of dehydrogenation of the alcohol Dodecanol.
Tetramethyl decynediol		Coating products, plant protection products, wetting/foaming agents. Very likely manmade, likely to be a contaminant from NWA 10853 curation history.
Dodecanol	12	Alcohol, found naturally in one plant family common to central and south America, and a plant family native to the UK. Used in detergents, lubricating oils, pharmaceuticals.
(o-hydroxy)biphenyl	12	Agricultural fungicide (specifically used in waxes for citrus fruits). The derivatised result "biphenyl" is used as a food preservative due to its antimicrobial properties, and is naturally found in crude oil and natural gas.
Dodecanoic acid	12	Carboxylic fatty acid, often used in fragrances. Alternative name: Lauric acid, often found in coconut oil, and is highly moisturising.
Diethylene-glycol	12*	Freezing sprays – one of which is used in the GC laboratory in the BECS labs.
Myristic acid	14	Carboxylic fatty acid. Soaps, key role in cell biology as a lipid anchor (holds proteins to cell membranes).
Tert-nonylphenol	15	Used in surfactants and detergents.
Pentadecanoic acid	15	Carboxylic fatty acid. Used in adhesives, sealant chemicals, agricultural chemicals, lubricants and lubricant additives. Is also used as a flavouring agent in foods.
Palmitic acid	16	Carboxylic fatty acid. Large components of palm, coconut, and other naturally-occurring oils. The most common fatty acid in animals and plants. The first fatty acid produced during fatty acid synthesis, thus consisting the base of all longer fatty acids. Also produced in palm trees.
Pentadecanoic acid	15	Carboxylic acid found primarily in fats of animal milk.
Palmitelaidic acid	16	Carboxylic trans-fatty acid. Trans-isomer of palmitic acid, unsaturated.
Oleic acid	18	Carboxylic (unsaturated) fatty acid. Naturally occurs in many oils and animal fats. Found in oils, fats such as milk and butter, and can be used in soaps.
Stearic acid	18	Carboxylic (saturated) fatty acid. Found in shea and coconut oil, in hardening soaps, candles, cosmetics, and plastics. Plays a role as a plant, human and algal metabolite.
Octabenzone/octyloxy biphenyl methanone	21	UV screener on coating products, adhesives, sealants and polymers. Occurs naturally in Japanese bamboo ferns and Siberian pine trees.

Figure 28: Compounds of interest detected in both the non-derivatised and derivatised experiments. It should be noted that some compound names changed upon derivatisation, so we have used basic names here, e.g. octabenzone likely reacted with the TMS group to form octyloxy-biphenyl-methanone. Thus some names in this table are used interchangeably. **Colour key:** detected in non-derivatised run only (green), detected in derivatised run only (blue), detected in both runs (red). **This has been estimated from the non-derivatised compound elements*.

Non-derivatised run	Compound name
NWA 10853	o-hydroxybiphenyl
U.M.	diethylene glycol
Derivatised run	Compound name
NWA 10853	biphenyl
	ocyloxy-biphenyl-methanone
U.M.	diethylene glycol

Table 14: The list of likely contaminants, due to either environmental contamination or contamination from curation.

5.3 Quantitative Analysis of Non-derivatised Samples

5.3.1 Calculating Concentrations

An example calculation in full is shown for decanoic acid, that was found in non-derivatised NWA 10853, with a retention time of 13.74 minutes. This is within the range for the first calibration curve (Figure 39), shown in Appendix 8E, which is for retention times between 0 and 25 minutes. Concentration is given by the peak area of the detected compound, divided by the gradient of the relevant calibration curve, so the concentration of decanoic acid per gram of NWA 10853 sample with peak area of 4126441.88 is:

$$\frac{4126441.88}{469138} = 8.796 \,\mu\text{g/ml}$$

Concentrations must be normalised to account for the sample volume used in GC-MS and the initial mass of the rock sample that went into solvent extraction. It is most convenient for our purposes to work in units of $\mu g/g$, as this is directly equivalent to working in parts per million. The word equation for normalised concentration is:

normalised concentration =
$$\frac{\text{concentration} \times \text{volume of sample}}{\text{initial mass of sample}}$$
 (3)

So again in the case of decanoic acid, its volume in the GC vial was 0.2ml, and it came from a rock of starting mass 0.3172g, so:

normalised concentration =
$$\frac{8.796\mu g/ml \times 0.2ml}{0.3172g}$$

= 5.546 $\mu g/g$ (ppm)

By repeating this equation for each compound, the list of normalised concentrations for each detected compound are given in Table 15. This process is how all normalised uncertainties, in both runs of the experiment, are calculated.

5.3.2 Uncertainty Analysis

Mathematically, the uncertainty on the non-normalised concentrations can only come from the peak area and the gradients of the calibration curves (as the formula for concentration is *concentration* = $\frac{peak area}{gradient of calibration curve}$). The peak area is automatically calculated in the *MassHunter* software and as there is no description of how this is generated, we are left with no choice but to ignore any uncertainty contributions from this parameter. So in order to calculate a value of uncertainty on non-normalised concentrations, we require the uncertainty on the gradients of the calibration curves made earlier. Each of the three curves generated are responsible for a section of peaks on the mass spectrum, based on the compound's retention times. The calibration curve for retention times between 0 and 24 minutes was based on the BECS Lab Standard spectrum for n-nonadecane, which has chemical formula C₁₉H₄₀. The second calibration curve, for compounds with retention times between 26-34 minutes, was based on the BECS Lab Standard spectrum for n-tricosane, C₂₃H₄₈. The final calibration curve was based off of the BECS Lab Standard spectrum for n-octacosane, C₂₈H₅₈. These curves can all be found in Appendix 8E.

The calibration curves for each compound are fitted as a straight line through each concentration, and the equation of the straight line can be used to extract the concentration of other compounds within the calibration curve's retention time span. Thus, we can calculate the combined uncertainty in the normalised concentrations, which require uncertainties on the concentration, volume of sample, and mass of the initial sample.

5.3.3 Uncertainty on calibration curve gradients

The uncertainty on the gradients of the calibration curves are relatively straightforward to calculate. Using the formula below,

$$\sigma_m = m\sqrt{\frac{\frac{1}{R^2} - 1}{n - 2}} \tag{4}$$

where σ_m is the uncertainty on the gradient, R^2 is the R-squared value, *m* is the gradient as given in the software, and *n* is the total number of data points (which is 3 for all calibration curves we generated), we can calculate each uncertainty. For the first calibration curve (for detections with retention times in the first 25 minutes) we obtain a gradient with uncertainty 469138±25734.377, corresponding to an uncertainty of ±5.49%. The calculation is laid out below for clarity:

$$\sigma_{m1} = 469138 \sqrt{\frac{\frac{1}{0.997} - 1}{3 - 2}}$$
$$\sigma_{m1} = 25734.33708$$
$$\sigma_{m1}(\%) = \frac{25734.33708}{469138} \times 100$$
$$\sigma_{m1}(\%) = \pm 5.49\%$$

Following this procedure for the next calibration curve (25-34 minutes) gives 520071 ± 46703.75 (i.e. $\pm 8.98\%$). And finally for retention times greater than 35 minutes, we have a gradient of 523098 ± 46975.59 (i.e. $\pm 8.98\%$ again).

5.3.4 Uncertainty on Normalised Concentrations

The normalised concentrations are calculated using the non-normalised concentration (the uncertainty on which was just calculated above), the volume of the sample and the initial mass of the sample. The volume uncertainty can be estimated easily as it was done manually and therefore is equal to the standard human error of analogue measurements of ± 0.5 of the smallest degree of measurement on the device used. In this case, the device used to measure the volume was a μl syringe whose smallest ticks are at intervals of 1μ l. Thus, the volume uncertainty is $\pm 0.5\mu$ l. The initial mass uncertainty comes from the digital scale used to measure the masses which, as stated in Chapter 3.2, is ± 0.0001 g.

Through a simple combining uncertainties equation, one can determine the final uncertainty on the normalised concentrations. To combine uncertainties, one must convert into percentages first. For the volume, this corresponds to a percentage uncertainty of 0.5%, and the mass uncertainty on NWA 10853 corresponds to 0.032%. For Murchison, this mass uncertainty is 0.034%.

5.3.5 Combining Uncertainties

The final step to obtaining a full understanding of the uncertainty in our measurements is to combine uncertainties from the lab stages (i.e. weighing, measuring with syringes). The process for combining percentage uncertainties (when subjected to multiplication of or division by each other) is to simply add them together. An example calculation is laid out below, for the non-derivatised run of NWA 10853 and the first detection, which was n-decanoic acid.

The uncertainty on the non-normalised (μ g/ml) concentration from Chapter 5.3.3 is $\pm 5.49\%$, calculated from considering the first calibration curve gradient. The absolute volume uncertainty is 0.5μ l, and 200μ l of DCM was measured out to add to the TLE before non-derivatised extractions, resulting in a percentage uncertainty of $\pm 0.25\%$. Finally, the absolute mass uncertainty of ± 0.0001 g results in a percentage uncertainty of 0.032% for NWA 10853. The equation to calculate the concentration in parts per million uses the product of the non-normalised concentration and the volume, divided by the mass. Percentage uncertainties can be combined in equation by addition, and so:

normalised concentration uncertainty (%) = non-normalised concentration uncertainty (%) + volume uncertainty (%) + mass uncertainty (%) normalised concentration uncertainty (%) = 5.49 + 0.25 + 0.03normalised concentration uncertainty (%) = $\pm 5.77\%$

Then by applying the percentage to the calculated ppm, this is returned in units of ppm. Thus, the final result of decanoic acid in NWA 10853 from the non-derivatised run is 5.55 \pm 0.32 ppm. These steps, from Chapter 5.3.3 through Chapter 5.3.5 was repeated for all non-derivatised compounds, taking note of their different calibration curves, and the non-derivatised concentrations with uncertainties are listed in Table 15. It is interesting to notice the difference in probabilities between the two samples, with the identifications made for the detected organics in NWA 10853 being considerably higher probability than those identified in Murchison.

Table 15: Normalised concentrations of compounds detected in NWA 10853 and Unheated Murchison (U.M.) after the non-derivatised run of the experiment. The probability percentage is given in the *MassHunter* software and provides a guideline for the sureness of the compound identification, and is given alongside the SNR of each detection.

Sample name	Compound name	Probability (%)	Normalised Concentration (ppm)	Signal to Noise Ratio (SNR)
NWA 10853	n-decanoic acid	74.4	5.55	16.3
	tetramethyl decynediol	73.9	1.19	0.9
	o-hydroxybiphenyl	51.2	7.80	12.9
	dodecanoic acid	60.7	2.18	2.2
	myristic acid	37.0	3.92	9.1
	palmitic acid	51.9	9.63	24.5
	oleic acid	11.2	3.57	3.5
	octabenzone	92.3	2.82	4.8
U.M.	dodecanal	17.0	57.48	24.9
	1-dodecanol	10.2	551.58	132.2
	diethylene glycol	53.15	53.15	15.9

5.3.6 Signal to Noise Ratio

The signal to noise ratio (SNR) is a signal processing statistic relating to the precision of an experiment result. It is in the same statistical group as standard deviation and coefficient of variation- all describe the precision of a measurement. An SNR of 1 signifies that a detection or signal is of the same size or effect as the noise of the measurement. A precise experiment, and therefore a repeatable experiment, will have a high SNR. Anything below 1 has more noise than signal, and so it is impossible to distinguish a true signal from the noise. It is standard practice in the BECS lab to use an SNR of 5 to determine statistical significance. This means that the following detections from the non-derivatised run can be ruled out of our search for extra-terrestrial compounds due to poor signal:

- tetramethyl decynediol in NWA 10853
- dodecanoic acid in NWA 10853
- oleic acid in NWA 10853
- octabenzone in NWA 10853.

5.4 Quantitative Analysis of Derivatised Samples

5.4.1 Calculating Concentrations

Following the same calibration protocol as outlined in the non-derivatised run, we obtain the following abundances. NWA 10853 now shows 12 compounds compared to the 8 detected in the first run, showing a range of chain lengths from 9 to 18 carbons long. The detections, normalised concentrations and SNR values are shown in Table 16. This table includes a column of calculated uncertainties using the process outlined in Chapter 5.3, with a small modification as detailed in the following section.

5.4.2 Uncertainty Analysis

The derivatised run has some other quantifiable uncertainties involved that do not need to be considered when calculating the non-derivatised uncertainties. More DCM was added to the GC vials before derivatisation. 150μ l was added to NWA 10853 and to U.M. To update the

volume uncertainty for derivatised samples, combine the absolute volume uncertainties for NWA 10853 to retrieve a total volume uncertainty for derivatised NWA 10853 of $0.5+0.5=\pm 1\mu$ l. A combined total uncertainty equation for normalised concentrations in derivatised NWA 10853 for decanoic acid (TMS, as it has been derivatised) is laid out below. First, calculate the uncertainty in the gradient of the calibration curve:

$$\sigma_{m} = m \sqrt{\frac{\frac{1}{R^{2}} - 1}{n - 2}}$$

$$\sigma_{m1} = 366404 \sqrt{\frac{\frac{1}{0.9997} - 1}{3 - 2}}$$

$$\sigma_{m1} = \pm 6347.256$$

$$\sigma_{m1}(\%) = \frac{6347.256}{366404} \times 100$$

$$\sigma_{m1}(\%) = \pm 1.732\%$$
(5)

For completeness, the uncertainties on the gradients for the second calibration curve is 3.164%, and for the third calibration curve it is 8.98%. Then, calculate the uncertainties from the lab, which were volume and mass:

$$\sigma_{vol}(\%) = \frac{1}{150} \times 100$$

 $\sigma_{vol}(\%) = \pm 0.667\%$
 $\sigma_{mass}(\%) = 0.03\%$

Now, combine by addition to get the total percentage uncertainty, before converting to absolute uncertainty in ppm and rounding to 2 decimal places. The normalised concentration in ppm as calculated in Chapter 5.4.1 is 3.174 ppm.

$$\sigma_{total}(\%) = 1.732 + 0.667 + 0.03 = \pm 2.429\%$$

 $\sigma_{total} = 3.174 \pm 2.429\% = 3.17 \pm 0.08$ ppm

This procedure has been repeated for each detection, taking note of differences in mass uncertainty for Murchison and using appropriate calibration curves. The uncertainties shown in the final analysis results table use a combined percentage uncertainty of $\pm 2.429\%$ for

compounds detected in NWA 10853 that have retention times between 0-24 minutes, an uncertainty of $\pm 3.861\%$ for those with retention times between 26-34 minutes, and $\pm 9.677\%$ for retention times greater than 35 minutes. For the Unheated Murchison samples, the percentage uncertainties are the same since the mass percentage works out to be proportionately equal.

5.4.3 Signal to Noise Ratio

Using the same statistical significance value of SNR = 5, the following detections in this run can be ignored due to poor signal:

- · dodecanoic acid in unheated Murchison
- tert-nonylphenol in unheated Murchison.

5.5 Contamination From Procedure

Now that we have eliminated some detections due to low SNR and literature searches, we can analyse the remaining "true" detections further, and consider whether any of these compounds could also be contamination. We determine this by looking at organics present in sample blanks, which will identify compounds that were picked up during the crushing procedure. As it has been deemed more reliable, we consider only the organics detected in the derivatised run.

The sample blank of the derivatised run contains several compounds (as seen in Appendix 8D) including 22-bipyridine (derivatisation catalyst), diphenyl sulfone, indicating some of the compounds which are present in the current lab set-up. Stearic, oleic and palmitic acids are detected in both the sample ("blank") and procedural ("sand") blanks, indicating contamination during either the ASE or the GC-MS steps of our process. Dodecanol was found in the procedural blank, but not in the sample blank, indicating potential contamination during crushing. However it was not present in every crushed sample, so the contamination was either limited to just the procedural blank and unheated Murchison, or dodecanol came into contact with the procedural blank and is indeed intrinsic to Murchison (or vice versa). At this stage, we cannot entirely discount the presence of dodecanol in Murchison, and so we

Table 16: Normalised concentrations of compounds detected in NWA 10853 and Unheated Murchison (U.M.) in the derivatised run of the experiment, with probabilities as given in the *MassHunter* software. * *This compound name has been shortened from "biphenyl, 2-[(trimethylsilyl)oxy]"*.

** This compound name has been shortened from "4-(Octyloxy)-2-[(trimethylsilyl)oxy]phenyl(phenyl)methanone".

*** This compound name has been shorted from "Ethylene glycol - Adipate - Diethylene glycol".

Sample name	Compound name	Probability (%)	Normalised Concentration (ppm)	Uncertainty (ppm)	SNR
NWA 10853	nonanoic acid (TMS)	60.8	11.41	0.28	31.7
	decanoic acid (TMS)	80.0	9.78	0.24	27.0
	biphenyl*	68.2	9.03	0.22	23.7
	dodecanoic acid (TMS)	90.2	7.55	0.18	18.7
	myristic acid (TMS)	94.6	21.79	0.53	50.0
	pentadecanoic acid (TMS)	85.5	6.10	0.24	10.0
	palmitelaidic acid (TMS)	52.3	12.44	0.48	20.8
	palmitic acid (TMS)	96.6	101.57	3.92	174.6
	oleic acid (TMS)	21.0	72.68	2.81	19.7
	stearic acid (TMS)	95.2	32.37	1.25	74.6
	octyloxy-biphenyl-methanone**	90.4	3.489	0.34	21.8
U.M.	nonanoic acid (TMS)	49.5	9.92	0.24	25.2
	dodecanol (TMS)	65.8	938.65	22.80	243.3
	diethylene glycol***	11.4	75.00	1.82	41.9
	dodecanoic acid (TMS)	87.6	25.47	2.13	2.7
	tert-nonylphenol (TMS)	8.87	11.37	0.28	4.4
	tetradecanol (TMS)	29.4	22.42	0.54	6.8
	myristic acid (TMS)	44.1	14.93	0.36	13.0
	palmitic acid (TMS)	94.9	79.53	3.07	74.1
	stearic acid (TMS)	87.7	28.05	1.08	93.0

will carry it through to the next stages of analysis. At this stage, we can discount the further following compounds:

- palmitic acid
- oleic acid
- stearic acid

from NWA 10853 and Unheated Murchison samples.

5.6 Limits of Detection and Quantification

The gradient and y-intercept of the standards from the non-derivatised run were used to calculate concentrations in parts per million. The limit of detection (LOD) is the the lowest concentration of an analyte at which a detection is possible, and the limit of quantification (LOQ) are the lowest concentration at which an analyte can be reliably detected and surpasses the bias goals of the BECS lab [81]. They can be calculated for each calibration curve by taking the standard deviation, S, in the y-plane, i.e. the regression line (we therefore call this S_y), and the gradient *m* of them, in the following ways:

$$LOD = 3.3 \times \frac{S_y}{m} \tag{6}$$

$$LOQ = 10 \times \frac{S_y}{m} \tag{7}$$

The multiplier of 3.3 in Equation 6 comes from the statistical value 3σ , which includes almost all of the relevant statistical information in each detection. The relevant information for each calibration curve, and their resulting LOD and LOQ, are in Table 17. The same for the derivatised run is shown below in Table 18.

The LOD gives the minimum limits of concentrations that can be detected in each run of an experiment. Therefore, any detections with concentrations less than these cannot be reliable. This means the non-derivatised detection of octabenzone (which was present in concentrations of $4.47\mu g/ml$ in NWA 10853, with a LOQ = $4.85\mu g/ml$) cannot be said to have been reliably detected. The only compound that doesn't meet these specifications is

Table 17: Limits of detection and quantification of non-derivatised run standards, given to two decimal places.

Curve number	S. of regression line (S_y)	Gradient (m)	LOD ($\mu g/ml$)	LOQ ($\mu g/ml$)
1	63530.67	469138	0.45	1.35
2	81597.00	520071	0.52	1.57
3	253682.77	523098	1.60	4.85

Table 18: Limits of detection and quantification of derivatised run standards, given to two decimal places.

Curve number	S. of regression line (S_y)	Gradient (m)	LOD ($\mu g/ml$)	LOQ ($\mu g/ml$)
1	36565.49	366404	0.33	1.0
2	61465.19	364378	0.56	1.69
3	166092.16	523098	1.05	3.18

Octabenzone, in the non-derivatised NWA 10853 results. This can be fully ignored in future analysis because its concentration doesn't meet the limit of quantification.

5.7 Summary of Analyses

We have calculated the concentrations of the detected compounds in both runs of the experiment in parts per million. These concentration calculations have been scrutinised by uncertainty analysis and contextual analysis from literature searches and considering statistical reliability of the detections. This has been achieved through considering environmental and curation contaminants, literature reviews, signal to noise ratios of detections, contaminants from the crushing lab, and finally the limit of detection and quantification of the equipment. Since the derivatised results has provided more precise spectra in the chromatograms, and it is providing more detections, we will go forward with analysis and discussion using these results. It should be noted that we are discounting dodecanol in Unheated Murchison as its concentration value in ppm is far beyond the amounts of alcohols previously detected in Murchison (expected values were around 11 ppm, as stated in Table 4).

5.7.1 Discounted Detections

The disregarded organics detections are listed in Table 20. This summarises the reasons why these compounds were initially disregarded, and their likely sources of contamination. It combines all reasoning- low SNR, man-made compounds, concentrations being too high to be intrinsic to the meteorite, and being present in sample blanks.

5.7.2 Extra-terrestrial Detections

Following the described analysis and considerations over the two runs, the compounds in Table 19 can confidently be said to originate from the sample, and not from contamination. The results indicate that in total, we detected 34.84 ± 0.94 ppm of organic compounds in NWA 10853, and 47.27 ± 1.14 ppm in unheated Murchison.

Table 19: The final list of indigenous organics in NWA 10853 and the unheated Murchison samples after accounting for laboratory or curation contamination, complete with concentration uncertainties. Note that the use of "indigenous" in this context signifies any compounds that were on the meteorite when it was found in its fall site, and so could include fall site contamination or extra-terrestrial organics.

Sample name	Compound name	Concentration (ppm)
NWA 10853	nonanoic acid	11.41 ± 0.28
	decanoic acid	9.78 ± 0.24
	dodecanoic acid	7.55 ± 0.18
	myristic acid	21.79 ± 0.53
	pentadecanoic acid	6.10 ± 0.24
	palmitelaidic acid	12.44 ± 0.48
U.M.	nonanoic acid	9.92 ± 0.24
	tetradecanol	22.42 ± 0.54
	myristic acid	14.93 ± 0.36

Table 20: Organic compound detections from the derivatised results that are regarded as contaminants following the analysis protocol outlined in Chapter 5.2. This table covers only detections that were disregarded due to low SNR, or being man-made compounds. Recall the sample blank is the uncrushed, unmeasured combusted sand, and the procedural blank was combusted sand which was weighed and crushed in the same procedure as the meteoritic samples.

Sample name	Compound name	Reason for disregarding	Contamination source
NWA 10853	biphenyl	man-made	curation/handling
NWA 10853	oleic acid	in sample & procedural blanks	ASE
NWA 10853	octyloxy-biphenyl-methanone	man-made	curation/handling
U.M.	diethylene glycol	man-made	GC-MS (antifreeze)
U.M	dodecanoic acid	low SNR	lab/curation
U.M	tert-nonylphenol	low SNR	lab/curation
NWA 10853, U.M	palmitic acid	in sample & procedural blanks	ASE
NWA 10853, U.M, H.M	dodecanol	concentration too high & in procedural blank	lab/curation
NWA 10853, U.M, H.M	stearic acid	in sample & procedural blanks	ASE
H.M.	benzenedicarboxylic acid,	in sample & procedural blanks	lab/curation
	bis(2-methylpropyl) ester		

6 Discussion

This chapter outlines the recommended re-classification of NWA 10853, and discusses the efficacy of the organics detection and analysis procedure. Conclusions about the effect of derivatisation upon organic extract samples are drawn, as well as conclusions from the results and analysis of the individual sample organic contents. We also outline routes for experimental and analytical improvements and future work.

6.1 NWA 10853 Classification

The SEM-EDS information showed that despite some areas of significant alteration throughout the studied thin section, some chondrules remain not entirely altered- there remains iron oxides and angular olivines within the chondrule relics, along with some primary textures. According to the Rubin scale (Table 1), a CM2.0 (CM1) should have completely altered silicates, and a CM2.1 should have 85-99% altered silicates. Both CM2.0 and CM2.1 meteorites have less than 0.02% abundance of Fe-Ni, and both classifications share the other listed diagnostic criteria. Therefore because of the signifying criteria of 100% altered silicates not being met in this thin section, there is strong evidence that NWA 10853 may be a CM2.1, and not a CM1 as previously identified and published on the Meteoritical Bulletin [69]. Within the allocated time in this project, the recommendation for re-classification is CM2.1 by the Rubin scale. The amount of preserved features is interesting however, and a new classification may even extend to that of CM2.2. The final re-classification will depend on modal mineralogy calculations to find the percentage of altered materials to preserved. Modal mineralogies may be studied using techniques such as PSD-XRD [44], or by using a software such as ImageJ. Additionally, there is only so much that can be said about an entire meteorite from one thin section of it. More thin sections of this meteorite are needed for SEM-EDS study to confirm or further elaborate on a re-classification proposition.

From an organics point of view, those detected in NWA 10853 are more consistent with those detected in less aqueously altered rocks, such as CM2s. Additionally, in CM, CV and Tagish Lake meteorites, the abundances of SCMA molecules decreases as the chain length of the compound increases [82, 83], and this trend is largely exhibited in our NWA 10853 results, as shown in Figure 29 where there is decreasing abundance with increasing chain length. This supports the inclusion of pentadecanoic acid as a final result. This simple

analysis is also unhindered by standards being too short- the calibration standards used in this protocol go up to C28, and the largest resultant compound we have is C16. Therefore the decrease in abundance cannot be due to standards failing at these chain lengths, and so the decreasing trend is certain to be true to the sample. From this, it is clear that myristic and palmitelaidic acids do not follow this trend, and so could be disregarded as contaminants intrinsic to the sample, likely from vegetation from the fall site. The below compounds are those that follow the trend expected from literature for intrinsic organic molecules to CM2s:

- Nonanoic acid (C9);
- Decanoic acid (C10);
- Dodecanoic acid (C12);
- Pentadecanoic acid (C15).

Although myristic and palmitelaidic acids do not follow the expected trend, they are not present in the sample blanks, and so with this level of analysis we cannot exclude these detections. However, the successful detection of multiple fatty acids is further evidence that the highly-altered classification of NWA 10853 may be incorrect. The classification on the Meteoritical Bulletin was determined through optical SEM at one institution, as far as the available data indicates. However, it is difficult to say whether these fatty acids formed in space, or if they are a result of the unknown period of time exposed to the elements on Earth as the meteorite lay in the desert of Northwest Africa.

6.2 Effect of Derivatisation

Derivatisation had multiple effects on the identifications of compounds in the samples. Firstly, there was an increased number of detections made upon derivatisation, with those detected in NWA 10853 rising from 8 to 11, and those in the unheated Murchison sample increasing from 3 to 9. This may indicate higher noise in the non-derivatised run and/or wide peaks concealing others. It also suggests that the samples could have been contaminated before or during derivatisation. However, most of the identified contaminants were already present in the non-derivatised run, largely ruling out this possibility. Secondly, the probabilities of



Fatty Acids in NWA 10853: Abundance against chain length

Figure 29: The abundances of the fatty acids detected in the sample of NWA 10853, plotted with respect to their carbon chain numbers. As demonstrated in [82] and [83], an exponentially decreasing relationship between these two variables is an indicator that monocarboxylic acids, such as these fatty acids, are potentially indigenous to the meteorite. The red points are those of myristic (C14) and palmitelaidic (C16) acids, which lie off of a clear exponentially decreasing relationship between abundance and chain length that the other compounds demonstrate. These compounds (nonanoic, decanoic, dodecanoic, pentadecanoic acids) have an R^2 value when fitted to an exponential trend of 0.9717, and an R^2 of 0.9367 when fitted to a linear trend.

correct identification changed between compounds that were detected in both runs, causing some inconsistencies and reducing confidence in the identified compounds. On the contrary, the SNR also widely improved after derivatisation.

6.2.1 Probabilities of Correct Identification

The *MassHunter* software automatically produces probabilities of the named compound being correctly identified upon peak integration. The probability of correct identifications upon detection in the GC-MS largely increased upon derivatisation for the compounds that were detected in non-derivatised run. These changes are shown in Table 21. Seven out of the ten compounds that were detected in both runs showed improved probability of a correct identification. A route for analytical improvement here could be to look into the alternative IDs suggested by the *MassHunter* software for the first, non-derivatised, run and compare to the derivatised results. This would give a clearer picture of how reliable non-derivatised results are, and perhaps influence or restrict expectations of potential contaminants.

Table 21: The percentage probabilities of compounds detected in both non-derivatised and derivatised runs being correctly identified. Only the compounds detected in both runs are shown, any incorrect identifications or compounds with similar retention times are excluded.

Sample name	Compound name	Probability- non-derivatised	Probability- derivatised
NWA 10853	decanoic acid	74.4%	80.0%
	dodecanoic acid	60.7%	90.2%
	biphenyls	51.2%	68.2%
	myristic acid	37.0%	94.6%
	palmitic acid	51.9%	96.6%
	oleic acid	11.2%	21.0%
	octabenzone/		
	octyloxy-biphenyl	92.3%	90.4%
U.M.	dodecanol	10.2%	65.8%
	diethylene glycol	22.5%	11.4%
	stearic acid	95.4%	87.7%

6.2.2 Chain Length and Complexity

One may also consider the effect of derivatisation on the complexity profile of the detected compounds. In Tables 22 and 23, the detections are shown for NWA 10853 and unheated Murchison, and are organised by chain length and complexity. In the cases where two com-

pounds have the same carbon number, the number of hydrogen atoms in the compound was then considered, then oxygen, then other elements ordered by the complexity or strength of their bonding type to the C chain. From these tables, it is clear that derivatisation has increased the number of mid-chain length detections, with the number of C12-C18 compounds in the NWA 10853 sample increasing by 3 detections, and increasing by 4 in the Murchison sample. Additionally, derivatisation has also picked up on shorter molecules than the nonderivatised run. From comparison with sample blank chromatograms, we know this increase in detection number is not due to contamination of samples between derivatisation. Therefore, derivatisation has increased the number of detections possible from our samples, and has allowed further detections in the range C12-C18 than possible from a procedure without derivatisation.

Table 22: The non-derivatised detected compounds organised by carbon chain length (C number) and complexity. It should be noted that the diethylene glycol compound formula is estimated from the combination of compounds given in its full *NIST* database name. The compounds highlighted in pink are contaminants.

NWA 10853			Unheated Murchison			
ID	Compound name	C number	ID	Compound name	C number	
1	decanoic acid	C10	7	dodecanal	C12	
2	o-hydroxybiphenyl	C12	8	dodecanol	C12	
3	dodecanoic acid	C12	9	diethylene glycol	C12	
4 myristic acid		C14	10			
5 palmitic acid		C16				
6	oleic acid	C18				

6.2.3 Detected Abundances

Using all concentrations calculated in the Supplementary Material lists in the Appendix 8D, the total concentrations detected between both NWA 10853 and the UM samples in the nonderivatised run was 702.15ppm. After derivatisation, this increased to 1895.33 ppm (noting that 551ppm of this comes from the contaminant dodecanol), more than doubling the detected organic abundance between the samples.

Looking more closely, the non-derivatised run detected 39.93ppm in NWA 10853, which increased to 292.26ppm in the derivatised run (an increase of 732%). This presents the question, what could have happened to increase the organics detected by such an amount?

Table 23: The derivatised detected compounds organised by carbon chain length (C number) and complexity. Again, the diethylene glycol compound formula is estimated from the combination of compounds given in its full NIST database name. All the carboxylic acids and alcohols in this table are TMS derivatives. The compounds highlighted in pink are contaminants.

NWA 10853			Unheated Murchison		
ID	Compound name	C number	ID	Compound name	C number
11	nonanoic acid	C9	21	nonanoic acid	C9
12	decanoic acid	C10	22	dodecanol	C12
13	1'1-biphenyl	C12	23	dodecanoic acid	C12
14	dodecanoic acid	C12	24	diethylene glycol	C12
15	myrsitic acid	C14	25	tetradecanol	C14
16	pentadecanoic acid	C15	26	myristic acid	C14
17	palmitelaidic acid	C16	27	palmitic acid	C16
18	octyloxy-biphenyl-methanone	C17	28	stearic acid	C18
19	oleic acid	C18			
20	stearic acid	C18			

The bulk of this increase comes from carboxylic acids (from 24.85ppm to 265.67ppm postderivatisation). Then, if we were to look at the concentrations in our final list of intrinsic organic compounds, Table 19, we can see that the concentration increased to a total organics abundance of 69.07ppm in NWA 10853 an increase of 1.73 times from the non-derivatised total abundance. Further, if we assume that myristic and palmitelaidic acids are to be disregarded as well after our investigation of the abundance and chain length relationship (see Figure 29), then the abundance after derivatisation is 34.84 ± 0.94 ppm. This is very close to the total organics concentration detected in the non-derivatised run, albeit without removing the contributions from known contaminants such as octabenzone. The largest contribution to the increased concentration upon derivatisation of the sample between completing the GC-MS run of non-derivatised samples, and sometime before the samples were placed in the GC-MS again after derivatisation. However, as seen in the subtraction of sample blank chromatograms from the chromatograms of meteoritic samples, there was no substantial new contamination that was not already present in the non-derivatised run.

Investigating Murchison shows similar trends- the concentration of all organics detected in Murchison went from 662.22ppm to 1233.11 ppm, nearly doubling- however the most contributions to this comes from dodecanol, which abundance itself had nearly doubled. If we exclude this, then the concentration of carboyxlic acids in the derivatised run was 157.9ppm, all of which went previously undetected in the non-derivatised results.

The final abundances are likely to have been increased upon derivatisation due to the effect of derivatisation on peak area, and the number of peaks that become detectable and identifiable. The derivatised run picked up on 11 significant compounds in NWA 10853, compared with 9 beforehand. These new detections were likely covered up by wider peaks in the first run chromatogram, demonstrating the power of derivatisation.

6.3 Discussion of Contaminants in Individual Samples

The following chapters discuss the contaminants as determined in Chapter 5.3.6 (detections rendered invalid due to low SNR), Chapter 5.5 (determined to be contamination picked up during crushing) and Chapter 5.6 (invalidated due to not meeting LOD or LOQ).

6.3.1 NWA 10853

Octabenzone is used in UV stabilisers and UV absorbers, and as a fragrance [84], though it is typically associated with protecting polymers, such as polyethylene, against UV damage. Octabenzone is currently patented for topical sunscreen [85]. However, recalling that this detection did not meet the limit of detection nor did it have significant SNR, the true presence of this compound is easily refutable. The derivatised version of this compound as identified by *MassHunter* is octyloxy-biphenyl-methanone, which also comes from a family of compounds used in sunscreens.

According to the available literature, biphenyl has been detected in Murchison before, but it does not appear in our sample of Murchison- however it is present in NWA 10853. The biphenyl detected in NWA 10853, o-hydroxybiphenyl (also known as phenylphenol), is typically used as a fungicide on waxed citrus fruits to preserve them as they are transported to shops [86]. It is also used as a germicide, in deodorants, and as laundry detergent [87]. In the derivatised run of the experiment, this compound no longer appeared and was replaced by a structurally-similar compound, 1'1-biphenyl, and it is understood that this compound is the result of the addition of the the derivatisation agent to the o-hydroxybiphenyl already in the sample.

Tetramethyl decynediol is used as a cleaning agent for hard floors, pre-moistened wipes, wood stains, surfactants, and in adhesives on plastic food wrappings [88]. Recently, it was found to be highly toxic to mammals, but is still used in the glues for labels and plastic wrappings on food products. The presence of this complex compound along with phenylphenol suggests that at some point in this sample's history, it was held by a person who had eaten a waxed citrus fruit which had been transported in plastic wrapping.

The fatty carboxylic acids (palmitic, oleic, and stearic) disregarded from this sample are present in the sample blanks. These peaks are removed from the final chromatogram for derivatised NWA 10853 when the blank chromatogram is subtracted from the initial sample chromatogram. It is understood that these came from the Accelerated Solvent Extractor (ASE) equipment, and in future it is recommended that this equipment is not used for meteoritic organics studies.

6.3.2 Unheated Murchison

At first glance, the detection of dodecanol (C12) was a promising one, with a very large chromatogram peak, a very large SNR and no trace in the sample blank. However, the concentration of 938.65ppm meant that it had overshot the expected alcohol abundances of Murchison by a multiple of 85. The option of this sample being a breccia high in alcohol compounds is unreasonable, since by the fact that abundance of SOM generally decreases with increasing chain length, we are left with the implication that alcohols of chain lengths C1-C11 would exist in huge quantities. Following the general rule that is displayed by the carboxylic acids in NWA 10853 as an example (where the compounds become 3 carbons shorter, the abundance increases by between approximately 124% and 151%), nonanol would exist at 1417ppm, hexanol at 2140ppm, and propanol at 3231ppm (based on the 151% increase). This is considerably higher again than what is expected of carboxylic acids in Murchisonone study by Jungclaus et al in 1976 [89] found that Murchison can be expected to contain a total of 11 ppm of alcohols, between C1 and C4 in length. It is not present in any other samples or blanks, and so did not come from the lab. The most realistic scenario is that the sample came into contact with a concentrated source of 1-dodecanol during previous study. Likely sources of this compound include coconut oil-based toiletries such as hand creams,

shampoos and conditioners- specifically those which treat coloured hair [90].

Diethylene glycol is a key ingredient in the anti-freezing agent used in the GC-MS lab at UofG. How this only affected this sample of Murchison and no other samples is unusualif it had been introduced at the GC-MS stage, it would have been difficult to only affect one sample out of the 5 (including the procedural and lab blanks). This suggests that the contamination occurred before introduction to the lab, and perhaps at an earlier stage in its study.

Dodecanoic acid and tert-nonylphenol were both disregarded due to low SNR. The final contamination detections in Table 16 were contaminants from the ASE equipment as discussed earlier.

6.4 Discussion of Individual Sample Results

6.4.1 NWA 10853

All results identified as intrinsic to NWA 10853 were straight chain monocarboxylic acids (SCMA). Since the organics in NWA 10853 has not been studied before, findings in other examples of altered CM2s may provide some comparative guidance.

Mautner et al [91] found that nonanoic acid can survive hydrothermal conditions in planetary environments, in temperatures of up to 350°C and 250 bars of pressure. And further, this compound can go on to form vesicles, a key role that nonanoic acid plays in building of cellular membranes in eukaryotes such as bacteria, and even humans. Other studies have shown high abundances of shorter-chained monocarboxylic acids, such as propanoic acid in Murchison [59]. Nonanoic acid was the shortest chain SCMA found in NWA 10853, but a GC-MS study of the Aguas-Zarcas CM2 meteorite found that beyond the expected C1 to C4 SCMA compounds, there were several unidentifiable "higher molecular weight compounds" [92]. It also found hydrocarbons of up to C30.

For the longer compounds detected in NWA 10853 (decanoic, dodecanoic, myristic, pentadecanoic and palmitelaidic acids), we look to other previous findings. The CM2, Yamato-791198 discovered in 1979 was found to contain monocarboxylic acids from length C1 to C12 [93]. Unfortunately there is no refinement on its classification within the CM2 group, so it is difficult to compare to a definitively-altered meteorite such as NWA 10853. Most studies use GC-MS machines that are calibrated for shorter chains, so there is little information available on longer fatty acids in meteorites. However, in Lai et al [50], abundances of SCMA are studied over a chain length range of C1 to C12, and shows that in 14 samples of CM1 and CM2 meteorites, a C9 SCMA, such as nonanoic acid, is present in 9 of them. The only CM1 in the study, ALH-84034, was shown to contain this C9 molecule, and also contains a C10 SCMA, such as decanoic acid. From this study, we know it is possible for CM1s to contain C9 and C10 monocarboxylic acids. Some examples of meteorites that have been shown to contain C12 SCMA are Asuka-881458 and Yamato-74662. This would indicate that the most robust results in terms of previous literature are those of nonanoic acid, decanoic acid and dodecanoic acid.

The unknown length of time the meteorite spent in an unknown location is another factor we must consider more carefully. Whether it landed in the desert, or in a vegetated area of Northwest Africa, is unknown. Vegetation can produce many fatty acids, most commonly linolenic acid (C18) in grasses [94], and palmitic and myristic acids from palm trees [95]. Without more specific location data as to where this meteorite was found, the mystery of where these fatty acids came from will remain until further research is undertaken- possibly by measuring compound-specific isotope ratios as in [96] which can aid in confirming or nullifying the indigenous nature of organic matter found in meteorites.

6.4.2 Unheated Murchison

Nonanoic acid, although longer than the more abundant organic molecules that are typically detected in Murchison, it has been found that particular breccias of the Murchison meteorite contains C9 SCMA [50].

Tetradecanol, C14, is simply the hydrogenated product of myristic acid. It is a fatty alcohol, and these are usually found in moisturisers, hair care products and makeup products. Myristic acid derives from palm and coconut oils, as well as mammalian milk [95]. It is also detected in an abundance (of 22ppm) which is double what is expected of alcohols in the Murchison meteorite as a whole [89]. Thus, the concentration of tetradecanol (and its length) is indicative that it is terrestrial contamination, perhaps from the fall site. Myristic acid was also detected in NWA 10853, which at first suggests lab contamination, but it wasn't detected

in sample blanks so it must be intrinsic to the sample.

The lack of carboxylic acids is surprising, as they are reported in literature to exist in concentrations over 300ppm in this meteorite and os would expect to see more of these compounds- however the long standards used for GC-MS calibration likely caused the bulk of these acids at C1-C4 to go undetected. There is also the added complication with Murchison, being that it is a brecciated meteorite. There is no record of which litholgy was supplied as a sample for this study, and so no way of knowing whether it was a more or less extensively aqueously altered sample. This will have affected the compounds present and their abundances.

6.4.3 Heated Murchison

The lack of detections in the Heated Murchison (H.M) sample compared to the other samples was expected, given its history of previous study where it was heated to 1100°C. Alkanes can be cracked at temperatures between 370°C, as was achieved in 1912 by W. Burton [97] at a pressure of about 6 bars (approximately 6 times our normal atmospheric pressure on Earth), and 800°C in modern-day catalytic and hydrogen cracking [98]. Generally, when breaking molecules apart, higher pressures require lower temperatures. In the absence of high pressure, higher temperatures alone will break the C-C bonds in organic molecules. Thus, regardless of pressure, it stands to reason that any extra-terrestrial organics heated to 1100°C would also be broken. However, due to the comparably small sample size, it is impossible to say whether the lack of detections was due to the thermal heating, or simply a small mass bias. Within the UofG planetary research team, one researcher, J. Douglas, found that GC-MS works optimally for igneous rock samples of 1.5 grams [21]- in this study the starting sample mass of H.M was 66.1mg, whereas the other masses all exceeded the 1.5g lower limit.

6.4.4 Procedural and Lab Blanks

From a contamination point of view, oleic acid, stearic acid and palmitic acid were detected in both the lab blank and the crushed sand procedural blank (as were dodecanol which was detected in small quantities in all meteoritic samples, and benzenedicarboxylic acid, bis(2methylpropyl) ester which was detected in the Heated Murchison sample). However, stearic acid was not detected until a second analysis of the results several months after the first reading, as the NIST Library had updated. Beforehand, the only contaminant that appeared in all samples was palmitic acid. For organic geochemists using this software, this may be something worth keeping in mind, as the contaminants changed after this software update.

6.5 Summary of GC-MS Results Discussion

It is interesting that a strong abundance of carboxylic acids has been detected in NWA 10853, but none in Murchison, as carboxylic acids have been detected in Murchison before at concentrations of 7480 ± 1237 ppm in other studies [99]. The lack of amino acids and PAHs are equally as interesting (amino acids have been detected in another study at 50 ± 3 ppm [65]), and suggests an equipment-based limit for detecting these compounds at UofG. Another point to note in terms of detection limits is that the shortest compound detected is a C9 SCMA. This is due to the standards used in the BECS lab, the shortest being of length C16. Literature and other studies indicate that CM2s are typically rich in very short (C1-C4) chain organic compounds, and so the standards used in the BECS lab are not ideally suited to meteoritic studies.

The organics detected in both NWA 10853 and U.M. samples were unexpected based on previous literature- there are no traces of isovaline or amino acids detected, due to the equipment at UofG being calibrated for longer molecules. Another point of interest as aforementioned is the chain length being considerably large, when many organic compounds detected in Murchison before have been of C-length 1-4. This has implications for the validity of the protocol after all, since if our equipment is only capable of detecting molecules of 10 carbons or more, then there is great potential that intrinsic organic compounds have gone undetected, along with other contaminants which may help to create a more full picture of the meteorite's history. However, it is important to note the possibility of investigating longer compounds in meteoritic samples which are often ignored in extra-terrestrial GC-MS studies.

Other routes for determining abiotic or biotic origins is to consider enantiometric ratios, which as discussed in Chapter 1.5.2, are known to be a good indicator of organic molecule formation origins. For example, an alternative route of study could be to carry out isotope-specific analyses, where investigating the δO ratios of oxygen in each compound are com-

pared to the Terrestrial Fractionation Line, and see where the overall molecule lies on this chart. However, this method is time-consuming and destructive, which would be challenging to achieve in the duration and financial restrictions of a Masters project. It would require approximately 10 grams of CM chondrite sample to obtain compound-specific carbon isotope results [53]. These routes are potential future work opportunities to continue to unravel the history of the NWA 10853 meteorite.

6.6 Future Work

6.6.1 Further Improving Experimental Technique

The pestle and mortar were purchased anew for this project, and so had never been used before. However, it was transported in a plastic wrapping, and its contamination history before this unknown. Simply rinsing it in deionised water and heating to 60° C may not be sufficient to consider it sterile. Additionally, once the samples are crushed, the grain sizes could be measured on a slide with an optical microscope. This was not done in this study due to limited samples sizes. To analyse grain sizes, it was suggested to use the software *ChemScan*. Since the recommended sample size from J. Douglas 2023 is between 1.5 grams, measuring grain sizes is more feasible for studies using larger samples masses than this one. Grain size will have affected the effectiveness of the GC-MS extraction protocol, so in future it is recommended to take this into consideration, but only if sufficient masses are available to use.

The ASE is attributed with a large portion of the long chain fatty acid contaminants in this project. This equipment is difficult to fully clean and is shared with other students. Instead, it is recommended by B. Cavazzin [private discussion] that extractions are done manually. This will be time consuming, however, far easier to control contamination and will offer more opportunity to develop the next scientist's analytical chemistry lab skills. One method of manual extraction is hot water extractions, and an example methodology can be found in [53].

The GC-MS is equipment at the University of Glasgow has a long-chain bias. The equipment would require the calibration standards used in the GC-MS machine to be changed to include a shorter carbon chain standard in order to detect shorter molecules. Carbonaceous chondritic meteorites contain high abundances of short chain molecules, as found in previous GC-MS studies, and despite using an evaporation and condensation protocol suited to extract shorter chained molecules, the calibration means that these molecules are not detected in the GC-MS. Instead, one may consider alternative means of identifying elements and shorter compounds, such as LC-MS.

6.6.2 Extra-terrestrial Identification Alternative Analyses

It may prove worthwhile to consider metabolomics- the study of metabolites, or the biochemical processes that go into forming biologically important compounds such as amino acids. Using analytical techniques, one can identify the presence of particular metabolic pathways, thus constricting the options for how certain compounds formed. Although this technique is typically used as a study of biological samples, it can be applied to compounds intrinsic in origin to samples of rocks, or to determine contaminants on rock samples [100, 101].

An attested means of determining extra-terrestrial or terrestrial origin of elements, compounds and molecules is to use isotopic studies where each oxygen, carbon or hydrogen isotope is analysed and compared to the terrestrial fractionation line and other groupings, as discussed in Chapter 1.4. The detected compounds could also be verified by studying enatiometric ratios, or δO ratios of oxygen in each compound are compared to the Terrestrial Fractionation Line. These analytical techniques are time consuming and highly destructive, and so were left beyond the scope of this MRes project.

6.6.3 Further Imaging Work

To gather more information on NWA 10853, it would be beneficial to make further use of the XCT imagery obtained as part of this project. Several characteristics could be examined, such as its porosity and sizes of chondrules or grains within them which are, as of writing, unknown. Many characteristics to study in XCT are described in [102].

More thin sections are required for SEM-EDS analysis to validate the extent of reclassification of NWA 10853, with a heavier focus on spectra comparisons to determine the specific minerals in the thin sections. It is recommended that three more thin sections, from different parts of the sample of NWA 10853, are made for study at UofG. Modal mineralogies could also be studied to add more quantitative mineralogical detail to this meteorite.

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6.6.4 A Bayesian Framework for Conditional Likelihood of Formation in Space

When determining an extra-terrestrial or contaminant source of organic matter, there are many routes one can take. As summarised in [103], one may use previous literature alongside assessing the probability of finding each compound on Earth's surface to determine whether a compound is contamination or extra-terrestrial in nature- if compounds are rare on Earth or at the collection site, or conversely are known to be unique to meteorites, it is highly suggestive of an extra-terrestrial nature. It would make sense to then consider the probability of the best matches given in the databases, as well as to consider the chemical reaction pathways and attach a probability to this as well, and start to consider statistical likelihoods.

Bayesian statistics utilises conditional probability to produce a statistical outcome of some event. This type of analyses suits scenarios where a result is dependent on some condition or some other event either happening, or not happening. For example, Catling et al [104] used Bayesian statistics to determine likelihoods of observing positive or negative biosignature detections from exoplanets . It considered stellar properties (such as age, spectral class, mass, radius, and activity), desirable planetary properties for life in terms of climate, surface properties and atmospheric conditions, alongside potential biosignature gases such as oxygen, ammonia and methane. Finally, the last component considered was that of false positive detections. After all these parameters were considered and probabilities modelled, the study was able to group exoplanets using these criteria in a Bayesian framework into five groups of confidence that a positive biosignature could be detected (very likely inhabited, likely inhabited, inconclusive, likely uninhabited, and very likely uninhabited). Bayes' theorem is stated below:

$$p(hypothesis|evidence) = \frac{p(evidence|hypothesis) \times p(hypothesis)}{p(evidence)}$$
$$p(hypothesis|data, info) = \frac{p(data|hypothesis, info) \times p(hypothesis|info)}{p(data|info)}$$

Where p(hypothesis|info) is known as the prior distribution, which describes the initial state of knowledge of a hypothesis (this is usually the value of a parameter, or a model), given some background information. The term p(data|hypothesis,info) is known as the likelihood, which describes the goodness of fit of a model or hypothesis to the measured data. The denomenator on the right hand side is the evidence, and this is constant for each data set

and therefore can often be ignored. The left hand side of this equation is the posterior, the resulting probability distribution after being updated by the new evidence and/or information. These probabilities are known as probability density functions, or "pdf"s for short, and vary from 0 to 1, or a 0% chance to 100% chance of happening or being true respectively.

A potential aid to constraining whether detected organic molecules formed in space or on Earth could be developed through a similar Bayesian framework. This would help astrobiologists and astrochemists to determine whether detected compounds from meteoritic samples are extra-terrestrial or terrestrial in origin, rather than relying on contamination tracking methods alone. Some suggested parameters for consideration could be;

- the likelihoods that a particular detected compound can form in space;
- the likelihoods that a particular detected compound can form on Earth;
- equally, the likelihoods that a compound cannot form in space;
- the likelihood that a compound can form on Earth;
- available elements on a parent body to form such a molecule (e.g. to form ammonia, NH₃, there must be nitrogen and hydrogen available)
- sufficient available energy to supply such a reaction (as most chemical reactions require heat);
- considering the concentrations detected in the results, are the abundances of the required elements existing in sufficient amounts?

Any events which always happen will have a pdf equal to 1- for example, we know that water can exist on Earth and, at the time of writing with our current climate, size of Sun, and so forth, it will always be able to form here. Therefore the likelihood that water can form on Earth is 100%, or 1. Conversely, let us say a scientist detected chlorophyll ($C_{55}H_{72}MgN_4O_5$) in a meteorite for example. Based on our current state of knowledge, there is no chlorophyll beyond the Earth, and therefore the current prior likelihood of chlorophyll forming in space is 0. It is also important to recognise that reactant concentration, the physical state of the reactants, and surface area, temperature, and the presence of a catalyst all determine the likelihood of a chemical reaction in the first instance. Additional descriptions to consider are

the abundance of relevant elements. For the organic molecules we have detected, this means we need the abundances of hydrogen, carbon, and oxygen in space at the time of formation.

This would be a long and potentially arduous task indeed, however if a Bayesian relationship could be created, this could be made available to scientists in a relatively simple machine learning algorithm. Such an algorithm would produce a likelihood grouping (a potential grouping could be 1-5, with 1 being very likely, 2 being likely, 3 being equally likely to unlikely, 4 being unlikely, and 5 being very unlikely, as in [104]) along with a confidence rate of which molecules are intrinsic to meteorites within seconds of data input. After this research, a more statistically-rigorous treatment of the detected compounds would allow one to say with more certainty if a compound could be intrinsic to the meteorite and be extraterrestrial in origin.

7 Conclusions

This final chapter summarises the conclusions from this work and the future work necessary to build a fuller picture of these samples and the capabilities at the University of Glasgow. The conclusions are separated into the following groups:

- Improvements to the experimental technique
- The classification of NWA 10853
- The organics detected in NWA 10853 and Murchison meteorites.

7.1 Improvements to the experimental technique

Due to the calibration of the equipment, the UofG BECS lab is not yet optimised for GC-MS work on meteoritic samples. However, the longer standards may allow longer molecules to have been detected in this study than in other studies which use a similar protocol but with shorter calibration standards on their GC-MS machines. For example, if other studies use GC-MS machines with standards that don't go past C10 in length, it is very likely that these types of equipment wouldn't detect longer molecules, explaining why the longest alcohol found via GC-MS in Murchison in previous literature is C6 [105]. It is also recommended for similar studies in future that ASE is not used on meteoritic samples, and alternative methods of solvent extraction are investigated prior to beginning work. However, it is recommended that meteoritic solvent extracts are derivatised when using this protocol.

7.2 The classification of NWA 10853

This work recommends that the meteorite NWA 10853 is re-classified to CM2.1, with scope for it being a CM2.2. This is based on findings in X-ray computed tomography, and scanning electron microscope-electron diffraction spectroscopy imaging techniques, which indicated less extensive alteration than previously thought from optical study. This re-classification is also supported by the presence of several organic compounds, which exist in abundances greater than that expected of CM1 meteorites.

7.3 The organics detected in NWA 10853 and Murchison meteorites

This work concludes that the long-chain organic compounds that are intrinsic to the chip of NWA 10853 used in this study are nonanoic acid, decanoic acid, dodecanoic acid, myristic acid, pentadecanoic acid and palmitelaidic acid. Those that are intrinsic to the sample of Murchison studied are nonanoic acid, tetradecanol and myristic acid. However, to determine whether these were picked up during these meteorite's time spent on Earth, or indeed during their curation prior to being brought into the crushing lab, is a far greater challenge.

We have also inferred the contamination history of NWA 10853 from those identified in the sample, as being held by a person who had held a waxed citrus fruit which had been transported in a glued plastic wrapping, or who had opened some plastic food packaging before or after holding a waxed fruit.

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8 Appendix

A. XCT Images of NWA 10853



Figure 30: Three cross-sections of NWA 10853. The nomeclature follows the "rgb" scheme, where red is the x-axis, green is the y-axis, and blue the z-axis. Note slight variations in size bars between images.

B: SEM-EDS Sites



Figure 31: An SEM-EDS image of NWA 10853, showing a pervasively altered matrix, indicating potential terrestrial weathering. The bright orange areas are Fe-S inclusions, which indicates extensive aqueous alteration of what was previously pure iron. The texturing is further indication of extreme alteration, and is an example of a radial quench texture, indicating that this meteorite cooled very quickly from a high temperature. Colour key: silicon (blue), calcium (pink), sulphur (yellow), iron (red), magnesium (green).



Figure 32: Another site of NWA 10853, focused on a crack in the thin section. Here we have a pseudomorphic chondrule replacement, with significant alteration. There remains some orange ironsulphur inclusions in the centre of the large pseudomorphosed ex-chondrule to the immediate left of the crack. The matrix has a lineated texture, which has appeared in studies of hot-desert meteorite finds [106] and shows the fibrous habit of typical of iron-silicates. Colour key: silicon (blue), calcium (pink), sulphur (yellow), iron (red), magnesium (green).



Figure 33: This site shows Fe-Ni sulphides and phosphates, which suggests that Iron and Nickel was present on the meteorite whilst still attached to its parent body before it was aqueously altered. Colour key: silicon (blue), calcium & phosphorus (pink), chromium (orange), iron (red), magnesium (green).



Figure 34: This site shows more phosphates, and not a lot of alteration in the veins, suggesting limited terrestrial replacements in this investigation site. Colour key: Phosphorus (purple), Iron (red), calcium (pink), silicon (blue), magnesium (green).



Figure 35: This site shows no real weathering in this close-up fracture, as there would be salts or calcites in fractures if it had been terrestrially weathered. Colour key: silicon (blue), calcium (pink), sulphur (yellow), iron (red), magnesium (green).



Figure 36: This image shows shows an aluminium-chrome-rich feature. Colour key (right): silicon (blue), calcium (pink), sulphur (yellow), iron (red), magnesium (green). Colour key (left): Phosphorus (purple), aluminium & chromium (orange), nickel (cyan), calcium (pink), sulphur (yellow).



Figure 37: This site shows carbonate globules, with twinning. In the upper left hand side, there is an aqueously altered Calcium inclusion around 80 μ m in diameter, which contains no Magnesium, whereas there is magnesium everywhere throughout the rest of this site. In the lower right hand side, we have several larger altered chondrule replacements, varying in size from approximately 40 μ m to $i 100 \mu$ m in diameter. Colour key: silicon (blue), calcium (pink), sulphur (yellow), iron (red), magnesium (green).



Figure 38: This area of investigation shows cavities where Fe metal or Fe-sulphides used to be and have been altered away. The vein-like features in the upper image used to be olivine before it was altered. It is possible that a secondary fluid came and removed silicates, and turned this into hydrated phyllosilicates, which we see in the matrix. This image also shows Ni features, which could have been a direct replacement of another element or mineral, or alternatively used to be sulphides before some alteration occurred. Colour key (left): Calcium (pink), iron (red), sulphur (yellow), silicon (dark blue), magnesium (green). Colour key (right): Calcium (pink), nickel (light green), oxygen (blue).

C. Results of Sample Losses and Final Masses

NWA 10853

The below table shows the starting masses of equipment and sample.

Measurement	Mass (g)
Empty beaker	18.7878
Initial sample + beaker	19.1115
Empty vial	11.4682
Initial sample mass	0.3237

The second table (below) shows final masses of equipment and sample after crushing, to demonstrate inability to completely empty all contents from mortar into the beaker, and to show sample loss during hand crushing.

Measurement	Mass (g)
Beaker + unmoving sample	18.7881
Final crushed sample + beaker	19.1068
Vial + sample	11.7854
Final sample mass	0.3172

The tables show that 0.0065 grams of sand was lost in the whole process.

Unheated Murchison

The below table shows the starting masses of equipment and sample.

Measurement	Mass (g)
Empty beaker	19.3495
Initial sample + beaker	19.6770
Empty vial	11.3821
Initial sample mass	0.4199

The second table (below) shows final masses of equipment and sample after crushing.

Measurement	Mass (g)
Beaker + unmoving sample	19.3305
Final crushed sample + beaker	19.6447
Vial + sample	11.6762
Final sample mass	0.2941

The tables show that 0.1258 grams of sand was lost in the process.

Heated Murchison

The below table shows the starting masses of equipment and sample.

Measurement	Mass (g)
Empty beaker	19.2800
Initial sample + beaker	19.3462
Empty vial	11.4167
Initial sample mass	0.0661

The second table (below) shows final masses of equipment and sample after crushing.

Measurement	Mass (g)
Beaker + unmoving sample	19.2804
Final crushed sample + beaker	19.3343
Vial + sample	11.4702
Final sample mass	0.0535

The tables show that 0.0126 grams of sand was lost in the whole process.

Sand

The below table shows the starting masses of equipment and procedural blank of crushed sand.

Measurement	Mass (g)
Empty beaker	18.5669
Initial sample + beaker	18.9942
Empty vial	11.3504
Initial sample mass	0.4247

Measurement	Mass (g)
Beaker + unmoving sample	18.5737
Final crushed sample + beaker	18.8898
Vial + sample	11.6622
Final sample mass	0.3118

The second table (below) shows final masses of equipment and sample after crushing.

The tables show that 0.1129 grams of sand was lost in the process.

D. Organics Detections & Calculations Supplementary Materials

Attached is a URL link to the Excel sheets used to record the initial organic detections, their peak areas, and concentration calculations. A "ND" in the sheet name refers to "non-derivatised", and a "D" in the sheet name refers to "derivatised". Also included in this dataset are the values used to create the calibration curves.

Link to supplementary material

Password: HHourston_2022

E: Non-derivatised Calibration Curves

This appendix contains the concentrations and peak areas of three standards used in the GC-MS machine, and their corresponding calibration curves which are used to calculate error uncertainties and concentrations of detections.

Below is the table of concentrations and peak areas for three data points within the first range of retention times, and its corresponding calibration curve. This gradient is used to calculate the unnormalised concentrations of compounds per millilitre of solvent ran through the GC-MS equipment.

Concentration (μ g/ml)	Peak area
2.5	971654
5	2177178
10	4825936

Table 24: This table outlines the peak area values for three different concentrations for the first range of retention times, 0-25 minutes.



Calibration Curve: 0-25 minute retention time

Figure 39: Calibration curve based on the compound C19 from the BECS Lab Standards. The equation of the straight line is y = 469138x, where y is the peak area of the compound being investigated, and x will be its concentration.

Below are the other two calibration curves for the two other retention time groups.

Concentration (μ g/ml)	Peak area
2.5	691651
5	1882789
10	4570373

Table 25: Peak areas in three different concentrations for the BECS standard $C_{23}H_{48}$.



Figure 40: Calibration curve based on the compound C23 from the BECS Lab Standards.

Concentration (μ g/ml)	Peak area
2.5	342834
5	1311580
10	4198266

Table 26: This table shows the peak areas that were plotted against three different concentrations for the final range of retention times, 35+ minutes.



Figure 41: Calibration curve based on the compound C28 from the BECS Lab Standards.

F: Derivatised Calibration Curves

This appendix contains the calibration curves for the derivatised run, as well as the peak areas that were used in concentration calculations.

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Table 27: ]
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This table outlines the peak area values for three different concentrations for the first range of retention times, 0-25 minutes.

Concentration (μ g/ml)	Peak area
2.5	621379.29
5	1488525.67
10	3359633.96





Figure 42: Calibration curve based on the compound C19 from the BECS Lab Standards.

Table 28:]	
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Peak areas in three different concentrations for the BECS standard $C_{23}H_{48}$.

Concentration (μ g/ml)	Peak area
2.5	448722.35
5	1277530.14
10	3165127.4



Figure 43: Calibration curve based on the compound C23 from the BECS Lab Standards.

Table 29:]

This table shows the peak areas that were plotted against three different concentrations for the final range of retention times, 35+ minutes.

Concentration (μ g/ml)	Peak area
2.5	288038.67
5	880309.13
10	2686310.02



Figure 44: Calibration curve based on the compound C28 from the BECS Lab Standards.